

ZeroFlow – new, environmentally friendly method of controlled gas nitriding used for selected car parts

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Abstract. This article presents new method of controlled gas nitriding called ZeroFlow, which is used for nitriding of selected car parts, such as crankshafts, camshafts, piston rings, poppet valve springs and discs, piston pins or nozzles for unit injectors. This article will discuss the essence of controlled gas nitriding process, with an emphasis on the influence of process parameters on results of nitriding process. This information are the basis to understand the issue of the kinetics of nitrided layer growth, and as it follows – for its practical application in designing, regulation and control of nitriding processes using simulation models (simulator of the kinetics of nitrided layer growth). This article will also present the simulator of the kinetics of nitrided layer growth, which supports nitriding using ZeroFlow method – through the use of simulator layers are obtained in the shortest possible time, which is connected with the lowest energy consumption; therefore, nitriding process using ZeroFlow method and simulator of the kinetics of nitrided layer growth is both economical and environmentally friendly.

1. Introduction

ZeroFlow is a new method of controlled gas nitriding, developed at the Poznan University of Technology, which enables precise forming of nitrided layers using nitriding kinetics. It is characterized by much lower consumption of gases, as well as simplification of the nitriding furnace and of the process itself, while full control over the kinetics of nitrided layer growth is still maintained. The same as in the traditional process, ZeroFlow method assumes the use of atmosphere consisting only raw ammonia. However, unlike to the traditional method, kinetics can be controlled by adjusting the chemical composition of the atmosphere in the furnace retort (by adjusting the nitriding potential) through the regulation of ammonia flow rate, or more precisely – through the regulation of ammonia inflow rate by stopping and reactivating ammonia feeding into the furnace retort. It is significant that in ZeroFlow method ammonia inflow rate is temporarily reduced to zero, which makes much easier to control the chemical composition of the atmosphere. To sum up, using a unary atmosphere makes the ZeroFlow method simpler than currently popular methods based on binary atmospheres, but simultaneously it allows to control the kinetics of nitrided layer growth by regulating of ammonia inflow rate [1]. Until now, ZeroFlow nitriding method has been introduced in 26 industrial plants in Poland and many other countries worldwide, such as: Italy, Great Britain, Canada, Sweden, Singapore, South Korea, Germany, Czech Republic, Belarus, Russia, India, Pakistan, Switzerland. 36 industrial installations have been constructed and implemented so far, another 4 are launched. Several thousands of nitriding processes for various parts of machines and vehicles have been conducted with positive results, which is the best verification of this method rightness.

Gathered experience shows that ZeroFlow method enables forming of nitrided layers with respect to the required phase structure, zone thicknesses, and hardness distribution. Through the use of



phenomenological models layers are produced in the shortest possible time, which is connected with the lowest energy consumption. Mathematical models of the kinetics of nitrided layer growth additionally allow determining nitrided layer phase structure and thickness of each zone that occurs in it as a function of process parameters: time, temperature and nitriding potential of the atmosphere. Layer obtained this way does not need costly and time-consuming grinding of iron nitrides, which leads to lower consumption of energy and materials. Several times lower consumption of gases in comparison with its consumption in another currently used nitriding processes, and as a result – much lower emission of post-process gases, also indicates on economical and environmentally friendly character of ZeroFlow method.

Thus, ZeroFlow is a new, rapidly evolving method of controlled gas nitriding, which fits into currently prevalent trends in the world: minimization of raw materials and energy consumption, as well as minimization of the negative impact on the environment [1]. However, it should be noted that ZeroFlow method is only general technological and structural solution, which enables carrying out processes in different, strictly selected parameters, such as temperature, nitriding potential of the atmosphere, time, speed of heating, reduction of potential etc. Therefore, each element requires the development of specially dedicated process with specific parameters; this task is supported by simulation models, which considerably speed up the development of new processes [2,3]. It is also worth mentioned that simulations of heat treatment processes are a really important issue and they allow observing various phenomena, which usually are not perceived in industrial practice (sometimes even in experimental research). They can also be a part of regulation and control of the processes [4].

Forming of nitrided layers occurs on steels that are most commonly used in transport machines engineering, like vehicles and aircrafts, or in technological machines and tools (used for example for the wood industry) engineering; therefore, ZeroFlow nitriding is used for parts of machines and vehicles such as: toothed wheels for wind power plants, plates for casting glass bulbs for lamps, inlet sleeves with the pushing piston, used in molds for aluminium pressure die casting, etc. Also many processes were conducted for parts of car engines: crankshafts, camshafts, piston rings, poppet valve springs and discs, piston pins or nozzles for unit injectors. Aim of nitriding of this elements is to obtain layer with higher surface hardness, improved fatigue life and corrosion resistance, increased wear resistant and antigallic properties. According to that, this layer increase durability of nitrided parts, and as a result – durability of machines and vehicles.

