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KINETIC PARAMETERS-ANALYSIS AND PROGNOSIS ITEMS OF THE NITRIDING PROCESS

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The theoretical base of the issue

Baram [1] gives as main use for the extended equation of the heterogeneous reactions' kinetics, (equation 1), to describe the phenomena that take place during the thermo-chemical processing of metals and alloys. The equation was obtained using the masses' action law and the phenomenological dependency of the time related variation of the inter phases separation areas' size (equation 2) in solid bodies undergoing thermo-chemical processes.

$$K^* = \frac{(1-\alpha)V^n}{S_0 t^{1-\alpha}} \int_{m_0}^{m} \frac{dm}{[CV-(m-m_0)]^n} \tag{1}$$

$$S = K' S_0 \frac{1}{t^\alpha} \tag{2}$$

where: S_0 represents the initial area of the solid phase; m_0 and m the mass of the solid phase at the beginning, respectively in the moment t of the process; V-the volume of the phase undergoing the processing; C – the limit concentration of the saturation element in the solid phase (the value will take into account the initial concentration of the element, respectively the chemistry of the process) n the grade of the inter phase reaction, depending on the type of the cementing element; α constant (kinetic parameter), depending on the individual property of the reacting phases; in case α→0, (1-α)→1, the process develops in the kinetic domain, the reactions on the interface reaction medium – metallic product are dominant and the inter phase reaction area is considered to remain unchanged; in case α→1,(1-α)→0, the speed of the layer forming process is limited by the speed at which develop the diffusion processes within the metallic matrix, the later ones representing the dominant processes, and the inter phase separation area changes; K^* – the constant of the process speed; its measuring units are the ones corresponding to the multiplication: $m^{1-n} V^{n} S^{-2} t^{\alpha-1}$, where *m*, *V*, *S* and *t* are the measuring units for mass, volume, area and time.

In case there is an exceeding of the cementing element in the medium, the variation in time of its concentration can be ignored (the most frequent case in the thermo-chemical treatment practice), the grade of the inter phase reaction becomes zero (*n*=0), and through the integration of the equation 1 results the relation (equation 3)

$$K_0^* = \frac{(1-\alpha)\Delta m}{S_0 t^{1-\alpha}} \tag{3}$$

where: $\Delta m = m - m_0$ represents the mass variation of the solid phase; If we consider the relation :

$$\delta = K' \Delta m \tag{4}$$

where: δ represents the size of the cemented layer, results:

$$K_0 = \frac{(1-\alpha)\delta}{t^{1-\alpha}} \tag{5}$$

where:
$$K_0 = K_0^* K' S_0 \tag{6}$$

The relations 3 and 5 are useful to ***calculate the constants of the speeds at which the thermo-chemical processing develop*** depending on the values of the mass variations or of the cemented layer size variations in time for the products being processed, the same relations in logarithmic coordinates [lg(Δm)-lgt, respectively lg δ -lgt] represent straight lines with tangents of the of the angles of inclination in relation with the lgt abscissa, themselves equal with the (1-α). This observation ensures the possibility to

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determine $(1-\alpha)$ and K_0^* (or K_0) using very few experimental data related to the size variation of the cemented layer or the mass variation recorded during a certain technological process.

Relation 4 allows determining the ratio between the cemented layer size and its mass variation, $\delta / \Delta m$ a constant for a certain process being analyzed.

The process ***activation energy*** [equation 7] can be calculated using the data related to the thermo-chemical process' ***average speeds***, determined at two temperatures, for the same amount of time.

$$E = \frac{\lg W_2 - \lg W_1}{\frac{1}{T_1} - \frac{1}{T_2}}.4{,}575 \qquad (7)$$

where: E(Kcal/mol)-represents the thermo-chemical process' activation energy; W$_1$ ($\frac{mg/cm^2}{ora}$) – the process' average speed, determined at temperature T_1, after the period of time t; W$_2$ ($\frac{mg/cm^2}{ora}$)-the process' average speed, determined at temperature T_2, after the period of time t;

$$W_t^T = \frac{K_0^*}{(1-\alpha)t^\alpha}; \text{ or } W_t^T = \frac{K_0}{(1-\alpha)t^\alpha} \qquad (8)$$

depending ob requirement the process' average speed can be expressed in $\frac{mg/cm^2}{ora}$, or in $\frac{\mu m}{ora}$.

Unfortunately, the data required for rigorous calculation in order to establish the thermo chemical treatment operations' parameters are almost nonexistent. The separate data from the specialty literature, related to values as ***D (the diffusion coefficient value), h (mass transfer relative coefficient) and K (adsorption speed constant)*** need to be verified for each situation taken aside. Knowing these values allows to understand the influence of various technological factors and to gain knowledge about ways to control thermo chemical processes. It is difficult and labor intensive to determine through experiments the values of interest D, h and K. A substantial help in resolving this issue comes from the graphic expressions of the criterial solutions of Fick's differential equations, $\Theta = f(Ti = h\sqrt{D.t}; \frac{x}{2\sqrt{D.t}})$ and respectively $\Theta = f(h\sqrt{D.t}; h.x)$ (where $\Theta = \frac{C_{x,t} - C_0}{C_{\lim} - C_0}$ [2; 3].

