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PREDICTIONS REGARDING THE EFFECTS OF NITRIDING APPLIED TO STEELS IN THE ABSENCE OR PRESENCE OF TITANALITING

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The paper presents the results of statistical processing of information on the growth kinetics of nitrided layers in the case of Fe-ARMCO and 34CrAlMo5(EN10085) nitriding steel grade, where nitriding is performed before (final process) or after titanaliting. It has been conclude that, if nitriding does not follow titanaliting, the layer growth kinetics is strongly influence by temperature, the degree of ammonia dissociation degree in the range of 45-70%, showing a significant influence especially at high temperatures. If nitriding succeeds titanaliting, the ammonia degree of dissociation influence is constantly significant throughout the temperature range tested (540-620^{0}C).

For the two metallic materials investigated and the two variants of thermochemical processing analyzed, the mathematical models of the interactions between nitriding temperature, the degree of ammonia dissociation and the total size of the nitrided layer were explained, thus becoming useful tools for predicting nitride layer thickness.

Keywords: nitriding, titanaliting and nitriding, layer growth kinetics, activ experiment, statistical data processing.

1. Introduction

A multitude of experimental researches discuss the effects of nitriding, in gaseous media or plasma, subsequent to titanization [1-3], on a wide range of characteristics of interest (tribological behavior, corrosion resistance, etc.). The conclusions of our own experimental researches on the combined effect of titanaliting (simultaneous saturation with titanium and aluminum) followed by nitriding (in partially dissociated ammonia) [4], lead to the idea that such an

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association is beneficial to the resistance characteristics due to an increase of the proportion of hardening phases in the surface layers, but does not ensure an intensification of the layer growth kinetics. The explanation of this last statement is related, in the opinion of the authors [4], to the fact that the flux of atoms / anionic complexes [9-11] adsorbed in the surface from the nitriding medium and available used to create the internal nitriding area, is diminished in the process of converting the defined chemical compounds from the titanalited layer into nitrides, the more intense as the metal matrix contains more elements with high affinity for nitrogen.

A special interest for the application of thermochemical treatments is the knowledge of the strict correlation between the nitriding temperature and the degree of ammonia dissociation, as well as the total layer thickness in which nitrogen diffusion occurred (in the absence or presence of a titanalied layer).

2. Theoretical Analysis, Methods and Experimental

The explanation of the correlation of interest between the defining quantities of the gaseous nitriding process in partially dissociated ammonia atmosphere and the process effects, in the absence or presence of a titanalited layer, expressed by the total nitrided layer thickness, becomes possible by experimental programming. The programming method used in the research was the central compositional orthogonal of the second order [5-7], the method of the active experiment.

The active experiment method involves the use of statistical methods in all stages of the experiments, as follows: prior to the experiments to establish the number of experiments required and the concrete conditions for their performance, during the experiments to process the results and finally (after the experiments), to outline the necessary conditions in order to achieve an optimum (if this stage is considered necessary).

The materials used in the research were Fe-ARMCO and 34CrAlMo5 (EN10085) nitriding steel grade. Samples of the two materials, with dimensions of 6x10x20 mm, after degreasing with isopropyl alcohol were subjected to titanaliting in a powdery solid medium composed of 30% mixture (35%TiO_2 + 2%Al + 2%CaF_2 + 2%Mg), 65%Al_2O_3 and 5%NH_4Cl, at 1050^0C, for 2 hours and after nitriding in partially dissociated ammonia ($\alpha_{NH3} \in$ [45-70%]), at different temperatures in the range of $540 \div 620^0$C, for 4 hours. The titanaliting was performed with the samples packed in the mixture intended for this processing, in refractory steel plate boxes, sealed with clay latches, in an electric chamber type oven (10 KW), with dimensions of the useful heating chamber 300x180x180 mm, provided with an automatic system for temperature regulation and control, and nitriding in a vertical electric oven (8 KW) with a retort in diameter of 190 mm and a height of 600 mm, provided with an automatic temperature regulation and control system. The degree of ammonia dissociation was controlled by the titration method.

In order to perform microscopy investigations (phase identification, dimensions of structural components), the microstructure was highlighted by chemical etching with Nital 3% reagent. Optical microscopy investigations were performed on an image analysis system consisting of: Reichert UnivaR microscope, Polaroid DMCe CCD camera, Buehler image analysis software - OmniMet Enterprise).

3. Results and Discussion

The quantification of the gas nitriding parameters variation effects made in partially dissociated ammonia, before or after the titanaliting of Fe-ARMCO, respectively 34CrAlMo5 nitriding steel grade, was performed by experimental programming (active experiment method), using the central compositional orthogonal method of the second order. It should be noted that, in the experimental researches, regardless of the matrix nature, the gaseous nitriding in a partially dissociated ammonia atmosphere was performed under the same conditions (mentioned in Table 1), with 4 hours of technological holding time at nitriding temperature. Cooling was performed in a nitrogen atmosphere up to 150^0C and then in air.

Some batches of samples were previously titanalited in powdery solid medium (1050°C, for 2 hours) and others were not.

Table 1

Correspondence between the natural and coded values of the independent parameters, respectively

Factor	**Independent Variables**				**Dependent Variable**
	Nitriding Temperature, [^{o}C]		Degree of Ammonia Dissociation, [%]		**Y,** Total Layer Tchickness, [μm]
	Z_1 Natural Values, [^{o}C]	**$X_{1,}$** Coded Values	**Z_2,** Natural Values, [^{o}C]	**X_2,** Coded values	
Basic Level	Z_o = 580	0	Zo = 57.5	0	-
Variation Range	ΔZ = 40	-	ΔZ = 12.5	-	-
Higher Level	Z_o+ΔZ = 620	+1	Z_o+ΔZ = 70	+1	-
Lower Level	Z_o-ΔZ = 540	-1	Z_o-ΔZ = 45	-1	-

The actual conditions for carrying out the experiments related to the gaseous nitriding performed as a singular thermochemical heat treatment or subsequent to the titanaliting of the two metallic materials already mentioned, respectively the actual obtained results, are presented in Table 2.

