ANALYTICAL METHOD FOR ESTIMATING NITRIDING EFFECTS

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Anticipation of the effects of gaseous nitriding carried out under certain strictly specified conditions can be ensured by a multitude of variants. Among the most convenient variants from the point of view efficiency, one can consider the experimental variant, which makes use of the regression equations obtained as result of the programming of the experiments-the active experiment method, or the analytical variant, which involves going through a sequence of steps that mainly take into account the solutions of the diffusion differential equations. This second option for estimating the effects of nitriding has been addressed in the paper, providing a rationale for the steps that need to be taken to answer a number of questions related to the kinetics of nitrided layer growth, the distribution of nitrogen in the layer, etc., for the particular case of nitriding of pure iron in undiluted ammonia. The corrections to be made in order to be able to use these solutions in case of nitriding of alloyed metal matrices were also indicated.

Keywords: hard nitriding; kinetic; analytical method for estimation; ammonia; nitriding potential.

1. Introduction

Taking place at relatively low temperatures, the kinetics of the gaseous hard nitriding process is slow, so that the rigorous correlation of environmental factors with those related to the material in order to obtain a certain distribution of nitrogen in the nitrided layer corresponding to a certain phase composition of it, in

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strict correlation with the requirements imposed by the operating demands of the product subject to processing, represents a major desideratum [1÷4;6]. Governed by the laws of diffusion, the distribution of nitrogen in the nitrided layer, under different processing conditions, can also be described with the help of the solutions of the differential equation of the diffusion equation, the solutions obtained under strictly specified conditions, which consider the peculiarities of the phases in equilibrium at a certain temperature [5;7÷10].

Related to this aspect in the specialized literature there are still slightly different points of view regarding the concentration limits in wich the solid solution are based on the compounds γ’ and ε respectively, their stoichiometry respectively their crystallography are stable). In this context, the particularity of the solid solution based on the defined chemical compound Fe_4N should be highlighted, namely the fact that it is stable in an extremely low range of nitrogen concentrations (for example, according to the Fe-N thermodynamic equilibrium). diagram, 5.3÷5.75% N at the eutectoid transformation temperature) [6]. The specialized literature in the field, taking into consideration the Fe_4N phase, corrects the information according to which the iron atoms are distributed in a CFC-type network with an ordered distribution of nitrogen atoms in the centers of the elementary cubes (1/2 1/2 1/2) [6]. Thus, according to Kooi's claims, Somers, Mittemeier et al. [18-19] in general the solid solutions of the Fe-N system can be considered as consisting of two interpenetrated subnetworks, one being related to iron atoms and the other to nitrogen atoms; the iron sub-lattice is considered to be completely occupied by the atoms of this metal, and the one related to nitrogen constituted by the octahedral interstices of the iron network, partially occupied by nitrogen atoms and partially by vacancies. If in the case of solid solutions α-Fe[N] (CVC-type iron sublattice), or γ - Fe[N] (CFC-type iron sublattice), the nitrogen atoms are distributed more or less randomly in their own sublattice, in in the case of the phase $\gamma'\text{-}Fe_4N_{1-x}$ (CFC-type iron sublattice), respectively $\varepsilon\text{-}Fe_2N_{1-z}$ (compact hexagonal iron sublattice) the nitrogen atoms present an ordered distribution over large distances (LONG-Range Order of Nitrogen) in their own sublattice . In the presence of alloying elements, part of the iron atoms from the γ' and ε phases respectively is replaced by the atoms of the alloying elements, thus appearing complex nitrides of the type $(Fe,M)_4N$, $(Fe,M)_3N$, $(Fe,M)_2N$ etc. Remarkable results regarding the prediction by calculation, using specialized computer programs, of the conditions in which a certain phase composition of the nitrided layer can be obtained were obtained by various groups of researchers: Lahtin et.al [1-3,5], Hosseini et al [12-14], Keddam et al [15-17] and others.

