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# Concept of an economical and ecological process of gas nitriding of steel

*An economical, ecological version of the gas nitriding process is presented. It allows a substantial reduction in the consumption of industrial gases compared with currently used processes. Also it leads to a simplification of nitriding installation as well as the process itself, while allowing maintenance of full control over the kinetics of the layer growth. The concept was developed from studies of the thermodynamics and kinetics of growth of nitrided layers on iron and steel. It has been verified in trials under industrial conditions.*

*Es wird eine ökonomische, ökologische Möglichkeit des Nitrierprozesses mit Gas vorgestellt.*

## 1 Introduction

The nitriding process, which improves the life expectancy of machine parts, may reduce at the same time the consumption of steel and energy and, as a result, the cost of the entire manufacturing process. For this reason, it may be qualified as economical and ecological.

Economical and ecological advantages will at the same time characterize a process, in which the formation of the nitrided layer occurs in the shortest time, with minimal consumption of gases, electrical energy, and water. Concurrently, it is assumed that the nitrided layer has an optimal structure in terms of expected performance i. e. the required zones of iron nitrides ( $\alpha$ ,  $\gamma' + \alpha$  or  $\epsilon + \gamma' + \alpha$ )<sup>1</sup>, correct thickness, nitrogen concentration profile and hardness, and a surface condition that allows immediate use of parts without any finishing operations.

Ecologically, the amount and composition of gas emissions emitted into the surrounding atmosphere are also important. Exhaust gas should contain only environmentally neutral components such as  $H_2$ ,  $N_2$  and  $H_2O$  and be free of nitrogen oxides or residual  $NH_3$ . Only by satisfying all these requirements the process is considered to be both, economical and environment-friendly, and therefore ecological.

The present concept of an economical, and at the same time ecological gas nitriding process creates the conditions for a substantial reduction in the consumption of industrial gases, as compared with currently used processes. Also, it leads to a simplification of the nitriding installation as well as of the process itself, while allowing full control over the kinetics of the layer growth. The process, based on the thermodynamics and kinetics of growth of nitrided layers, has been tested and verified in industrial application.

<sup>1</sup> The term  $\epsilon + \gamma' + \alpha$  represents a nitrided layer composed of:  $\epsilon$  at the surface,  $\gamma'$  more or less beneath  $\epsilon$  and an  $\alpha$  diffusion zone underneath; the term  $\gamma' + \alpha$  denotes a layer composed of  $\gamma'$  at the surface and an  $\alpha$  diffusion zone underneath; the term  $\alpha$  denotes an  $\alpha$  diffusion zone adjacent to the surface.

## 2 Review of current processes of gas nitriding

To date, traditional nitriding, with very limited control over the growth of the nitrided layer is still very much in use worldwide [1]. It is performed using only ammonia and the resulting layer is composed of superimposed  $\epsilon + \gamma' + \alpha$  phases. In industrial practice, the superficial zone of iron nitrides  $\epsilon + \gamma'$  (as a rule exceedingly thick and brittle) is usually removed by grinding [2, 3], which substantially adds to the cost of the manufacturing process. Moreover, as will be demonstrated later, the formation of an  $\epsilon + \gamma' + \alpha$  layer uses much more ammonia ( $NH_3$ ) than the formation of a layer composed of  $\gamma' + \alpha$ . It is because the growth of an  $\epsilon + \gamma' + \alpha$  layer occurs at a much higher nitriding potential ( $K_N$ ) value. This then calls for a greater flow of  $NH_3$  through the retort and consequently its higher consumption. The lowest potential  $K_N$  and the lowest  $NH_3$  consumption is required for the creation of the diffusion (precipitation) layer  $\alpha$ . Therefore, in the traditional production process, the  $\epsilon + \gamma'$  layer and its subsequent removal is, from the economical point of view doubly disadvantageous.

Controlled gas nitriding, performed for over 60 years, represents an advancement over an earlier (but still encountered today) 'traditional' method, using 100 % ammonia atmospheres. Two-component atmospheres of ammonia and dissociated ammonia ( $NH_3 + NH_{3,diss.}$ ) [4, 5], as well as ammonia and molecular nitrogen ( $NH_3 + N_2$ ) came into use about 50-60 years ago [6-8]. Through proper selection of atmosphere composition and adjustment of atmosphere flow rate through the retort, it is possible to form layers of the required phase composition (consisting of  $\epsilon + \gamma' + \alpha$ ,  $\gamma' + \alpha$  or  $\alpha$  zones) of required thickness of individual zones, along with a limited nitrogen concentration at the surface. Diluting ammonia with dissociated ammonia ( $NH_{3,diss.}$ ) or with molecular nitrogen ( $N_2$ ) results in a diminishing supply of atomic nitrogen to the surface, leading to a reduction of the superficial nitrogen concentration, and in consequence to a limitation of growth or even to a removal of the undesirable brittle nitride zones. Also, similar layers with a limited  $\epsilon$  or  $\epsilon + \gamma'$  zone can be obtained in the 'vacuum nitriding' process (Nitrovac) [9], or through plasma nitriding [2, 3].