Table 2

The central compositional orthogonal programming matrix of second order; actual conditions for carrying out the experiments and the results obtained

Exp. No.	X_o	Independent Variables (X_i)							Y_{tot}, [μm]			
									Fe-ARMCO		34CrAlMo5	
		X_1	X_2	X_1X_2	X_1^2	X_2^2	X_1'	X_2'	*N*	*TA+N*	N	TA+N
1	+1	-1	-1	+1	+1	+1	+1/3	+1/3	***484***	***383***	**200**	**178**
2	+1	-1	+1	-1	+1	+1	+1/3	+1/3	***477***	***396***	**160**	**146**
3	+1	+1	+1	+1	+1	+1	+1/3	+1/3	***1007***	***954***	**302**	**272**
4	+1	+1	-1	-1	+1	+1	+1/3	+1/3	***1224***	***1150***	**313**	**307**
5	+1	+1	0	0	+1	0	+1/3	-2/3	***1113***	***1053***	**309**	**291**
6	+1	-1	0	0	+1	0	+1/3	-2/3	***479***	***390***	**180**	**165**
7	+1	0	+1	0	0	+1	-2/3	+1/3	***682***	***587***	**172**	**180**
8	+1	0	-1	0	0	+1	-2/3	+1/3	***696***	***645***	**213**	**190**
9	+1	0	0	0	0	0	-2/3	-2/3	***685***	***613***	**201**	**179**

*Note: **Y_{tot}**, [μm] - total thickness layer measured after: **N**-gaseous nitriding;**TA+N**- titanaliting in powdery solid medium folowed by partially dissociated ammonia gaseous nitriding*

A- The results of experimental research on Fe-ARMCO nitrided in a partially dissociated ammonia atmosphere.

The statistical processing results of the data regarding the nitriding in partially dissociated ammonia gaseous atmosphere of Fe-ARMCO, contained in Table 2, are mentioned in Table 3.

Table 3

Results of Fe-ARMCO experimental data statistical processing on nitriding in a partially dissociated ammonia gaseous atmosphere

Nr.	*Statistically Parameter*	Nr.	*Statistically Parameter*
1	$So^2=108.27$	6	$t_{0,05;9}=2.26$
2	$S_{bo}^2 = 12$	7	$\lvert\Delta b_1\rvert = \lvert\Delta b_2\rvert = \pm 9.58$
3	$S_{b1}^2 = S_{b2}^2 = 18$	8	$\lvert\Delta b_{11}\rvert = \lvert\Delta b_{22}\rvert = \pm 16.6$
4	$S_{b12}^2 = 27$	9	$\lvert\Delta b_{12}\rvert = \pm 11.7$
5	$S_{b11}^2 = S_{b22}^2 = 54.1$	10	$\lvert\Delta b_0\rvert = \pm 7.83$

Subsequent to the stage of statistical verification of the nonlinear model coefficients (Table 3), its particular coded form resulted is (Eq. 1):

$$Y=\delta_{tot}=687.7+317.3X_1-39.6X_2-52.5X_1X_2+109.6X_1^2 \quad (1)$$

were: X_1, X_2 represents the coded expressions of the independent parameters, nitriding temperature (X_1) and the degree of ammonia dissociation (X_2) from Table 1.

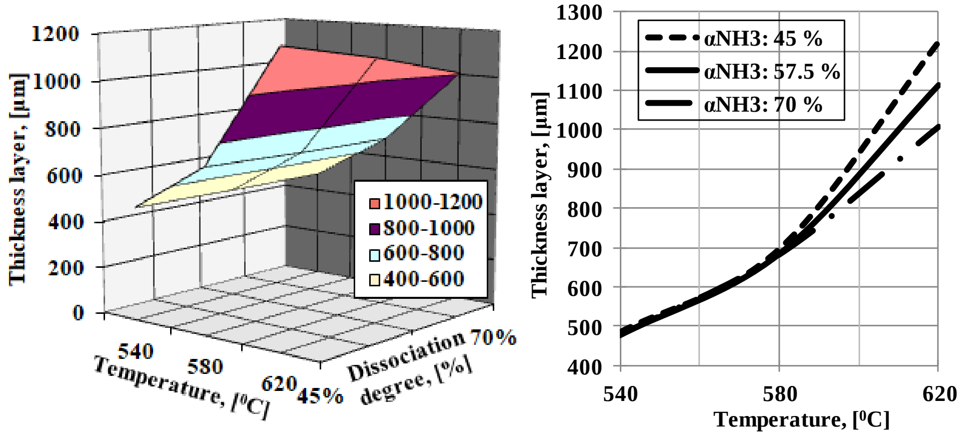
The statistical verification of the concordance of the calculated nonlinear model results expressed by equation 1, are presented in Table 4 and confirm that it, with a probability of 95%, expresses the correlation between the independent parameters considered (the technological maintenance temperature and the degree of ammonia dissociation) and the Fe-ARMCO total nitrided thickness layer.

Table 4

Verification of the concordance between the calculated nonlinear model (Eq. 1) and the experimental results

$Y = f(X_1, X_2)$	S_{conc}^2	F_{calc}	F_{tab}
Equation 1	7746	7.15	19.25

The graphical expressions of the nonlinear model expressed by equation 2 - Fig. 1 and Fig. 2, complement in a particularly suggestive way the conclusions regarding the way in which the interest parameters influence the growth kinetics of the nitrided layer in the case of Fe-ARMCO.



a) b)

Fig. 1. Dependence of the nitrided total thickness layer on the temperature and the degree of ammonia dissociation, in the case of Fe-ARMCO; a) the response area of the function $\delta = f(T; \alpha_{NH3})$; b) sections through the ternary diagram*(a)*, at different values of the degree of ammonia dissociation.

Thus, the strong positive effect of the temperature increase is clearly highlighted and, on the contrary, negative, when the ammonia dissociation degree increase over 45% (considered optimal).

