

L. Maldziński, J. Tacikowski

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 nitrified 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 nitrified layer occurs in the shortest time, with minimal consumption of gases, electrical energy, and water. Concurrently, it is assumed that the nitrified layer has an optimal structure in terms of expected performance i. e. the required zones of iron nitrides (α , $\gamma' + \alpha$ or $\varepsilon + \gamma' + \alpha$)¹, 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 nitrified layers, has been tested and verified in industrial application.

¹ The term $\varepsilon + \gamma' + \alpha$ represents a nitrified layer composed of: ε at the surface, γ' more or less beneath ε and an α diffusion zone underneath; the term $\gamma' + \alpha$ denotes a layer composed of γ' at the surface and an α diffusion zone underneath; the term α denotes an α 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 nitrified layer is still very much in use worldwide [1]. It is performed using only ammonia and the resulting layer is composed of superimposed $\varepsilon + \gamma' + \alpha$ phases. In industrial practice, the superficial zone of iron nitrides $\varepsilon + \gamma'$ (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 $\varepsilon + \gamma' + \alpha$ layer uses much more ammonia (NH_3) than the formation of a layer composed of $\gamma' + \alpha$. It is because the growth of an $\varepsilon + \gamma' + \alpha$ 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 α . Therefore, in the traditional production process, the $\varepsilon + \gamma'$ 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 ($NH_3 + NH_3\text{diss.}$) [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 $\varepsilon + \gamma' + \alpha$, $\gamma' + \alpha$ or α zones) of required thickness of individual zones, along with a limited nitrogen concentration at the surface. Diluting ammonia with dissociated ammonia ($NH_3\text{diss.}$) 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 ε or $\varepsilon + \gamma'$ 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, $NH_3 + NH_3\text{diss.}$ and $NH_3 + N_2$, the second one (with N_2) is more widely used in industrial practice. It is usually cheaper than the $NH_3 + NH_3\text{diss.}$ atmosphere, as nitrogen N_2 is in most cases cheaper than dissociated ammonia. Moreover, production of $NH_3\text{diss.}$ 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].

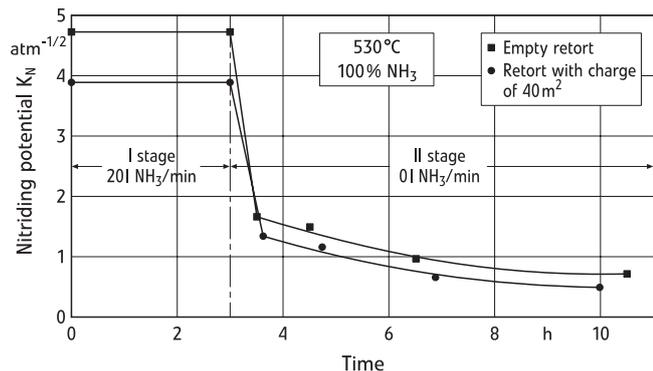


Fig. 3. Decrease in the nitriding potential K_N after closing NH_3 inflow into the retort, in an empty furnace (retort surface area - 11 m²) and in the same retort with charge (surface area - 40 m²)

Bild 3. Deutsche Übersetzung fehlt!!! • mnb mnb • mnb mnb mn • mnb mnb mnb mnb mnb mnb mnb • mnb mnb mnb mnb mnb • mnb mnb

In turn, a higher inflow rate of NH_3 (or of a two-component atmosphere) counteracts the drop of K_N and, in a certain range of flow and dissociation, rates may improve or worsen the homogeneity of atmosphere in the furnace [10, 19].

4 Experimental verification of the concept in the case of an industrial furnace

Within this investigation two experiments with two-stage processes were carried out. They both involved, in the initial period of the process (3 h), a high ammonia inflow into the retort, followed by closing the inflow entirely.

The first of these experiments was carried out with an empty retort (nominally 11 m² surface area of the retort, no charge), the second with a large-surface charge (ca. 40 m² surface area). Fig. 3 shows the variation of the nitriding potential as a function of time, for both processes. It illustrates that after stopping the supply of NH_3 to the retort, the potential K_N falls rapidly at first, then very gradually. This pattern appears regardless of whether the retort is empty or filled, and the differences in K_N between the two processes are not too big.

The rapid initial drop of K_N is a favourable phenomenon from the point of view of process regulation and control. It allows a low level of potential to be reached quickly, where further regulation of composition may be effected, through a continuous or pulsating dosage of NH_3 to the retort⁶.