2. The framework of the problem. Its solving

In strict accordance with the type of demands to which the nitriding product is subjected in operation, the phase composition of the nitrided layer will present at the thermochemical processing temperature one of the following sequence of phases: $\alpha_N \rightarrow \alpha$, $\gamma' \rightarrow \alpha_N \rightarrow \alpha$, $\varepsilon \rightarrow \gamma' \rightarrow \alpha_N \rightarrow \alpha$. Regardless of the situation analyzed, the stages of the calculation are similar, having however, a series of distinctive features. The calculation algorithm and respectively the computer program, generated to increase the efficiency in order to quickly design hard nitriding technologies, was generated considering a pure iron matrix and later customized for a complex matrix alloyed with molybdenum, aluminum and chromium of a steel improvement type Nitralloy 39MoAlCr15 - STAS 791/88 (Romanian standard) or equivalent DIN 1.8504 (average element concentration values: 0.39% C, 0.45% Mn, 1.5% Cr, 0.2% Mo, 0.32% Si, 0.9% Al. The input data of the anticipatory estimation program of the kinetics of the growth of nitrided layers obviously contain the chemical compositions of the metal matrices subjected to thermochemical processing and the conditions in which this is carried out - the temperature (for example, the temperature of 520˚C > 793K was chosen and respectively the medium: 100% ammonia). In order to control the phase composition of the nitrided layer, it is necessary to determine the correlation between the nitrogen potential of the atmosphere used - undiluted ammonia and its degree of dissociation at the processing temperature. Achieving this goal becomes possible through the rigorous correlation of the information obtained from the explanation of the dependence between the degree of dissociation of ammonia α_{NH3}, the nitrogen potential of the ΠN atmosphere and the overpressure in the working space of the thermal aggregate (p=1.012 atm) - rel.1, respectively the limits of demarcation of domains $\alpha_N \leftrightarrow \gamma'$ and $\gamma' \leftrightarrow \varepsilon$ (rel. 2, 3).

$$\pi_N = \frac{(1-\alpha)(1+\alpha)^{0,5}}{(1{,}5\cdot\alpha)^{1,5}} \cdot p_t^{-0,5} \tag{1}$$

$$\lg \pi_N^{\alpha\leftrightarrow\gamma'} = \frac{1120}{T} - 2{,}1 \tag{2}$$

$$lg\pi_N^{\gamma'\leftrightarrow\varepsilon} = \frac{1900}{T} - 2{,}3 \tag{3}$$

The variation in the degree of ammonia dissociation within the limits of 10÷90% determines a change in the nitrogen potential within the limits of 16.17 $atm^{-0.5}$ and 0.087 $atm^{-0.5}$ respectively (Fig.1).

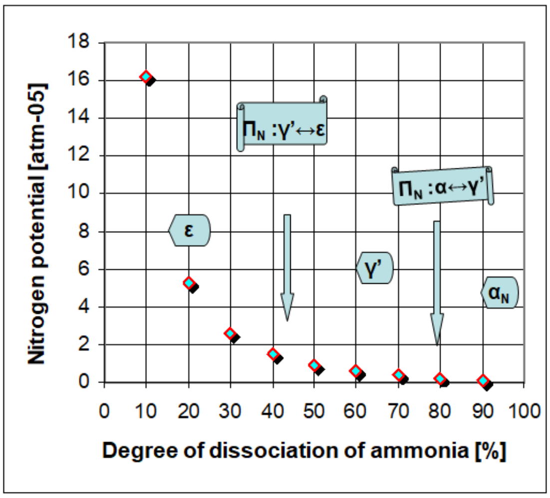

Fig.1 Variation of the nitrogen potential of the undiluted ammonia atmosphere depending on the degree of ammonia dissociation (ref.rel.1) T=ct=793K