An interesting aspect of the problem is highlighted by the images of the sections made in the ternary diagram (Fig. 1a), at different values of the degree of ammonia dissociation in the range 45-70%. The analysis of this diagram (Fig. 1b) highlights the fact that in the range of lower nitriding temperatures ($540\,^{0}C$), which represents the lower limit of the tested range, the variation of the degree of ammonia dissociation in the range 45-70% is negligible in terms of the influence manifested on the nitrided layer growth kinetics; as the temperature increases towards the upper limit of the range, this influence acquires more and more significant values, each increase by 12.5% of the degree of ammonia dissociation implying a decrease by approximately 100 microns of the total nitrided thickness layer. The explanation can be related to the value of the nitrogen diffusion coefficient in the non-alloy metal matrix and to the way it varies with temperature, respectively to the ratio between the speed with which nitrogen accumulates by adsorption and the dissipation rate by diffusion in the matrix, at various temperatures.

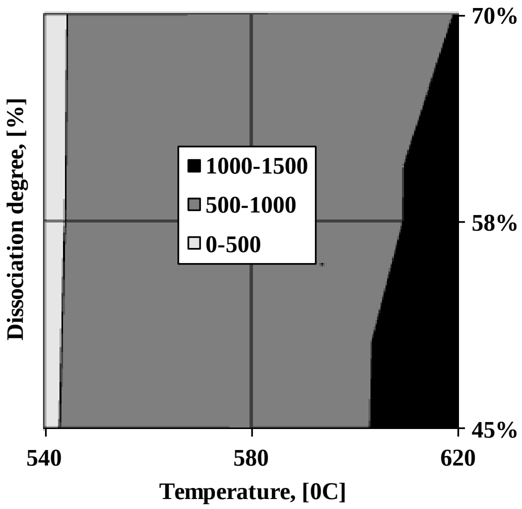


Fig. 2. Isoproperty domains of the function $\delta = f(T, \alpha_{NH3})$ determined in the case of Fe-ARMCO nitrided in partially dissociated ammonia atmosphere.

At lower temperatures ($540^{\circ}C$), the change in environmental activity generated by the increase in the degree of ammonia dissociation, has obvious repercussions on the amount of nitrogen adsorbed in the layer (it's decrease). The relatively low values of the diffusion coefficient in the non-alloyed metal matrix make them not have obvious (notable) effects on the layer growth kinetics. As the temperature increases, by increasing the diffusion coefficient, the differences in the amount of adsorbed nitrogen, generated by the decrease of atmospheric activity by increasing the degree of ammonia dissociation in relation to its optimal value, will have noticeable negative effects on the growth kinetics (increasingly stronger as the temperature increases).

The analysis of the isoproperty domains (Fig. 2) shows that the probability of obtaining the highest layer thicknesses increases when the nitriding temperature increases and the degree of ammonia dissociation stabilizes at values as close as possible to the optimal value (lower limit of the range taken in analysis).

A- Results of experimental research on Fe-ARMCO-nitrided in a partially dissociated ammonia atmosphere after titanaliting in a powdery solid medium

Actual conditions for conducting experiments related to the nitriding of Fe-ARMCO in this new context (prior to nitriding in a partially dissociated ammonia atmosphere the samples of Fe-ARMCO were titanaliting in powdery solid medium at 1050^{o}C, for 2 hours), and the obtained results are mentioned in Table 2. The results of the data statistical processings regarding the nitriding in gaseous atmosphere of partially dissociated ammonia subsequent to the titanaliting in powdery solid medium contained in Table 2 are mentioned in Table 5.

Table 5

The results of the data statistical processings regarding the nitriding in gaseous atmosphere of partially dissociated ammonia subsequent to the titanaliting in powdery solid medium

No.	*Statistical Parameter*	No.	*Statistical Parameter*
1	$S_o^2 = 103$	6	$t_{0.05;\,9} = 2.26$
2	$S_{bo'}^2 = 11.44$	7	$\lvert\Delta b\rvert = \lvert\Delta b\rvert = \pm 9.36$
3	$S_{b1}^2 = S_{b2}^2 = 17.16$	8	$\lvert\Delta b\rvert = \lvert\Delta b\rvert = \pm 16.2$
4	$S_{b12}^2 = 25.7$	9	$\lvert\Delta b\rvert = \pm 11.45$
5	$S_{b11}^2 = S_{b22}^2 = 51.5$	10	$\lvert\Delta b\rvert = \pm 7.64$

Subsequent to the stage of statistical verification of the nonlinear model coefficients (Table 5), its particular coded form resulted according to the Eq. 2:

$$Y=\delta_{tot}=615.6+331.3X_1-40.1X_2-52.2X_1X_2+106X_1^2 \qquad (2)$$

were:X_1 and X_2 represents the coded expressions of the independent parameters, nitriding temperature (X_1) and the degree of ammonia dissociation (X_2) from Table 1; Y represents the real value of the dependent parameter (total layer thickness).

The concordance results of the calculated nonlinear model statistical verification of the calculated nonlinear model according to the Eq. 2, are presented in Table 6.

Table 6

Verification of the concordance between the calculated nonlinear model (Eq. 2) and the experimental results

$Y = f(X_1, X_2)$	S_{conc}^2	F_{calc}	F_{tab}
Equation 2	94.7	0.92	19.25

These results confirm that it (with a probability of 95%) expresses the correlation between the independent parameters under discussion (temperature and degree of ammonia dissociation) and the total nitrided layer thickness in partially dissociated ammonia, after titanaliting, made in the case of Fe-ARMCO.

The graphical expressions of the nonlinear model expressed by equation 2, presented in Fig. 3 and Fig. 4, complete in a particularly suggestive way the conclusions regarding the way in which the parameters of interest influence the growth kinetics of the nitrided layer, obtained after the titanaliting, in the case of Fe-ARMCO. Thus, as in the previous case, the strong positive effect of the temperature increasing is clearly highlighted and, on the contrary, the negative, at the increasing of the ammonia dissociation degree at more than 45% (considered optimal).