These processes allow the elimination of final grinding, thus reducing the cost of the whole manufacturing process. However, as will be shown below, nitriding using two-component atmospheres involves a considerable consumption of gases, hence a higher cost of the process.

From the two mentioned atmosphere types,  $NH_3 + NH_{3,diss.}$  and  $NH_3 + N_2$ , the second one (with  $N_2$ ) is more widely used in industrial practice. It is usually cheaper than the  $NH_3 + NH_{3,diss.}$  atmosphere, as nitrogen  $N_2$  is in most cases cheaper than dissociated ammonia. Moreover, production of  $NH_{3,diss.}$  requires a dissociator, which adds to the cost of the installation. The dissociator, generating a high-hydrogen mix often represents a psychological barrier to potential industrial users. On the other hand, in the case of  $NH_3 + N_2$  atmospheres, the control of the kinetics of layer growth is much more difficult and limited because of the non-equilibrium character of the process [10]. The same is true for plasma nitriding [2, 3].

Installations of vacuum and plasma nitriding are technically more complex and therefore more expensive than installations of controlled nitriding [3, 4].

### 3 Essentials of the concept of economical and controlled nitriding

The present concept assumes carrying out the process of controlled nitriding with  $\text{NH}_3$  alone. This is a simpler process than that using two-component mixes of ammonia diluted with  $\text{N}_2$  or  $\text{NH}_3$  diss.<sup>2</sup> The regulation of the chemical composition of the atmosphere in the retort, and therefore the regulation of  $K_N$ , is obtained through the variation of the inflow rate of  $\text{NH}_3$  into the retort<sup>3</sup>. The authors accept that the inflow of  $\text{NH}_3$  into the furnace may at times be reduced to zero, which widens the range of the gas composition in the retort (and by the same token, of the nitriding potential  $K_N$ ). The amount of  $\text{NH}_3$  introduced into the furnace is regulated (controlled) with the aid of a gas analyzer (for example an infrared analyzer). The gas analyzer opens or closes periodically the  $\text{NH}_3$  inlet valve at a frequency required for maintaining a desired gas composition (a desired  $K_N$ ) in the retort. The concept presented here is not an entirely new solution. In existing practice, from early years on, the composition of the atmosphere has been controlled through the variation of the flow rate of  $\text{NH}_3$  into the furnace, but in a relatively narrow range, without closing the inflow entirely. In rare instances (aerospace industry), considerable limitations of ammonia inflow have been applied, accompanied by a large drop in the  $K_N$  potential. However, in the case of the most widely used processes of controlled nitriding, the established practice is focused on „gas-guzzling” processes using two-component diluted atmospheres. This raises the question: why, to this day, has gas nitriding based on a single-component –  $\text{NH}_3$  – atmosphere has not been implemented on a larger scale?

It may be supposed that the reasons have been: an insufficient knowledge of the fundamental physico-chemical mechanisms of nitriding as well as the complexity of nitriding processes in industrial installations. Literature on the subject does not answer the question whether the dissociated ammonia formed in the furnace (on the surfaces of the retort and of the load) is equivalent in its effect on the nitriding kinetics to  $\text{NH}_3$  diss. generated in an upstream dissociator. Therefore there was no answer to the question whether a mix containing  $\text{NH}_3 + \text{NH}_3$  diss. formed in the retort would lead to the same surface nitrogen concentration, and as a consequence to the same layer structure as a  $\text{NH}_3 + \text{NH}_3$  diss. mix with  $\text{NH}_3$  diss. supplied from a dissociator, assuming the same nitriding potential  $K_N$  in both cases.

There was an unfounded opinion among many practitioners that the rate of the inflow of ammonia (and also of the  $\text{NH}_3 + \text{N}_2$  and  $\text{NH}_3 + \text{NH}_3$  diss. mixes) into the retort has an effect not only on the atmosphere composition in the furnace but also, independently, on the kinetics of the layer growth. They considered, apart from maintaining a required nitridding potential  $K_N$ , for ensuring a correct growth kinetics, it also necessary to provide a certain flow rate of the atmosphere through the retort. For this reason, relatively high flow rates of atmosphere have been used to this day.

<sup>2</sup> This refers to N<sub>2</sub> and NH<sub>3</sub> diss. introduced together with ammonia into the retort, and not to the same components formed in the retort as products of NH<sub>3</sub> dissociation.

<sup>3</sup> The inflow rate of atmosphere into the retort is more relevant to this discussion than the flow rate *through* the retort. The latter, because of  $\text{NH}_3$  dissociation and thermal expansion of gases, is difficult to measure and practically unimportant.

The absorption isotherm of nitrogen dissolved in  $\epsilon$ -Fe<sub>2</sub>N<sub>1-x</sub> denotes the relationship between the nitriding atmosphere (nitriding potential  $K_N$ ) and the amount of nitrogen in the  $\epsilon$  phase under equilibrium conditions at constant temperature.