Obs. Π_N (α↔γ') =0.205, Π_N (γ'↔ε) = 1.247, values calculated at T=793K.
The evolution of the nitrogen potential of the atmosphere used for nitriding - undiluted ammonia - as a function of the degree of ammonia dissociation is in apparent contradiction with the information from the specialized literature, it can be explained by taking into account the stepwise decomposition mechanism of ammonia (mechanism proposed by Gräbke) by successive loss of hydrogen atoms, associated with the ionic mechanism of nitriding, generator of NH_x^- type anionic complexes (where x = 3, 2, 1) [11], both extremely probable from an energetic point of view. The information provided by Fig. 1. they are in perfect agreement with those provided by the Lehrer diagram. For such values of the thermodynamic potentials of nitrogen in the α_N solid solution, respectively the solid solutions based on chemically defined compounds Fe_4N and $Fe_{2-3}N$, the phase equilibrium diagrams: nitrogen potential-degree of ammonia dissociation-temperature-phase in equilibrium [2,4] indicate the minimum necessary values of the degree of ammonia dissociation as 80% for the stabilization of the α_N phase, between 50% and 80% for the γ' phase, respectively 30% and 50% for the ε phase. Using the relationship between the potential of nitrogen and the degree of dissociation of ammonia at the processing temperature (rel.1), particularized for the strict case of the nitriding atmosphere composed of undiluted ammonia, the validity of these statements based on the phase balance diagrams is obtained. Thus, for a degree of dissociation of 30% and a total pressure in the working space of the enclosure where the nitriding takes place pt=1.012 atm [5] results in a value of the nitrogen potential Π_N = 2.628, higher than the one calculated as minimum necessary to ensure the stability of the ε phase; for α_{NH3}=60% (value in

the stability range of the γ'' phase) results in a nitrogen potential value of Π_N = 0.59 (value in the range (0.205÷1.247)), and for α_{NH3}=80% results in Π_N = 0.2029, lower value compared to the limit value (0.205). These values will be used in the future to specify the concrete conditions in which the hard nitriding is to be carried out in order to achieve one or another desired. It should be stated that the demarcation limits of the different phases in the Fe-N system determined with the help of rel.2; 3, calculated for the temperature of 793K are Π_N (α↔γ') = 0.205, respectively Π_N (γ'↔ε) = 1.247. They change relatively little with temperature variation within the limits characteristic of hard nitriding (773↔863K) - Fig.2.

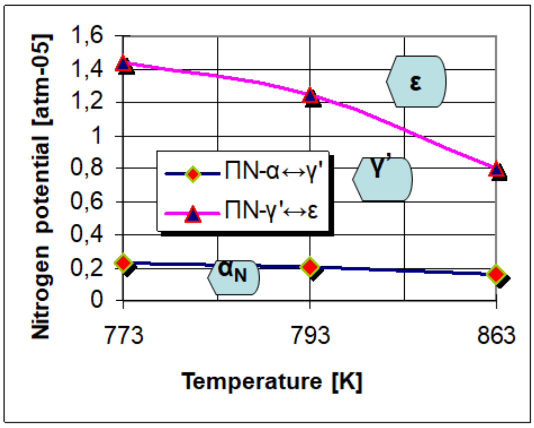

Fig.2 Variation of the potential of nitrogen corresponding to the limits of demarcation of domains αN ↔γ'respectively γ' ↔ ε when the temperature changes

The analysis of the information provided by the evolution of the demarcation limits of the α_N, γ' and ε phases with temperature variation lead to the conclusion that they are much more stable in the case of the α_N↔γ' limit compared to γ'↔ε. The explanations are related to the concentration limits between which the phases in question are found.

A) Phase sequence $\alpha_N \rightarrow \alpha$;

The desired can be achieved, according to previous estimates, under the conditions: $\pi_N^{\alpha} < \pi_N^{\gamma'} = 0.2029$, α_{NH3}=80%.

The following aspects of interest are taken into analysis.

- How the size of the area of the nitrided layer composed exclusively of nitroferrite evolves over time.
- How is nitrogen distributed over time in a nitrided layer with such a phase composition.