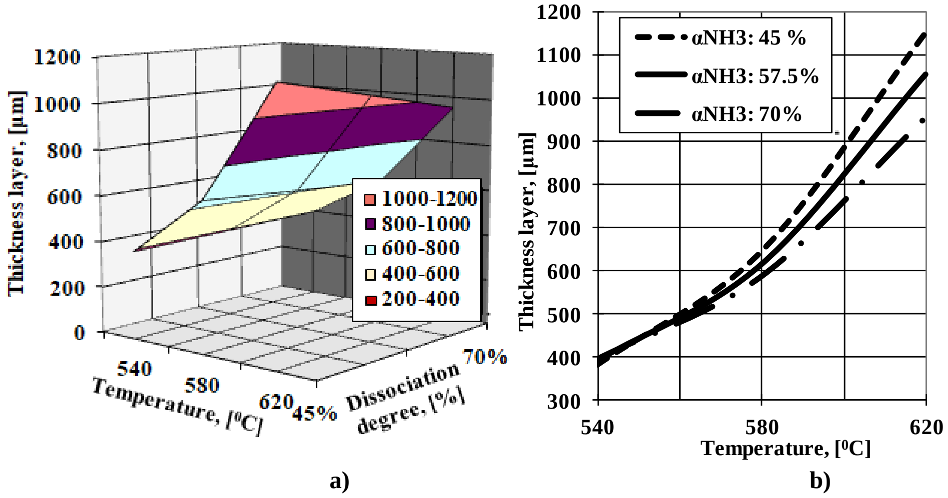


Fig. 3. Dependence of the total titanalited and subsequently nitrided thickness layer, on the temperature and degree of ammonia dissociation in the case of Fe-ARMCO; a) the response area of the function $\delta = f(T; \alpha_{NH3})$; b) sections by the ternary diagram(*a*), at different values of the degree of ammonia dissociation

Comparing the results regarded to the nitrided layer growth kinetics, obtained by applying a singular process or performed after titanaliting in powdery solid medium, at 1050°C for 2 hours (see Eq. 1,2 and Fig. 1-4), a slight decrease of the nitrided growth kinetics of the layer is found. This phenomenon is due to the existence of an area enriched with titanium and aluminum (titanalited layer), whose composition includes compounds of aluminum with titanium, aluminum with iron, iron with titanium [4] and which acts as a light brake in nitrogen diffusion.

According to experimental research [4] in this area, processes of conversion of these compounds into nitrides of different elements (Al, Ti, Fe) are carried out, with the release of nitrogen capable of diffusing and forming the internal nitriding zone. However, the nitrogen flow in this case is lower compared to the situation in which the titanalited layer is absent, an aspect with immediate consequences on the total layer thickness. On the other hand, the analysis of the dependencies in Fig. 3b compared to those in Fig. 1b highlights the similarity of the consequences deriving from the change of the degree of ammonia dissociation, the explanations regarding the aspect of the curves being similar to those exposed in case of titanalited layers absence.

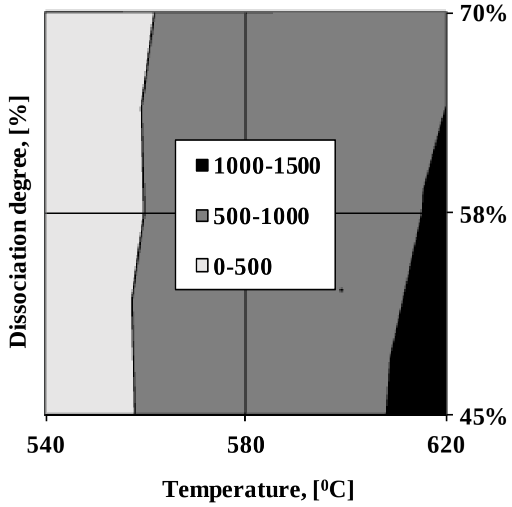


Fig. 4. Isoproperty domains of the function $\delta = f(T, \alpha_{NH3})$ determined in the case of Fe-ARMCO titanalited and nitrided in partially dissociated ammonia atmosphere.

From the analysis of the isoproperty domains (Fig. 4) it is found that the probability of obtaining the highest layer thicknesses increases with nitriding temperature increasing and stabilizing the ammonia dissociation degree at values as close as possible to the optimal value (lower limit of the studied range). In this case, there is a decrease in the field in which the combination of interest parameters (nitriding temperature and the degree of ammonia dissociation) can lead to values of total layer thickness greater than 1 mm, compared to the Fe-ARMCO simply nitrided (Fig. 2).

The microstructures comparative analysis of the nitrided Fe-ARMCO, in the absence (Fig. 5a) or the presence (Fig. 5b) of the titanalited layer, highlights an internal nitriding area, common to both situations and as a particular element, if prior to nitriding a titanaliting was carried out (Fig. 5b), a marginal area in which titanium and aluminum nitrides are found and also iron compounds $FeAl_3$ type [4], which give the layer higher hardness, wear resistance, etc.

