Plasma nitriding – theory and praxis

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1. Introduction

Plasma nitriding technology is a process performed in a vacuum with the assistance of a low ionized plasma of an anomalous glow discharge. The electric DC discharge makes it possible to physically dissociate the gaseous medium under conditions where the activity of the medium would not have taken place during conventional gas processing. This effect can be used to advantage. It is possible to use various gases (N_2, Ar, H_2, C_3H_8…) for which thermal cleavage of molecules during nitriding is out of the question, or to completely eliminate ammonia from the nitriding process.

Fig. 1 shows a graph of the mass spectrum of the occurrence of individual ammonia ions during the nitriding process at 510°C for 6 hours, and these values are compared with the spectrum of the atmosphere without discharge. By comparing both spectra, it is possible to determine the formation of individual ions during dissociation of ammonia by discharge and during thermal dissociation. A significant difference is evident and this difference specifies the whole process of plasma nitriding. The activation of particles for nitrogen diffusion is incomparably higher in the discharge and therefore the activated nitrogen potential is also higher than in nitriding in gas. This difference affects the speed of the process and is one of the main advantages of plasma.

On the other hand, the physical nature of the process has the disadvantage that where the gas is not dissociated by the electric discharge, nitriding does not occur at all, and that the nitriding field and its geometry are affected by the cathode dark space. The properties of the cathode dark space are influenced by a number of physical properties, such as particle weight, current density, potential at the cathode, etc. This is therefore a very complex process that requires special knowledge.

There are a number of theoretical works that explain the physico-chemical processes at the cathode. Although many theories complement or contradict each other, it is clear that the resulting reactions are dependent:

- on parameters of electric discharge (ion energy, ion current density…)
- on the type of gases used (dissociation potential, chemical activity…)
- on the macro physical properties of the environment (temperature, pressure ..)
- on cathode material and surface condition (electron emission…)

From the user's point of view, these are quantities that must be converted into adjustable and controllable values. E.g. voltage, current, pulse length, gas flow, pressure, time, etc.

Another advantage of the plasma process is the actual activation of the treated surface by the continuous flow of energetic ions to the cathode. There is a significant "self-cleaning" effect and the surface becomes atomically clean and without diffusion barriers. Also, the

absence of oxygen, or the marked ability of the split hydrogen to bind oxygen to each other, means that the process proceeds without oxide and without addtional chemical reactions. In addition to physical activity, chemical activity also plays an important role. The participation of hydrogen ions H^+, $H2^+$ with an energy of several eV ensures the extraction of Fe, resp. other elements from oxide bonds, either by a reduction or dissociation mechanism.

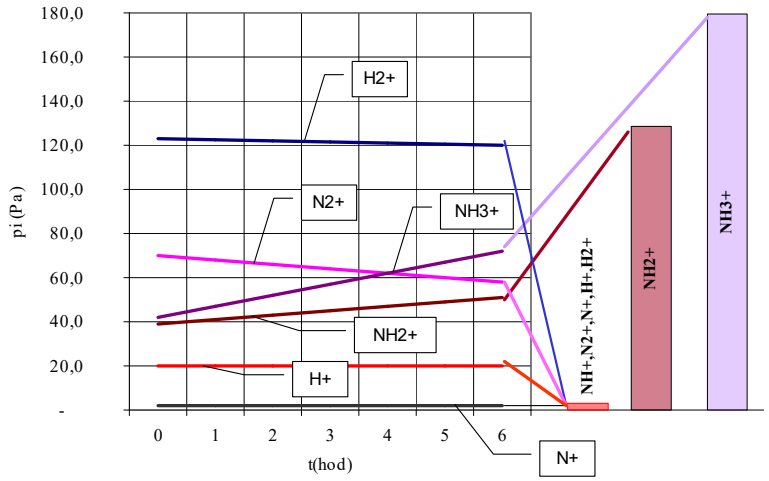


Fig. 1 *Measured values of the mass spectrum of the atmosphere of undissociated ammonia NH3 with discharge and without discharge at total pressure pT = 320 Pa (measured by Balzers QMG511)*

2. Diffusion

Nitrogen atoms are adsorbed on the surface, either in the form of N^+ particles or radicals such as NH^+, NH_2^+, NH_3^+. Due to the low energy up to 10 eV, they are not implanted into the surface of the components. Nitrogen passes into the material by other mechanisms and the moment it penetrates the Fe lattice, its behavior is affected only by diffusion laws. From this point on, nitrogen is transferred by the same mechanism to the core material as in other diffusion processes. The benefits of plasma are slowly lost and at times above 16 - 20 hours the nitriding completely disappears.

The diffusion equation has the form:

$$x = k * \sqrt[2]{Do * e^{(-Q/RT)} * t}$$

where **Q** is the activation energy of diffusion, $\mathbf{D_o}$ diffusion coefficient - a temperature-independent constant, dependent only on the lattice structure, **t** the process time.

