AMMONIA BEHAVIOR DURING HEATING IN THE PRESENCE OF “NON-INERT” SURFACES - ATOMIC/MOLECULAR MECHANISM VERSUS IONIC MECHANISM OF ADSORPTION

Mihai Ovidiu COJOCARU[1], Mihai BRANZEI[2], Sorin CIUCĂ[3], Ruxandra Elena DUMITRESCU[4], Adrian BIBIȘ[5]

In an ammonia atmosphere under convective heating, nitrogen saturation is initiated via an atomic/molecular adsorption mechanism. Ammonia molecules near the metal surface are adsorbed within the electric double layer, which acts as a catalyst. In this adsorbed state, ammonia molecules or NH_x *radicals form* NH_x^- *anionic complexes, releasing energy. This process facilitates electronic emission from the metal surface, triggering the ionic adsorption mechanism. These anionic complexes also form within the furnace atmosphere, followed by their subsequent adsorption. Consequently, applying voltage between the furnace chamber (cathode) and the parts (anode) enhances nitride layer kinetics (anodic effect) while providing cathodic protection to the chamber.*

Keywords: ammonia atmosphere, plasma nitriding, anodic effect, ion adsorbtion, surface activation

1. Introduction

Ammonia is of particular importance in the practice of thermochemical treatments of metal products such as nitriding and nitrocarburizing, representing the main source of nitrogen that ensures superficial saturation. The overall kinetics of the nitrogen saturation process is dependent on the kinetics of the processes/phenomena that take place in the reaction medium, respectively on the kinetics of the processes that take place at the medium-metal product interface, both in strict correlation with the temperature and the surface chemical nature,

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[1] Prof., Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, Romania, National University of Science and Technology POLITEHNICA Bucharest, Romania, e-mail: mihai.cojocaru@upb.ro

[2] Assoc. Prof., Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, e-mail: mihai.branzei@upb.ro

[3] Assoc. Prof., Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, e-mail: sorin.ciuca@upb.ro

[4] Lect., Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, corresponding author, e-mail: ruxandra.dumitrescu@upb.ro

[5] Scientific Researcher III, National Research and Development Institute for Gas Turbines – COMOTI, e-mail: adrian.bibis@comoti.ro

respectively. So, an increase in temperature in the reaction medium implies an increase in the degree of ammonia dissociation and implicitly a decrease in the nitrogen potential of the atmosphere, with negative consequences on the processes at the interface (i.e. adsorption rate). A similar effect on the processes at the interface is the possible dilution of the environment with nitrogen, for example, or the modification of the chemical nature of the superficial layers of the metallic product in the presence of elements or chemical compounds that reduce the value of the mechanical work of extracting the electron from the surface, the intensity of the processes at the interface being thus amplified and favoring adsorption. Modifying the temperature, or the degree of dilution of the medium, or the chemical composition of the surfaces of products subjected to thermochemical processing, or the presence in some situations of electrostatic fields, all of these have major consequences on the intensity with which the various adsorption mechanisms occur, molecular/atomic or ionic, and thereby on the global kinetics of the formation of nitrogen-saturated layers, respectively their phase composition.

2. Processes and Phenomena in Undiluted Ammonia at the Non-Inert Ferrous Interface

The saturation of product surfaces with nitrogen during the thermochemical nitriding carried out in an atmosphere of undiluted ammonia occurs as a result of a sequence of phenomena in the reaction medium, at the interface of the medium - product and in the product. The ammonia decomposition reaction results in the production of molecular nitrogen, which in the temperature range usual for nitriding and nitrocarburizing processes (below 650 °C) is stable/neutral and does not participate in the superficial saturation with nitrogen. The ammonia molecule is particularly unstable and decomposes into the elemental gaseous components, nitrogen and hydrogen, starting at 0 °C, so that in the temperature range where the nitriding process usually takes place, in the absence of "non-inert" components in the medium, nitrogen and hydrogen molecules will be found alongside undissociated ammonia molecules (according to Equation (1)) [1-3].

$$2NH_3 \leftrightarrow N_2 + 3H_2 \tag{1}$$

It follows that the nitrogen potential (π_N – Equations (2)÷(4)) [2, 4] of an atmosphere consisting exclusively of ammonia will change (decrease) continuously, simultaneously with the increase in the degree of ammonia dissociation, as it is shown in Fig. 1.

$$\pi_N = \frac{(1-a)(1+a)^{0.5}}{1.5a^{1.5}} \cdot p_t^{-0.5} \tag{2}$$

where: π_N - nitrogen potential, atm$^{-0.5}$
A - the degree of ammonia dissociation, %
p_t - preassure, atm.

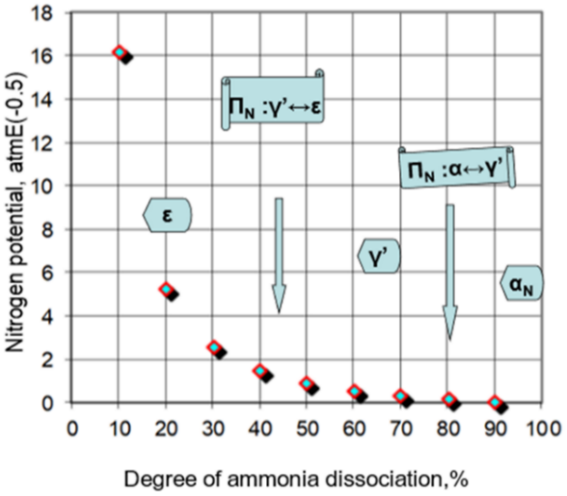


Fig. 1. Variation of the nitrogen potential of the undiluted ammonia atmosphere as a function of the ammonia dissociation degree, at T=793 K [5].

The separation boundaries of the domains corresponding to the different phases in the Fe-N system, α↔γ’ and γ’↔ε, dependent on the nitrogen medium potential, strictly correlated with the ammonia dissociation degree and, implicitly with the processing temperature, can be determined by a series of Equations (3) and (4):

$$lg\pi_N^{\alpha\leftrightarrow\gamma'} = \frac{1120}{T} - 2.1 \tag{3}$$

$$lg\,\pi_N^{\gamma'\leftrightarrow\varepsilon} = \frac{1900}{T} - 2.3 \tag{4}$$

The increase in the degree of ammonia dissociation, determined by the increase in temperature (within the limits of the temperature range in which the hard nitriding process is currently carried out), determines a continuous decrease in the nitrogen potential of the environment (Fig. 1) with the reconfiguration of the phase composition of the superficial layers of the metallic matrices, "non-inert" in the medium.