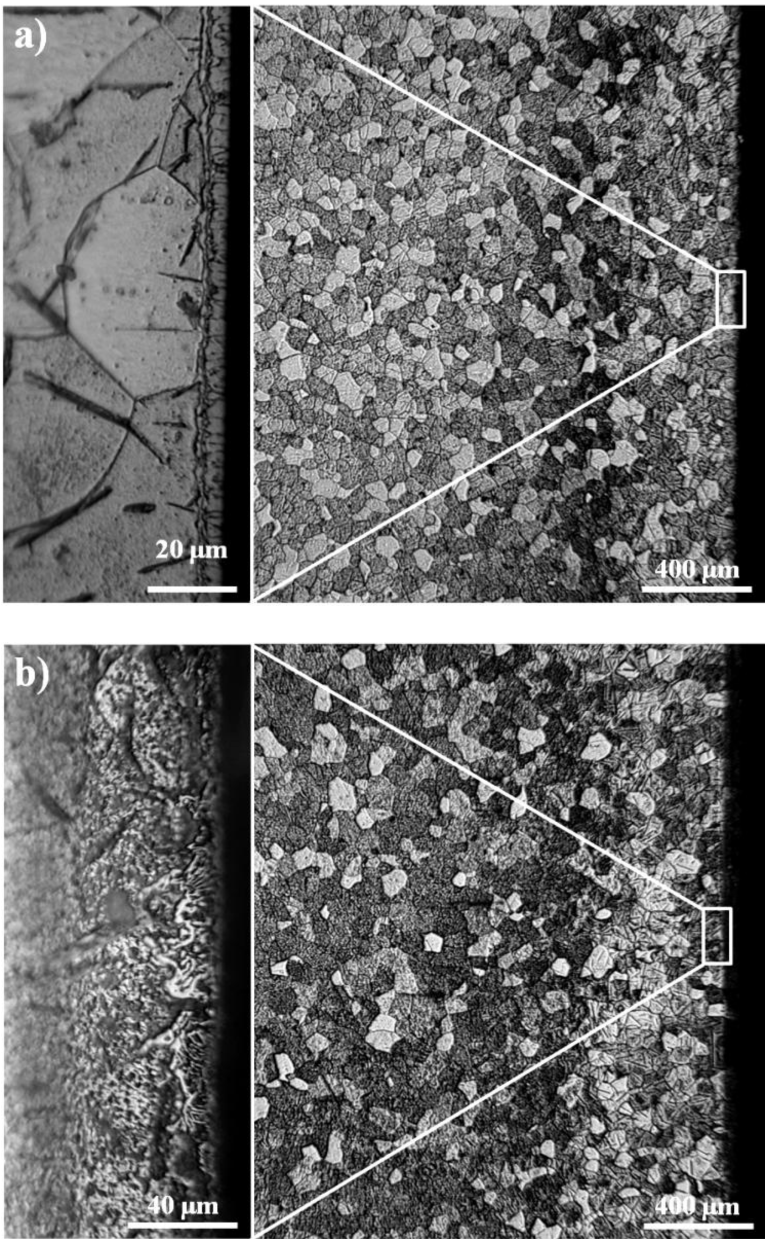


Fig. 5. Optical microscopy of Fe-ARMCO: a) nitrided (540^{0} C /4h / α_{NH3} = 45%); b) titanalited in powdery solid medium (1050^{0} C /2h) and subsequently nitrided in partially dissociated ammonia (540^{0} C /4h / α_{NH3} = 45%).

A- Results of experimental research on 34CrAlMo5 (EN10085) steel grade, nitrided in a partially dissociated ammonia atmosphere

The actual conditions for carrying out the experiments related to the nitriding of the alloy metal matrix of 34CrAlMo5 steel and the obtained results are mentioned in Table 2. The results of the data statistical processing regarding the nitriding of 34CrAlMo5 nitriding steel grade in a partially dissociated ammonia atmosphere contained in Table 2 are mentioned in Table 7.

Table 7

The results of the data statistical processing regarding the nitriding of 34CrAlMo5 steel in a partially dissociated ammonia atmosphere

No.	*Statistical Parameter*	No.	*Statistical Parameter*
1	$So^2 = 30.3$	6	$t_{0.05;\,9} = 2.26$
2	$S_{bo'}^2 = 3.36$	7	$\|\Delta b\| = \|\Delta b\| = \pm 5.06$
3	$S_{b1}^2 = S_{b2}^2 = 5.05$	8	$\|\Delta b\| = \|\Delta b\| = \pm 8.79$
4	$S_{b12}^2 = 7.57$	9	$\|\Delta b\| = \pm 6.21$
5	$S_{b11}^2 = S_{b22}^2 = 15.5$	10	$\|\Delta b\| = \pm 4.13$

Subsequent to the stage of statistical verification of the nonlinear model coefficients (Table 7) its particular coded form resulted according to the Eq. 3:

$$Y = \delta_{tot} = 194.3+64X_1-15.3X_2+7.25X_1X_2+50.6X_1^2 \qquad (3)$$

were: X_1 and X_2 represents the coded expressions of the independent parameters, nitriding temperature (X_1) and the degree of ammonia dissociation (X_2) from Table 1; Y represents the real value of the dependent parameter (total layer thickness)

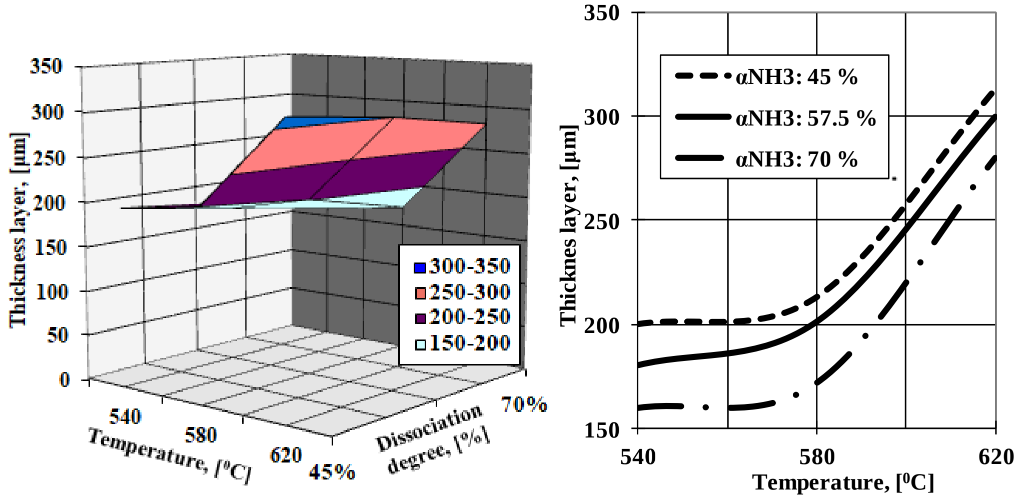
The concordance results of the calculated nonlinear model statistical verification of the calculated nonlinear model expressed by Eq.3, are presented in Table 8 and confirm that it with a probability of 95% expresses the correlation between the independent parameters under discussion (temperature and degree of ammonia dissociation) and the total nitrided thickness layer in partially dissociated ammonia, made in the case of 34CrAlMo5 steel.