The comparison of the two curves of the variation of K_N also indicates that the dissociation rate of NH_3 is mainly determined by the surface area of the retort. The charge, despite its much larger surface area, influences NH_3 dissociation to a lesser degree. This happens for two reasons. Firstly, the increase in the catalytic surface of the retort and charge does not result in a proportional increase of the dissociation rate of NH_3 because as the ammonia content in the atmosphere decreases (due to an increase in the surface area of the retort and charge), the driving force of the dissociation reaction is diminished. Secondly, the effective catalytic surface area of the retort is, after a longer service, much larger than the surface of the charge. The influence of the surface area on the dissociation is therefore greater than that of the charge.

⁶ During the drop of K_N , the possibility of regulation (or control) of the growth of the nitrided layer is suspended until the potential reaches a level programmed for the 2nd process stage. From this moment onwards K_N is regulated through a continuous, or intermittent inflow of NH_3 into the retort.

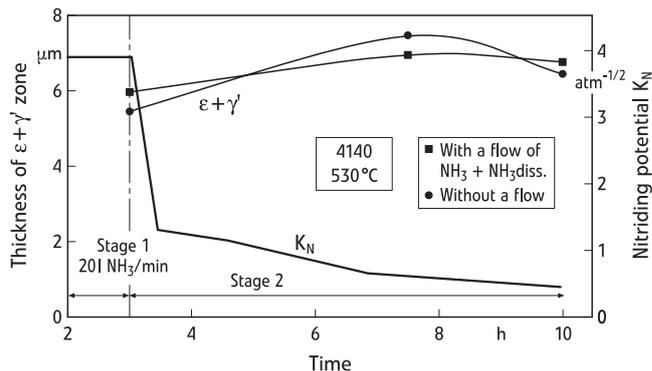


Fig. 4. Kinetics of growth and reduction of the ε+γ zone in a two-stage process: stage 1: 100 % NH_3 , stage 2: NH_3 inflow entirely closed (variant 1) or atmosphere changed to $NH_3 + NH_3diss.$ (variant 2)

Bild 4. Deutsche Übersetzung fehlt!!! • mnb mnb • mnb mnb mn • mnb mnb mnb mnb mnb mnb mnb • mnb mnb mnb mnb mnb • mnb mnb

In the following section of the investigation a comparison was made between the growth of the e+g zone on 4140 steel during nitriding according to the new concept (with occasional stopping of the ammonia flow into the retort) and the growth of the same zone in a controlled standard process. In both cases a two-stage process was used. Stage 1, the same in both compared processes, was carried out in 100 % NH_3 , at $K_N = 4 \text{ atm}^{-1/2}$ for three hours. Stage 1, according to the new concept, was run with a closed NH_3 supply. In the course of the process the potential decreased, as plotted in the graph in Fig. 3. In variant 2 of the process, stage 2 was run using the $NH_3 + NH_3diss.$ atmosphere, the composition of which was varied so as to produce the same time-dependent decrease of the potential K_N as in the first variant.

Fig. 4 also shows the changes in the thickness of the ε+γ zone, formed in both processes. As may be seen, differences in the thickness of comparable zones are small and practically negligible. These results prove again that closing the NH_3 supply to the retort does not affect the growth rate of the nitrided layer. Growth is determined only by the process parameters (T, K_N and time). In the following two processes, samples of the 4140 steel were inserted into the retort during stage 2. Fig. 5 shows the surface hardness (measured with the Vickers

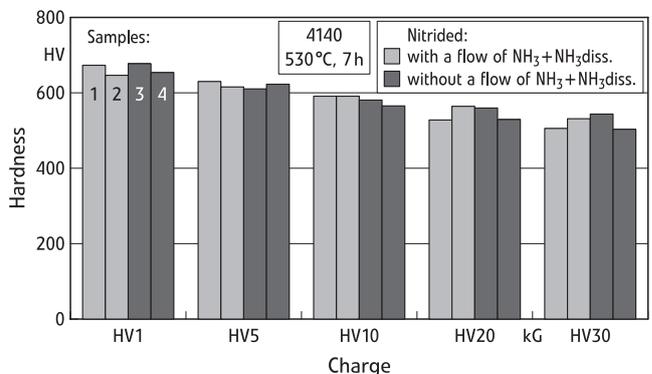


Fig. 5. Comparison of surface hardness of nitrided 4140 steel, obtained in a stage 2 (as in Fig. 3) with $NH_3 + NH_3diss.$ inflow, and in a process with a closed supply of 100 % NH_3 . Variation of potential during second stage as in Fig. 3. Time - 7 h

Bild 5. Deutsche Übersetzung fehlt!!! • mnb mnb • mnb mnb mn • mnb mnb mnb mnb mnb mnb mnb • mnb mnb mnb mnb mnb • mnb mnb

