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EMPIRICAL EXPOSITION OF THE ADSORPTION'S IONIC MECHANISM ON GASEOUS NITRIDING

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Introduction

The classic theory of the adsorption of the Nitrogen resulted through thermal catalytic dissociation of the ammonia cannot explain a series of situations appearing repeatedly during nitriding:

– the non monotonous variation of the adsorbed nitrogen quantity on the increase of the ammonia dissociation degree;

– the intensifying of the nitriding process kinetics through the existence of transition metals in contact with the nitriding media, of a completely different nature to that of both the nitrogen and the material subject to nitriding.

The comparative analysis, on energy grounds, of the ammonia thermal catalytic dissociation reaction s and respectively ionization of the molecules with their creation of anions or cations, has led to the conclusion that the most likely decomposition mechanism is the one of ionization with the creation of anions.

a) a) the ammonia thermal catalytic dissociation global reaction:

$$NH_3 \rightarrow N + H \qquad \text{(ec.1)}$$

represents a strongly endothermic reaction, the quantity of energy necessary for it to develop being of 11,2eV, the sum of the necessary energies for the three phases of decomposition:

$$NH_3 \rightarrow NH_2 + H \qquad \text{(ec.2)}$$

$$NH_2 \rightarrow NH + H \qquad \text{(ec.3)}$$

$$NH \rightarrow N + H \qquad \text{(ec.4)}$$

4,2eV (reaction 2), 3,64eV (reaction 3), and respectively 3,36eV (reaction 4), there for a total consumption of 11,2eV.

b) The ionization of the ammonia molecule with the creation of its anions

$$NH_3 + \bar{e} \rightarrow NH_3^- \qquad \text{(ec.5)}$$

is exothermal, the quantity of energy released being +2,8eV

c) The ionization of the ammonia molecule with the creation of its cations

$$NH_3 \rightarrow NH_3^+ + \bar{e} \qquad \text{(ec.6)}$$

is strongly endothermic, the quantity of energy necessary for it to develop being of the order of 10,34eV.

All these observations lead to the conclusion that in the conditions in which the nitriding process in gaseous atmosphere develops it is very probable the apparition of type NH_3^- anions (along with type NH_X, neutral radicals or other types of ions), conclusion which if proved valid, would allow the understanding of the noted possible contradictions and in the same time modify the current perception on the adjustment and control mode of the classic nitriding parameters.

Materials, working method and equipment used for research

The experimental research have pursued the empiric exposition of the presence of type NH_3^- anions on the gaseous nitriding occurring in ammonia atmosphere and by this the communality on the adsorption's ionic mechanism in the case of this variant of thermal processing, compared to the free atoms adsorption mechanism, in active status. The starting point was the idea that the creation of the ammonia anions is possible in the conditions specific to the development of the classic nitriding process and the hypothesis that, in this situation, the presence of a electric field of a certain intensity should result in an orientation and an acceleration of the ions in the electric field, with consequences on the forming kinetics of the different polarity samples layers existing in the field. Considering the desired outcome, in the first stage of the research it was sought to determine through calculations the thermal and electric conditions in which it is possible the formation of type NH_3^- anions and following that, through experiments it was sought to confirm the theoretical reasoning.

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The material on which the research were performed was technical pure iron, as it allows the more precise exposing of different structural components of the nitrided layer, respectively their dimension in real processing conditions.

The assembly used for research is presented in figure1, it allowed a strict control of the processing's electric and geometric parameters.