Table 8

Verification of the concordance between the calculated nonlinear model (Eq. 3) and the experimental results

$Y = f(X_1, X_2)$	S_{conc}^2	F_{calc}	F_{tab}
Eq. 3	34.8	1.15	19.25

The graphical expressions of the nonlinear model according to the Eq. 3, presented in Fig. 6 and Fig. 7, complement in a particularly suggestive way the conclusions regarding the way in which the parameters of interest influence the growth kinetics of the 34CrAlMo5 steel nitrided layer. Thus, it is clearly highlighted once more, the strong positive effect of the temperature increasing and, on the contrary, the negative, at the ammonia dissociation degree increase over 45% (considered optimal).



a) b)

Fig. 6. Dependence of the total nitrided thickness layer, on the temperature and degree of ammonia dissociation in the case of 34CrAlMo5 steel; a) the response area of the function $\delta = f\,(T;\ \alpha_{NH3})$; b) sections by the ternary diagram(*a*), at different values of the degree of ammonia dissociation.

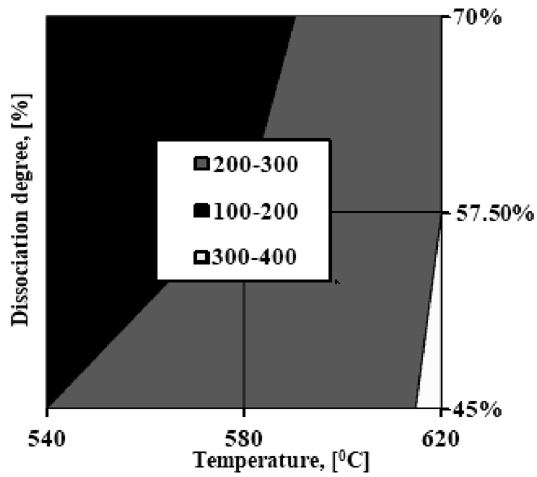


Fig. 7. Isoproperty domains of the function $\delta = f\,(T,\ \alpha_{NH3})$ determined in the case of 34CrAlMo5 steel, nitrided in partially dissociated ammonia atmosphere.

As seen in the Fig. 1 and Fig. 6 (in the case of nitrided alloyed metal matrix) there are notable differences in terms of the layer nitrided kinetics growth compared to the Fe-ARMCO.

Thus, in steels containing alloying elements, the excess nitrides separation is difficult, or frequently blocked, the microstructural analysis not showing their presence [12]. All the alloying elements, to a greater or lesser extent, diminish the value of the nitrogen diffusion coefficient in the alloyed ferrite and implicitly reduce the size of the internal nitriding zone. Nitrogen atoms decreased mobility, in the case of alloyed ferrite, is closely in relation to the diffusion activation energy increasing in the presence of alloying elements dissolved [12]. In the presence of 2-4% alloying elements (Cr, Mo), dissolved in ferrite, the activation energy increases from 18 kcal (at g)$^{-1}$ to 20-23 Kcal (at g)$^{-1}$.[12].

The 34CrAlMo5 nitriding steel grade has about 1.12%Cr and 0.33%Mo, and after titanaliting the Ti percentage in the surface layers reaches the value of 0.9% [4]. The presence of Ti influences extremely strongly the activation energy value, at about 1.29%Ti, reaching a value of 23.8 Kcal (at g)$^{-1}$ [12].

The isoproperty domains analysis (Fig. 7) highlights the fact that by nitriding the 34CrAlMo5 steel in a partially dissociated ammonia atmosphere for 4 hours, at different temperatures, the internal nitriding area would frequently have dimensions in the range of 200-300 µm, obtaining higher values at high temperatures, above the eutectoid one in the Fe-N system and preferably low dissociation degrees, close to the optimal level.

A- Results of experimental research on 34CrAlMo5 steel (EN10085) - titanalited in a powdery solid medium and nitrided in a partially dissociated ammonia atmosphere.

The actual conditions for carrying out the experiments on 34CrAlMo5 steel related to the titanaliting in a powdery solid medium and nitriding in a partially dissociated ammonia atmosphere and the obtained results are mentioned in Table 2. The results of the data statistical processing regarding the titanaliting in a powdery solid medium and nitrided in a partially dissociated ammonia atmosphere of 34CrAlMo5 steel contained in Table 2 are mentioned in Table 9.

Table 9

The results of the data statistical processing regarding the titanaliting in a powdery solid medium and nitrided in a partially dissociated ammonia atmosphere of 4CrAlMo5 steel.

No.	*Statistical Parameter*	No.	*Statistical Parameter*
1	$So^2 = 65.34$	6	$t_{0.05,9} = 2.26$
2	$S_{bo'}^2 = 7.26$	7	$\lvert\Delta b\rvert = \lvert\Delta b\rvert = \pm 7.46$
3	$S_{b1}^2 = S_{b2}^2 = 10.89$	8	$\lvert\Delta b\rvert = \lvert\Delta b\rvert = \pm 12.9$
4	$S_{b12}^2 = 16.33$	9	$\lvert\Delta b\rvert = \pm 9.13$
5	$S_{b11}^2 = S_{b22}^2 = 32.67$	10	$\lvert\Delta b\rvert = \pm 6.08$

Subsequent to the stage of statistical verification of the nonlinear model coefficients (Table 9) its particular coded form resulted expressed by Eq. 4:

$$Y = \delta_{tot} = 176.5+63.5X_1-15.6X_2+50.9X_1^2 \quad (4)$$

were: X_1 and X_2 represents the coded expressions of the independent parameters, nitriding temperature (X_1) and the degree of ammonia dissociation (X_2) from Table 1; Y represents the real value of the dependent parameter (total layer thickness). The concordance results of the calculated nonlinear model statistical verification of the calculated nonlinear model according to the equation 4, are presented in Table 10 and confirm that it with a probability of 95% expresses the correlation between the independent parameters under discussion (temperature and degree of ammonia dissociation) and the total nitrided thickness layer in partially dissociated ammonia, made in the case of 34CrAlMo5 steel.