In order to determine the values of interest *D*, *h* and *K*, one can use the data related to the correlation between the size of the diffusion area and the isothermal maintaining time at the thermo chemical processing temperature, the same data that were used also to estimate the constants of the speeds at which the thermo chemical process develops, its activation energy and its average speeds of development.

In order to determine the values *D*, *h* and *K* related to a certain type of thermo chemical processes, undergoing in rigorously set conditions, it is necessary to go through the following phases; determine the relative concentration Θ; graphic estimation of the time after which the time variation curve of the size of layer enriched with the element transferred through diffusion from the medium (the cementing element), separates form the abscissa (in this application this is time t_1); from the graphic expression of Fick's differential equation solution, obtained by resolving it in grade II limit conditions, $\Theta = f(Ti = h\sqrt{D.t}; \frac{x}{2\sqrt{D.t}})$, for $\frac{x}{2\sqrt{D.t}} = 0$ and the value of the relative concentration Θ previously determined, the value $h\sqrt{D.t}$ =Ti (Tihonov criterion) can be determined; for strictly set thermal processing conditions (temperature and medium conditions) the values *D*, *h* and *K* are constant, thus it can be approximated $Ti_1 = Ti_x\sqrt{\frac{t_1}{t_x}}$; the Tihonov criterion's values, determined after various periods of isothermal maintaining, t_x, along with the value corresponding to the relative concentration Θ, allow to determine the values corresponding to the Biot criterion ($Bi = h.x$) (the graphic expression $\Theta = f(h\sqrt{D.t}; h.x)$ will be used); the values of the mass transfer relative coefficient, *h*, will be calculated starting from the graphic determined values for the Biot criterion and respectively the size of the diffusion layers, x, in relation with them; the value of the diffusion coefficient D, will be calculated, taking into account the estimated value of the Tihonov criterion (Ti_1) and the one referring to the mass transfer relative (average) coefficient:

$$D = \left(\frac{Ti_1}{\bar{h}}\right)\frac{1}{3600.t_1} \quad (\mathrm{cm}^2/\mathrm{s}) \tag{9}$$

the value of the adsorption speed constant will be calculated, K (cm/s)

$$K=h.D \tag{10}$$

The calculation of the kinetic parameters and their significance

***Materials and equipment used for experiments**

Experimental test intended to gather a minimum of information related to the kinetics of the gaseous nitriding process applied to the pure iron parts (Fe-ARMCO) and respectively to an alloyed steel for improvement intended for nitrding-nitralloy-39MoAlCr15 (0,38%C; 45%Mn; 0,25%Si;1,4%Cr;0,20%Mo; 1,1%%Al). The nitralloy samples were used in an improved status (quenching 930°C/oil followed by tempering 630°C/oil). he test samples had the dimensions Ø10x15mm and were subsequently nitrided in ammonia, in a vertical muffle furnace, with an useful space of Ø300x600mm, electrically heated (*P*=24KW).

By choosing two materials, beside verifying the calculation methods for the kinetic parameters, it was intended to determine the effect of the ferrous matrixes alloying on the level of kinetic parameters.

***Calculation of the kinetic parameters**

The experimental data used for the calculation of the kinetic parameters, using the Baram method are stated in table 1, for pure technical iron, for periods of isothermal maintaining of 4, 8 and 12ore, at a nitriding temperature of 500° C, respectively 580°C. Using the calculated values of the reaction speeds, K_0^* and K_0 and of the kinetic parameter α, can be anticipated by calculation the size of the nitrided layers, respectively the mass variations of the samples undergoing thermal processing, for any other value of time for isothermal maintaining at the processing temperature.

Therefore:

$$\left(\frac{\Delta m}{S_0}\right)_{calc} = \frac{K_0^* t^{1-\alpha}}{1-\alpha}\text{, from relation 3} \tag{11}$$

respectively $\delta_{calc} = \dfrac{K_0 t^{1-\alpha}}{1-\alpha}$, from relation 5 (12)

where K_0^* and K_0 represent their average values (arithmetic average of the values obtained using experimental data).