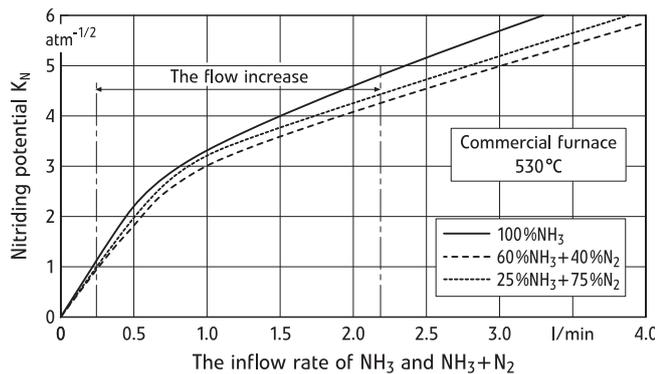


Fig. 7. Effect of the inflow rate of NH_3 and $NH_3 + N_2$ atmospheres and nitrogen content in the $NH_3 + N_2$ atmosphere on the nitriding potential in the retort. Industrial nitriding pit-type furnace, 1 m^3 working chamber

Bild 7. 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 mnb mnb

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 nitrided layer, the transfer coefficients β 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 NH_3 with a $NH_3 + N_2$ mix leads to an increase in the consumption of NH_3 up to several times over, depending on the N_2 content. Concurrently, the additional consumption of nitrogen has to be considered. In consequence, a process utilizing a $NH_3 + N_2$ atmosphere has to be more expensive than that run with NH_3 only. However, consumption of the $NH_3 + N_2$ mix is still much lower than that of the $NH_3 + NH_3$ 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_3

A process which utilizes only 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 $NH_3 + N_2$ atmosphere is controlled by two parameters (nitriding potential K_N and the N_2 content), the design of processes requires many more experimental trials than in the case of atmospheres of NH_3 or $NH_3 + NH_3$ 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 NH_3 (also when using $NH_3 + NH_3$ diss.) than when using $NH_3 + N_2$. These additional economical factors argue in favor of processes in 100 % NH_3 .

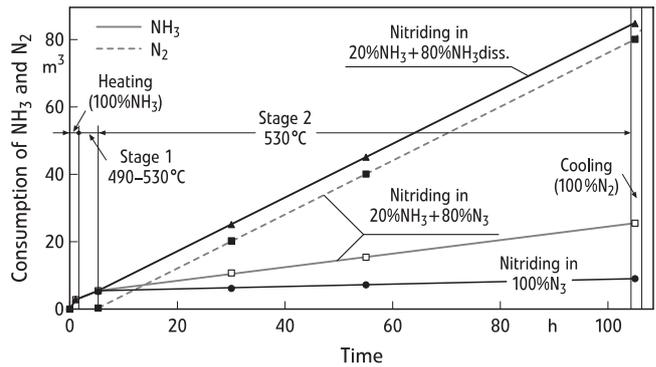


Fig. 8. Comparison of consumption of $NH_3 + N_2$, $NH_3 + NH_3$ diss. and NH_3 atmospheres in the total nitriding process. Industrial nitriding pit-type furnace, 1 m^3 working chamber

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 mnb mnb

A process with only NH_3 requires only one gas flow controller, while for processes with $NH_3 + N_2$ and $NH_3 + NH_3$ diss. atmospheres, two such controllers have to be used.

For precise regulation and control of the chemical composition of atmosphere obtained from NH_3 (also from $NH_3 + NH_3$ diss.), it is sufficient to determine one gas component in the retort, whereas in case of the $NH_3 + N_2$ atmosphere two are necessary. Also from this point of view, the process in NH_3 is simpler and less expensive than that using $NH_3 + N_2$. The $NH_3 + NH_3$ 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 NH_3 (also $NH_3 + NH_3$ diss.) may be designed, and even controlled with the aid of existing models of kinetics of growth [15-18, 21]. The $NH_3 + N_2$ atmosphere requires the development of more involved models and additional physico-chemical data (transfer coefficients of nitrogen to ϵ and γ' phases at the surface of iron and steel workpieces). Unfortunately, because of the complex mechanisms of processes in the $NH_3 + N_2$ 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 NH_3 is necessary. Also, this does not apply to the consumption of gases (NH_3) during heating up as well as during the cooling period (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 % 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 NH_3 alone it is possible to produce nitrided layers identical to those obtained in two-component atmospheres.

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 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 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 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 $\text{NH}_3 + \text{N}_2$.

The authors acknowledge the support received from Nitrex Metal Inc. of Montreal, Canada. We also wish to thank Dr. George Tymowski for constructive help in the investigation and preparation of this paper.