In the case of alloy steels, the diffusion coefficient depends on the amount and type of alloying elements that have the ability to bind nitrogen. The amount of alloying elements affects not only the rate of nitrogen diffusion but also its solubility. The larger the amount of alloying elements, the higher its solubility. Various structural components are formed according to the

schemes MeN or Me_2N , $(Fe,Me)_{2-3}(N,C)$, $(Fe,Me)_x(N)$, where Me = W, Mo, Cr, Al, Ti, V, Nb, Zr, and these phases have a inhibitory effect on nitrogen diffusion. For the same reason, the required diffusion activation energy also increases [1]. The effect of carbon is minimal.

The diffusion coefficient - corrected for the temperature of the experiments 510 C, and the activation energies have the following regression equations [2] depending on the nitride-forming alloying elements:

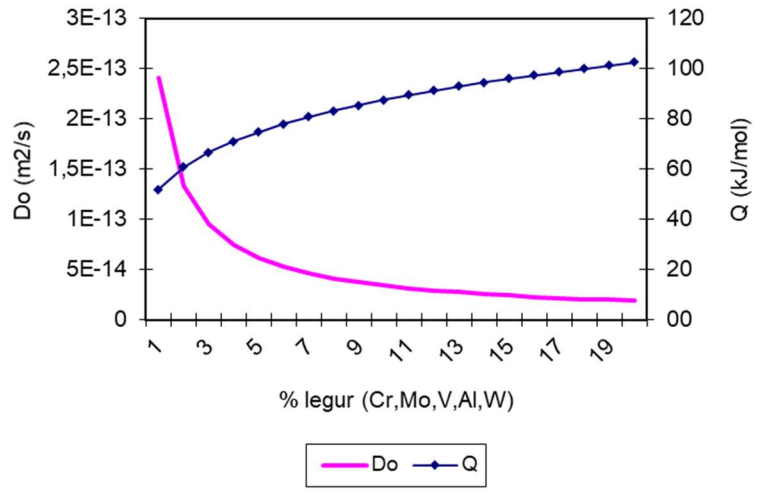
$$D_{0(510)} = 2{,}4086 * 10^{-13} * (\%legur)^{-0{,}849}$$

The above equations were compiled from experiments with the following steels:

$$Q = 51{,}917 * (\%legur)^{0.227}$$

Steel	Do*E-13	Q	Alloy Elements						
	(m2/s)	(kJ/mol)	C	Cr	Mo	V	Al	W	Total
11500/1.0050	**2,44**	**44,20**	0,4	0,0	0,0	0,0	0,0	0,0	**0,0**
14140/1.7034	**2,09**	**46,90**	0,4	1,0	0,0	0,0	0,0	0,4	**1,4**
14220/1.7131	**2,23**	**46,20**	0,2	1,0	0,0	0,0	0,0	0,0	**1,0**
14340/1.8504	**1,33**	**73,16**	0,4	1,6	0,0	0,0	1,2	0,0	**2,8**
15330/1.7707	**0,99**	**66,50**	0,3	2,5	0,3	0,2	0,0	0,0	**3,0**
15340/1.8509	**1,11**	**79,60**	0,4	1,5	0,2	0,0	1,0	0,0	**2,7**
19436/1.2080	**0,18**	**83,10**	2,0	12,0	0,0	0,0	0,0	0,0	**12,0**
19541/1.2365	**0,36**	**101,40**	0,3	3,1	3,1	0,7	0,0	0,0	**6,9**
19550/AISIS7	**0,78**	**66,00**	0,6	3,3	1,2	0,1	0,0	0,0	**4,6**
19552/1.2343	**0,28**	**89,80**	0,4	5,0	1,4	0,5	0,0	0,0	**6,9**
19830/1.3343	**0,26**	**93,60**	0,9	4,2	5,0	1,9	0,0	6,3	**17,3**
19852/1.3243	**0,26**	**93,60**	1,3	4,4	0,0	4,0	0,0	11,0	**19,4**

Tab. 1 *Table of experimental steels with calculation of coefficients $D_{0(510)}$ and Q*



Fiug. 2 *Dependence of diffusion coefficient and activation energy on the amount of nitride-forming alloying elements*

Each material has a different alloying, ie a different diffusion rate. Ie. that the nitriding time required to achieve the same diffusion depth is different for each material. For high-alloy ledeburitic 12% steels of the 1.2080 type, or austenitic stainless steels, we can also talk about the unreachability of certain depths in realistically achievable times (> 100 hours). In each case, these simplified equations allow the basic nitriding parameters, ie temperature, time and diffusion depth, to be estimated for each material.