It starts with the simplified solution of Fick's differential equation obtained by analytical and criterion solution in limit conditions of order III.

$$\theta = \frac{C(x,t)-C_0}{C_{lim}-C_0} = erfC\frac{x}{2\sqrt{D_N^{\alpha}\cdot t}} \qquad (4)$$

where $C_{(x,t)}$ is adopted as the maximum value of nitrogen in nitroferrite at 793K

$$C_{(x,t)} = C_{Nmax}{}^{\alpha} = \exp(-4575/T+3) = 0{,}0627\%\ N \quad [4] \qquad (5)$$

C_{lim} - represents the maximum nitrogen concentration in nitroferrite corresponding to the precalculated nitrogen potential, Π_N=0.2029. C_{lim} results from the relationship between nitrogen potential and temperature, respectively nitrogen concentration:

$$\lg[N]=\lg\Pi_N-4400/T+5{,}1 \qquad [2]\ (6)$$

Result % N_{max}=C_{lim}=0.07227%

Co - initial concentration of nitrogen in the layer (considered 0%N)

$D_{N\alpha}$ - the diffusion coefficient of nitrogen in nitroferrite at the thermochemical processing temperature (793K)

$$D_{N\alpha}=6.60\cdot 10\text{-}3\exp(-18600/RT) \qquad (7)$$

R=1.986cal/mol·K.

Result: $D_N\alpha$=4.93·10-8cm^2/s

erfcY=1-erfY function complementary to the Gaussian error function.

For different values of the holding time at the nitriding temperature, information can be obtained regarding the size of the nitroferrite zone (Fig.3).

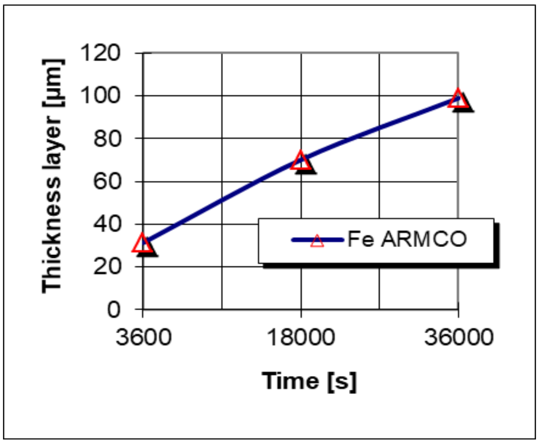

Fig.3 Variation over time of the size of the nitroferrite zone obtained by nitriding pure iron at 793K, under the following conditions:
$\pi_N^{\alpha} < \pi_N^{\gamma'} = 0{,}2029$, α_{NH3}=80%

Using the same solution of Fick's differential equation (eq.4) and considering the fact that the calculated maximum value of the nitrogen concentration in nitroferrite (C_{lim}) is 0.0627% (rel.5), the evolution over time of the concentration can be determined of nitrogen in any microvolume of interest in the layer. In the particular situation in which it is of interest, for example, the evolution over time of the concentration of nitrogen in nitroferrite, at a distance of 10 μm from the surface, equation 5 will take the following particular form (rel. 8):

$$\frac{C(10\mu m;t)}{0{,}0627} = erfC\frac{0{,}001}{2\sqrt{4{,}93\cdot 10^{-8}\cdot t}} \tag{8}$$

with the help of which the imposed desired can be achieved (Fig. 4).

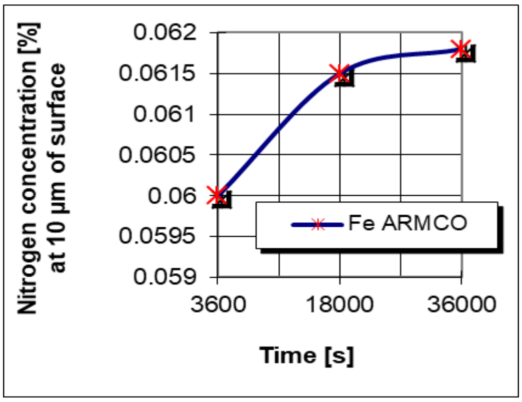

Fig.4 Variation over time of nitrogen concentration in nitroferrite measured at a distance of 10μm from the surface