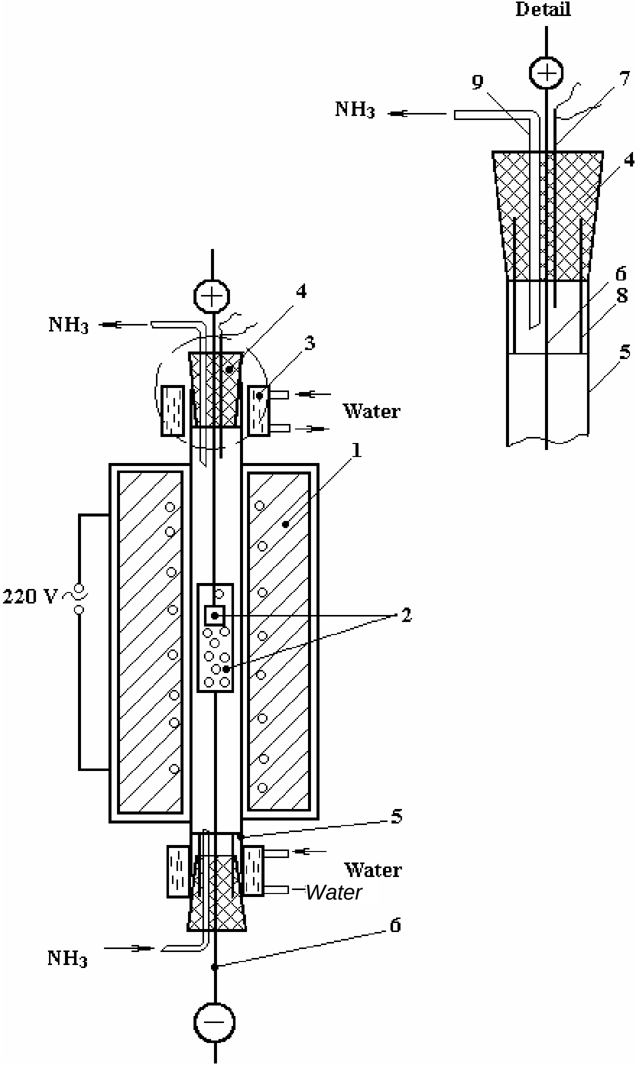

Fig.1 Installation for exposing the presence of anions on gaseous nitriding
1 – electric furnace; 2 – coaxial electrodes
3 – water coolers; 4 – insulators;
5 – refractory steel pipe; 6 – electrode;
7 – thermocouple; 8 – centering elements;
9 – exhaust pipe for ammonia dissociation products

Cylindrical samples were used d20X30mm (anodes), in a dimensional relation with the coaxial central electrode, the cathode, D28X150mm, D/d=1.4. The anodes and the cathodes were executed from technical pure iron (Fe-ARMCO). The nitriding results were analyzed through specific metallographic methods, respectively optical microscopy using a Reichert microscope. There were also done measurements of the samples' mass variation as the nitriding process underwent in various conditions.

Theoretical and experimental researches. Results. Interpretation

The analysis on energy grounds of the ammonia molecule ionization emphasizes the fact that the forming of the ammonia's negative ion, in case there are condition created in order for the phenomenon to occur, can develop with an energy probability higher than that of the thermo catalytic dissociation. One such mechanism of electron exchange between the gas' molecules, used for the saturation of the metallic surface is made possible by the existence of the double electric layer in the zone near the metallic surface. Beside this on the surface of the metal the crystalline matrix is not electrically balanced, phenomenon equivalent to an exceeding number of electrons in these areas. When the ammonia molecules make contact with the metallic surface it is possible to occur a transfer of electrons towards the gas molecules. The possibility for the electrons to adhere is ensured by the presence of stable external orbits for the atoms that compose the molecules of gas. The ammonia neutral molecules' affinity for the electrons can be explained using the energy released or on the contrary consummated during the process of merging between the electron and the molecule (the value correspondent to the affinity towards the electron is +2.85 eV for the ammonia molecule). The energy release when forming the metallic anions by the contact of the gas molecules with the metallic surface represents a necessary but not sufficient condition for the electron to adhere. The value of energy necessary for the interaction of the gas molecules with the metallic surface must be equivalent to the value of energy to tore apart the electron, which in case of the iron matrixes is of 4.31 eV , and in the presence of sub-micron (oxide films a real occurrence in the thermo chemical processing) this value is 3.0eV.

The energy necessary to tore apart the electron and to overpass the barrier of potential is composed by the electrons , kinetic (thermal) energy, the molecule's kinetic energy transferred to the electron in the moment the molecule impacts the metallic surface and the energy correspondent to the molecule affinity towards the electron.