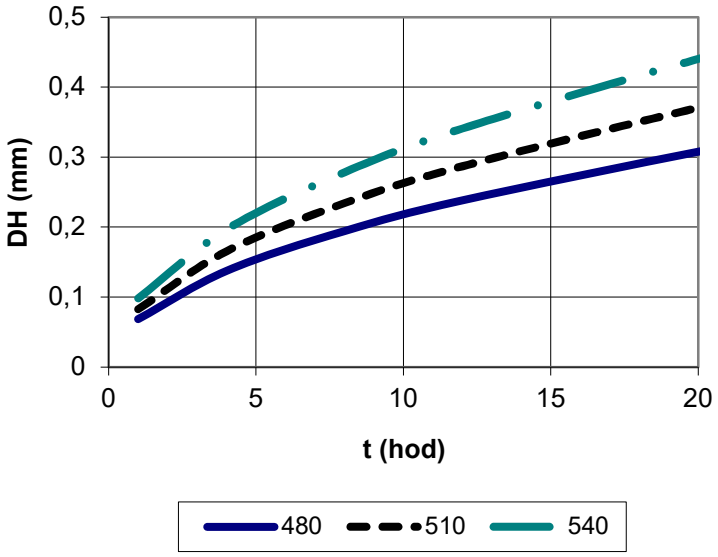


Fig. 3 *Calculated diffusion equations for steel 14220 / 1.7131/16MnCr5*

3. New generation equipment

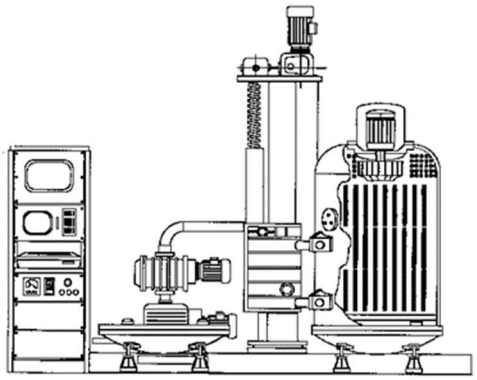
It can be seen from the above diagram that the process temperature is one of the most important nitriding parameters. To achieve this, only electric direct discharge is used in conventional devices. Energy ions bombard the cathode - the component, and their kinetic energy is converted into thermal energy. Although this method provides all the necessary process parameters, the disadvantage is the possibility of concentrating the discharge in places with more complex geometry or in cavities. In these places, local overheating or even melting of parts may occur.

Another disadvantage is the need for perfect pre-cleaning of the surface. If the surface is not clean, the glow discharge is unstable and tends to switch to arc discharge mode. In the first phase of the process, therefore, only the impurities are separated from the surface, but no heating occurs because the steady ionic current is small. The process is therefore prolonged and in the event of adverse pollution, it is difficult to achieve economical use of the equipment. In extreme cases, the process cannot be started at all.

In the new generation of equipment, only a part of the power is transferred from the plasma (30-70%), the remaining heat output is then transferred mainly from external heating. It can be convection or radiation. Thus, the process of component heating and discharge cleaning can take place at the same time.

Due to the fact that many impurities are bound only by weak absorption forces, many impurities are organic in nature and thermal decomposition can significantly speed up the process of their removal, then the whole process is significantly accelerated.

The effect of suppression of electric discharge power is also favorable for the formation of concentrated discharges or places with a higher ionic current density. Therefore, different components can be better combined in these devices, and the risk of a large temperature difference is significantly reduced.



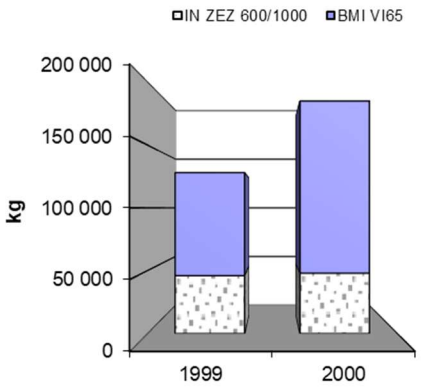


Fig. 4 *New generation equipment with external radiation heating in three zones*
Fig. 5 *Comparison of performance of old and new generation equipment (annual sales in kg)*

In most cases, this device concept is further combined with a pulsed plasma source, which allows better process control and reduces the risk of short circuits and surface damage. The combination of the power part of the pulse and the pulse gap is another parameter that allows to improve the process control

4. Conclusion

All of the above parameters are reflected in the productivity of the device. Fig. 5 compares the "performance" of the old ION ZEZ 600/1000 cold wall concept device and the BMI VI65 device with radiation heating and pulsed plasma. Although the devices are not completely identical in size, the productivity of work on the new generation of devices is significantly higher. However, the reliability of nitriding parameters, especially temperature, is also significantly higher. With the old generation equipment, a better result than +10 C cannot be achieved, but in many cases the temperature difference is > 100 C.

With the new generation of devices, it is possible to regulate with an accuracy of +/-1 C even for very complicated batches, and these values can be achieved reproducibly and permanently.

[1] Lachtin J. – Azotirovanije stali, Masinostrajenije, 1976, Moskva
[2] Stanislav J – Iontová nitridace a nitrid titanu – disertační práce, říjen 1991, Liberec