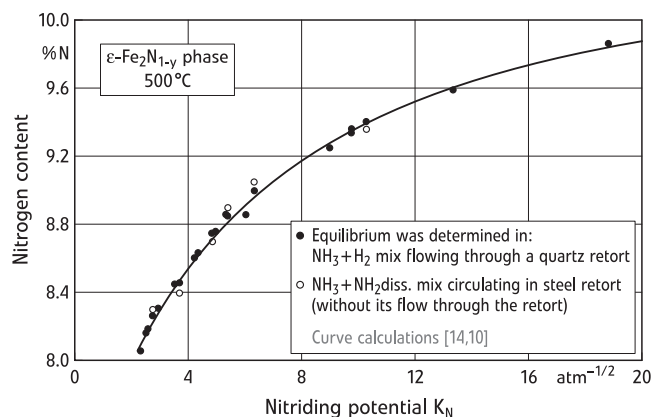


Fig. 1. Absorption isotherm of nitrogen in the  $\epsilon\text{-Fe}_2\text{N}_v$  phase, determined experimentally in atmospheres obtained from  $\text{NH}_3$ ,  $\text{NH}_3 + \text{H}_2$  and  $\text{NH}_3 + \text{NH}_4\text{diss.}$  Curve - calculated according to [14, 10]

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In the following section, we discuss the essential aspects of the proposed concept of controlled nitriding, employing  $\text{NH}_3$  only. These aspects will involve thermodynamic, kinetic and technological considerations. In the final section the economical impact will be considered.

### 2.1 Thermodynamic aspect of nitriding in atmospheres obtained from $\text{NH}_3$ and from two-component $\text{NH}_3 + \text{H}_2$ and $\text{NH}_3 + \text{NH}_3$ diss. mixes

*Maldziński et al.* [11-14] investigated the equilibrium between the atmosphere obtained from  $\text{NH}_3$ , or  $\text{NH}_3 + \text{H}_2$ ,  $\text{NH}_3 + \text{NH}_3\text{diss.}$  and  $\text{NH}_3 + \text{N}_2$  mixes, and nitrogen in the  $\gamma'$  and  $\epsilon$  phases of Fe-N alloys. They used thin, porous (open-pore structure) iron foils. Processing was performed in a laboratory furnace with a quartz tube and also in an industrial furnace with a steel retort and a circulating fan. The main difference between the two experiments was that in the quartz retort there was practically no dissociation of  $\text{NH}_3$  while it was considerable in the steel retort. This means that in the steel retort a substantial amount of  $\text{NH}_3\text{diss.}$  was generated on the walls of the retort and surfaces of the charge racking.

These studies demonstrated that the equilibrium conditions between the retort atmosphere and nitrogen in the nitride phases are neither affected by the type of the atmosphere nor that of the furnace, but only by the composition of the atmosphere or, in other words, the nitriding potential  $K_N$  at the sample surface. The absorption isotherm of nitrogen dissolved in  $\epsilon\text{-Fe}_2\text{N}_{1-y}$ , shown in Fig. 1, has been determined experimentally, taking into account data points obtained for:  $\text{NH}_3$ , the  $\text{NH}_3 + \text{H}_2$  and  $\text{NH}_3 + \text{NH}_3$  diss. mixes and the two furnace types, one with quartz- the other with the steel retort and fan. In the quartz retort, the equilibrium was obtained in atmospheres  $\text{NH}_3 + \text{H}_2$  and  $\text{NH}_3 + \text{NH}_3$  diss. in conditions of their constant flow (filled circles). In the furnace with the steel retort, the equilibrium was achieved using only  $\text{NH}_3$ , with its supply entirely closed, though with an operating circulation fan (open circles).

The above results confirm that the equilibrium between the atmosphere in the retort and nitrogen in the Fe-N phases depends only on the composition of the atmosphere, or  $K_N$ , at the nitriding surface.

Also, when the  $\text{NH}_3$  supply to the retort is entirely stopped (in the furnace with the steel retort), the equilibrium concentration of nitrogen in the  $\gamma'$  and  $\epsilon$  phases is a function of the  $K_N$  poten-