It should be noted that the demarcation lines of the different phases in the Fe-N system calculated using equations 3 and 4, for a temperature of 793 K, are π_N

(α↔γ’) = 0.205, and π_N (γ’↔ε) = 1.247 respectively. These parameters exhibit minimal sensitivity to temperature fluctuations within the typical range for hard nitriding (773–863 K), as illustrated in Fig. 2.

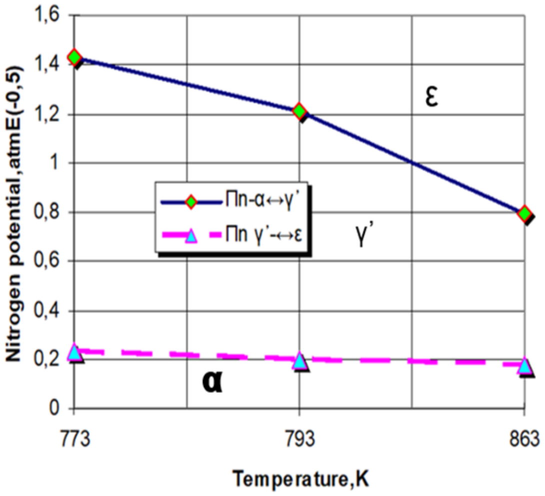


Fig. 2. Variation of the nitrogen potential corresponding to the demarcation lines of the α↔γ’ and γ’↔ε domains, respectively, upon changing the nitriding temperature [5].

The modification of ammonia dissociation degree implies a continuous change in the ratio between the proportion of "inert" nitrogen molecules and those of undissociated ammonia in the medium that actively participate in the saturation of "non-inert" surfaces and thereby implicitly on the nitrogen potential of the atmosphere.

The schematic representations of the processes/phenomena that take place during thermochemical processing, and that lead to the formation of nitrogen-saturated layers, in the absence or presence of electrostatic fields, are suggestively represented in Fig.s 3 and 4.

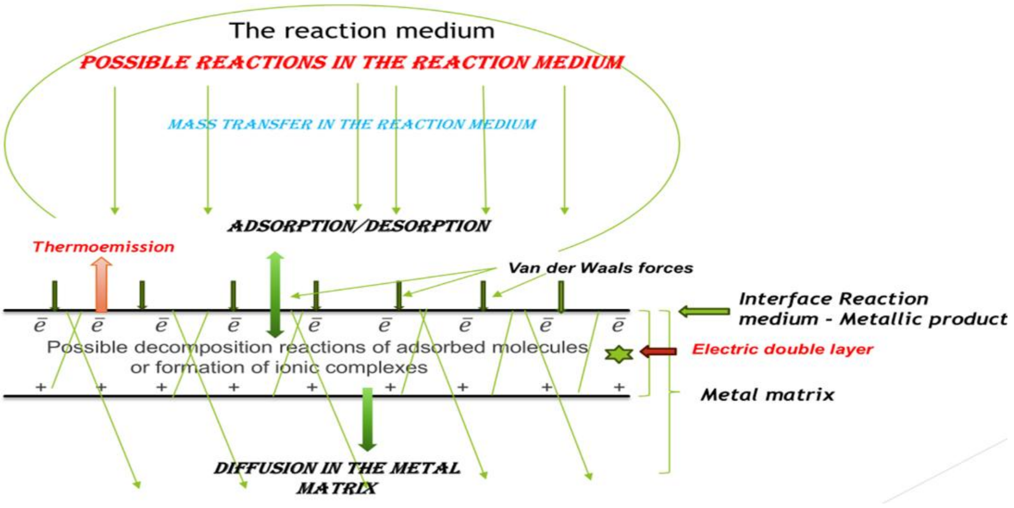


Fig. 3. Schematic/general representation of the processes/phenomena that take place in the reaction space, during thermochemical processing

At the level of non-inert surfaces, the decomposition reaction of ammonia molecules (undissociated in the reaction medium) becomes possible with the molecules in the adsorbed state and proceeds according to the mechanism proposed by Gräbke, in steps [6,7], through successive losses of hydrogen atoms (successive dehydrogenations).

$$2NH_3(g) \leftrightarrow 2NH_3(ad) \tag{5}$$

$$2NH_3(ad) \leftrightarrow 2NH_2(ad) + 2H(ad) \tag{6}$$

$$2NH_2(ad) \leftrightarrow 2NH(ad) + 2H(ad) \tag{7}$$

$$2NH(ad) \leftrightarrow 2N(ad) + 2H(ad) \tag{8}$$

$$2N(ad) \leftrightarrow N_2(ad) \leftrightarrow N_2(desorbed) \tag{9a}$$

$$\downarrow$$

$$2N(diffused) \tag{9b}$$

$$2H(ad) \leftrightarrow H_2(ad) \leftrightarrow H_2(desorbed) \tag{10}$$

Stepwise dehydrogenation reactions of NH_x radicals, Equations (11)-(13), are more probable from the energetic point of view compared to the direct decomposition of ammonia into nitrogen and hydrogen, Equation (14).

Thus:

$$NH_3 \rightarrow N_2 + H;\ \textit{requires a consumption of 4.20 eV} \tag{11}$$

$$NH_2 \rightarrow NH + H;\ \textit{requires a consumption of 3.64 eV} \tag{12}$$

$$NH \rightarrow N + H;\ \textit{requires a consumption of 3.36 eV} \tag{13}$$

compared to the 11.2 eV required for the direct decomposition of ammonia into nitrogen and hydrogen:

$$NH_3 \rightarrow N + 3/2H_2 \tag{14}$$

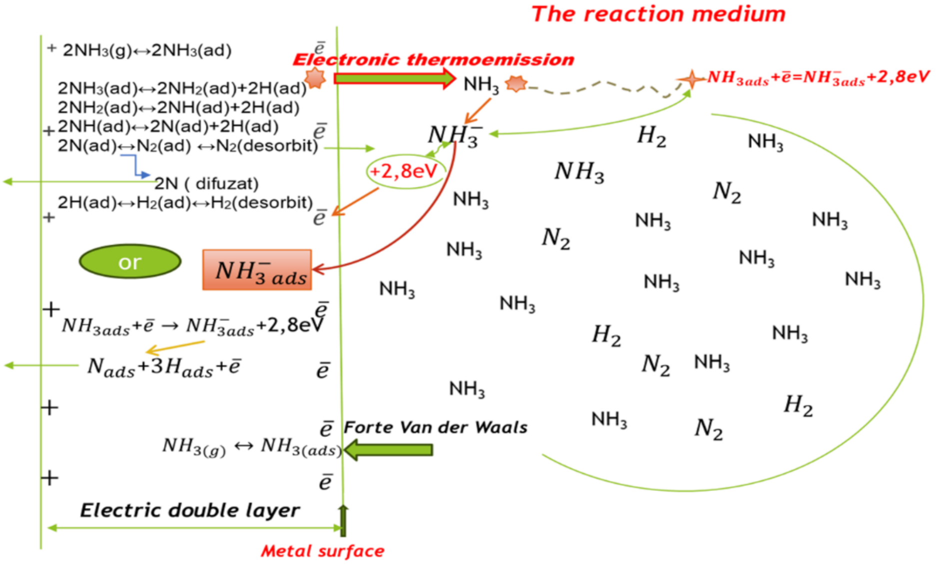


Fig. 4. Particular aspects of the nitrogen adsorption mechanisms, atomic/molecular and respectively ionic, on metal surfaces in the presence of ammonia as a reaction medium

The energies related to the unfolding of these reactions are high enough to ask if they can unfold, if the ammonia molecules are found in an adsorbed state in the metal surface, in the area of the electric double layer. The total energy of the electrons in the electric double layer, W_{et}, Equation (15) represents a sum of energies, their kinetic energy (W_c), to which is added their thermal energy, (W_T).

So:

$$W_{et} = W_c + W_T \tag{15}$$

Ammonia molecules in the adsorbed state have the ability to take up electrons located in the electric double layer [10,11,14], thus releasing a considerable amount of energy, equivalent to their affinity for electrons (E_a), about 2.8 eV, as it is shown in Equation (16).

$$NH_{3\,ads} + e^- \rightarrow NH_{3ads}^- + 2.8\,eV \tag{16}$$

This energy is given to other electrons located in proximity, in the electric double layer, which already have a quantity of energy, dependent on the temperature at which the processing takes place (kinetic plus thermal: about 0.2 eV at T=723 K), thus ensuring their possibility to overcome the potential barrier, therefore to reinitiate the phenomenon of electronic emission (see Table1 and Fig. 5).

Table 1

Modification of electron energy in the electric double layer of the iron matrix, a submicron of the ferric oxide film type, maintained in undiluted ammonia medium [15].

T, [°C]	T, [K]	$E_C \cdot 10^2$, [eV]	$E_T \cdot 10$, [eV]	W_a, [eV]	W_{et}, [eV]
100	373	3.2125	0.4880	2.8	2.88092
200	473	4.0750	0.6121		2.90196
300	573	4.9400	0.7415		2.92355
400	673	5.8000	0.8710		2.94510
500	773	6.6680	1.0000		2.96668
600	873	7.5300	1.1298		2.98828
700	973	8.3930	1.2592		3.00985
800	1073	9.2560	1.3860		3.03142

It results that, in the temperature range 450-700 °C (temperature range in which steel nitriding frequently occurs), in the case of nitriding in an undiluted ammonia atmosphere, in the absence of electrostatic fields, the interaction of adsorbed ammonia molecules with electrons in the electric double layer is possible, resulting in the formation of anionic complexes of the type NH_3^- and the release of a quantity of energy (the energy corresponding to the electron affinity of ammonia molecules, equal to 2.8 eV), transferable to electrons in the electric double layer. Through this energy transfer, electrons overcome the potential barrier of the electric double layer (3.0 eV for the submicron ferric oxide film on the iron matrix). Once transferred to the furnace medium near the surface, these electrons attach to ammonia molecules, generating new anionic complexes. These complexes are subsequently adsorbed onto the metal surface, where they decompose according to Equations (17) and (18).

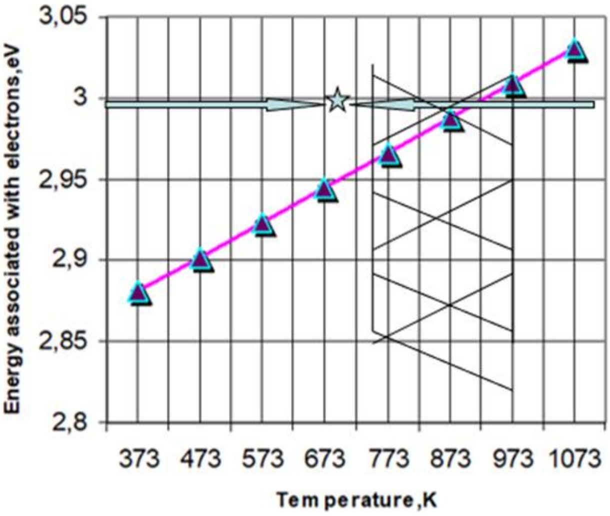


Fig. 5. Variation of electron energy within the electric double layer of iron matrices covered by submicron ferric oxide films in undiluted ammonia. Note: The potential barrier energy is 3.0 eV; the cross-hatched area indicates the temperature range of interest.

$$\underset{\substack{\downarrow \\ \textit{diffuse}}}{NH_{3\,ads}} \rightarrow N_{ads} + 3H_{ads} + e^- \tag{17}$$

or:

$$NH_{ads} + e^- \rightarrow N_{ads}^- + 0.04\ eV \tag{18}$$

In contrast to ammonia molecules, which generate anionic complexes and release significant energy upon capturing electrons, adsorbed nitrogen species exhibit different energetic behaviors. Nitrogen atoms release only minimal energy when attaching an electron (with an affinity of approximately 0.04 eV, as per Equation 18). Furthermore, adsorbed nitrogen molecules require an energy input of about 0.6 eV [12, 14] to form an anion, representing an energy-consuming rather than a heat-releasing process. It results that, in this temperature range, it is possible to manifest both atomic/molecular and ionic nitrogen adsorption mechanism.

