

ZEROFLOW® GAS NITRIDING IS A MODERN TECHNOLOGY THAT MINIMIZES THE CONSUMPTION OF PROCESS MEDIA AND REDUCES EMISSIONS OF POST-PROCESS GASES.

Tomasz Przygoński

Thermal Process Equipment Development Director

Historical view of nitriding

Gas nitriding of iron and its alloys is a heat and chemical process for steel treatment with over one hundred years of history. It is assumed that the technology originated with development of a nitriding method in an ammonia and hydrogen mixture atmosphere by A. Machlet, covered with patent granted in 1913. At the same time, A. Fry developed, and in 1923 obtained, a patent for a nitriding method in pure ammonia with a specially developed steel dedicated for nitriding containing chromium and aluminium.

These methods, based on gas carburizing, with requirements only for layer depth and thickness, initially consisted of creating thick phase ϵ of maximum nitrogen concentration, located at $(\epsilon+Y') + \alpha$ phases. Such layers had significant porosity and brittleness, and a network of iron carbon nitrides on the boundaries of grains, therefore required grinding, and with the increase of structural requirements, could not meet expectations.

In the 1930's the development by E. Lehrer of the equilibrium diagram Fe-N gave a helping hand, connecting ranges of the existence of nitrogen phases with temperature and ammonia content in a mixture of $NH_3 + H_2$. It quickly became a price-less tool for developing the technological processes.

As a consequence, the search for solutions aimed for use of atmospheres of reduced nitriding capability were undertaken, and the turning point was patented by C. Floe with the two-stage nitriding process in an ammonia and adissociated ammonia mixture [13].

This method allowed for adjusting the process in such way that the minimum layer of ϵ was created in the first stage and was maintained in a second stage with the simultaneous effect of maintaining the development of an internal nitriding zone. This process created the foundations for the adjusted gas nitriding of steel.

Modern gas nitriding

In many ways, the principles of gas nitriding as originally developed are still the source for the technology. In the 1990's, after analyzing the results of experiments with the use of thin iron foils, the Lehrer diagram was updated by L. Małdziński with isoconcentration curves. Today all gas nitriding methods available on the market are based upon this modified system.

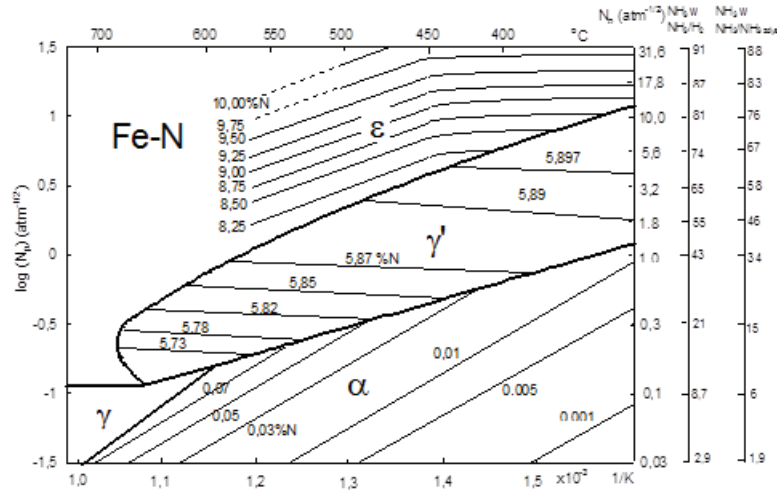


Fig. 1. Lehrer diagram modified by L. Małdziński [16].

Many types of nitriding differ in the method of changing the atmosphere nitriding capability due to its dilution with other gases and/or changing the flow rate through the retort at a given temperature. Use of the first method is connected with the necessity of using more complex equipment, and in some cases, due to disequilibrium of realized processes, besides determination of nitriding potential, it is also required to control the atmosphere composition at the furnace entry. Although the development of control and measurement instruments has significantly improved conditions of process control with the use of most available methods, the "centre of gravity" has been moved towards the economy and ecology which determines the actual advantages of solutions in use.

ZeroFlow® is a fully automatic and single-component process (only ammonia), adjusted by the flow rate of NH_3 through the retort (including temporary complete flow cut-off), and at the same time the "equilibrium" process (in terms of metal/gas interaction), gives full control of the phase development of the layer, corresponding directly to the "pure form" of classic nitriding of A. Fry.

ZeroFlow® connects tradition and modernity.

History has come full circle and today the most economical process of gas nitriding - ZeroFlow®, from the physical point of view, connects tradition with modernity while overcoming the obstacles of the most demanding industrial applications.

Review of available gas nitriding systems

Currently there are a few methods of gas nitriding offered on the market, which depending on the assumed criteria may be divided into various categories. Putting aside deeper theoretical considerations, from a practical point of view, the following systems may be distinguished.

The widest group is represented by systems (equipment and methodology) that are based on the use of retort furnaces in horizontal or pit configurations. Full automation, visualization, tools for creating the technological recipes, diagnostics, trends, and archiving allow the user a relative sense of comfort in safely obtaining repeatability.

Those systems are mostly based upon nitriding with two gases - ammonia plus dissociated ammonia as a dilution gas, prepared with the use of a dissociator, being an integral part of the system. A significant part of those systems additionally has the process nitrogen line, aimed for extending their functionality according to the supplier's assumptions.

Much of the equipment used today for nitriding are based upon common concepts of complex controls and recipes, but are often far from optimum. These systems utilize exemplary recipes which are based on the furnace manufacturer's extensive databases. In many cases they are enriched with advanced graphics using known relationships, but only a few of them include optimizing prediction algorithms. Most of them are only able to show the current working point in a graphical manner.

Processes are controlled according to the indications of sensors, mostly the hydrogen analyzers, usually in a version where the heat conductivity of gas is compared with the reference gas. Less frequently the measurement is realized with use of analyzers based upon infrared radiation absorption by the polyatomic gases - here: ammonia.