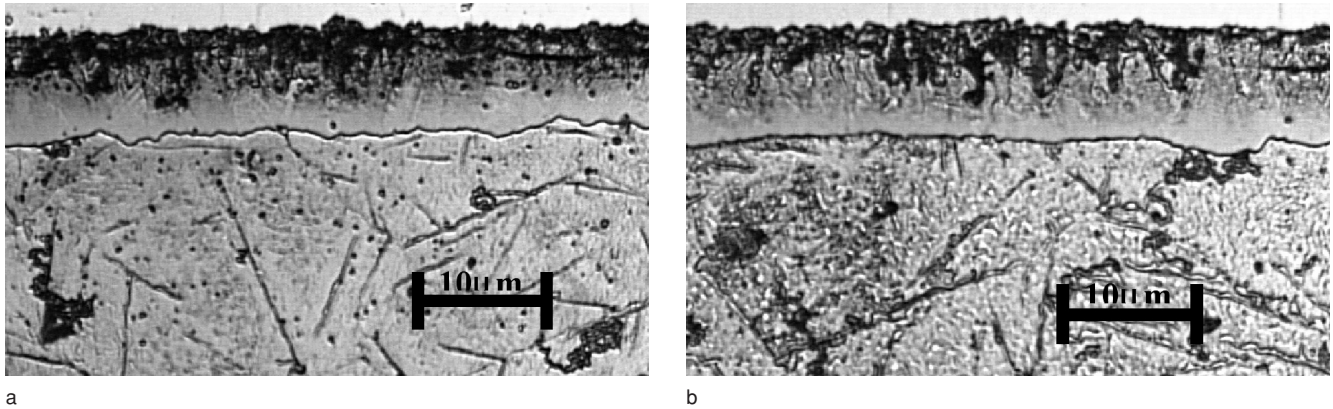


Fig. 2. Micrographs of the nitrated layer on Armco iron, nitrated in a furnace with a quartz retort at  $550^{\circ}\text{C}$ ,  $K_N = 1.3 \text{ atm}^{-1/2}$ , for 10 hours, with a linear velocity along the sample surface: (a)  $1 \text{ cm/s}$ , (b)  $7.5 \text{ m/s}$

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tial only. In these experiments different linear atmosphere flow velocities along the sample surface were used. In the quartz retort this velocity varied between 3 cm/s and 10 cm/s, in the steel retort, due to the action of the fan, varied from 0,2 m/s to 1,5 m/s. This result indicates that the linear velocity of flow along a sample surface does not affect the equilibrium between the nitriding atmosphere and nitrogen in the iron foil.

On the basis of the above considerations it follows that from the perspective of thermodynamics, dissociated ammonia generated in a separate dissociator is equivalent to the same  $\text{NH}_3$  diss. formed inside the steel retort (furnace with a fan).

### 3.2 Kinetic aspect of nitriding in atmospheres obtained from $NH_3$ and from two-component $NH_3 + H_2$ and $NH_3 + NH_3$ diss. mixes

The above conclusion is also important from the point of view of kinetics, as the nitrogen concentration at the surface determines the growth rate of the layer and its phase structure. But in the condition of equilibrium between the atmosphere and nitrogen in a thin iron foil there is no net diffusion of nitrogen atoms from the surface into the sample core. This raises the question of the influence of the above-analyzed factors on the surface concentration of nitrogen ( $c_s^N$ ) and, in consequence, on the kinetics of layer growth on samples of considerable thickness. In this event there is a diffusion of nitrogen atoms from the surface into the core, and the surface concentration of nitrogen tends to be determined by the relative fluxes of nitrogen atoms from the atmosphere to the metal surface and from the surface into the metal [15-18]. In such a case, the linear component of atmosphere flow velocity parallel to the metal surface can also have an effect on the layer growth. If it is too small, it may slow down the growth kinetics. On the other hand, some practitioners are concerned that too high a linear velocity may also have a detrimental effect on the kinetics of nitriding. It could supposedly 'destroy' the Nernst layer and as a result impede the supply of atomic nitrogen to the surface.

Within the scope of this investigation, the effect of linear flow velocity of the  $\text{NH}_3 + \text{NH}_3\text{diss.}$  atmosphere along the sample surface on the kinetics of growth of the  $\epsilon + \gamma'$  zone on Armco iron was studied. The experiments were carried out using a quartz tube furnace, within the range of linear flow velocity from 0.25 cm/s to 7.5 m/s, at a constant temperature and nitriding potential  $K_N$ . It turned out that the flow velocity of atmosphere parallel to the nitrided surface has only an effect with very low velocities 0.25–1 cm/s, and this solely in the initial period of the

nitriding process, when the absorption of nitrogen by the iron surface is highest<sup>5</sup>. In the range of 1 cm/s to 7.5 m/s the linear velocity has no effect on the growth of the above-mentioned layer anymore. The  $\epsilon+\gamma'$  zone on Armco iron shown in Fig. 2a was obtained with a linear velocity of 1 cm/s, and with 7.5 m/s in Fig. 2b. Both cases yielded a similar thickness of the whole  $\epsilon+\gamma'$  layer and of the individual  $\epsilon$  and  $\gamma'$  zones. These results show conclusively that the kinetics of layer growth does not depend on the linear flow along the treated surface but only on the composition of the atmosphere.

In the presence of nitrogen diffusion into the metal, the type of the employed two-component atmosphere is not unimportant. In the  $\text{NH}_3 + \text{N}_2$  atmosphere with a high  $\text{N}_2$  content, the supply of the atomic nitrogen to the surface is reduced, thus decreasing the nitrogen concentration at the surface. In this event the process is controlled by two factors: the nitriding potential  $K_N$  of the atmosphere in the retort, and the degree of its dilution with  $\text{N}_2$ . In an atmosphere obtained from  $\text{NH}_3$  or  $\text{NH}_3 + \text{NH}_3$ , diss.  $\text{N}_2$  is also present, but its content is low and in practice the process is controlled only by the potential  $K_N$ .