3. Electrochemical Phenomena and Mass Transfer Mechanisms under Applied Electric Potential

In the case of nitriding temperatures in the range of 450÷700 ºC, in the presence of a potential difference applied between the part subjected to nitriding in undiluted ammonia medium (as role of anode) and the furnace muffle (or an additional electrode) acting as cathode [16,17], an acceleration of the anionic complexes (formed in the vicinity of the surface as a result of the bonding of electrons emitted by the surface with ammonia molecules located in the immediate vicinity of the surface, according to the Equation (16) towards the anode occurs, resulting in an increase in their density in the area adjacent to the anode and thereby an intensification of adsorption (and implicitly diffusion). The role of the ionic adsorption mechanism thus becomes predominant (Fig. 6).

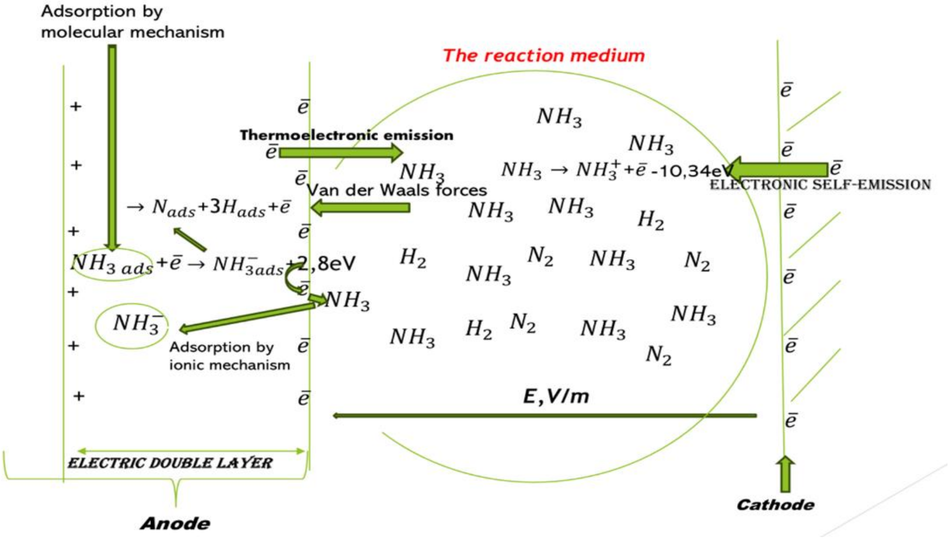


Fig. 6. Particular aspect of the atomic/molecular adsorption mechanism on metal surfaces in the presence of ammonia and an electrostatic field of a certain intensity, E.

Based on thermodynamic considerations of ammonia decomposition, Kogan and Solodkin [4,18] concluded that during nitriding in a nitrogen-diluted ammonia atmosphere (radiation heating), the nitrogen potential (Π_N) depends on the ammonia dissociation degree (α), the initial ammonia percentage (λ), and the dilution gas percentage ($100 - \lambda$), according to Equation (19).

$$\Pi_N = \frac{\lambda(1-\alpha)(1+\alpha\lambda)}{(1.5\alpha\lambda)^{3/2}} = \frac{(100-\%N_2)(1-\alpha)[1+\alpha(100-\%N_2)]}{[1.5\alpha(100-\%N_2)]^{3/2}} \tag{19}$$

Note. The initial gas mixture is formed exclusively of ammonia and nitrogen ($\%NH_3 + \%N_2 = 100\%$)

It follows that, notable effects in terms of the nitrogen potential variation are recorded when changing the ammonia dissociation degree from the ammonia-nitrogen gas mixture. Exemplifying, for a 30% nitrogen dilution degree of the nitriding medium, the decrease of ammonia dissociation from 70% to 45% has the effect of an increase in the nitrogen potential by about 235% (about 240% for a 60% dilution degree), as it is shown in Fig. 7, while for the same degree (45% or 70%), the increase in the nitrogen degree dilution of the medium from 30% to 60% induces a significantly lower change in the nitrogen potential (an increase of about 14-15%, therefore an order of magnitude smaller than the variation in the degree of ammonia dissociation).

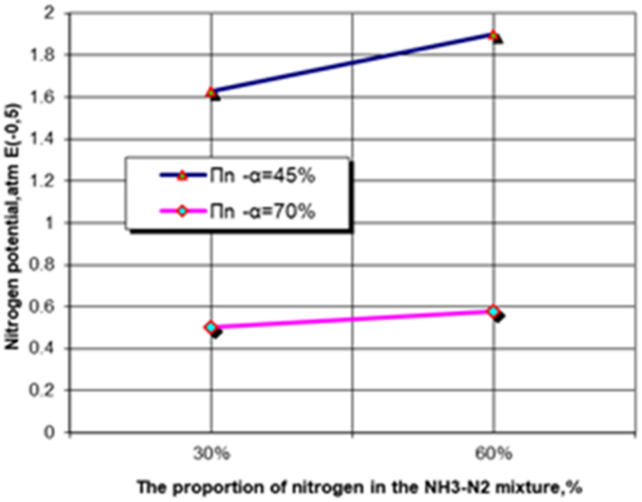


Fig. 7. Variation of the ammonia nitrogen potential - nitrogen gas mixture used in nitriding, depending on the degree of ammonia dissociation (45%;70%) and the dilution gas-nitrogen percentage [18].

The immediate implications of this conclusion, confirmed by our own experimental research, are related to the phase composition of the nitrided layer and related to the nitrogen concentration of the ε-phase. The ε-phase ($Fe_{2-3}N$) is formed as a result of the reaction between the γ'-phase (Fe_4N) and the ζ-phase (Fe_2N), through a reaction like the one below [5-7]:

$$[Fe_4N]\varepsilon + NH_3 = 2[Fe_2N]\varepsilon + 3/2H_2 \tag{20}$$

Note that ε signifies that the two nitrides are part of the solid solution ε-$Fe_{2-3}N$.