The analysis of the data related to the kinetic parameters of the gaseous nitriding process applied to pure technical iron underlines the following aspects:

– at 500°C the nitrogen cementing process develops in the kinetic range, (1–α)>0,5, therefore the phase of the process that slows its development speed is represented by the reactions on the inter phases separation level;

– at 580°C the development speed of the nitrogen cementing process is limited by the intensity of the diffusion within the metallic matrix, (1-α)<0.5;

– the nitrided layer growth speeds increase with the increase in nitriding temperature, but they decrease noticeably in time;

– the nitriding process activation energy in the range of temperatures 500÷580°C, determined using the average speed of the process, is close to the data existing within the specialty literature related to this value [4; 5].

Following the previously presented succession of calculations necessary to determine the diffusion coefficient, the mass transfer relative coefficient and respectively the adsorption speed constant's value, based on a minimal number of experimental data existing in table 1, related to the nitriding of pure technical iron, the following values were obtained (table. 2).

Table 1. Summary of the pure technical iron nitriding kinetic parameters (using Baram method)
A) nitriding conditions: $500^oC;\alpha_{NH3}=40\%$

t, ore	**$[\Delta m/S_0]_{exp}$**	**$\delta,_{exp}$**	**$[\Delta m/S_0]_{calc}$**	**$\delta,_{calc}$**	**1-α**	K_0^*	K_0	**W**	**$E_{500-580oC}$**
4	0,89	133,5	-	-	0,65	0,235	35,23	33,4	17,0
8	1,46	222,8	-	-		0,245	37,51	27,9	12,0
12	***1,83***	***272,8***	-	-		***0,236***	***35,28***	***22,7***	***11,6***
20	-	-	*2,56*	*388,3*		$\overline{K_0^*}$ =0,238	$\overline{K_0}$ =36,01	*19,4*	$\overline{E_{\overline{W}}}$ =14,1
30	-	-	*3,34*	*505,4*				*16,8*	

Note. Measuring units:: $\Delta m/S_0$=mg/cm^2; δ-μm; K_0^*= mg/[cm^2.hour $^{1-\alpha}$]; K_0 =μm/ hour $^{1-\alpha}$; δ/Δm=[μm.cm^2]/mg;W=μm/hour;E=Kcal /mol

B)Nitriding conditions: 580^oC; α_{NH3}=40%

***t*, ore**	**$[\Delta m/S_0]_{exp}$**	**$\delta,_{exp}$**	**$[\Delta m/S_0]_{calc}$**	**$\delta,_{calc}$**	**1-α**	K_0^*	K_0	**W**
4	2,52	374,5	-	-	0,34	0,535	79,6	93,7
8	3,06	463,8	-	-		0,512	77,7	57,9
12	3,68	553	-	-		0,536	80,6	45,9
20	-	-	*4,29*	*645,8*		$\overline{K_0^*}$ =0,527	$\overline{K_0}$ =79,3	*32,3*
30	-	-	*4,92*	*741,3*				*24,7*

Table 2. Summary of D, h, and K kinetic parameters calculation
Nitriding temperature 520^oC

t_x, hours	Ti$_{calc}$=Ti$_1$: $\sqrt{\frac{t_1}{tx}}$	X,cm	hx	h,cm^{-1}	$\overline{h}$,cm^{-1}
2	0,140	0,0148	0,10	6,75	9,60
4	0,353	0,0193	0,20	10,36	
6	0,288	0,0238	0,25	10,50	
8	0,250	0,0282	0,30	10,63	
10	0,230	0,0327	0,32	9,78	
$D=\left(\frac{0,07}{9,60}\right)^2 . \frac{1}{3600.0,5} = 2,95.10^{-8} \cong 3.10^{-8} \text{cm}^2/\text{s}$ $K=\overline{h} * D$=9,60*2,95*10^{-8}=28,3*10^{-8} cm/s					

The calculated values are in close accordance with the data from the specialty literature related to the nitrogen diffusion in non alloyed ferrite [6].

In case of alloyed matrixes, as for example improvement alloyed steel 39MoAlCr15, the nitrogen diffusion process kinetics in clearly modified, an aspect confirmed by both the experimental data and the corresponding values of the calculated kinetic parameters (tables 3; 4;).

Comparing the results obtained (table 3) with the ones correspondent to the pure technical iron nitriding (table 1) it can be noted that in both cases, at low temperatures, the saturation process phase that develops at the slowest speed is the one in the cementing media [(1–α)>0,5], and that at high temperatures, $\geq 550^oC$, the layer forming speed will be hindered by the diffusion processes within the metallic matrix [(1-α)<0,5]. It can also be observed the diffusion speeds and the reaction speeds' constants in the case of

39MoAlCr15 steel are substantially lower than the ones recorded in the case of pure technical iron nitriding. Implicitly, given the connection between the reaction speed's constant and the process activation energy, a decrease of the reaction speed's constant value will cause an increase of the activation energy.