Even less frequently the measurement of hydrogen content is realized in a direct way. Special probes detect changes of pressure in the measurement chamber proportionally to the hydrogen partial pressure in the tested atmosphere. There are also solutions based upon a calculation of atmosphere constitution according to changes in its operational pressure directly in the furnace chamber, in the time interval due to dissociation. One may also encounter a solution using catalytic ammonia oxidation, where atmosphere properties are determined upon the basis of oxygen partial pressure measurement with use of oxygen probe. Other methods use two hydrogen analyzers with measurement in the operational chamber and another one after complete ammonia dissociation, or a system consisting of a hydrogen analyzer and an oxygen probe.

In the case of processes using nitrogen as the technological admixture, the situation is even more complex, as measurement of nitriding potential does not fully determine the nitriding capability of atmosphere.

In the case of processes using nitrogen as the dilution gas, the situation is even more complex, as measurement of the nitriding potential does not fully determine the nitriding capability of the atmosphere. This necessitates continuous calculation and tracking of the flow of gases.

In the case of repeatable charges, arranged in the same number and having similar catalytic surfaces, the situation is simplified and repeatable; otherwise the process engineer must use the appropriate corrections. Moreover, the very determination of the mixture ratio requires an arbitrary decision resulting from previous experiment. Therefore, that method is sensitive to changes in actual production runs which might not be properly modelled by the prior reference conditions.

The advancement, today, in nitriding systems, has been based on the minimization of those risk factors which are known in common systems. This second group of nitriding systems actually account for the many additional known factors

Systems based upon ZeroFlow® method have competitive investment and operational costs and high reliability indices.

which result in variability in the nitrided metals. These modern systems consist not only of properly prepared "tools" (e.g. equipment interior made from Inconel), but also predictive technology, for example, the packet of information with specifications for heat processing,

described precisely in terms of type, initial properties, number, arrangement, expected final properties, etc.

All of this technology in the second case adds to costs. Therefore, while it would seem that these solutions should have better market position, it is not so due to high investment costs and low process flexibility. These factors present an

opportunity for a third group, represented by the ZeroFlow® method, which combines the best properties of both of the previous groups. Systems based upon this solution include all required tools (furnace with control system), which due to the process differences are actually very simple. This concept translates directly into very competitive investment costs and also significantly impacts the reliability indices, operational costs, and spare parts availability and management. Moreover the method itself, due to the use of ammonia only, causes a range of process gas savings, which is described below. Limiting the number of process control parameters, as well as the “equilibrium” nature of this new process, allows for easy adaptation of the updated process requirements, which assures high flexibility and repeatability of results, thanks to the process simulator developed over many years of experience by the ZeroFlow inventor L. Małdziński.

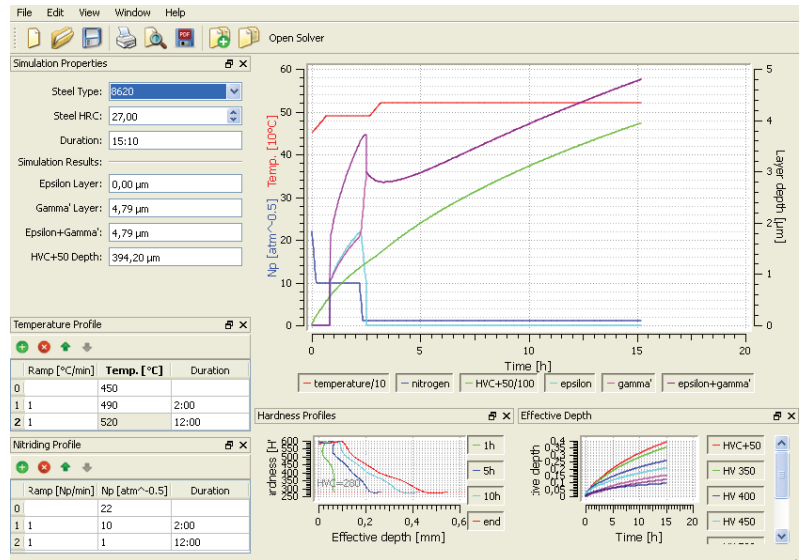


Fig. 2. Screen Shot of Nitriding Process Simulator developed by L. Małdziński.

What does gas nitriding with use of the ZeroFlow® method consist of?

Gas nitriding is defined as a process of diffusion saturation of top layer of iron and its alloys with nitrogen, usually in a temperature range of 490 - 570°C (900 - 1050°F) realized in an atmosphere containing partially dissociated ammonia.

The foundation for the ZeroFlow method is an observation resulting from theoretical studies and supported by appropriate tests that growth speed and phase structure of the nitrided layer is not connected with the atmosphere or furnace type, but with the atmosphere nitriding potential K_N , determined in appropriate process phases. On the other hand, that nitriding potential in the given conditions depends on ammonia dissociation speed in the retort, intensity of atmosphere circulation and intensity of supply of process gases to the furnace.

Therefore, the use of only ammonia gas and the periodic complete stopping of its flow turned out to be the logical consequence of those observations. Valve closing and opening allows for full control of the atmosphere chemical composition (rep. by K_N) and so impacts the process kinetics. The amount of ammonia supplied to the furnace in such way is adjusted according to the measurement of hydrogen content in the atmosphere, realized in the continuous way with use of a thermoconductometric analyzer. Using the recorder values, the control system prepares a response, controlling the temporary opening/closing of the valve supplying ammonia to the process chamber, where the system in the adjustment loop aims for reaching the assumed nitriding potential K_N .

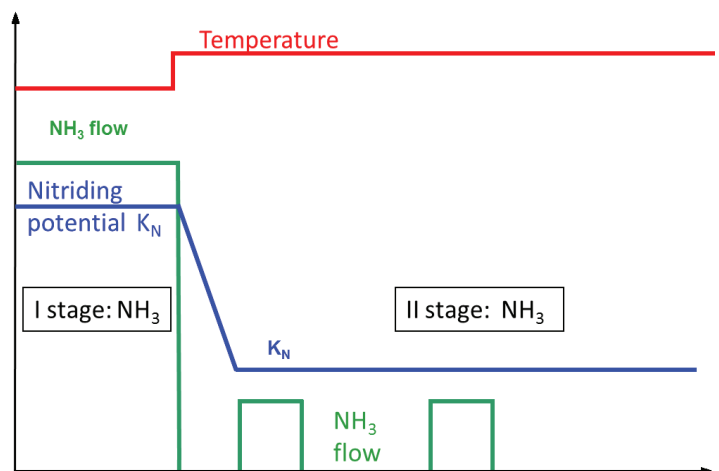


Fig. 3. Chart showing nitriding adjustment for ZeroFlow® method

Applications of ZeroFlow Gas Nitriding

Due to its many advantages, gas nitriding is widely used in the industry.

