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# CONTROLLED NITRIDING AND GAS NITROCARBURIZING WITH THE ZEROFLOW™ METHOD[1]

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**Abstract**
This article presents two case studies controlled nitriding and gas nitrocarburizing of steel using the ZeroFlow method for automotive and wind gear applications. Both nitriding and nitrocarburizing using this method enables the precise forming of diffusion layers in the phase structure and zones (phases) thickness of hardness distribution. These processes are characterized by lower ammonia consumption during nitriding, and lower ammonia and carbon dioxide consumption during nitrocarburizing when compared with currently used processes. They are also characterized by a much lower emission of subprocess gases to the environment. The ZeroFlow method of nitriding and nitrocarburizing utilizes a simplified system for gas adjustment and control.
**Keywords:** Nitriding; Nitrocarburizing; Control gas nitriding; Nitrided layer; Nitriding furnace.

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## 1 CONTROLLED GAS NITRIDING WITH THE ZEROFLOW METHOD

The article published in HTM in 2006[1] presented the theoretical basics of the new, economical and environmentally-friendly nitriding method, defined afterwards as the ZeroFlow method. In this method, the nitriding process is performed with use of a single-component atmosphere – $NH_3$. The concept is to use a simpler atmosphere than the two-component atmospheres, $NH_3$+$N_2$ and $NH_3$+$NH_3$ diss., that are used currently in most commercial processes. The regulation of atmosphere chemical composition in the retort, and therefore the control of nitriding potential $K_n$, is performed by a temporary stop and reactivation of $NH_3$ feeding into the furnace. The amount of $NH_3$ fed into the furnace is adjusted (and controlled) with use of a gas analyzer (e.g. $NH_3$ or $H_2$ analyzer). The gas analyzer stops and reactivates the $NH_3$ feeding temporarily into the retort with a frequency sufficient to assure the required gas chemical composition (required $K_n$ potential) in the retort. This method was developed based on experimental research and theoretical analysis of the thermodynamic and kinetic aspects of nitriding. The research was conducted in a laboratory furnace with the quartz retort and in an industrial furnace with the steel retort and convection fan. The atmospheres used: $NH_3$, $NH_3$+$H_2$ and $NH_3$+$NH_3$ diss., with different linear velocity along the sample surface. In the research conducted in the industrial furnaces, the option with temporary stop of the $NH_3$ feeding to the furnace retort was tested.

This research has shown[2] that the growth of the nitrided layer and its phase structure are not impacted directly either by the type of atmosphere supplied into the furnace, nor by the furnace type (laboratory or industrial). It is also not determent by velocity of atmosphere along the sample surface. The process is impacted only by the chemical composition of the atmosphere ($K_n$ nitrogen potential) inside the furnace retort. The atmosphere composition in the steel retort with the fan is determined directly by three fundamental factors:[2] velocity of $NH_3$ dissociation in the furnace retort, by the intensity of the nitriding atmosphere circulation in the furnace retort and by the intensity of the nitriding atmosphere inflow ($NH_3$, $NH_3$+$NH_3$ dissociated, $NH_3$+$H_2$) into the retort.

The intermittent stopping of the $NH_3$ flow into the retort (therefore the name of the method Zeroflow) did not impact directly either the kinetics of the nitride layer growth, it impacted only the gas composition ($K_n$ potential) that was set in the retort. The research has demonstrated a considerable reduction of $NH_3$ consumption using this method compared with gas consumption in processes using $NH_3$+$NH_3$ diss. and $NH_3$+$N_2$, as well as the possible elimination of the dissociator and gas flow-meters, and consequently the simplification of the control system.

The next stage of research on gas nitriding development using the ZeroFlow method included industrial applications.[3,4] SECO/WARWICK S.A. designed and built a prototype industrial furnace (Fig. 1). The furnace was equipped with the proper control system for nitriding using the ZeroFlow method.

In 2008, ZeroFlow furnaces were put into operation in service hardening shops in Germany, England, India and Pakistan.

The following cases are presented to demonstrate two applications of the ZeroFlow method and selected findings.