### 3.3 The technological aspect of nitriding in industrial furnaces

In a typical furnace, incorporating a steel retort and a circulating fan, the atmosphere composition depends directly on three basic factors [10, 19]:

- the dissociation rate of  $\text{NH}_3$  in the furnace retort;
- circulation flow of the nitriding atmosphere in the retort;
- inflow of nitriding atmosphere ( $\text{NH}_3$ ,  $\text{NH}_3 + \text{NH}_{3\text{diss.}}$ ,  $\text{NH}_3 + \text{N}_2$ ) into the retort.

Dissociation of  $\text{NH}_3$  results in the drop of potential  $K_N$ , and thus in a decreased supply of nitrogen to the metal surface. Insufficient circulation of atmosphere in the retort may lead to an inhomogeneity of the atmosphere composition.

The circulation (imposed by a fan) produces a high linear velocity of the atmosphere along the surface of the nitrided charge. It improves the homogeneity of the atmosphere composition in the retort [10, 19]. It also improves the uniformity of temperature. In addition, in the early stages of the process, circulation increases the heat flow from the retort walls to the charge.

<sup>5</sup> This velocity is so low that, were it not for a risk of atmosphere inhomogeneity, no fan would be necessary and convection flows of gas in the retort would be sufficient. A linear velocity of the order of 7.5 m/s may be found in modern industrial furnaces.





pyramid under loads of 1 kg to 30 kg). The lack of difference between the hardness levels of both layers is evidence of the same kinetics of nitriding, whether the  $\text{NH}_3$  supply to the retort is constant or occasionally closed.

The experiment was continued for a total duration of 10 hours. Its extension would, in accordance with the laws of thermodynamics, cause almost complete dissociation of  $\text{NH}_3$ <sup>7</sup>. Thus, prolonging the process would require a small, constant supply of  $\text{NH}_3$  in order to maintain the required nitriding potential in the retort.

## 5 Comparison of consumption of $\text{NH}_3$ , $\text{NH}_3 + \text{NH}_3\text{diss.}$ and $\text{NH}_3 + \text{N}_2$ atmospheres

For a comparison of consumption of  $\text{NH}_3$ ,  $\text{NH}_3 + \text{NH}_3\text{diss.}$  and  $\text{NH}_3 + \text{N}_2$  atmospheres, it has to be assumed that processes using these gas mixes are carried out at the same temperature, and the resulting nitrided layers have the same phase structure, same thickness and the same concentration profiles of nitrogen in individual zones. In other words, that in the analyzed processes the same amount of nitrogen is introduced into the metal in every case.

This is equivalent for each of the atmospheres under consideration, to the equality of diffusion flows of nitrogen,  $J_N^g$ , into the metal. Satisfying this condition requires setting up a specific composition of the atmosphere in the retort. This composition, in the case of 100 %  $\text{NH}_3$ , is determined only by the inflow rate, while for  $\text{NH}_3 + \text{NH}_3\text{diss.}$  and  $\text{NH}_3 + \text{N}_2$ , by both the inflow and the ratio of their components.

### 5.1 Comparison of consumption of $\text{NH}_3$ and $\text{NH}_3 + \text{NH}_3\text{diss.}$ atmospheres

A comparison of consumption of  $\text{NH}_3$  with that of  $\text{NH}_3 + \text{NH}_3\text{diss.}$  is relatively simple. In order to ensure the equality of flows of nitrogen atoms from either of the atmospheres to the surface, it is necessary to adjust the intensity of flow of  $\text{NH}_3$  and of  $\text{NH}_3 + \text{NH}_3\text{diss.}$  and the composition of the latter so as to obtain in the retort, in both cases, the same nitriding potential  $K_N$ . According to previous considerations (sections. 3.1, 3.2 and 3.3), in processes using  $\text{NH}_3$  and  $\text{NH}_3 + \text{NH}_3\text{diss.}$  the nitriding potential  $K_N$  is the only factor determining the flux of nitrogen atoms  $J_N^g$  from the gas phase to the surface and, in consequence, the kinetics of the layer growth. In order to analyze the consumption of atmosphere in both cases we utilized the relationships, determined experimentally on an industrial furnace, between the flow of the atmospheres  $\text{NH}_3$  and  $\text{NH}_3 + \text{NH}_3\text{diss.}$ , and the nitriding potential  $K_N$  inside the retort. Such relationships are shown in Fig. 6 for 530 °C.