2. The essence of nitriding process using ZeroFlow method

Controlled gas nitriding ZeroFlow is carried out in a heightened temperature (usually from range between 490°C÷590°C), using an atmosphere consisting of ammonia. The low durability of the ammonia molecules (at average nitriding temperature ammonia is in unstable thermodynamic state) results in their disintegration after contact with a metal surface, as shown in the following catalytic reaction of dissociation:



As a result of atomic nitrogen diffusion into the steel surface, layer with different properties than original material (material of the core) is formed. Its phase structure, zone thicknesses, and as a consequence – its properties – depend both on the type of the steel and the parameters of the nitriding process: time, temperature and nitriding potential of the atmosphere. As a nitriding potential of the atmosphere is understood a ratio of partial pressures of the atmosphere active ingredients. Atomic nitrogen and hydrogen, obtained by dissociation of ammonia, tends to recombine into diatomic molecules as soon as possible, whereas nitrogen diffusion occurs only when it is in atomic state – that means it is necessary to feed fresh amount of ammonia continuously into the furnace retort in order to carry out the process. Therefore, atmosphere in furnace retort during the process consist of nitriding gas NH_3 and denitriding gas H_2 , which are the active ingredients of the atmosphere, and inert gas N_2 [1,5,6]. Thus, we can describe nitriding potential of the atmosphere with a following formula:

$$N_p = \frac{p_{NH_3}}{p_{H_2}^{3/2}} \quad (2)$$

Depending on the activity of nitrogen in the atmosphere (which is connected with nitriding potential), nitriding of steel may be accompanied by growth of the single-, double- or triple-phase layer (α , $\gamma' + \alpha$, $\epsilon + \gamma' + \alpha$). The connection between phase structure and parameters such as nitriding potential and temperature is shown on T- N_p phase equilibrium diagram, also known as a Lehrer's diagram. The boundaries of phases occurrence (α/γ , α/γ' , γ/ϵ , γ'/ϵ) are presented at this diagram as a function of temperature and nitriding potential. It is worth noting that the chemical potentials of nitrogen in particular phases are equal at boundaries between them, and at equilibrium conditions with atmosphere $NH_3 + H_2$ they are equal to chemical potential of nitrogen in this atmosphere.

As far as Lehrer's diagram predict in some measure phase structure of the nitrided layer, it does not deliver any information about the concentration of nitrogen in α , γ' and ϵ phases as a function of temperature and nitriding potential, however, these data are the basis for description of the kinetics of nitrided layer growth. L. Małdziński, on the basis on his own analysis and research, had determined lines and curves of iso-concentration (constant values of nitrogen concentration) in T- N_p phase equilibrium diagram, which allowed for the development of a modified T- N_p -N phase equilibrium diagram (figure 1). It delivers essential information required to develop models of the kinetics of nitrided layer growth [1,4].

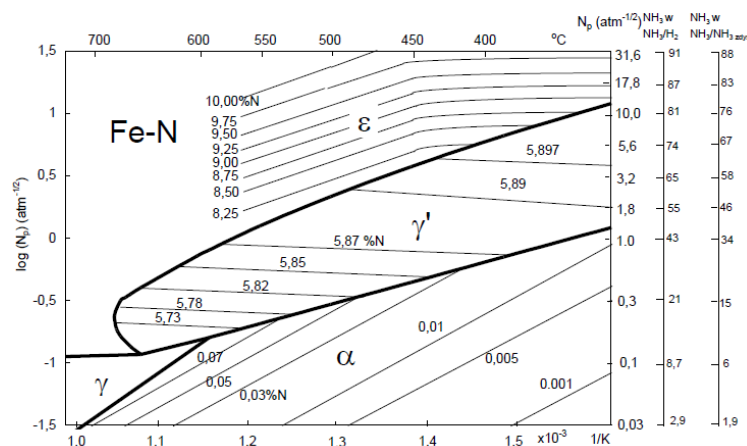


Figure 1. T- N_p -N phase equilibrium diagram.

From T- N_p -N phase equilibrium diagram we can conclude that depending on the nitriding potential of the atmosphere (if process temperature remains the same), nitrided layer can have three different forms. At the nitriding potential N_p^a , located in the graph on the range of α phase occurrence, only diffusion zone will increase – that means we get single-phase layer α (figure 2), which does not contain any iron nitrides (γ' and ϵ). This is the simplest case of nitrided layer growth, analogous to the growth of carburized layer. Furthermore, because of the low activity of nitrogen in α phase (low concentration of nitrogen), growth of this layer is not accompanied by reaction of nitrogen recombination, which is an additional simplification [4].