**Figure 1.** Horizontal furnace for nitriding using ZeroFlow process.

In general, during the 1,5 year – operation of these furnaces several hundred process cycles of industrial nitriding carried out. Nitrided parts included crankshafts, distribution shafts, gear wheels made of constructional steel for toughening (5140, 4140, N135 acc. to AISI) and die blocks for aluminum casting under pressure, tools for plastic working made of tool steel (H11, H13, D2 acc. to AISI). The obtained results turned out to be similar to the results obtained on the prototype furnace.

### 1.1 Nitriding of Crankshafts for Engines of Racing Cars Manufactured by an American Company

This example refers to the nitriding of crankshafts from 4340 steel using the ZeroFlow method for a company producing car engines. Because of their application, the company has set very high requirements regarding, among others, the nitrided layer phase structure, thickness of layer zones, its effective hardness, thickness as well as dimensional and geometrical changes. Required was:

- iron nitrides zone with the thickness 5 ÷ 6$\mu$m;
- nitrided layer effective thickness with core hardness criterion not less than +50HV – 0.4 mm;
- nitrided layer effective thickness with hardness criterion not less than 600HV $g_{600}$ = 0,15mm;
- surface hardness – approx. 63 HRC.

The first stage was the developing the nitriding technology. The simulations of kinetics of nitrided layer growth with use of kinetics of nitrided layer growth model[5,6] have been performed.

**Figure 2.** Crankshaft to engines of racing cars.

In the calculations the double-stage nitriding process due to temperature (490 and 530ºC) and the triple-stage due to atmosphere nitriding potential have been assumed. Fig. 3 shows the simulation of effective layer thickness growth. Fig. 3 shows, that required effective thickness at HV400 (core hardness was 350HV) is obtained by the layer after approx. 29 hours of nitriding (490ºC, 2 h, and 530ºC, 27 h). It has to be mentioned, that the core hardness was 350HV. In further calculations the nitriding potential $K_n$ has been selected in the way to obtain the required iron nitrides zone thickness $g_{mp}$ = 5 ÷ 6μm during 29 hours. Those conditions have been fulfilled by potential $K_n$ = 25 in the first stage of process, $K_n$ = 0.6 in the second stage, and $K_n$ = 0.4 in the third stage. Times of individual stages are accordingly: 2, 15, and 12 h (Fig. 4).

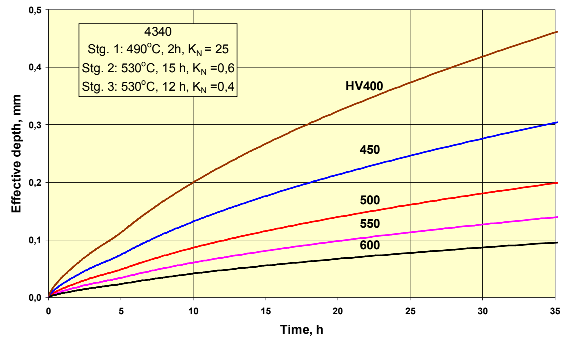


**Figure 3.** The growth of effective depth case on 4340 steel.

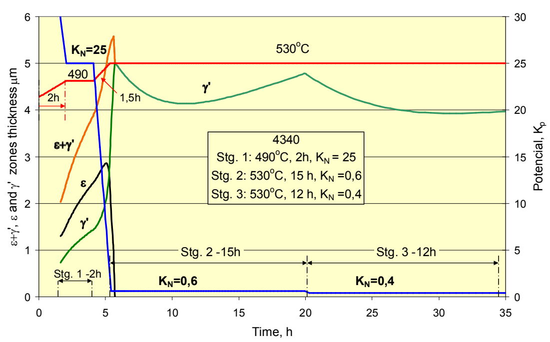


**Figure 4.** The growth of white layer on 4340 steel.

According to the set parameters, after their slight correction, (Fig.7) the crankshafts and the samples of steel 4340 for metallographic researches were nitrided. Photographs of metallographic microsections are shown in Fig. 5, and the hardness distribution in the section perpendicular to the surface – in Fig. 6.