It illustrates that in order to replace 100 %  $\text{NH}_3$  with a 60 %  $\text{NH}_3 + 40$  %  $\text{NH}_3\text{diss.}$  mix., maintaining the same potential  $K_N = 0.35 \text{ atm}^{-1/2}$ , it is necessary to increase its flow 7.7 times, in comparison with 100 %  $\text{NH}_3$ . Taking into account the expansion of  $\text{NH}_3\text{diss.}$ , this is equivalent to a 5.6-times higher consumption of  $\text{NH}_3$ . Still larger differences would appear in the case of replacing the  $\text{NH}_3$  with a 20 %  $\text{NH}_3 + 80$  %  $\text{NH}_3\text{diss.}$  mix (this mix is frequently used in the stage 2 of nitriding of alloy steels). In this case (Fig. 6), in order to maintain the potential of  $0.35 \text{ atm}^{-1/2}$ , the flow of 20 %  $\text{NH}_3 + 80$  %  $\text{NH}_3\text{diss.}$  would have to be increased 50 times, compared with the inflow of pure  $\text{NH}_3$ . This is equivalent to a 30 times higher consumption of  $\text{NH}_3$  when using a two-component mix. From this comparison, it also emerges that diluting  $\text{NH}_3$  with dissociated  $\text{NH}_3\text{diss.}$  leads to an increased consumption of  $\text{NH}_3$ , and the higher the dilution,

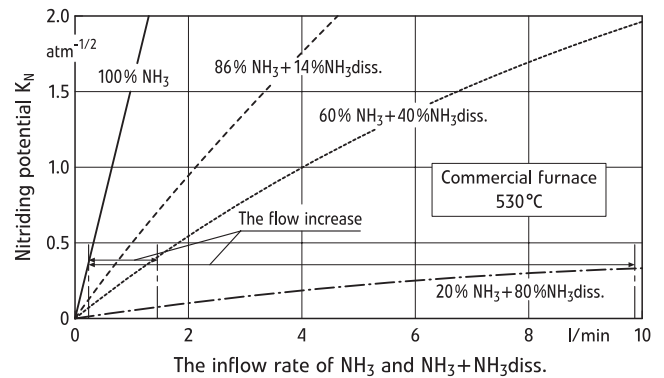


Fig. 6. Effect of the inflow rate of  $\text{NH}_3$  and  $\text{NH}_3 + \text{NH}_3\text{diss.}$  atmospheres on the nitriding potential in a furnace retort. Industrial nitriding pit-type furnace, 1 m<sup>3</sup> working chamber

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the higher the consumption. Replacing 100 %  $\text{NH}_3$  with a  $\text{NH}_3 + \text{NH}_3\text{diss.}$  mix at other temperatures shows the same tendency.

### 5.2 Comparison of consumption of $\text{NH}_3$ and $\text{NH}_3 + \text{N}_2$ atmospheres

Comparison of consumption of  $\text{NH}_3$  and  $\text{NH}_3 + \text{N}_2$  atmospheres is much more difficult than the comparison of consumption of  $\text{NH}_3$  and  $\text{NH}_3 + \text{NH}_3\text{diss.}$  ones. In a process using the  $\text{NH}_3 + \text{N}_2$  mix, the net flux of nitrogen atoms from the gas phase to the surface,  $J_N^g$ , is controlled by the following parameters: composition of the atmosphere in the retort, its nitriding potential  $K_N$ , kinetic parameters (such as diffusion coefficients). The relationship applies:

$$J_N^g = \beta \cdot (c_N^g - c_N^s) \quad (1a)$$

where  $\beta$  is the transfer coefficient from the gas to the solid phase (also called the reaction constant), and is expressed as:

$$\beta = \beta_0 \cdot p_{H_2} \cdot \exp(-Q_1 / RT) \quad (1b)$$

$\beta_0$  – experimental constant in m/s/atm,  $p_{H_2}$  – partial pressure of hydrogen,  $Q$  – activation energy,  $R$  – gas constant,  $T$  – absolute temperature,  $c_N^g$  – surface concentration of nitrogen in equilibrium with the atmosphere, which is a function of the nitriding potential of the atmosphere,  $c_N^s$  – actual nitrogen concentration at the metal's surface. Using Fick's first law it follows:

$$\beta \cdot (c_N^g - c_N^s) = D_M^N \frac{dc}{dx} \quad (2)$$

$D_M^N$  – diffusion coefficient of nitrogen in the superficial layer on steel;  $dc/dx$  – concentration gradient at the surface of the superficial layer.

Diluting  $\text{NH}_3$  with molecular nitrogen lowers the partial pressure of hydrogen  $p_{H_2}$ , and, in consequence (according to 1b) diminishes the transfer coefficient  $\beta$  of nitrogen. Apart from this, the presence of  $\text{N}_2$  has two counter-acting effects on the potential in the retort and concurrently on the equilibrium concentration of nitrogen  $c_N^s$ . On the one hand, a simultaneous lowering of the  $\text{NH}_3$  and  $\text{H}_2$  partial pressures increases the potential  $K_N$ . On the other hand, according to Le Chatelier's rule, it promotes the dissociation of  $\text{NH}_3$ , decreasing  $K_N$ . The resulting effect of both tendencies depends on the surface area of

<sup>7</sup> At the nitriding temperatures (500–570 °C), and at equilibrium, over 99,5 %  $\text{NH}_3$  is dissociated.