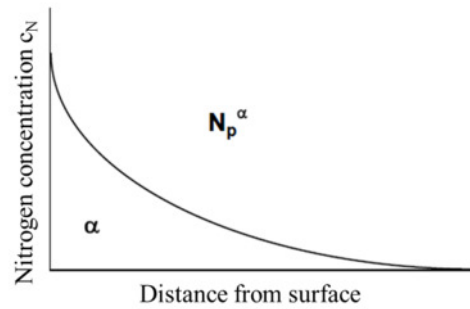


Figure 2. Single-phase layer α structure.

At the higher nitriding potential $N_p^{\gamma'}$, located in the graph on the range of γ' phase occurrence, double-phase layer $\gamma'+\alpha$ (figure 3) will increase. This is a case much more complex than single-phase layer growth, and it proceeds in several stages. At first stage α phase increases until saturation of the ferrite surface with nitrogen. Then second stage – nucleation of γ' phase – occurs, and immediately after second stage starts third stage – coalescence of γ' crystals, which lasts until a continuous γ' phase is formed on the iron surface. At fourth stage the γ' phase increases with a variable (or more precisely – with an increasing) nitrogen concentration at the surface $c_N^{s/\gamma'}$. After nitrogen at the surface reaches the local equilibrium with an atmosphere, starts the last, fifth stage – γ' phase growth on ferrite ($\gamma'+\alpha$ layer growth) with a fixed nitrogen concentration at the surface $c_N^{s/\gamma'}$ [4].

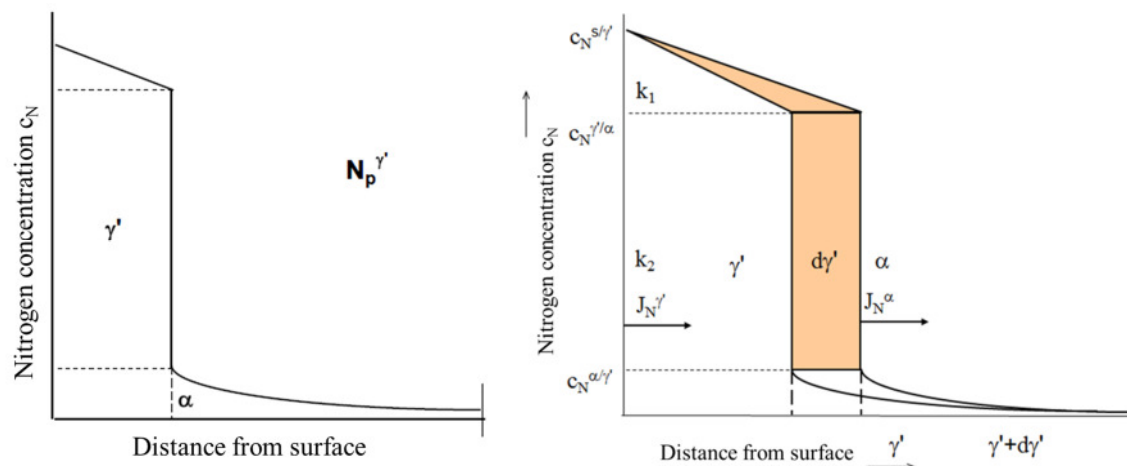


Figure 3. Double-phase layer $\gamma'+\alpha$ structure.

Growth of the triple-phase layer $\epsilon+\gamma'+\alpha$ (figure 4) occurs at the nitriding potential N_p^ϵ , located in the graph on the range of ϵ phase occurrence, or in other words – at the nitriding potential higher than border potential $N_p^{\gamma'/\epsilon}$. Triple-phase layer growth in initial stages is the same as the double-phase layer growth, but this case is even more complex. After the $\gamma'+\alpha$ layer is formed, at the γ' layer surface occurs the nucleation of ϵ phase; the next stage is coalescence of ϵ phase crystals until a continuous ϵ phase is formed. Then starts its growth – first with a variable, and next with a fixed concentration at the surface $c_N^{s/\epsilon}$. Therefore, ϵ phase growth is analogous to the γ' phase growth, however, because of accompanying phenomena this case is more difficult to mathematical description. In fact, ϵ phase growth can occur not only on continuous γ' phase with maximum, border nitrogen concentration at the surface, but also on apexes of that phase embryos before they form a continuous γ' phase. Complications are also connected with nitrogen concentration at the surface $c_N^{s/\epsilon}$, which does not reach equilibrium value due to the strong desorption of atomic nitrogen to atmosphere [4].