The process, designed properly for the final operational properties of a given material type, allows for improving the mechanical properties for increasing hardness (up to 1200HV for steel for nitriding and up to 1500HV for high-alloy steels), abrasion resistance, seizure resistance, fatigue strength, and corrosion resistance. Nitriding is suitable for alloy structural steels, carbon and alloy steels for hardening & tempering as well as for carburizing, corrosion-resistant steels, tool steels for cold and hot work, and high-speed steels [9].

From the application point of view the nitrided elements include parts used in automotive industry, like crankshafts and camshafts, sleeves, injector nozzles, valve springs, suspension springs, piston rings and pins, gears and shafts, hydraulic pump components, etc. In the case of parts used for machines, sleeves, pins, shafts, rings and cylinders are nitrided.

A significant group of nitriding applications include tools for machining and forming, where nitriding is used for cutting tools, drop forging dies, die inserts, reciprocating screws of plastic injection machines, elements of permanent moulds for aluminium casting, moulds for extrusion of aluminium profiles, press moulds, forming inserts, etc. The expected processing result is in such cases is a general increase of durability, which often rises by a few times [9].

What does it mean that nitriding is an economical and ecological process?

By definition, nitriding itself is an economical process as it allows for the reduction of manufacturing technological costs due to the increase in durability of the processed work.

Due to wide and still increasing global consumption, either in range of applications or in weight of processed products, the influence of even the smallest savings or limiting the negative impact on the environment leads to great potential for real improvements in local economies and the environment; The level of improvement can be for individual users, or can benefit businesses with significant competitive advantages.

The influence of even the smallest savings or limiting the negative impact on the environment leads to great potential for real improvements in economy and the natural environment.

The advantages of gas nitriding include:

- Relatively low temperature of processing:
 - Capable of hardening parts after previous hardening & tempering
 - Allows for the reduction in energy costs, and uses equipment that is simple and reliable at a relatively low investment cost
- Full automation of the process, allowing for final results during a single cycle
- Minimum dimensional changes of processed parts, allowing for limiting or even eliminating (in some cases) final mechanical processing (grinding)

Some of these advantages may be supplemented with positive (or not) individual properties of processing methods used. Moreover, depending on experience, the designed layers may be more or less accurately selected, therefore the final properties of products will also be different, but this is not the subject of this paper.

Let's just assume that the measure of quality of a given method in range of economy will be the ability to create the required layer in the shortest possible time with the lowest gases consumption. Various methods may be assessed and compared in the ecological aspect, where the measure of quality may be their ability to reaching the goal with minimum environmental impact. In case of gas nitriding, the risk factors, connected with the potential negative impact on the environment may be divided into two areas:

1. Infrastructure, assuring gases availability and design of installation
2. The effects of the finished process

ZeroFlow® significantly reduces ammonia consumption.

In case of the ZeroFlow process, benefits in both areas may be expected. Particularly in the case of high capacity installations, the significant reduction of ammonia consumption is an improvement in safety, based on the results from actual industrial experience. Limiting the need for ammonia storage for the processes on a scale of tons may really impact investment decisions. In this specific case, ZeroFlow has allowed for a radical reduction of risk connected with potential leaks in the system causing environment pollution.

The second area of concern with nitriding equipment is connected mostly with the risk of a negative influence on the environment through the emission of post-process gases. According to regulations valid in the individual countries, and often in various geographical regions of one country, the final requirements for allowable emission may vary.

Therefore it is a common practice to adapt the solutions for utilization of exhaust gases to the actual requirements of users while assuring appropriate conditions of safe workplace, resulting from the regulations. Generally speaking, the components of gas nitriding that require emission control are nitrogen oxides and ammonia. Depending on these requirements as well as system type and size, the dissociators allowing for ammonia dissociation (and combustion of produced hydrogen) and the whole series of afterburners are used.

Omitting the technical details of combustion processes whose efficiency also indirectly impacts the environmental effect of the nitriding process, the best way to assess the processes and their potential for generating risk is through the comparison of the absolute amounts of emissions in the post-process gases.

In such situation, methods of higher demand for process gases and having long periods of work with atmosphere created by poor combustion require a higher capital outlay for utilization. It refers to additional afterburner units, energy consumption, occupied space, operational costs, etc.

Comparison of consumption of process gases / absolute emissions for various methods is presented below.

What influences nitriding process costs?

The costs associated with the nitriding process depend on several factors, which may be grouped according to different criteria. For instance, when evaluating indirect costs, one may distinguish amortization of equipment, costs of fixtures (jigs, baskets, trays), costs of repairs and maintenance, costs of unplanned shutdowns, operational costs, costs of purchase of energy media, etc. These costs are monitored and according to the current indices that determine a user's operational decisions.

Direct costs include:

- Consumption of process gases
- Electrical consumption
- Consumption of auxiliary media (water, compressed air, natural gas, etc.)

Those costs expressed in relative values [€/kg] of charge net will depend not only on the energy efficiency of the equipment, but also their suitability for the final task (size of chamber, type of design, power, efficiency), as well as knowledge and experience of the user in operating the equipment, part arrangement method and possible charge mix, etc.

An additional element which cannot be assigned directly to any of these categories and which may strongly impact the actual, global level of costs of the actual process is the efficiency of the equipment. This refers to the absolute number of processing cycles executed within a time frame, in comparable conditions, in order to achieve the determined goal. Such expressed efficiency will depend mostly on the relevance of the recipe selection, assumed processing time, and equipment efficiency which, in summary, translates into the total cycle time.

The key to minimizing nitriding costs will be the reduction of process gas consumption and process cycle time.

What influences the demand for gases in nitriding processes?

Factors influencing the consumption of technological gases in nitriding processes include:

- Temperature
- Type of atmosphere
- Flow rate of atmosphere
- Preset nitriding potential of atmosphere
- Intensity of atmosphere circulation
- Material of interior of furnace
- Effective catalytic surface in the operational space (retort, radiators, fixture, charge itself)
- Indirectly, the phase composition of layer and its thickness.