Table 3. Summary of the 39MoAlCr15 nitralloy nitriding kinetic parameters (using the Baram method)
A)Nitriding conditions; 500^oC;α_{NH3}=40%

***t*, hours**	**$\delta_{\mu m}$, exp**	**$\delta_{\mu m}$, calc**	**1–α**	**K_o $\frac{\mu m}{ora^{\alpha-1}}$**	**W, $\frac{\mu m}{hour}$**	**E 500-600^{o}C, Kcal/mol**
10	200	-	0,608	29,98	19,99	9836,3
20	300	-		29,51	14,99	8214,8
30	390	-		29,98	12,99	8023,7
40	-	458,3		$\overline{K_0}$ =29,59	$\overline{W}$ =15,99	$\overline{E}$ =8691,6
50	-	525				

B) Nitriding conditions: 600^oC;α_{NH3}=40%

***t*, hours**	**δμm,$_{exp}$**	**δμm,$_{calc}$**	**1–α**	**K_o, $\frac{\mu m}{hour^{\alpha-1}}$**	**W, $\frac{\mu m}{hour}$**
10	410	-	0,487	65,06	41
20	599	-		61,82	27,3
30	700	-		65,05	23,33
40	-	792		$\overline{K_0}$ =63,97	$\overline{W}$ =30,54
50	-	883			

Table 4. Summary of D, h, and K kinetic parameters calculation
T=520^{o}C; α_{NH3}=40%

t_x, hours	$Ti_{calc}=Ti_1: \sqrt{\frac{t_1}{tx}}$	*X*,cm	*hx*	*h*,cm^{-1}	$\overline{h}$,cm^{-1}
10	0,223	0,0251	0,30	11,95	14,8
12	0,204	0,0273	0,40	14,65	
20	0,158	0,0358	0,55	15,36	
30	0,129	0,0456	0,80	17,20	
$D=\left(\frac{0,07}{14,8}\right)^2 . \frac{1}{3600.0,5} = 12,43.10^{-9} \cong 1,2.10^{-8} cm^2/s$ $K=\overline{h} * D$ =14,8*12,43*10^{-9}=18,4*10^{-8} cm/s					

The information gathered regarding the *D*, *h* and *K* kinetic parameters have a very distinct importance both in theory and in practice: in theory, they certify that by ferrite alloying, the diffusion coefficient decreases (2,5 times compared to the value recorded for pure technical iron nitriding) this in turn causing the increase in the mass transfer relative coefficient, h. The increase of the mass transfer relative coefficient at the same time with a decrease of the diffusion coefficient and a constant value of the adsorption constant leads to the conclusion that in case 39MoAlCr15 steel nitriding the probability of type ε nitrogen rich phases forming on the surface is much greater than in the case of pure technical iron nitriding; in practice, it is necessary to modify the activity of the atmosphere used for nitrididng in such way that the process of nitrogen rich phases forming is strictly controlled, thus avoiding the appearance of the networks generated by these phases and therefore the inconveniences related to them. In this context, the specialty literature confirms by practical observations the theoretical reasoning previously presented: an increase in the degree of ammonia dissociation up to 60÷65% (even 70% at a temperature towards 600^{o}C) does not have a significant effect on the macro hardness and respectively on the size of the nitrided layer obtained in certain processing conditions (temperature-time) but greatly reduces the tendency of the type ε nitrogen rich phase to appear.

Conclusion

The kinetic parameters of any thermo chemical process can represent efficient analysis and prognosis instruments for the said processes. It is possible to determine them in an analytical manner using the heterogeneous reactions' kinetics extended equation and using minimum o information related to process kinetics, gathered through experiments. Thus it can be obtained data referring to the phase of the process that develops at the lowest speed (using the kinetic parameter α), the reaction speed constant, process activation energy, layer forming current speed.

The values of the diffusion coefficient, the mass transfer relative coefficient and of the adsorption speed constant can be estimated using the graphic expressions of the criterial solution to Fick's equation, again using minimum o information related to process kinetics, gathered through experiments.

The data referring to the two materials used for study, Fe-ARMCO and 39MOALCR15 are in accordance with the information from the specialty literature and confirm the validity of the analytical methods of calculation for the kinetic parameters, presented in this paper.

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Summary

The lack of practical information regarding the kinetics of a thermal process can be compensated by estimating the kinetic parameters of the process. Using the methodology imposed by Baram, as well as to one resulted form the use of the solution to the Fick's differential equation, through a minimum number of experiences, can be obtained sufficient information to estimate the process' average speed, its activation energy, the diffusion coefficient, etc., and forecast the saturation effects in conditions different from those used for experiments to obtain preliminary information. This paper presents the experimental results obtained during the nitriding of pure technical iron and respectively of a nitraloy type alloyed steel for improvement, regarding the kinetic of the nitrided layers' growth and starting from this results, the calculated values of the of the kinetic parameters, respectively the forecasted values of the kinetics in conditions different from those effectively used during experiments.