The equilibrium constant of the Equation (20) can be expressed by means of its free energy, ΔG^0:

$$lg\,K_1 = \frac{\Delta G^0}{4.47T} \tag{21}$$

or, taking into account the formation energy of iron nitrides [19] in the simplified form:

$$lg\,K_1 = -\frac{2670}{T} + 2.93 \tag{22}$$

On the other hand, $K_1 = \frac{a_\epsilon}{a_{\gamma'}}\frac{1}{\Pi_N}$ [1, 4, 20] where Π_N represents the nitrogen potential of the atmosphere, and a_ε together with $a_{\gamma'}$ the nitrogen activities in the nitrides that are part of the ε phase (Fe_4N and Fe_2N). Accepting that the ε phase represents an ideal solid solution, formed by the nitrides Fe_4N and Fe_2N, the nitrogen activities in the two nitrides can be replaced by the molar fractions [1,4]. Consequently, the last expression of the equilibrium constant will take the following form:

$$\frac{N_\varsigma^2}{1 - N_\varsigma} = \Pi_N K_1 \tag{23}$$

Kogan and Solodkin [1, 4], starting from the expression of the relation that allows the quantification of the nitrogen concentration in the ε-phase, an expression that takes into account the masses of the nitrides that enter into its composition, $m_{\gamma'}$ and m_ζ , as well as their molar masses, $M_{\gamma'}$ and M_ζ, go to a simplified relation that links the nitrogen concentration in the ε phase, $[N]_\varepsilon$, to the molar participation of the Fe_2N nitride, in the composition of the ε-nitride:

$$[N]_\varepsilon = \frac{0.06}{1 - 0.47 N_\varsigma} \cdot 100 \; [\%] \tag{24}$$

Replacing Equation (22) in Equation (23) and together with Equation (24), a system of equations will result: Equation (25) and (26).

$$\frac{N_\varsigma^2}{1 - N_\varsigma} = \Pi_N \cdot 10^{-\frac{2670}{T} + 2.93} \tag{25}$$

$$[N] = \frac{0.06}{1 - 0.47 N_\varsigma} \cdot 100 \tag{26}$$

The nitrogen level in the workpiece's surface layer (ε-phase) is determined by the equilibrium established with the furnace atmosphere's nitrogen potential.

The results regarding the nitrogen concentration in the nitrided surface layer obtained by processing in gas mixtures with different nitrogen potentials, at different temperatures, determined by running the algorithm presented previously, are presented in Fig. 8.

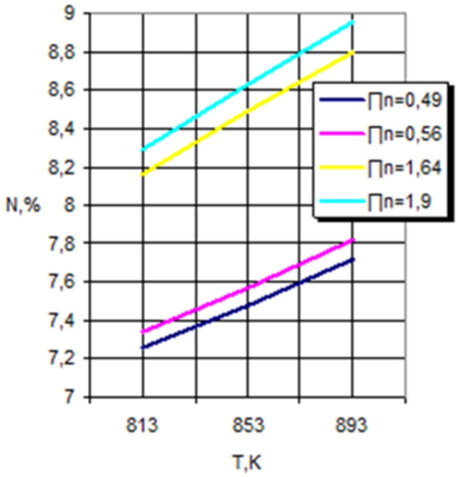


Fig. 8. The nitrogen concentration change in the superficial areas of the nitrided layer, adjacent to the surface, as a function of the nitriding temperature and the nitrogen potential of the gas mixture [18].

At nitriding medium temperature values outside the mentioned range, below 450 °C and above 700 °C, a series of particularities of the process appears:

– **above 750 ^{0}C**, ammonia is completely dissociated and nitrogen and hydrogen molecules will be found in the furnace medium (the percent of undissociated ammonia molecules, under theoretically ideal conditions, represents about 0.1% at 773 K and continues to decrease as the temperature increases [3]). The stability of nitrogen molecules being extremely high (ΔG>>0), as it is shown in Fig. 9, the nitrogen saturation of metallic matrices in this temperature range (metals and refractory alloys) will be based predominantly on a molecular mechanism of adsorption. In this temperature range (often above 900/1000 °C) mainly refractory metals such as Ti, Mo, Nb, V, Cr and their alloys are subjected to nitrogen saturation, the heating being carried out by radiation or in plasma media.

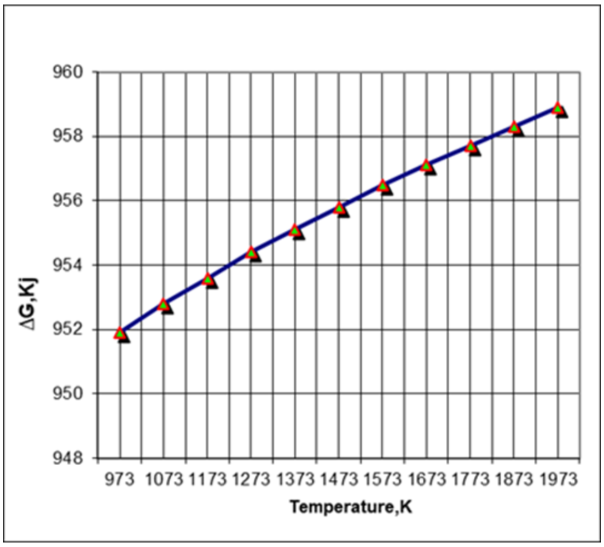


Fig. 9. The variation of the free enthalpy (ΔG) of the decomposition reaction of molecular nitrogen into atomic nitrogen depending on temperature [21]

In the case of these metallic matrices the energy associated with the electron in the electric double layer is of the order of 3.94 eV in the case of Ti and, 4.5 eV in the case of W, values that can be reached in the temperature range 900-1200 °C, temperatures at which their thermochemical processing takes place, according to the Equations (27-29) [1]:

$$N_2(g) \leftrightarrow N_2(ad) \tag{27}$$

$$N_2(ad) \leftrightarrow 2N(ad)\text{; } \textit{requires a consumption of 9.76 eV } [11] \tag{28}$$

$$N(ad) \leftrightarrow [N] \rightarrow diffused \tag{29}$$

The formation of the anionic complex N_{2ads}^{-} is also very likely in the case of nitriding in a nitrogen medium (resulting from the ammonia dissociation, or intentionally introduced into the reaction space), at high temperatures, the reaction taking place with the release of energy of about 0.6 eV, unlike the cationic complexes of the N_{2ads}^{+} type, whose formation is however unlikely due to the high energy consumption it requires about 9.0 eV [11]. It can be concluded that in the case of nitrogen saturation in the high temperature range both adsorption mechanisms are also manifested, the molecular and the ionic one.