Some of these elements are beyond the influence of system user, others may be optimized within a narrow range. These are the factors which significantly influence costs:

Consumption of ammonia

Gas nitriding is based upon nitrogen transfer from the gaseous phase (atmosphere containing partially dissociated ammonia) to the solid phase (steel) with accompanying reactions [17]:

- Nitriding/denitriding:

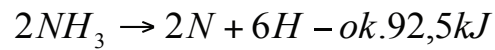


- Denitriding through nitrogen recombination:



In the multi-gas methods the additional gases, i.e. nitrogen, dissociated ammonia, or hydrogen do not participate directly in the nitriding reaction and their role consists in adjustment of the nitriding capability of atmosphere, whose effect in terms of cost will be discussed below. Therefore, regardless of the method used, ammonia remains the main component of process atmosphere and its consumption has a vital impact on costs.

Being subjected to heat decomposition on the catalytic surfaces of retort, equipment, and processed charge according to the general reaction [13]:



it requires refilling and simultaneous removing of reaction products.

Demand for ammonia corresponds to its dissociation speed expressed by equation [17]:

$$\frac{1}{A} \frac{dn_{N_2}}{dt} = k'_v \frac{P_{NH_3}}{(P_{H_2})^3} - k_v [N]_{Fe} P_{H_2}^{1/2} + v_2 ([N]_{Fe})$$

where the successive segments are:

A - Size of active surface

$\frac{dn_{N_2}}{dt}$ - Speed of ammonia dissociation

and on the other side:

$k'_v \frac{P_{NH_3}}{(P_{H_2})^3}$ - Nitriding potential of atmosphere

(A) $k_v [N]_{Fe} P_{H_2}^{1/2}$ - Influence of the increase of concentration of nitrogen dissolved in iron and hydrogen content (action weakening dissociation)

(B) $v_2 ([N]_{Fe})$ - Influence of the increase of concentration of nitrogen dissolved in iron on intensity of nitrogen recombination reactions (action strengthening dissociation)

where:

$[N]_{Fe}$ - Nitrogen concentration in iron

k'_v, k_v - Reaction constants, increasing with temperature and depending on the catalytic properties of active surfaces.

It results from the above that the elements which may be influenced in order to reduce ammonia consumption are used in nitriding potential, and therefore:

- Increase of potential increases the intensity of ammonia dissociation, where
- An increase of potential requires an increase of ammonia flow rate

An increase of temperature intensifies ammonia decomposition, therefore process optimization is looking for a solution which determines a set of those parameters in time for which the economic effect, i.e. processing cost, will be the lowest and the furnace efficiency the highest.

However, there are also limitations in the range of selection of nitriding potential used in a given case.

As it results from Lehrer diagram, the nitriding potential strictly defines the surface nitrogen concentration, and through its control in time allows for forming the desired phase composition of layer. Operating in a given temperature with low potential corresponding to existence of α phase will result in creation of monophase α layer, at the higher potential corresponding to γ' phase the double-zone $\alpha+\gamma'$ layer will be created, and in range of ϵ phase stability the triple-zone $\epsilon+\gamma'+\alpha$ layer will be created.

Industrial studies

Thanks to numerous studies realized in the industrial conditions, L. Małdziński has determined many technical characteristics helpful in the economic analysis (and other aspects). Results of those studies have been used and described in detail in [8] and are discussed below.

The initial point is a chart allowing for quantitative analysis including the influence of temperature and nitriding potential of atmosphere on equilibrium nitrogen concentration on the iron surface in a function of ammonia flow rate for the tested furnace. It results from the chart that the lowest used ammonia flow rates allowed for creation of mono- and double-phase layers, and at the maximum flow rates in the whole range of temperatures, the triple-phase layer $\epsilon+\gamma'+\alpha$ was created.

Influence of nitriding potential

In order to show the impact of the process parameters used on ammonia consumption, it was necessary to determine the kinetic characteristics, which has been modeled with the use of a simulator.

In effect, it has been observed that particularly at higher potentials of 3.6 and 6.0, its increase resulted in a relatively small increase of layer thickness in a given time (approx. 10%) while simultaneously over two times higher ammonia consumption. That conclusion confirms previously mentioned relationships and shows even more the disadvantages of classic nitriding, where disproportionally increasing costs of creating thick layers in the single-stage processes of high nitriding potential additionally implicate the additional costs of subsequent mechanical processing.

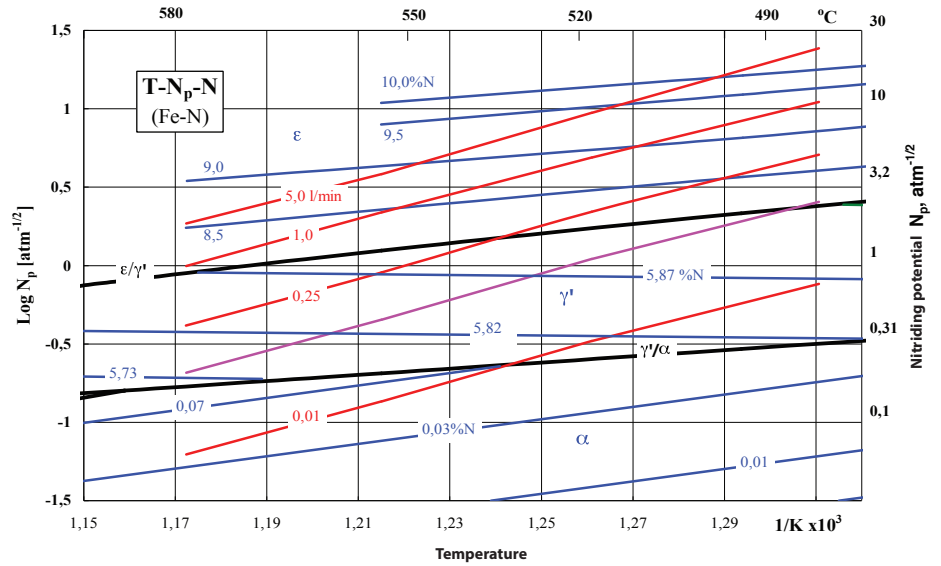


Fig. 4. Influence of temperature and nitriding potential of atmosphere on equilibrium nitrogen concentration on the iron surface in a function of ammonia flow rate through the furnace retort [8].