The kinetic energy of the ammonia molecule at different temperatures can be calculated with the relation:

$$W_1 = \frac{m\varpi^2}{2} = kT \tag{7}$$

where: ϖ – represents the average speed of the molecule; m – the mass of one molecule; k – the Boltzmann constant $=1.38*10^{-23}$ J/K$=\frac{1.38*10^{-23}}{1.6*10^{-19}}$ eV.

The average kinetic energy (thermal energy) of the electrons at different temperatures can be determined with the relation:

$$W_2 = \overline{\varepsilon_i} = 3/2kT \tag{8}$$

The calculated values for the electron's energy in the area of contact between the metallic surface and the molecule of nitriding gas (ammonia), in the range of temperatures between 100÷700^{o}C are summarized in table1.

Table 1. The energies of the electrons in the electric double layer, after the contact with the nitriding gas, ammonia

T,^{o}C	T,K	W1,eV	W2,eV	$W=W_1+W_2+S_{NH3}$ **AMMONIA**
100	373	$3.21*10^{-2}$	$4.81*10^{-2}$	2.9302
200	473	$4.07*10^{-2}$	$6.10*10^{-2}$	2.9517
300	573	$4.94*10^{-2}$	$7.41*10^{-2}$	2.9735
400	673	$5.80*10^{-2}$	$8.7*10^{-2}$	2.995
500	773	$6.66*10^{-2}$	$9.99*10^{-2}$	***3.0165***
600	873	$7.53*10^{-2}$	$11.29*10^{-2}$	***3.0382***
700	973	8.39*10-2	$12.58*10^{-2}$	***3.0597***

The analysis of the results stated in table 1 confirm an information verified in common practice: nitriding in ammonia can develop at temperatures at of over 450 °C, at which temperature it is certain the apparition of type NH_3^-; on the contrary, in nitrogen it is impossible for the process to develop, the calculation confirming the great stability of the molecule in the ranges of temperatures at which the gaseous nitriding develops.

The analysis of the electronic interaction mechanism, specific for the initial stages of the adsorption process creates the possibility to anticipate the temperature range in which the thermal processing can occur, but can also be estimated the conditions in which it develops with maximum intensity. This is possible because the forming process of the negative ions depending on the electron energy presents an extreme character. The adherence of the electron to the neutral molecule takes place after the first one has sufficient energy to overpass the barrier of potential. It is also noteworthy that both the electron and the molecule must have relatively reduced kinetic energies, of ~0.1eV. At higher values (speeds) the electron will slide alongside the molecule unable to interact with the later. For values of energy equivalent to the energy necessary to overpass the barrier of potential, the electron at the end of the mid free way will have a kinetic energy close to zero value, this fact supporting the maximal development of the process of „adherence" to the neutral molecule, therefore, in other words, of the anions forming process. When the electrons have energy values higher than the energy value necessary to overpass the barrier of potential, an increasingly higher proportion of the electrons will slide along the molecules unable to interact with the later ones, a phenomenon that implies a decrease in the proportion of anions.

Following this first phase, it became necessary to determine in theory the energy conditions that must be created in order to make possible an acceleration of the anions in the electric field created. The causes that determine this problem to be solved are:

– At reduced values of the electric field intensity generated in the space between the electrodes (anode-the part to be nitrided; cathode – the muffle in which the process develops), it can't happen an orientation and an effective acceleration of the anion in the field, the energy ceded to the electrons from the electric double layer of the product's surface being insufficient to stimulate the emission of the electrons in the surface:

– At values to high of the applied electric field intensity it is possible to initiate the spark type electrical discharge. An explanation can be: the increase in the energy of the electrons emitted by the anode surface, following the energy intake caused by the anions strongly accelerated in the electric field, causes an increase in the number of electrons who can't interact with neutral molecules of ammonia, phenomenon which will cause a reduction of the anion proportion in the space between the electrodes and as a consequence decreases kinetics for layer forming. In the same time with the increase in the energy of the electric field applied it is also amplified the proportion of the rapid electrons capable through collision with the neutral molecules to lead to the ionization of the later, with the formation of the type NH_x^+ cations.