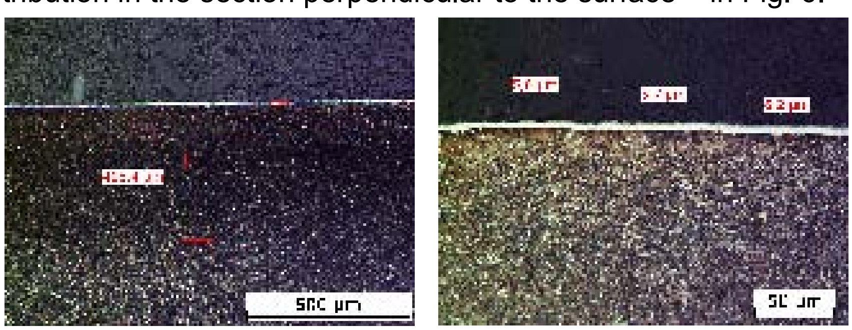

**Figure 5.** Micrographs of the nitrided layer (a) and iron nitrides (b) on 4340 steel nitrided using ZeroFlow process at: I stage – 490°C, $K_N$ = 22 atm$^{-1/2}$, 2 h, II stage – 530°C, $K_N$ = 0,8 atm$^{-1/2}$, 15 h, $K_N$ = 0,7 atm$^{-1/2}$, 12 h.

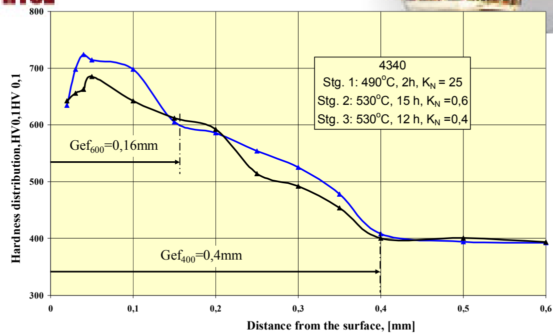


**Figure 6.** Hardness distribution of nitrided layer on 4340 stee.

Fig. 5a shows that the total thickness of nitrided layer is approx. 0.4 mm, and Fig. 5b – iron nitrides zone thickness is 5.7 – 6.2 µm, which meets expectations. The same effective thickness ($g_{400}$) has been marked out from the hardness distribution in the layer (Fig. 6).

Fig. 6 shows also that the effective thickness for hardness HV600 is approx. 0.16 mm, which also meets the expectations.

It has to be mentioned, that in order to prevent the shape deformation, the crankshaft has been placed vertically in the special holder. Moreover, the furnace heating and cooling time has been extended for this purpose. As a result, according to the company, deformations were small and have not exceeded the allowed deviations.

Fig. 7a shows the course of the most important, registered process parameters: temperature, ammonia and nitriding potential flow intensity in the retort. The most interesting thing is the ammonia consumption in the ZeroFlow process. In the analysis particular stages have been separated: rinsing, the 1st, the 2nd and the 3rd nitriding stage and cooling.

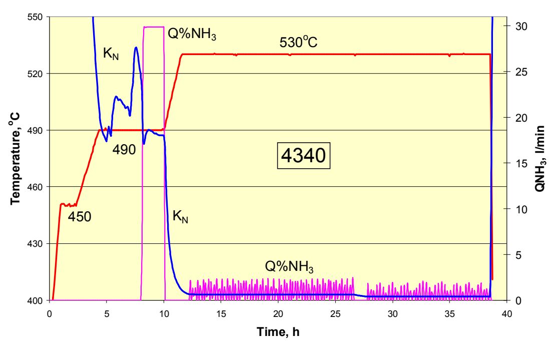


**Figure 7.** The variations of: temperature, inflow rate of $NH_3$ into the retort and $NH_3$ , nitriding potential during nitriding of crankshaft.