– **below 450 °C**, therefore also in an almost entirely medium of nitrogen molecules, there are apparently similarities with the phenomena that occur at temperatures above 700 °C. In reality, however, if the adsorption of nitrogen molecules (or also ammonia remaining undissociated) occurs through an atomic/molecular mechanism, they will be found in an adsorbed state in a layer with molecular dimensions, generating a "barrier" zone in the way of continued adsorption. The ionic mechanism of adsorption cannot manifest itself due to the low energy of the electrons in the electric double layer, and mass transfer by diffusion under the action of concentration gradients is extremely slow due to low temperatures (the diffusion coefficient of nitrogen in unalloyed ferrite at a temperature of 673 K, is of the order of $6.59 \cdot 10^{-10}$ cm^2/s) [22].

– **within the range of 450÷700 ºC**, in the presence of a potential difference applied between the part subjected to nitriding in undiluted ammonia medium (as role of anode) and the furnace muffle (or an additional electrode) acting as cathode [16,17], an acceleration of the anionic complexes (formed in the vicinity of the surface as a result of the bonding of electrons emitted by the surface with ammonia molecules located in the immediate vicinity of the surface, according to the Equation (16) towards the anode occurs, resulting in an increase in their density in the area adjacent to the anode and thereby an intensification of adsorption (and implicitly diffusion). The role of the ionic adsorption mechanism thus becomes predominant.

The extreme character recorded by the growth kinetics of the nitride layer in undiluted ammonia medium at a temperature within the range of optimal temperatures from the point of view of the probability of formation of anionic complexes in the electric double layer (about 560 ºC/833 K – see Fig. 5) can be explained by the accelerations gained by the anionic complexes formed in the space between the electrodes, and the energies associated with the electrons in these areas. Thus, simultaneously with the increase in the potential difference between the anode (the part) and the cathode (the furnace muffle or an additional electrode coaxial to the part) between 1500 V and 2500 V (at a constant value of the electrostatic field intensity (E), and respectively the geometric factor, R/r presented in Figs. 10 and 11), there is an increase in the percent of anionic complexes in the area adjacent to the anode with immediate effect on the adsorption rate (expressed by the relative mass increase of the anode, respectively the size of the structural components of the nitrided layer - the size of the ε phase in compare to the entire layer thickness).

It should be noted that between the three variables, E, U and R/r, there is the following relationship:

$$E = \frac{U}{r \cdot ln(R/r)} \tag{30}$$

where: *R* is radius of the furnace muffle or of the additional electrode coaxial to the workpiece; *r* is radius of the workpiece.

So that changing one of them automatically implies changing the others.

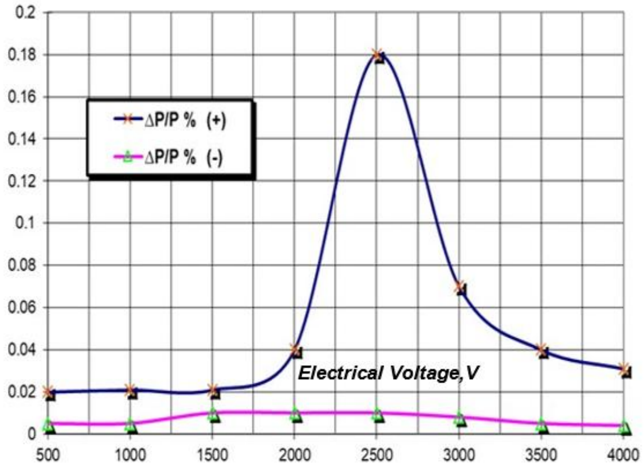
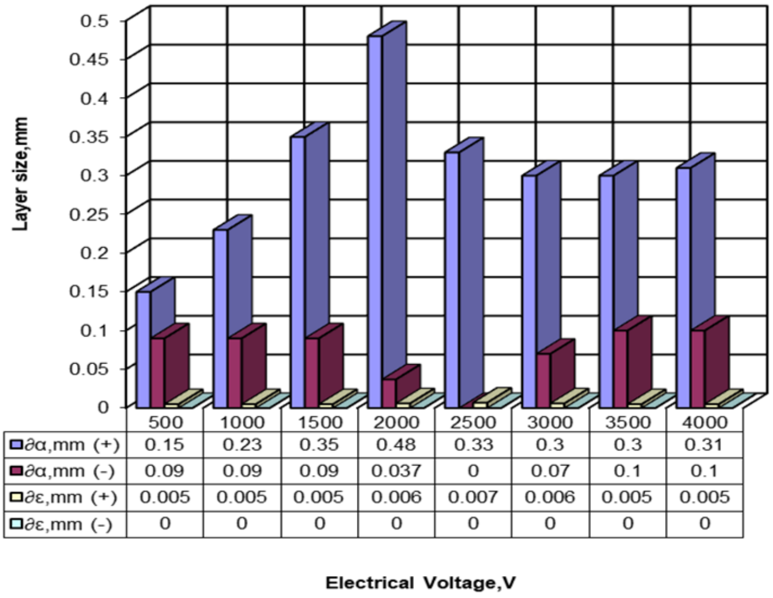


Fig. 10. Relative mass variation of technical-grade pure iron samples, nitrided in partially dissociated ammonia (αNH3=20-30%) for 2 hours at 560 °C. The process was conducted under an electrostatic field E=(0.72-5.77)·10^5 V/m, across various applied potential differences, with a geometric factor R/r=4.0 (for R=2·10^{-2} m; r=0.5·10-2m) [15]

When the voltage increases above 2500 V (under the experimental conditions previously exposed), the electron energy far exceeds the value corresponding to the potential barrier energy, a phenomenon that has as a consequence an increase in the number of electrons that, being transferred into the inter-electrode space, fail to interact with neutral ammonia molecules and thereby form anionic complexes. At the same time, when the potential difference increases, the number of fast electrons increases, capable of pulling electrons through the collision of neutral molecules, thus leading to the formation of cationic complexes of the type NH_3^+- Equation (31), a phenomenon that involved once in plus the decrease in the percent of anionic complexes and thus the medium activity, generating favorable conditions for the initiation of electric gas discharges.

$$NH_3 \rightarrow NH_3^+ + e^- - 10.34\ eV \tag{31}$$

The analysis of the effects of the potential difference variation on the phenomena that occur at the cathode surface (Figs. 9 and 10) highlights an expected phenomenon namely the modification of the anionic complexes percentage in the inter-electrode space with direct effect on the nitrided growth layer kinetics in the anodic zone (the part), respectively the cathodic zone (the furnace muffle) [15].