**The alloying of metallic matrices has implications both on the degree of solubilization of nitrogen in nitroferrite and on the diffusion coefficient. The type and concentration of the alloying elements in the metallic matrix can be considered through the activity coefficients of these elements ($\prod \gamma_{EA}$ -the cumulative effect of of their presence - used to highlight the effect of the presence of alloying elements on the limit concentration of nitrogen in nitroferrite), respectively $\eta^{\alpha}_{D_N}$- (used to highlight the effects of the presence of alloying elements on the value of the diffusion coefficient)[1;2]. In the particular case of the improvement alloy steel 39MoAlCr15 $\prod \gamma_{EA} = \gamma_C \cdot \gamma_{Cr} \cdot \gamma_{Mo} \cdot \gamma_{Al} = 0{,}304$, which determines a substantial increase in the solubilization capacity of nitrogen in $C_{N_{max}}^{\propto aliat} = \frac{C^{\propto}_{N max}}{\prod \gamma_{EA}} = 0{,}223\ \%$ nitroferrite (compared to 0.0627% in the case of pure iron), $\eta_{D_N}^{\alpha aliat} = 0{,}0098$ and also implies a considerable change in the diffusion coefficient in alloyed nitroferrite

$$D_N^{\alpha aliat} = 6{,}60\cdot 10^{-3}\exp(-\frac{18600}{RT})\cdot \eta_{D_N}^{\alpha aliat} = 0{,}048\cdot 10^{-8} cm^2/s$$

(compared to $4.93\cdot 10^{-8}$ cm^2/s).

B) Phase sequence $\gamma'>\alpha_{N}.>\alpha$

B1) γ' -Fe_4N_{1-x} phase

The desired can be achieved, according to previous estimates, under the conditions: Π_N=0.59; α_{NH3}=60% for T=793K-according to the previously stated reasons.

The following aspects of interest are analyzed.

-a) How the size of the area of the nitrided layer composed exclusively of the phase evolves over time - Fe_4N_{1-x}-$\delta_{\gamma'}$=f(t)

-b) How is nitrogen distributed over time in a Fe_4N_{1-x} compound area

a)According to the methodology of Hosseini et.al [12÷14], the size of the solid solution zone that is the basis of the compound γ'-$\delta_{\gamma'}$ varies over time according to a dependence of the type:

$$\delta_{\gamma'} = [\sqrt{(b_\varepsilon + 0{,}02\sqrt{D_\alpha})^2 + 0{,}2D_\gamma} - (b_\varepsilon + 0{,}02\sqrt{D_\alpha})] \cdot \sqrt{t} \tag{9}$$

where: $b_\varepsilon = \sqrt{4D\varepsilon - 0{,}2\ D_{\gamma'}}$ represents the layer growth rate constant.

$$D_\varepsilon = 2{,}1 \cdot 10^{-8}\exp(-\frac{93517\frac{J}{mol}}{RT})$$

the nitrogen diffusion coefficient in the ε phase; R=8.3145 J/mol·K

$$D_{\gamma'} = 1{,}7 \cdot 10^{-9}\exp(-\frac{64000\frac{J}{mol}}{RT})$$

the nitrogen diffusion coefficient in the γ phase D_α- nitrogen diffusion coefficient in nitroferrite (calculated in the previous step). At the thermochemical processing temperature T=793K, the following values will result:

$D\varepsilon = 1{,}45 \cdot 10^{-10}\ cm^2/s\ ;\ D_{\gamma'} = 1{,}0349 \cdot 10^{-9}\ cm^2/s\ ;\ D_\alpha = 4{,}93 \cdot 10^{-8}\ cm^2/s\ ;\ \rightarrow\ b_\varepsilon = 2{,}009 \cdot 10^{-6} \cdot \sqrt{t}[cm \cdot s^{0{,}5}]$

The graphic expression of time variation of the size of the γ'-Fe_4N_{1-x} compound area is represented in Fig.5.