As the furnace and the retort are designed for use in vacuum conditions, the air used for surface activation has been removed from the retort with use of a vacuum pump, the purging with ammonia has been limited only to filling the retort with this gas. Due to this fact, the consumption of $NH_3$ has been equal to the retort volume, and amounted approx. 1 $m^3$.

The 1st nitriding stage (490ºC), lasting 2 hours, has been performed with $NH_3$ feeding intensity 30 l/min. It has generated consumption 1.8 $m^3$. In the 2nd and the 3rd nitriding stage the average $NH_3$ feeding was measured at 0.8 and 0.7 l/min respectively. The consumption of $NH_3$ was measured at 1.2 $m^3$. Cooling has been performed with closed $NH_3$ feeding, which has been removed with use of a vacuum pump in temperature close to environment. Total ammonia consumption amounted to 6.6 $m^3$.

In the traditional, controlled process using the $NH_3$+$NH_3$ diss. atmosphere, the purging and the 1st stage of nitriding are performed in the same way as in the ZeroFlow method. Therefore the consumption of $NH_3$ will be the same as in the ZeroFlow process. Differences in $NH_3$ consumption will appear in the second and the third nitriding stage. The amount of that consumption is determined by the chemical constitution of the atmosphere $NH_3$+$NH_3$diss., fed into the furnace. Document[2] shows, that the more $NH_3$ is diluted with $NH_3$diss., the higher will be the flow intensity of that mixture into the furnace retort in order to assure the required nitriding potential $K_n$, therefore the higher the $NH_3$ consumption will be. For comparison the typical atmosphere composition of 30%$NH_3$ + 70%$NH_3$diss. used in industry has been taken. The research results have indicated that the consumption in the second and the third stage is 21.5 $m^3$, so it is 18 times higher than the consumption in the ZeroFlow process. Total consumption of $NH_3$ is 24 $m^3$, so it is 4 times higher than in the ZeroFlow process. It has to be mentioned, that in the case of different charges this difference will increase together with the process time.

The consumption of $NH_3$ + $N_2$ atmosphere has not been measured. According to the previous researches,[1] for a typical industrial atmosphere (25%$NH_3$ + 75%$N_2$) the consumption of $NH_3$ in the 2nd and the 3rd stage is 2 times higher than in the ZeroFlow process. In the whole nitriding process that difference drops to approx. 1.5 times.

However, in the process in atmosphere $NH_3$ + $N_2$ the nitrogen is used in amounts few times higher than $NH_3$. The consumption of the nitrogen that is not used in the ZeroFlow method, amounts in the discussed case approx. 30$m^3$ $N_2$.

### 1.2 Nitriding of Gear Wheels for Wind Power Plants

For a European customer, the technology has been developed for processing gear wheels made of 42CrMo4, 31CrMoV9, 34CrNiMo6 steel (EN). These parts, used for wind power plants, are nitrided using the ZeroFlow process. The wheels in this study had diameter from 30 to 180 cm (Fig. 10 shows the smallest wheel). Due to the high surface pressure of teeth, a thick nitrided layer (0.6 ÷ 0.8 mm) without the iron nitride zone was required. The same method has been used as in paragraph 1.1. In order to increase the kinetics of layer growth the nitriding temperature has been increased to 550ºC. The expansion of the nitriding time was required, dependent on the steel type up to 60 ÷ 80 h and lowering the nitriding potential $K_n$ of the atmosphere in the 2nd and the 3rd process stage to the values 0.3 and 0.2. Purging and the first stage of nitriding have been performed in the same way as in case of crankshafts (par. 2.1), and in the $2^{nd}$ and $3^{rd}$ stage of the process the obtaining of required $K_n$ required the decreasing of the $NH_3$ flow to 0,5 and 0,4 l/min. As the time of the second and the third stage was longer (approx. 50 ÷ 78 h), the consumption of $NH_3$ amounted 1.7 ÷ 2.3 $m^3$, and in the whole process 7.3 ÷ 7.9 $m^3$.