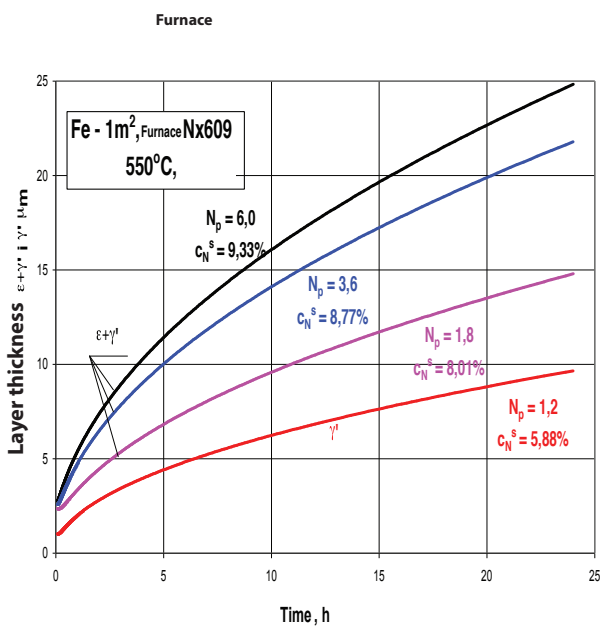


Fig. 5. Influence of atmosphere nitriding potential on layer growth speed [8].

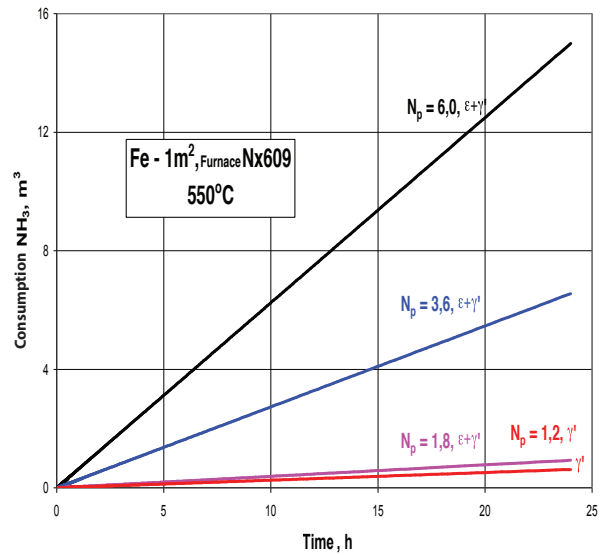


Fig. 6. Influence of nitriding potential on ammonia consumption [8].

Influence of temperature

In order to assess the temperature impact on ammonia consumption the following simulation has been conducted. For the expected layer consisting of zone of compounds ε+γ' of thickness of 25 μm the nitriding potentials have been selected corresponding to identical expected surface concentration of nitrogen of 9.33% for two comparable temperatures of 550°C (1020°F) and 520°C (960°F), i.e. 6.0 and 8.8 atm. correspondingly. According to obtained data, despite the higher potential, layer growth in 520°C is significantly slower than in 550°C (44h/24h), and the ammonia consumption is lower (12m³/15m³). The chart also includes the consumption of electric energy.

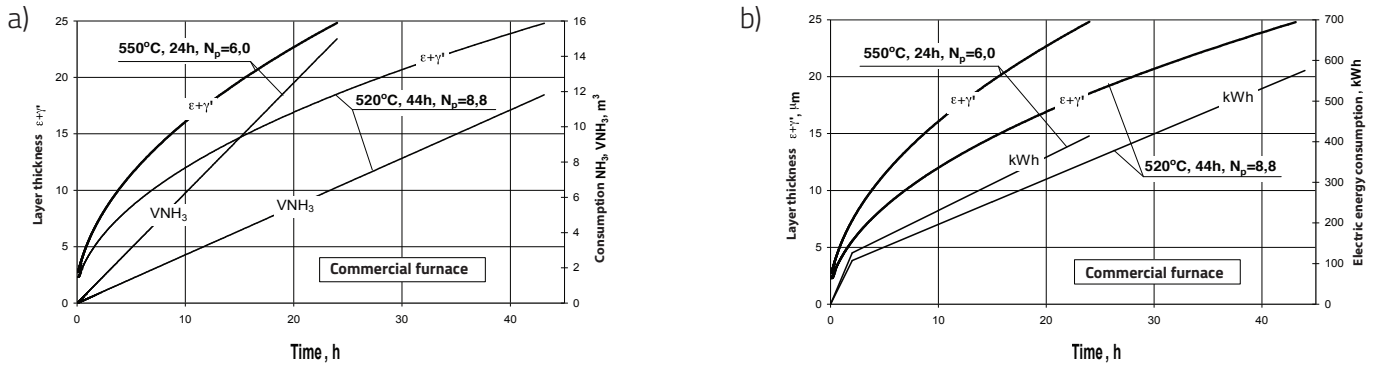


Fig. 7. Influence of process temperature on $\epsilon+\gamma'$ layer growth speed and: a) ammonia consumption, b) electric energy consumption [8].

The experiment above clearly shows what the optimization actions should be aimed for.

On one hand, in the range of general principles of nitriding processes, where the operating temperature should not be higher than 30°C (85°F) below the tempering temperature due to mechanical properties of processed details, it is always recommended to use the maximum allowable temperature. On the other hand, just designing the layers and their selection to a given application should be made with proper care due to the law of parabolic growth of the diffusion layer [15]:

$$\Delta X_i = k_i \cdot t$$

where:

- ΔX_i ▪ Thickness of i-th phase in nitrided layer
- k_i ▪ Parabolic constant of i-th phase growth
- t ▪ Time

Excessive thicknesses will result in a disproportionately high cost of media consumption, a cost resultant from limiting of the equipment potential capacity and cost of grinding.