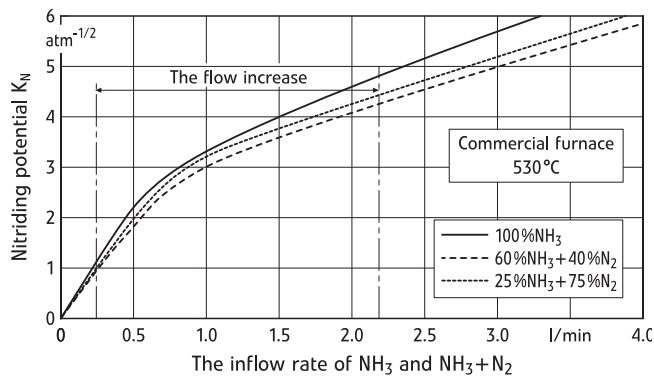


Fig. 7. Effect of the inflow rate of  $\text{NH}_3$  and  $\text{NH}_3 + \text{N}_2$  atmospheres and nitrogen content in the  $\text{NH}_3 + \text{N}_2$  atmosphere on the nitriding potential in the retort. Industrial nitriding pit-type furnace, 1 m<sup>3</sup> working chamber

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the retort and of the charge, temperature, atmosphere flow, and  $N_2$  content. In typical industrial retorts, these tendencies are approximately balanced, which is shown in Fig. 7.

This finally leads to the conclusion that diluting of ammonia reduces the flux  $J_{N^g}$ . Accordingly, in order to maintain the same flux  $J_{N^g}$  in the  $NH_3 + N_2$  as in an atmosphere of  $NH_3$ , it is necessary to increase the equilibrium concentration of nitrogen  $c_{N^g}$ , or nitriding potential  $K_N$ . This is shown schematically in Fig. 7, where a horizontal arrow indicates the degree of dilution of ammonia with nitrogen, and a vertical arrow the required increase of potential  $K_N$ . For a more accurate calculation of the effect of  $N_2$  content on the consumption of the  $NH_3 + N_2$  atmosphere, it would be necessary in the determination of the flux  $J_{N^g}$ , to employ the relationship (2).

However, in view of the lack of physico-chemical data required for this approach (diffusion coefficients of nitrogen in the different phases of the nitrified layer, the transfer coefficients  $\beta$  of nitrogen from the gas phase to the metallic phases) this is not possible.

The analysis of many processes carried out in industrial furnaces has proven [20] that replacing  $\text{NH}_3$  with a  $\text{NH}_3 + \text{N}_2$  mix leads to an increase in the consumption of  $\text{NH}_3$  up to several times over, depending on the  $\text{N}_2$  content. Concurrently, the additional consumption of nitrogen has to be considered. In consequence, a process utilizing a  $\text{NH}_3 + \text{N}_2$  atmosphere has to be more expensive than that run with  $\text{NH}_3$  only. However, consumption of the  $\text{NH}_3 + \text{N}_2$  mix is still much lower than that of the  $\text{NH}_3 + \text{NH}_3\text{diss.}$  atmosphere. In the latter case, mentioned above, the cost of a dissociator has to be added to the high price of the atmosphere.

## 6 Other benefits and limitations of nitriding in 100 % NH<sub>3</sub>

A process which utilizes only  $\text{NH}_3$ , brings, in comparison with processes making use of two-component mixes, other substantial benefits, both practical and economical. Because the kinetics of the layer growth in the case of the  $\text{NH}_3 + \text{N}_2$  atmosphere is controlled by two parameters (nitriding potential  $K_N$  and the  $\text{N}_2$  content), the design of processes requires many more experimental trials than in the case of atmospheres of  $\text{NH}_3$  or  $\text{NH}_3 + \text{NH}_3\text{diss.}$ , in which the kinetics is controlled by one parameter only ( $K_N$ ). For this reason, the precision of predicting as well as the reproducibility of results is higher for processes in  $\text{NH}_3$  (also when using  $\text{NH}_3 + \text{NH}_3\text{diss.}$ ) than when using  $\text{NH}_3 + \text{N}_2$ . These additional economical factors argue in favor of processes in 100 %  $\text{NH}_3$ .

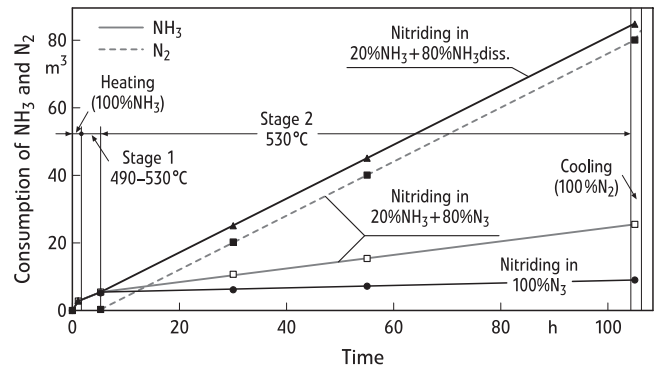


Fig. 8. Comparison of consumption of  $\text{NH}_3 + \text{N}_2$ ,  $\text{NH}_3 + \text{NH}_3\text{diss.}$  and  $\text{NH}_3$  atmospheres in the total nitriding process. Industrial nitriding pit-type furnace, 1 m<sup>3</sup> working chamber

*Bild 8. Deutsche Übersetzung fehlt!!! • mnb mnb • mnb mnb mn • mnb mnb  
mnb mnb mnb mnb mnb mnb • mnb mnb mnb mnb mnb • mnb mnb mnb mnb  
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A process with only  $\text{NH}_3$  requires only one gas flow controller, while for processes with  $\text{NH}_3 + \text{N}_2$  and  $\text{NH}_3 + \text{NH}_3\text{diss.}$  atmospheres, two such controllers have to be used.