In the traditional, controlled process[7] performed in order to compare the consumption in the second and the third stage, the typical atmosphere 20%$NH_3$ + 80%$NH_3$diss. was used. The consumption of $NH_3$ amounted 52 ÷ 70 $m^3$, and in the whole process 58 ÷ 72 $m^3$. It is 7.5 ÷ 9 times higher than in the ZeroFlow process.

**Figure 8.** Gear to wind power stations.

## 2 GAS NITROCARBURIZING USING ZEROFLOW METHOD

The positive results obtained in the processes of industrial nitriding encouraged the authors of this article to use this method for low-temperature ferritic nitrocarburizing. As it comes to low-temperature processes, ferritic nitrocarburizing is used as often as nitriding. Ferritic nitrocarburizing is used mainly for low-carbon, middle-carbon and low-alloyed steel, and the purpose of this process is to create the thick iron nitrocarburized zone on the surface in a short period of time.[7,8] Often the oxidation process is carried out after the nitrocarburizing.[8] The created layer reaches the hardness up to 400HV and is characterized by good corrosion resistance.

There are $NH_3$ atmospheres used with the $CO_2$ addition, not so often with the addition of endothermic atmosphere or with the CO addition. The advantage of $CO_2$ is the possibility of the supply in large bottles, and above small the toxicity, in contrast to CO. That is why $CO_2$ does not endanger the health and life of the staff. It is characterized by relatively low carbon activity and consequently it allows to saturate the layers maximal up to 0,7%C. The disadvantage of the $NH_3$+$CO_2$ atmosphere is the release of the ammonium carbonate powder on the cold parts of the retort, and especially in the outlet pipes. It clogs the system and results in errors in the chemical composition analysis. CO show the high carbon activity and allows to reach up 3,5%C with the surface 2,5 and does not cause the releasing of the ammonium carbonate.[8] The endothermic atmosphere contains CO, but $CO_2$ as well, which is why it is characterized by the intermediate properties compared with the ones analyzed above.

The common feature of all atmospheres is the ability to use higher process temperatures (570-580$^o$C) and the acceleration of the growth kinetics of the iron carbonitride zone.

As mentioned above, the atmosphere most often used in the industry is the $NH_3$+$CO_2$ mixture with the 2-3% contents of this gas. The iron carbonitrides zone is, with such chemical composition of the atmosphere, porous to a large extent. In this connection, in many industrial applications the $NH_3$ diss. (dissociated ammonia) or $N_2$ is added to the atmosphere to limit the nitrogen feeding to the layer. Through this, it is possible to create layers with limited porosity, less brittle and after additional oxidation – more resistant to corrosion. However, putting in the additional gases complicates the system and the control of the layer growth kinetics. The authors of this work used the ZeroFlow method for regulation and control of the atmosphere composition in the furnace retort. Instead of adding $NH_3$ diss. (dissociated ammonia) or $N_2$ to the $NH_3+CO_2$ atmosphere, it was decided to carry out the control of the atmosphere composition by the temporary stop and reactivation of the inflow of the $NH_3+CO_2$ mixture into the furnace retort. This restriction of this atmosphere inflow into the retort causes the fast $NH_3$ dissociation in the retort, and consequently – the fast decrease of its contents (decrease of the $K_n$ nitrogen potential) to the required value.

Figure 9 shows the distribution of nitrogen and carbon concentration in the layer, and Figure 10 shows the hardness distribution. These results are similar to those obtained during the nitrocarburizing in conventional processes.

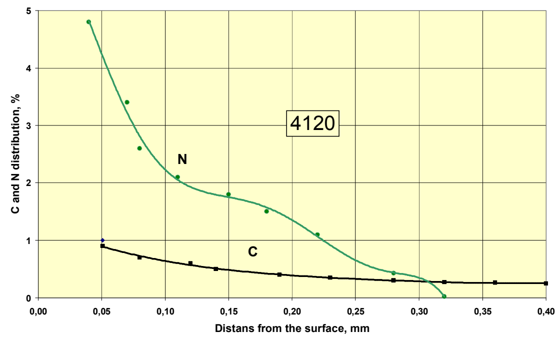


**Figure 9.** The distribution of the nitrogen and carbon concentration in the layer carbonitrided with the ZeroFlow method.