It results that there must be an optimal value of the electric field intensity in order for the effect of the anions' presence to become noticeable by the intensification of the nitriding process of the anode in the same time with a reduction of the of the cathode nitriding kinetics.

The general level of ion's energy in the presence of the electrical field can be calculated with the relation:

$$W=E\lambda+kT+S \tag{9}$$

where: E – is the electrical field intensity ,V/m; λ – the length of the average free way, m

$$\lambda_i=\lambda_0\,\frac{T_i}{T_0} \tag{10}$$

$\lambda_0=12.8.10^{-8}$ m, at $T_0=293$K and p=101,3KPa

k – Boltzmann's constant

$$k=\frac{1,38.10^{-23}}{1,6.10^{-19}}=0,862.10^{-4}\,\text{eV}$$

T – temperature (K)

S – ammonia molecule's affinity for electron

$$E=\frac{U}{r.\ln\frac{R}{r}} \tag{11}$$

U – applied voltage (V), r – the anode's radius , m (the part to be nitrided), R – the coaxial electrode radius, m, acting as cathode (see fig. 1)

Note: During the cycle of experiences performed, the anode radius was set to r=10 mm and the cathode's to R=14 mm, thus R/r=1.4.

The results of the calculus regarding the modification of the anion's energy in the presence of the electric field are summarized in table 2

Table 2. The modification of the NH_3^- *anions' energy under the influence of the electric field (Note: The data in the table does not include the corresponding value for ammonia molecule's affinity for the electron)*

U,V	**E,V/m**	**W, eV-S(2.8eV),for T[K],**							
		573		**673**		**773**		**873**	
		K.T	**E.λ**	**K.T**	**E.λ**	**K.T**	**E.λ**	**K.T**	**E.λ**
500	148800	0.049	0.037	0.058	0.043	0.066	0.050	0.075	0.056
1000	297600		0.074		0.086		0.099		***0.112***
1500	446400		0.115		0.135		***0.156***		0.176
2000	515200		0.148		***0.174***		0.200		0.226
2500	744000		***0.185***		0.218		0.250		0.282
3000	892800		0.221		0.260		0.299		0.337
3500	1041600		0.260		0.305		0.350		0.396
4000	1190400		0.297		0.349		0.401		0.453

For the range of temperature set for analysis, 300÷600°C and respectively voltage (500÷4000V, DC), the calculated values for the anions' energies, superior to those marked in the table, represents the necessary minimal values for the electrons to overpass the barrier of potential (3.0eV in the case of iron matrixes with sub-micron oxide films), in order to extract themselves from the double electric layer and perform the ionization of the molecule.

The calculations made have led to the conclusion that the actual experiments intended to expose the presence of the anions and therefore the adsorption's ionic mechanism must be performed in the range of corresponding values for the intensity of the electric field of: $1.48.10^5 \div 7.44.10^5$ V/m (applied voltage 500÷2500 V, for a value of the geometric factor of R/r=1.4), when the temperature of the nitriding process would in theory vary between 300^{o}C and 600^{o}C.

The experiments were effectively done on the installation presented in figure 1 , at a temperature below the corresponding eutectoid transformation temperature in the Fe-N system (591^{o}C) namely 560^{o}C, in partially dissociated ammonia atmospheres, with 2 hours of maintain at temperature, varying the applied voltage in the range of 500÷4000V. The results obtained were evaluated by calculating the mass variations and respectively measuring the total layer and the combination zone. The results obtained are summarized in figures 2÷3.