References

1. Patent US 1,487,554 (1924)
2. Knerr, C. H.; Rose, Th. C.; Filkowski, J. H.: Gas Nitriding. ASM HandbookTM, Vol. 4, Heat Treating, 1991, p. 387-425
3. Sinha, A. K. (Ed.): Physical Metallurgy Handbook. McGraw-Hill, New York, 2003, p. 16.89. - ISBN 0-07-057986-5
4. Floe, C. F.: A Study of the Nitriding Process. Transactions for American Society for Metals 32 (1944), p. 134-149
5. Bever, M.; Floe, C. F.: Case hardening of steel by nitriding. In: Surface Protection Against Wear and Corrosion, H. S. Avery (Ed.). ASM, 1953, p. 123-143
6. Minkevich, A. N.: Thermochemical treatment of metals and alloys. Mashinostroenie (1965), p. 331
7. Sorokin, Yu V.; Minkevich, A. N.: Nitriding steel in a mixture of nitrogen and ammonia. MİTOM (1966) 5, p. 49-52
8. Patent PL85924B (1976)
9. Haś, Z.; Kula, P.: Nitrovac'79 - Nowa technologia obróbki cieplnochemicznej elementów maszyn i narzędzi. Inżynieria Materiałowa 16 (1983) 5, p. 127-132
10. Maldzinski, L.: Thermodynamic, kinetic and technological aspects of the producing nitrided layers on iron and steel in processes of gas nitriding (in Polish). Habilitation thesis, Technical University Poznan, Poland, Wydawnictwo Politechniki Poznańskiej, 2002. - ISBN 83-7143-564-9
11. Przyłęcki, Z.; Maldzinski, L.: Investigation of equilibrium conditions in the system NH_3 - H_2 - N_2 -nitride ϵ . Proc. III. Int. Conf. Carbides, Nitrides, Borides, Poznań-Kolobrzeg/Poland, 1984, p. 116-129.
12. Przyłęcki, Z.; Maldzinski, L.: Conditions of equilibrium between NH_3 - H_2 gas mixture and nitrogen in γ' nitride. Proc. IV. Int. Conf. Carbides, Nitrides, Borides, Poznań-Kolobrzeg/Poland, 1987, p. 153-162
13. Maldzinski, L.; Przyłęcki, Z.; Kunze, J.: Equilibrium between ammonia-hydrogen mixtures and the ϵ -phase of iron. Steel Research 57 (1986) 12, p. 645-649
14. Somers, M. A. J.; Kooi, B. J.; Maldzinski, L.; Mittemeijer, E. J.; van der Horst, A. A.; van der Kraan, A. M.; van der Pers, N. M.: Thermodynamics and long-range order of interstitial in an h. c. p. lattice; nitrogen in ϵ -Fe₂N_{1.2}. Acta Metal. Mater. 45 (1997), p. 2013-2025
15. Mittemeijer, E. J.; Somers, M. A. J.: Thermodynamics, Kinetics, and Process Control of Nitriding. Surface Eng. 13 (1997) 6, p. 483-497
16. Mittemeijer, E. J.; Somers, M. A. J.: Thermodynamics, Kinetics, and Process Control of Nitriding. Proc. 10th Congr. of IFHT, 1-5.9.99, Brighton/UK, T. Bell, E. J. Mittemeijer (Ed.), p. 83-117
17. Torchane, L.; Bilger, P.; Dulcy, J.; Gantois, M.: Control of Iron Nitride Layers Growth Kinetics in the Binary Fe-N System. Metall. Mater. Trans. A, 27A (1996) July, p. 1824-1834
18. Somers, M. A. J.; Maldzinski, L.; Sommer, T.: The Growth of the $\epsilon + \gamma'$ nitrides on pure iron. In preparation
19. Maldzinski, L.; Lilliental, W.; Tymowski, G.: Causes of Inhomogeneity of Chemical Composition of Nitriding Atmospheres in the Furnace Retort. Proc. 19th ASM, 1-4 November, 1999, Cincinnati, Ohio, USA, S. J. Midea (Ed.), p. 178-186
20. Tacikowski, J.: unpublished report, 1998
21. Maldzinski, L.; Lilliental, W.; Tymowski, G.; Tacikowski, J.: New Possibilities of Controlling the Gas Nitriding Process by Utilizing Simulation of Growth Kinetics of Nitride Layer. Proc. 12th Int. Conf. on Surface Modification Technologies, 12-14 October, 1998, ASM Rosemont, Illinois, USA, p. 215-226 and Surface Eng. 15 (1999) 5, p. 377-384

The authors of the paper

Prof. Dr. hab. Inz. Leszek Maldzinski, born in • ??? • ??? •, is Professor at the University of Technology, Poznan/Poland and scientific adviser of Nitrex Metal Inc. Canada.

Prof. Dr. Inz. Jan Tacikowski, born in • ??? • ??? •, is Professor at the Institute of Precision Mechanics, Warsaw/Poland.

Manuscript submitted in November 2006.

Dieser Beitrag hat die Dokumentennummer
HT 100••• und steht unter www.HTM-Journal.de
für Sie zum Download bereit.

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 nitrated 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.