The influence of atmosphere type

As mentioned in the beginning, there are many methods of gas nitriding, and it is obvious that due to their existing technical differences they may be classified according to economic criteria (and/or emissions). For objectivity purposes creating such comparisons requires assuming identical reference conditions; therefore we assume the same temperature and assess differences in outlay for creating the identical layer. The diagram below shows comparison for the single-gas method with ammonia and the double-gas method with ammonia/dissociated ammonia.

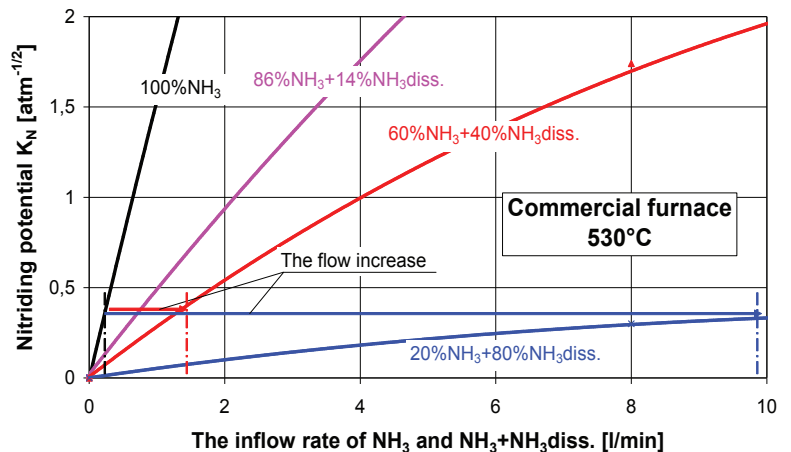


Fig. 8. Influence of process mixture composition in the industrial test in 530°C on consumption of atmosphere for the specified nitrogen potential [8].

Dilution of ammonia with dissociated ammonia always results in a higher atmosphere flow rate for the preset nitriding potential in comparison to an ammonia only atmosphere. For both methods, the nitriding potential clearly determines the nitriding capability of atmosphere, and therefore the process kinetics. As a consequence, for the preset potential dilution of ammonia with dissociated ammonia always leads to an increase of the atmosphere flow rate, and at the higher dilution

Dilution of ammonia with dissociated ammonia always results in a higher atmosphere flow rate for the preset nitriding potential in comparison to an ammonia only atmosphere.

level, the higher flow rate. Typical mixtures (shown on the diagram) in the test conditions required significantly higher ammonia consumption (sum: ammonia plus raw ammonia processed with dissociator) from few to tens of times!

Comparison and assessment of an alternative nitriding method, i.e. that one where the molecular nitrogen is used as diluting gas, requires taking some important differences into consideration. The characteristic property of that method is the fact that change of the nitriding potential does not have to be accompanied by the automatic change of nitriding capability and kinetics.

In practice, controlling the process course is much more complex and the "non-equilibrium" process, unlike processes discussed previously and based only upon ammonia, besides the control of nitriding potential it also requires the continuous control of the atmosphere chemical composition (a calculation of process gases distribution).

According to the results of analysis of many industrial processes, L. Małdziński specifies that the increase of consumption of ammonia only, when compared with the corresponding processes realized with use of ZeroFlow method, is up to two-fold better. Also the additional nitrogen consumption should be added, which besides higher direct costs (atmosphere) means additional higher costs of utilization of post-process gases.

Comparison of process gas consumption (and emissions) in industrial processes

Collected conclusions have been verified in industrial conditions. The analysis included nitriding processes with use of four methods (ZeroFlow®, classic, Floe, and ammonia plus nitrogen) for representatives of medium- and long-term nitriding, i.e. crankshafts of engines for racing cars and toothed wheels used in wind turbine gears. The double-stage processes have been assumed, as well as identical temperatures of individual stages, and typical nitriding mixtures.

Nitriding of crankshafts

According to requirements of engines manufacturers the appropriate processes have been designed in a way to assure the diffusion layer of thickness of 0.4 mm below 5 μm of Y' zone. The diagram below shows a comparison of consumption of

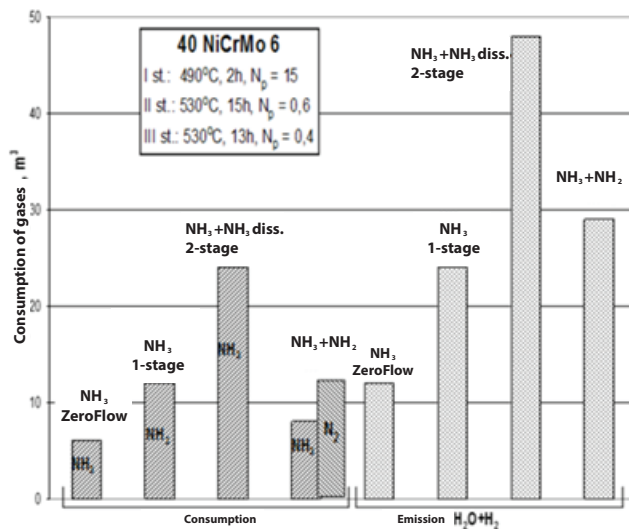


Fig. 9. Consumption of ammonia and nitrogen in nitriding processes of crankshafts from steel 40NiCrMo6 with use of methods: ZeroFlow®, traditional, Floe, and ammonia + nitrogen [8].

According to the conclusions from the laboratory tests, ZeroFlow has the lowest consumption of process gases. In comparison to the classic process it allows for saving half of ammonia. It requires only approx. 25% of demand of Floe process, and comparing to ammonia plus nitrogen process it allows savings of tens of percent of ammonia and additionally two times more of nitrogen.

As a consequence, ZeroFlow allows for a significant reduction of demand for process gases, as well as limiting their utilization costs through the absolute reduction of volume of exhaust gases.

Nitriding of wind turbine gears

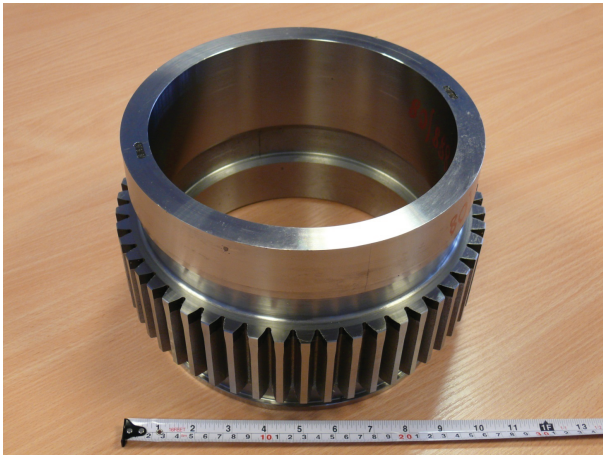


Fig. 10. A sample of the gears subjected to the comparison processes.