	500	1000	1500	2000	2500	3000	3500	4000
🟦 ∂α,mm (+)	0.15	0.23	0.35	0.48	0.33	0.3	0.3	0.31
🟪 ∂α,mm (-)	0.09	0.09	0.09	0.037	0	0.07	0.1	0.1
🟨 ∂ε,mm (+)	0.005	0.005	0.005	0.006	0.007	0.006	0.005	0.005
□ ∂ε,mm (-)	0	0	0	0	0	0	0	0

Fig. 11. Growth kinetics of different phases of the nitrided layer (the thickness of the compound zone ε and the diffusion zone α) for pure technical iron nitrided parts in a partially dissociated ammonia medium (αNH_3=20-30%) / 2 h / 560 ºC, in the presence of an electrostatic field $E=(0.72\text{-}5.77)\cdot10^5$ V/m, applied at different values; R/r=4.0 (for $R=2\cdot10^{-2}$ m; $r=0.5\cdot10^{-2}$m) [15].

Fig. 12 analyzes nitriding in an undiluted ammonia medium under an electrostatic field ($E=2.16\cdot10^5\text{-}2.88\cdot10^5$) V/m; R/r=4 and $r=0.5\cdot10^{-2}$ m). The analysis identifies the specific potential difference range required between the anode (workpiece) and cathode (muffle) to maximize nitrided layer growth kinetics while ensuring cathodic protection [15–17] across various process temperatures.

Particular conditions: $E=(2.16\cdot10^5\text{-}2.88\cdot10^5)$ V/m; R/r=4.0 and $r=0.5\cdot10^{-2}$ m [15].

This ensures the achievement of two major goals:

1. intensification of the nitrogen saturation process;
2. the possibility of increasing the life of nitriding furnace muffles and replacing them with low-alloy steels.

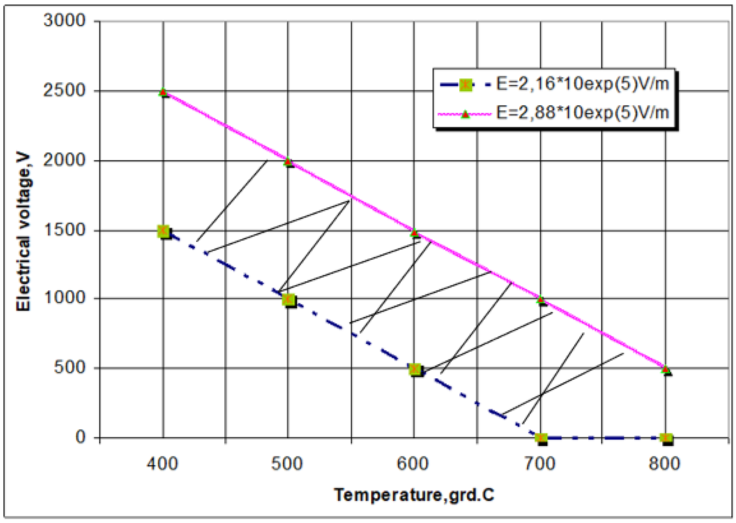


Fig. 12. The domin within which the necessary conditions for nitriding in undiluted ammonia medium (αNH_3=20-30%), in the presence of the electrostatic field, which simultaneously ensures cathodic protection while accelerating the process of nitrogen saturation of the anode.

Particular conditions: $E=(2.16\cdot10^5-2.88\cdot10^5)$ V/m; R/r=4.0 and $r=0.5\cdot10^{-2}$ m [15].

This ensures the achievement of two major goals:

3. intensification of the nitrogen saturation process;
4. the possibility of increasing the life of nitriding furnace muffles and replacing them with low-alloy steels.

4. Discussion and Conclusions

1. At temperatures within the range of 450 °C-700 °C, the initiation of superficial nitrogen saturation process of metallic matrices is based on the atomic/molecular mechanism of adsorption, after which, by generating the necessary conditions for stimulating electronic emission, the ionic mechanism of adsorption also begins to manifest;

- the dominant adsorption mechanism—whether atomic/molecular or ionic—is determined by the system's activation energy. While thermal conditions favor molecular adsorption, the application of an electric potential shifts the process toward a predominantly ionic regime, significantly enhancing the nitriding kinetics;
- increasing the medium temperature (max. 700 °C) in which nitriding occurs ensures an increase in the two energy components associated with the electrons in the electric double layer, E_c and E_T and thereby the probability

of initiating the phenomenon of electronic emission, with immediate effect on the ionic mechanism of adsorption;

- at temperatures above 700 °C, temperatures at which refractory metals and their alloys are currently subjected to nitrogen saturation, the medium, initially of ammonia, is composed of its decomposition products, nitrogen saturation is based on both molecular and ionic mechanisms, the nitrogen source being the adsorbed molecular nitrogen (molecular adsorption mechanism) and subsequently decomposed, or the anionic complexes resulting from the interaction with electrons in the electric double layer (ionic adsorption mechanism);
- at temperatures below 450 °C the nitrogen saturation process is theoretically and practically improbable: the medium is also composed of the decomposition products of ammonia-nitrogen and hydrogen; through a molecular adsorption mechanism nitrogen molecules can be found in the layer, but due to the low temperature and implicitly the extremely low percentage of nitrogen in the metal matrix, this adsorbed monomolecular layer plays a role of barrier to the continuation of the adsorption process.

2. It has been analytically demonstrated and experimentally confirmed that the ammonia dissociation degree from the ammonia-nitrogen gas mixture, together with the medium nitrogen dilution degree, significantly influences the nitrogen potential of the gas mixture used for nitriding and therefore implicitly on the nitrogen concentration in equilibrium at the interface, during the thermochemical process.

3. By applying a potential difference between the part, acting as anode, subjected to nitriding in an undiluted ammonia medium and the furnace muffle (or an additional electrod coaxial to the part/batch), acting as cathode, the ionic mechanism of adsorption becomes predominant;

- the nitrided layer growth kinetics (expressed by the relative mass variations or the dimensions of the different phases of the nitrided layer) in an undiluted ammonia medium, in the presence of electrostatic fields, presents an extreme character, strictly dependent on the value of the applied potential difference and that of the geometric factor: under certain strictly determined conditions (potential difference, geometric factor) a maximum value of the layer growth kinetics is recorded in the anodic zone and a minimum (blocking tendency) in the cathodic zone - cathodic protection;
- by exceeding the conditions that ensure maximum nitrogen saturation kinetics and simultaneously cathodic protection, the proportion of anionic complexes is reduced and the premises for initiating electrical discharges in gases are simultaneously created.