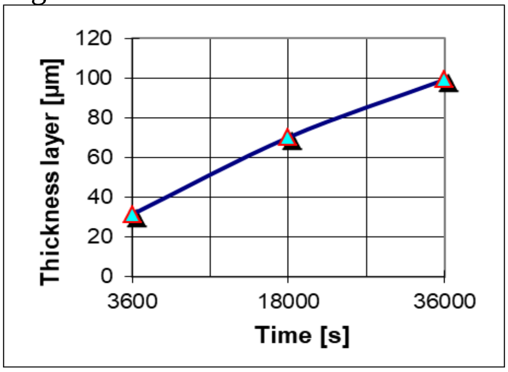

Fig.5 Variation over time of the size of the γ'-Fe_4N_{1-x} compound area

(b) To describe the time variation of the nitrogen concentration on the γ' -Nγ' phase section, one can refer to the solutions of Hosseini et.al [12]:

$$N_{\gamma'} = \frac{0{,}14 \cdot \lambda_{\varepsilon} + 5{,}90 \ \cdot \lambda_{\gamma'}}{\lambda_{\gamma'}} - \frac{0{,}28\sqrt{D\gamma' \cdot t}}{\lambda\gamma'} \cdot \mathrm{erf}\left(\frac{x}{2\sqrt{D_{\gamma'} \cdot t}}\right) \tag{10}$$

Where the size of the compound area γ’ [µm]:

$$\lambda\varepsilon = \sqrt{(4 \cdot D\varepsilon - 0{,}2 \cdot D\gamma') \cdot t} \tag{11}$$

$$\lambda\gamma' = 0{,}5\left[-\left(b\varepsilon + 0{,}02\sqrt{D\alpha}\right) + \sqrt{\left(b_{\varepsilon} + 0{,}02\sqrt{D_{\alpha}}\right)^{2} + 0{,}2D_{\gamma'}}\right] \tag{12}$$

Result: $\lambda\varepsilon = 1.93 \cdot 10^{-5} \cdot \sqrt{t}$; $\lambda\gamma' = 1.25 \cdot 10^{-3} \cdot \sqrt{t}$ and respectively:

$N_{\gamma'} = 5{,}902 - 7{,}206 \cdot 10^{-3} erf \frac{x \cdot 10^{5}}{6{,}434\sqrt{t}}$

Table 1

Distribution of nitrogen concentration in time (T=ct=793K) on the section of the compound area γ'- Fe_4N_{1-x}

Time,s	***The size of the compound area γ', µm***		
	1,206	*2,69*	*3,81*
3600	5,899	-	-
18000	5,899	5,899	-
36000	5,9	5,899	5,899

A constant concentration of nitrogen was found on the section of compound γ' (~5.9%) when the holding time varied between 1-10 hours (T=ct=793K).

B2) Phase α_N

Nitrogen distribution in the nitroferrite (Nα) solid solution substrate.

$$N_{\alpha} = 12{,}3exp - \frac{4175{,}9}{T}\left(1 - erf\frac{x}{2\sqrt{D_{\alpha} \cdot t}}\right) \quad [12] \tag{13}$$

At 793K, relation (13) takes the particular form: $N_{\alpha} = 0{,}063\left(1 - erf\frac{x}{2\sqrt{D_{\alpha} \cdot t}}\right)$ with the help of which the correlations between the nitrogen concentration in nitroferrite estimated at different distances in relation to the interface γ'/α_N can be calculated at different nitriding temperature (793K) (table 2).

Table 2

Nitrogen distribution in the nitroferrite substrate

	Distance in relation to the γ'/α_N interface, cm		
Time,s	***0,003***	***0,005***	***0,010***
3600	0,055%	0,0498%	0,0375%
18000	0,0594%	0,0570%	0,0511%
36000	0,0604%	0,0587%	0,0546%

C) Phase sequence ε>γ' > α_N>α

The desired can be achieved, according to previous estimates, under the conditions: $\Pi_N \geq 2.628$, $\alpha_{NH3} \leq 30\%$ for T=793K-according to the previously stated reasons.

The following aspects of interest are analyzed.