Gears for wind turbines are critical components operating in conditions of high unitary pressures on the tooth surface, where the main structural criterion is the fatigue strength. In order to fulfil those requirements, thick nitrided layers are required, free from compound zones. Processes corresponding to those requirements need tens of hours of processing at low nitriding potential.

In this specific case for steel 31CrMoV9 nitriding, the diffusion layer of approx. 0.8 mm required approx. 70 - 90 hours of nitriding. Such particular conditions definitely revealed differences in the consumption of gases for the individual methods, which is graphically shown in the diagram below.

The ZeroFlow process with use of approx. 8 m³ of ammonia, classic process required a supply of 42 m³ (5.25 times more), Floe process required 66 m³ (8.25 times more), and ammonia plus nitrogen has been realized with use of approx. 12 m³ (1.5 times more) of ammonia, but additionally required a supply of 53 m³ of nitrogen (additionally 6.6 times volume of used ammonia in the ZeroFlow method).

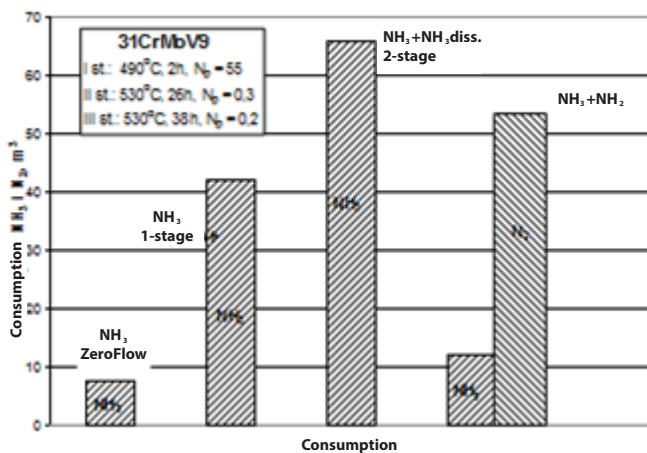


Fig. 11. Consumption of ammonia and nitrogen in nitriding processes of toothed wheels of wind turbines with use of methods: ZeroFlow®, traditional, Floe, and ammonia + nitrogen [8].

SECO/WARWICK furnaces for gas nitriding

In view of current experience, ZeroFlow technology is in use in many applications around the world. These installations cover the whole spectrum of nitriding applications, various materials and components, from structural parts to tools.

Practice has revealed that ZeroFlow surpasses other methods, has a relatively lower consumption of process gases and consequently, proportionally lower emission to the atmosphere. Besides the technology, the equipment for obtaining optimal results is manufactured by SECO/WARWICK. Design solutions used in those furnaces add new advantages to the system performance beyond those resulting directly from ZeroFlow.

ZeroFlow features lower consumption of process gases and proportionally lower emissions to the atmosphere.



Fig. 12. Production line for gas nitriding with using the ZeroFlow method with HRN horizontal retort furnaces.

These furnaces are available with electric or natural gas heating systems, vacuum, additional external (blower), and internal (by-pass cooler) systems of accelerated cooling. They are delivered in the basic version for gas nitriding with the use of the ZeroFlow method, but as an option, may be equipped for ferritic nitrocarburizing, sulfonitriding, chemical activation of the surface, and passivation. All devices have the CE mark and are manufactured according to the highest safety standards. They have very good temperature distribution, better than $\pm 5^{\circ}\text{C}$, and on demand, are delivered in accordance to AMS standards (2750E and 2759-12). The control system are designed with Siemens PLC controllers and industrial computers.

All devices have the CE mark and are manufactured according to the highest safety standards. They have very good temperature distribution, better than $\pm 5^{\circ}\text{C}$, and on demand, are delivered in accordance to AMS standards (2750E and 2759-12).



Fig. 13. Pit furnace of VRN type for gas nitriding using the ZeroFlow method.

Control applications, in addition to the basic functions connected with the creation of recipes, processes database, multi-criteria module for trend analysis, reporting module, diagnostics module, and visualization module supports the operator's work through safety monitoring and alarms.

The system allows for remote diagnostics, the function of remote event and alarms reporting is also available. Furnaces are delivered with all wiring, equipped with a process gas panel, control cabinet, optional cooling system and afterburner unit.

After delivery, the system is installed by qualified technicians, with start-up and commissioning realized by specialized process engineers. After the first period of operation, SECO/WARWICK provides practical training in the work place, aimed at the discussion of current technological problems and improvement of processes. SECO/WARWICK continuously supports users of ZeroFlow throughout the life of the system. The company professionals share their experience, offer expert help, refer to reference processes in R&D department with use of test furnaces, access large process databases, and utilize dedicated software (nitriding process simulator).

The characteristic properties of SECO/WARWICK equipment, that supports the economic advantages resulting from use of ZeroFlow method are:

- High heat dynamics allowing for optimization of heating and cooling cycles
- Low heat accumulation for minimization of heating and cooling costs
- High heat efficiency of cooling systems
- Effective chamber aerodynamics for better heat transfer in convection conditions
- Cold vacuum purge before and after the process (savings of time and nitrogen)
- Hot vacuum purge (savings of time and nitrogen)
- Direct retort back-fill with ammonia (savings of time, nitrogen, and ammonia)
- Hardware and software integration of activation operation of surfaces of processed details (the whole processing in one furnace and one operation)
- Efficient heat insulation
- Efficient afterburner units
- Precise control of temperature and nitriding (carbon) potential
- Full automation of processes and optional remote monitoring of operation
- Intuitive and safe software for elimination of operational mistakes

- Compact design (saving of space), low infrastructure requirements and mobility (easy relocation)
- Simple design translating into high reliability and low maintenance and servicing costs
- Use of commercial subassemblies of known brands gives access to spare parts competitive in range of price (= independence) and limits risk of down-time while waiting for parts
- Competitive price