Table 10

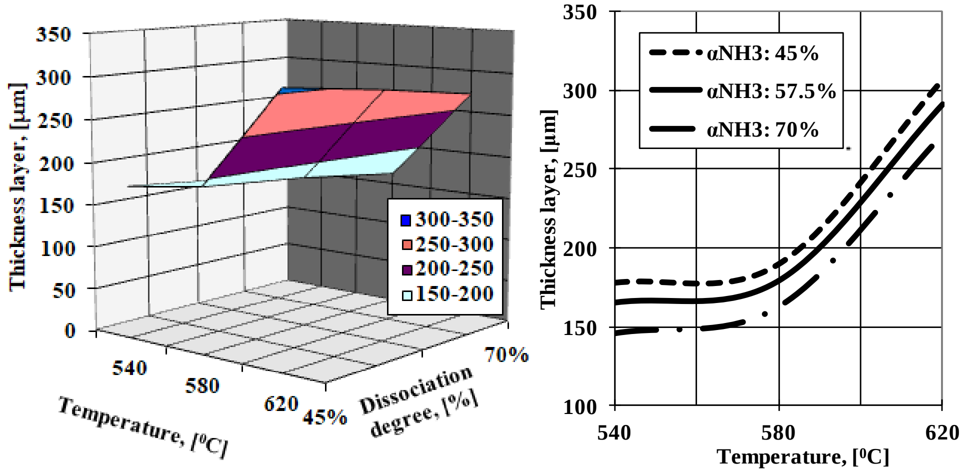
Verification of the concordance between the calculated nonlinear model (Eq. 4) and the experimental results

$Y = f(X_1, X_2)$	S_{conc}^2	F_{calc}	F_{tab}
Equation 4	6.76	0.103	19.30

The graphical expressions of the nonlinear model experssed by the equation 4, presented in Fig. 8 and Fig. 9, complement in a particularly suggestive way the conclusions regarding the way in which the parameters of interest influence the growth kinetics of the nitrided layer obtained subsequent titanaliting in a powdery solid medium 34CrAlMo5 steel. Thus, it is clearly highlighted once more, the strong positive effect of the temperature increase and, on the contrary, the negative, at the ammonia dissociation degree increase over 45% (considered optimal).

The graphical expressions of the regression equation (4) obtained in the case of titanaliting and subsequent nitriding of 34CrAlMo5 steel and especially of the sections by the ternary diagram (Fig. 8), are extremely similar to those obtained in the case of plain nitrided steel (Fig. 6), the presence of the titanalited layer producing this effect.

The isoproperty domains comparative analysis (Fig. 5-7) afferent to the two situations in which 34CrAlMo5 steel is found, after nitriding, respectively titanaliting and nitriding, performed in the same conditions (temperature and degree of ammonia dissociation), highlights the slight deceleration effect in the growth kinetics of the nitrided layer in the presence of the titanaliting layer.



a) b)

Fig. 8. Dependence of the total titanalited and subsequent nitrided thickness layer, on the temperature and degree of ammonia dissociation in the case of 34CrAlMo5 steel; a) the response area of the function $\delta = f(T; \alpha_{NH3})$; b) sections by the ternary diagram(*a*), at different values of the degree of ammonia dissociation

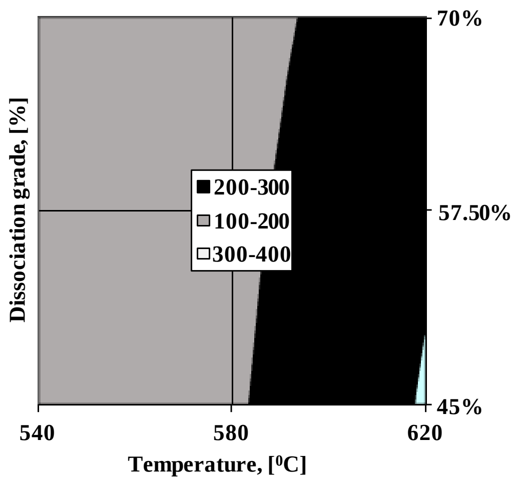


Fig. 9. Isoproperty domains of the function $\delta = f(T, \alpha_{NH3})$ determined in the case of 34CrAlMo5 steel, titanalited and subsequent nitrided in partially dissociated ammonia atmosphere.

The microstructural differences highlighted by metallographic etching of the samples surface area in 34CrAlMo5 steel (Fig. 10a) and titanalited in powdery solid medium respectively (1050^0 C /2h) and subsequently nitrided in partially dissociated ammonia medium (Fig. 10b), are related both to the structure of the internal nitriding zone and to that of the area strictly adjacent to the surface. In the area strictly adjacent to the surface, in the case of simple nitriding, a strictly delimited area highlighted, occupied by the phase's $\varepsilon + \gamma'$ in excess.