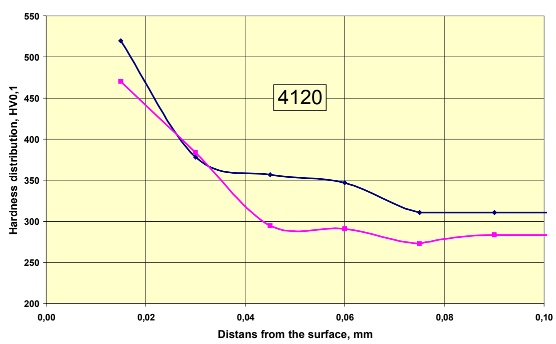


**Figure 10.** The distribution of hardness in the layer carbonitrided with the ZeroFlow method.

It was also noticed, that the $NH_3 + CO_2$ atmosphere consumption in the carbonitring port using the ZeroFlow method is 1,2 up to 1,5 times lower than the consumption of these gases in the traditional process. These differences are not as significant as in case of the nitriding because of the short process (2-4h). However, the unquestionable advantage of the nitrocarburizing with the ZeroFlow method is the simpler gas system and simpler control system.

## SUMMARY

This article presents the results of the laboratory and industrial research regarding the steel nitriding and gas nitrocarburizing using the ZeroFlow method. The nitriding using the ZeroFlow method has proven to be as efficient a process as previously used methods of controlled nitriding. The process produces layers with the phase structure required by industrial specification, with the required thicknesses and

hardness. According to previous research and analysis, the ZeroFlow process has proven to be much more economical in terms of gas consumption than historical methods used to date.

The ferritic nitrocarburizing with the ZeroFlow method has demonstrated performance by executing the controlled forming of the layer structure (thickness of iron carbonitride zone, thickness of the porous zone). The consumption of the gases ($NH_3$ i $CO_2$) is slightly lower in this method than in the traditional method, but the advantage is – similar as in case of nitriding – the simpler installation as well as the simple control of the atmosphere composition in the furnace retort.

Both processes, because of the lower gas consumption and lower emission levels of the after-process gases, is more environment-friendly than traditional processes.

## REFERENCES

1 Małdziński L., Tacikowski J.: "Concept of an economical and ecological process of gas nitriding of steel", HTM, 9/2006, 61Band, p. 296-302.
2 Maldziński L., Liliental W., Tymowski G., Causes of Inhomogeneity Composition of Nitriding Atmospheres in the Furnace Retort, w: Proceedings of the 19th ASM, 1-4 November, 1999, Cinncinati, Missouri, USA.
3 Małdziński L.: "Controlled nitriding using ZeroFlow process", HTP, August 2007, p 57-59.
4 Małdziński L., et. al: "Industrial experiences with cotrolled nitriding using a ZEROFLOW METHOD", HTP, 7/8 2009, p, 19-22.
5 Maldziński L., Liliental W., Tymowski G., Tacikowski J., New Possibilities of Controlling the Gas Nitriding Process by Utilizing Simulation of Growth Kinetics of Nitride Layer, w: Proceedings of the Twelfth International Conference on Surface Modification Technologies, ASM Rosemont, Illinois, USA, 12-14 October, 1998, s. 215-226 oraz w: Surface Engineering, 1999, Vol. 15, No. 5, s. 377-384.
6 Małdziński L.: „Termodynamiczne, kinetyczne i technologiczne aspekty wytwarzania warstwy azotowanej na żelazie i stalach w procesach azotowania gazowego" Wydawnictwo Politechniki Poznańskiej, Seria Rozprawy Nr 373, Poznań, 2002.
7 Physical Metallurgy Handbook" authored by Kumar Sinha Anil, McGraw-Hill, 2002, ISBN, No: 0-07-057986-5, s. p. 16.89.
8 "Warmebehandlung von Eisenwerkstoffen – Nitriren und nitrocarburiren" by Ruth Chatterjee-Fischer und 7 Mitautoren, expert verlag, 1986.