For precise regulation and control of the chemical composition of atmosphere obtained from  $\text{NH}_3$  (also from  $\text{NH}_3 + \text{NH}_3\text{diss.}$ ), it is sufficient to determine one gas component in the retort, whereas in case of the  $\text{NH}_3 + \text{N}_2$  atmosphere two are necessary. Also from this point of view, the process in  $\text{NH}_3$  is simpler and less expensive than that using  $\text{NH}_3 + \text{N}_2$ . The  $\text{NH}_3 + \text{NH}_3\text{diss.}$  atmosphere not only requires two gas flow controllers and the determination of one component in the atmosphere but also, as mentioned above, a separate dissociator, which adds to the cost of the equipment.

A process using only  $\text{NH}_3$  (also  $\text{NH}_3 + \text{NH}_3\text{diss.}$ ) may be designed, and even controlled with the aid of existing models of kinetics of growth [15-18, 21]. The  $\text{NH}_3 + \text{N}_2$  atmosphere requires the development of more involved models and additional physico-chemical data (transfer coefficients of nitrogen to  $\epsilon$  and  $\gamma'$  phases at the surface of iron and steel workpieces). Unfortunately, because of the complex mechanisms of processes in the  $\text{NH}_3 + \text{N}_2$  atmosphere, and due to the lack of experimental data, the development of such models is as yet not feasible.

Savings in the consumption of gases, indicated above, concern only the second stage of the nitriding process, in which the supply of nitrogen atoms from the gas phase to the metal surface has to be restricted. There is no opportunity for savings in the first stage, during which, in view of the required intensive supply of atomic nitrogen to the surface, a high flow of  $\text{NH}_3$  is necessary. Also, this does not apply to the consumption of gases ( $\text{NH}_3$ ) during heating up as well as during the cooling period ( $\text{N}_2$ ). Thus, to estimate realistic savings in gas consumption, attributable to the new method, it is necessary to consider total gas consumption in all process stages.

The corresponding results are presented in graphical form in Fig. 8. It has to be recognized that the benefits of using 100 %  $\text{NH}_3$  for nitriding increase with the process (stage 2) time. Thus, it is not reasonable to seek savings in short-term processes (such as those applied to non-alloyed steel), which are performed in 100 % ammonia at high inflow rate.

## 7 Conclusions

The results of the investigation indicate that by performing the process using  $\text{NH}_3$  alone it is possible to produce nitrided layers identical to those obtained in two-component atmos-

pheres  $\text{NH}_3 + \text{NH}_3$  diss. and  $\text{NH}_3 + \text{N}_2$ . In such a process it is possible to control the composition of the atmosphere through the regulation of  $\text{NH}_3$  flow into the retort, with occasional closing of the flow, thereby obtaining a precision of control similar to that available with the  $\text{NH}_3 + \text{NH}_3$  diss. atmosphere.

The process using only  $\text{NH}_3$  brings the benefit of low consumption of gas and can be realized with a simpler and, by the same token, less expensive control system, compared with processes using two-component atmospheres  $\text{NH}_3 + \text{NH}_3$  diss. and  $\text{NH}_3 + \text{N}_2$ .

The process using  $\text{NH}_3$  alone is similar to that using  $\text{NH}_3 + \text{NH}_3$  diss. in terms of easy control of the kinetics of growth of the nitrided layer. Easier, in fact, than in the case of the atmosphere  $\text{NH}_3 + \text{N}_2$ .

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**Concept of an economical and ecological process of gas nitriding of steel**

*L. Maldziński, J. Tacikowski*

HTM 61 (2006) 6, p. 000–000, 8 figs., 21 literature references

An economical, ecological version of the gas nitriding process is presented. It allows a substantial reduction in the consumption of industrial gases compared with currently used processes. Also it leads to a simplification of nitriding installation as well as the process itself, while allowing maintenance of full control over the kinetics of the layer growth. The concept was developed from studies of the thermodynamics and kinetics of growth of nitrided layers on iron and steel. It has been verified in trials under industrial conditions.

**Konzept eines ökonomischen und ökologischen Prozesses des Nitrierens von Stahl mit Gas**

*L. Maldziński, J. Tacikowski*

HTM 61 (2006) 6, S. 000–000, 8 Bilder, 21 Literaturangaben

Es wird eine ökonomische, ökologische Möglichkeit des Nitrierprozesses mit Gas vorgestellt.