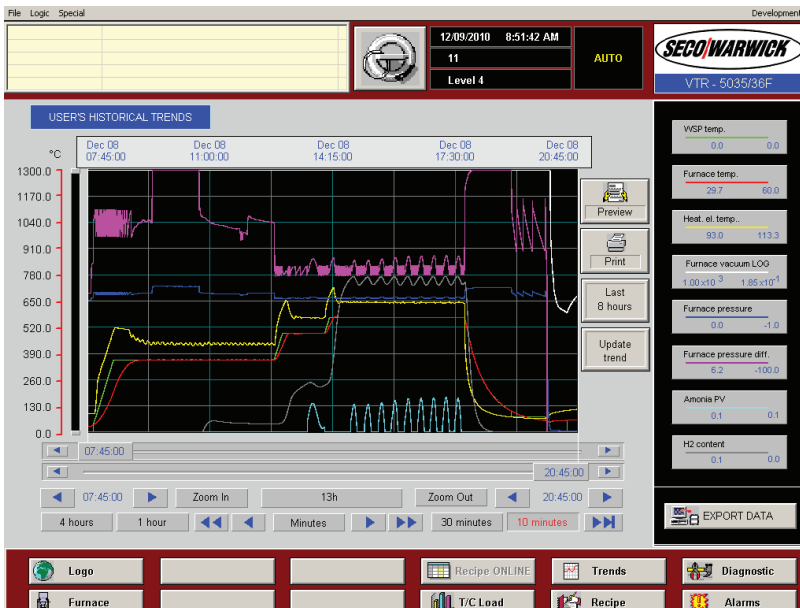


Fig. 14. Trend screen in control application for ZeroFlow® gas nitriding furnace.

Moreover ZeroFlow assures the user indirect advantages that are often overlooked.

They include:

- Full repeatability of processes regardless the amount and configuration of charge
- "Compensation" of changes of catalytic properties of internal equipment
- Relatively simple (= inexpensive) preparation of recipes for new materials due to limited number of process variables
- Lower investment and operational costs of utilization of post-process gases due to:
 - reducing the consumption of process gas (ammonia)
 - limiting the costs connected with lack of necessity of processing a large volume of atmosphere highly diluted with nitrogen

Summary

Modern gas nitriding with the use of ZeroFlow technology, using SECO/WARWICK products, perfectly fits into the current trends and demands of modern industry.

On one hand, we deal with an innovative method of process control which maximizes the use of the factors that influence processing costs, on the other hand, there is modern equipment that improves economy through the further reduction of energy consumption and cycle times.

Savings, flexibility, precision, and simplicity of the ZeroFLOW process makes it the ideal replacement for traditional nitriding systems.

Savings, flexibility, precision, and simplicity - this is ZeroFlow.

References:

1. ASM Handbook, rev. vol. 4: Heat Treating, Prepared under the direction of the ASM International Handbook Committee, Fifth printing, March 2001
2. Patent, "Method of gas nitriding", Poland, 11.06.1977, No 85924.
3. Małdziński L., Tacikowski J.: „Regulowane azotowanie gazowe z oszczędnym wykorzystaniem amoniaku” Inżynieria Powierzchni 2006 nr 4
4. Małdziński L., Tacikowski J.: "Concept of an economical and ecological process of gas nitriding of steel" Harterei-Technische-Mitteilungen" 61 (2006) 6 p. 295-302
5. Małdziński L.: "Controlled Nitriding using a Zeroflow process", Heat treating Progress", August 2007, Vol 7, Number 5, p. 53-57
6. Małdziński Leszek, M. Bazel, M. Korecki, A. Miliszewski, T. Przygonski: "Controlled nitriding using a "ZeroFlow" method, Industrial experiences" Heat treating Progress, July/August, 2009, p. 19-22
7. Małdziński Leszek, M. Bazel, M. Korecki, A. Miliszewski, T. Przygonski: „Przemysłowe zastosowania azotowania gazowego metodą „ZeroFlow” 3/2010, s. 48-54, Inżynieria Powierzchni,
8. Małdziński L., Ostrowska K., Okonowicz P., Hofman A., Kowalska J.: „Zużycie i emisja gazów technicznych w procesie regulowanego azotowania gazowego ZeroFlow oraz w dotychczas stosowanych procesach” Piece Przemysłowe & Kotły, I-II 2014, s. 8-14
9. Monografia: Kula P.: „Inżynieria warstwy wierzchniej” Wydawnictwo Politechniki Łódzkiej, Łódź, 2000.
10. Gulikhandanov E.L., Budzynowski T.W.: „Nawęglanie, węgloazotowanie, azotowanie stali” Wydawnictwo Politechniki Radomskiej, Radom, 2003.
11. Monografia: Gawroński Z.: „Technologiczna warstwa wierzchnia w kołach zębatych i mechanizmach krzywkowych” Wydawnictwo Politechniki Łódzkiej, Łódź, 2006.
12. Jaroński J.: „Techniki czystego spalania” Wydawnictwo Naukowo-Techniczne, Warszawa, 1996.
13. Zyśk J.: „Rozwój azotowania gazowego stopów żelaza” Wydawnictwo Instytutu Mechaniki Precyzyjnej, Warszawa, 2008.
14. Praca zbiorowa: „Materiały szkoleniowe kursu – obróbka cieplna stopów metali” Wydawnictwo Instytutu Mechaniki Precyzyjnej, Warszawa, 2014.
15. Michalski J.: „Charakterystyki i obliczenia atmosfer do regulowanego azotowania gazowego stali” Wydawnictwo Instytutu Mechaniki Precyzyjnej, Warszawa, 2011.
16. Praca habilitacyjna: Małdziński L.: „Termodynamiczne, kinetyczne i technologiczne aspekty wytwarzania warstwy azotowanej na żelazie i stalach w procesie regulowanego azotowania gazowego” Poznań, 2003.
17. Małdziński L.: "Consumption of ammonia in the regulated Zero Flow® gas nitriding and other processes used in the world", prezentacja użyta w czasie webinarium SECO/WARWICK, Świebodzin, 2015.