-a) How the size of the area of the nitrided layer composed exclusively of the Fe_2N_{1-z} - ε phase evolves over time

-b) How is nitrogen distributed over time in a Fe_2N_{1-z} - ε compound area

(a) Time variation of the size of the solid solution zone based on an ε-Fe_2N_{1-z} compound (δ(ε))

$$\delta\varepsilon = \sqrt{\left(4 \cdot D_\varepsilon - 0{,}2 \cdot D_{\gamma'}\right) \cdot t} \quad [12] \qquad (14)$$

where:

$D\varepsilon = 1.45 \cdot 10^{-10}$ cm^2/s and $D\gamma' = 1.0349 \cdot 10^{-9}$ cm^2/s.

For different values of the holding time in the range of 1-10 hours, it is found that the size of the compound area ε varies in the range of 11.58÷36.62μm (Fig.6).

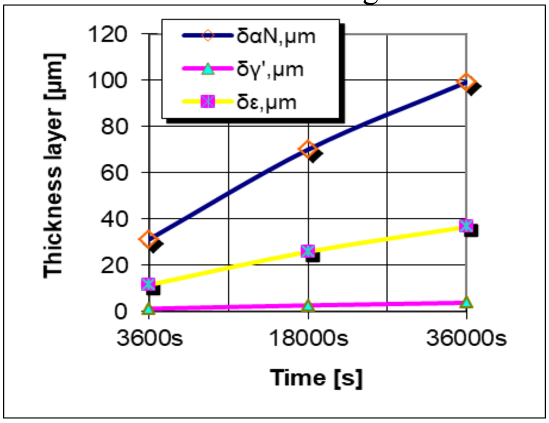

Fig.6 Comparative analysis of the growth kinetics over time, at T=ct =793K, of the structural components of the nitrided layer obtained in the case of pure iron.

(b) Variation over time, at different distances in relation to the product-environment interface, of the nitrogen concentration (Nε) of the solid solution based on the compound ε-Fe_2N_{1-z}.

It can be estimated using the relation:

$$N_{\varepsilon} = N_S + \frac{7{,}712 - N_S}{erf\frac{\lambda_S}{2\sqrt{D_{\varepsilon}\cdot t}}} \cdot erf\frac{x}{2\sqrt{D_{\varepsilon}\cdot t}} \quad [12] \qquad (15)$$

where $\lambda\varepsilon$ has the same meaning as δ_{ε} from rel.14 ($\delta_{\varepsilon}=K_{\varepsilon}\cdot\lambda_{\varepsilon}$, for a value of the coefficient $K_{\varepsilon}=1$-correction coefficient), N_s-nitrogen concentration on the surface of the ε phase is assumed to be 8% at the processing temperature.
It follows that, for $\lambda\varepsilon=1.93\cdot10^{-5}\cdot\sqrt{t}$; $D_{\varepsilon}=1.45\cdot10^{-10}$ cm^2/s >> $N_{\varepsilon}=8-0.388$ erf $(x\cdot10^5)/(2.408\cdot\sqrt{t})$ (tab. 3).

Table 3

Time distribution of nitrogen on the thickness of the compound ε

Time,s	*Distance in relation to the surface, cm*		
	0,001	*0,002*	*0,003*
3600	7,739%	-	-
18000	7,868%	7,76%	-
36000	7,905%	7,82%	7,749%

3. Conclusions

1. Obtaining a monophasic structure of nitroferrite requires high values of the degree of ammonia dissociation (if the atmosphere contains exclusively ammonia), therefore low values of the nitrogen potential of the atmosphere. It was also certified by calculation that, in the presence of the elements of alloying increases the solubility of nitrogen in the alloyed nitroferrite but drastically decreases the rate of layer formation.
2. By changing the requirements imposed on the phase composition of the layer (from a monophasic layer to a biphasic or triphasic one), it determines a change in the activity of the environment (its nitrogen potential) ensured by the variation of the degree of dissociation of ammonia from the working space of the heat aggregate), with immediate implications on the kinetics of each structural component of the layer.
3. The generated algorithm considers the entire sequence of steps that must be followed to ensure a certain phase sequence in the nitrided layer, and a certain size associated with each phase.

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