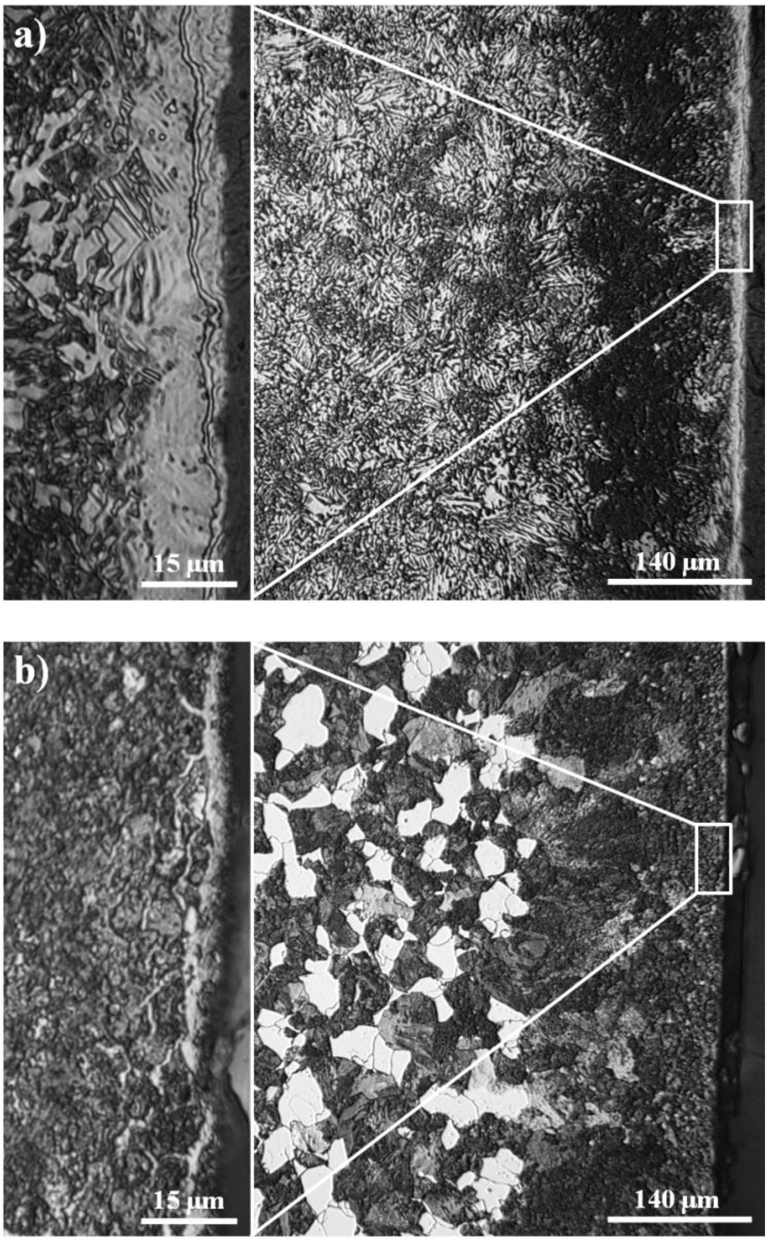


Fig. 10. Optical microscopy of 34CrAlMo5 steel: a) nitrided in partially dissociated ammonia atmosphere (540^{o} C /4h / α_{NH3} = 45%); b) titanalited in powdery solid medium (1050^{o} C /2h) and subsequently nitrided in partially dissociated ammonia (540^{o} C /4h / α_{NH3} = 45%).

Related to this area, by X-ray analysis is highlighted a three-phase area consisting of $\varepsilon + \gamma' + \alpha$. The presence of the ε phase along with the α phase can be explained by the displacement of the ε phase along the grain boundaries.

The main component of the nitrided layer is the diffusion zone (internal nitriding zone), strongly differentiated from the rest by the etching grade with chemical reagent (Nital 3%) and consisting of α_N solid solution poor in alloying elements, in which the γ' phase was separated in excess - $(Fe,Me)_4N$, nitrides of the alloying elements and most likely carbides of the alloying elements type Me_3C.

In the case of 34CrAlMo5 steel nitrided after titanalited, without other intermediate thermal processing, the matrix will result in an annealing structure (superheated) due to the fact that the cooling from the technological maintaining temperature is slow (samples were packed in the powdery solid mixture). Consequently, in order to ensure the core tenacity, it will be necessary that after the titanaliting (before nitriding) the parts/samples be subjected to quenching and tempering in conditions that ensure the preservation of the titanaliting layer structure. A processing alternative that can be considered in the case of quenching and tempering steel products subjected to titanaliting and subsequent nitriding, is to perform after titanaliting only the bulk martensitic quenching, the role of tempering being ensured by the nitriding process. In this processing alternative, it's possible to accelerate the layer kinetics growth of due to the presence of internal stresses introduced by the quenching.

Regardless of whether or not there is an quenching and tempering heat treatments cycle between titanaliting and nitriding, in the area adjacent to the surface, (the one in which there was previously a titanalited layer), will be characterized by a higher proportion of hardening phases (iron nitrides and nitrides of their own alloying elements, and the elements introduced during titanaliting, Al-Ti, Al-Fe compounds of $FeAl_3$ type, Mo-Ti respectively, detectable by X-ray analysis) [4]. In the internal nitriding zone are to be seen, due to a higher chemical etching, nitrides of the alloying elements separated in excess, together with the α_N solid solution (also poor by the alloying elements), and most probably alloying elements carbides proper to the matrix.

6. Conclusions

The mathematical models of interactions between the nitriding technological parameters, applied as a single treatment or after titanaliting, and the total nitrided layer thickness obtained in the case of the two metallic materials analyzed (Fe-ARMCO and 34CrAlMo5 steel), expressed as regression equations, provides:

A. How the nitriding temperature influences the nitrided layer growth increasing at the variation of the degree of ammonia dissociation within the limits of 45-70%. If nitriding is a singular thermochemical treatment or was apply after titanaliting, it is noteworthy that an ammonia dissociation degree increasing above 45% (value considered optimal) ensures a decreasing in the layer growth, regardless of the situation, but still slightly different in the two situations considered. Thus, if in the case of simple nitriding the degree of ammonia dissociation was accelerate by the temperature rise, in the case of titanaliting the effect remains constant.

B. The determination/anticipation by calculation of the total size of nitride layer for certain values imposed on the technological holding time temperature and the degree of ammonia dissociation (in the adopted intervals of variation in the cycle of experiments carried out) respectively.

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