REFERENCES

[1] *E. J. Mittemeijer, M. A. J. Somers,* Kinetics of thermochemical surface treatments, Thermochemical Surface Engineering of Steels, Woodhead Publishing Series in Metals and Surface Engineering, Cambridge, UK, vol. **62,** 2015, pp. 113-139;

[2] *Yu. M. Lakhtin, Ya. D. Kogan, H. J. Spies, S. Böhmer*, Teoria i Tehnologhia Azotirovania (Theory and Technology of Nitriding), Metallurghia & VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, Germany, 1991; pp. 144–182;

[3] *C. D. Nenițescu*, Chimie generală (General Chemistry); Edit. Didactică și Pedagogică, București, România, 1979;

[4] *Yu. M. Lakhtin, Ya. D. Kogan, G. A. Solodkin*, Thermodynamic principles of controlling nitriding processes, Metal Science and Heat Treatment**,** Vol. **23**, No. 4, 1981, pp. 16–20;

[5] *M. O. Cojocaru, M. Brânzei, S. Ciucă, F. Bogdan, M. A. Ghinea, F. G: Călin*, Analytical Method for Estimating Nitriding Effects, U.P.B. Sci. Bull., Series B, **85**(3), 2023, pp. 123-134;

[6] *H. J. Grabke*, Conclusions on the Mechanism of Ammonia-Synthesis from the Kinetics of Nitrogenation and Denitrogenation of Iron, Zeitschrift für Physikalische Chemie Neue Folge, vol. **100**, 1976; pp. 185–200;

[7] *H. J. Grabke*, Reaktionen von Ammoniak, Stickstoff und Wasserstoff an der Oberfläche von Eisen I. Zur Kinetik der Nitrierung von Eisen mit NH_3-H_2-Gemischen und der Denitrierung (Reactions of ammonia, nitrogen and hydrogen on the surface of iron I. On the kinetics of the nitriding of iron with NH_3-H_2 mixtures and the de-nitriding), Berichte der Bunsengesellschaft für Physikalische Chemie, vol. **72,** 1968, pp. 533-541

[8] *E. Florian, M. O. Cojocaru*, Comportarea amoniacului in timpul încălzirii, explicate prin mecanismul ionic de adsorbţie (Behavior of ammonia during heating, explained by the ionic mechanism of adsorption), Metalurgia, vol. **30**, Iss. 9, 1978, pp. 461–463.;

[9] *M. O. Cojocaru, E. Florian,* Cementarea cu azot, rezultat al schimbului de electroni între metal şi amoniac (Nitriding, a result of the exchange of electrons between metal and ammonia), Metalurgia, vol. **30,** Iss. **7**, 1978; pp. 406-409.

[10] *M. O. Cojocaru, E. Florian,* Theoretical and practical aspects regarding the mechanism of nitriding in gas and plasma, Buletinul Institutului Politehnic „Gheorghe Gheorghiu-Dej”-București, Seria Chimie-Metalurgie, vol. **XLI**(2), 1979; pp. 101–108;

[11] *V. I. Vedeneev, L. V. Gurvich, V. N. Kondratiev, V. A. Medvedev, E. L. Frankevich*, Energii razryva khimicheskikh svyazey. Potentsialy ionizatsii i srodstvo k elektronu (Bond Energies, Ionization Potentials and Electron Affinities), Spravochnik, Izdatelstvo Akademii Nauk SSSR, Moskva, 1962, pp. 124;

[12] *I. K. Kikoin*, Tables for Physical Quantities, Atomizdat Publisher, Moscow, **1976**; pp.423;

[13] *E. Florian, M. O. Cojocaru*, Aspects Regarding the Thermodynamics and Kinetics of Ammonia Dissociation During Heating in the Nitriding and Carbonitriding of Steels, Metalurgia, vol. **30**, Iss. 6, 1978, pp.362-364;

[14] *G. S. Kaplina, G. L. Zhunkovskii*, K voprosu o mekhanizme nachal'noy stadii protsessa azotirovaniya (Regarding the mechanism of the initial stage of the nitriding process), Zashchitnye Pokrytiya na Metallakh, vol. **1**, 1966, pp. 73-80;

[15] *M. O. Cojocaru*, Azotirovanie v electrostaticescom pole (Nitriding in electrostatic field), Doctoral Thesis, Moscow, 1976, pp. 49, 53, 51–53 and 69–81;

[16] *Yu. M. Lakhtin, Ya. D. Kogan, V. A. Alexandrov, M. O. Cojocaru*, Sposob khimico-termicheskoy obrabotki (Method of thermochemical treatment), Patent no. **519499**/5 -03-1976, 1976;

[17] *M. O. Cojocaru, T. Dulămiță, L. Lazăr*, Procedeu pentru protecția cuvelor utilizate la tratament termochimic (Method for the protection of tanks used in thermochemical treatment), Patent no. **94205**/14, 1987;

[18] *M. O. Cojocaru, M. Branzei, A. M. Ghinea, L. N. Drugă*, The Effects of Modifying the Activity of Nitriding Media by Diluting Ammonia with Nitrogen Materials, vol. 14, Iss. 9, 2021;

[19] *M. Hillert, M. Jarl,* A thermodinamic analysis of the iron-nitrogen system, Metallurgical Transactions A, vol. **6A** (3), 1975;

[20] C*. E. Wicks, F. E. Block,* Thermodynamic Properties of 65 Elements: Their Oxides, Halides, Carbides, and Nitrides, Bureau of Mines, Bulletin **605**, U.S. Government Printing Office, Washington, D.C.**,** 1963;

[21] *A. Roine,* HSC Chemistry Software, Version 6.12. Outotec Research Oy, Pori, Finland, available from: www.outotec.com, 2006**;**

[22] *Yu. M. Lakhtin, Ya. D. Kogan*, Azotirovaniyestali (Nitriding of steels), Mashinostroenie, Moskcow, 1976, pp. 53 - 90, 225, 234.