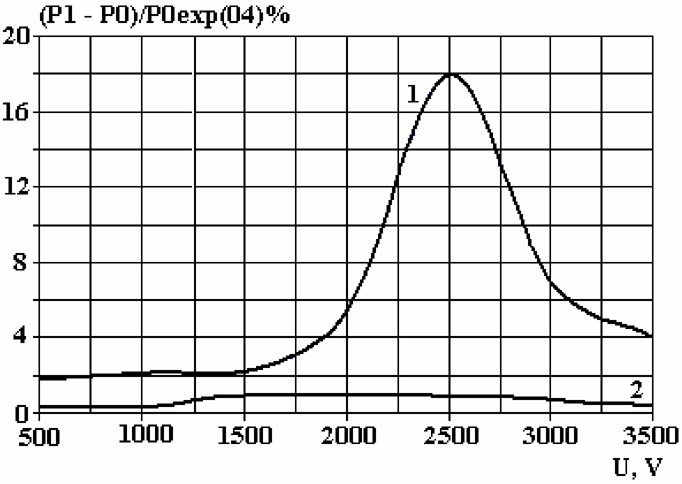

Fig.2 Mass variations of the pure iron samples (anode and cathode) nitrided at 560^{o}C, 2 hours, in the presence of an electric field

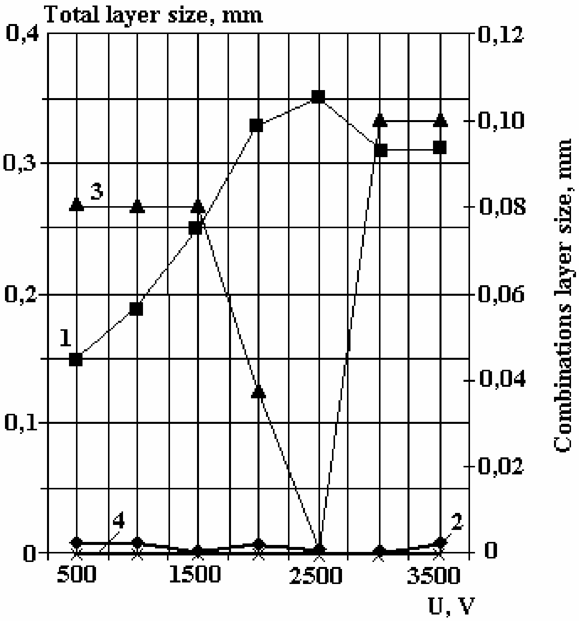

Fig. 3 The variation of the dimension of different structural components of nitrided layers in electric field, obtained on pure technical iron samples T=ct=560oC,t=ct=2ore)

The results obtained confirm the theoretical reasoning previously given: around the value of 2500V there are both the maximum corresponding to the increase in the size of the nitrided layer (in general dimension and in size of the components area) and the maximum correspondent to the mass increases. Over passing this value implies an increase in the anions' energy, with effect on the proportion of anions in the space between the electrodes and respectively on the energy associated to the electrons that leave the electric double layer. On over passing this value the effects of the presence of the electric field begin to diminish and over a certain value 3500V, begins to occur the spark type electric discharge, a phenomenon that favors the amplifying of the cathode saturation kinetics.

Conclusions

It was demonstrated through experiments the existence of the anions on gaseous nitriding in ammonia therefore in the working enclosure can coexist depending on the created conditions, non dissociated ammonia molecules, their dissociation products represented by type NH_x radicals, anions, cations, etc. It was underlined the possibility to accelerated the process by applying electric field whose intensity is dependent on the process temperature and the geometric factor of the charges.

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Received 01.07.08

Summary

Countless contradictions, of practical or theoretical kind, associated to the gaseous nitriding process, for a long time have forced the researcher to study in depth the theoretical aspects of the process. The analysis of the main phases of the mass transfer process occurring within the nitriding process led to the conclusion that the phases responsible for the series of noted contradictions are the ones correspondent to the reactions in the environment, respectively on the interface environment-product. Through theoretical studies and experimental verification it was exposed that, in the reaction space, in conditions specific for the gaseous nitriding to occur, the ammonia undergoes, most probably, in areas close to the metallic surfaces, in the same time with the thermal catalytic dissociation, an ionization process that is followed as a consequence by the apparition in greater number of anions and anionic complexes. In this paper are presented the results of the studies and experimental researches related to the adsorption's ionic mechanism on nitriding in a gaseous medium.