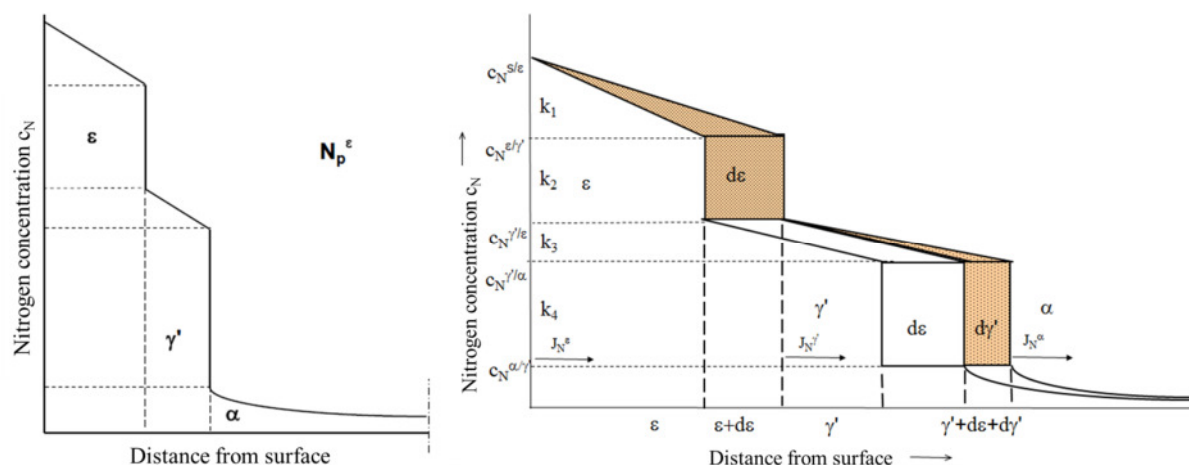


Figure 4. Triple-phase layer $\varepsilon+\gamma'+\alpha$ structure.

Assuming a fixed nitrogen concentration at the surface c_N (which means local equilibrium or stationary state between nitrogen and atmosphere at the surface) and local equilibrium of nitrogen in ε , γ' and α phases on borders γ'/ε and α/γ' , the growth of iron nitrides is determined by streams of nitrogen atoms J_N . The values of that streams are connected with gradient of nitrogen concentration at the surface c_N on the border of the individual phases [4,7]. Influence of nitrogen concentration at the surface c_N on the growth of phases has been shown on figure 5. At the nitriding potential $N_p^\varepsilon (c_N^{s/\varepsilon} > c_N^{\varepsilon/\gamma'})$, located in the graph T- N_p -N on the range of ε phase occurrence, both ε and γ' phases will grow. With increasing nitrogen concentration at the surface $c_N^{s/\varepsilon}$, ε phase will grow faster and faster; if the stream of nitrogen atoms $J_N^{\gamma'}$ will be bigger than the stream of nitrogen atoms J_N^α , then the γ' phase will be consumed towards the ε phase. The reverse situation occurs at nitriding potential of the atmosphere equal to the border nitriding potential $N_p^{\varepsilon/\gamma'}$, when the gradient of nitrogen concentrations at the surface $c_N^{s/\varepsilon}$ and $c_N^{\varepsilon/\gamma'}$ will be equal to 0 ($c_N^{s/\varepsilon} = c_N^{\varepsilon/\gamma'}$); then the stream of nitrogen atoms $J_N^{\gamma'}$ will be smaller than the stream of nitrogen atoms J_N^α and the ε phase will be consumed towards the γ' phase [7].

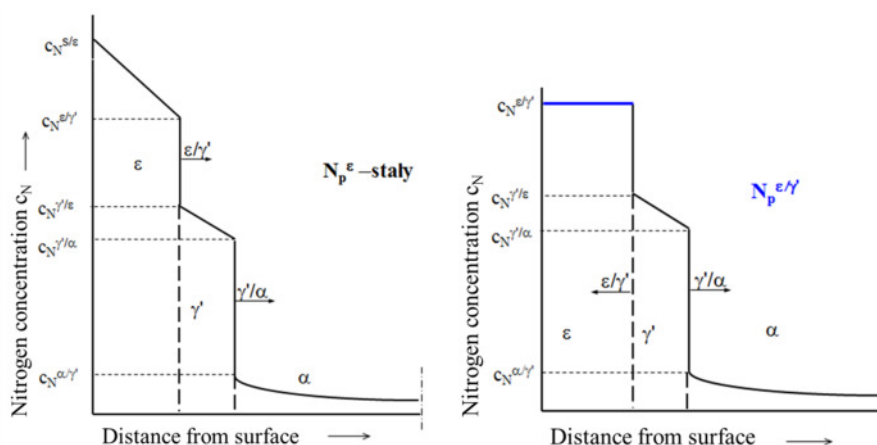


Figure 5. Influence of nitrogen concentration at the surface c_N on the growth of phases.

As seen from above, nitriding potential of the atmosphere is one of the most important parameters determining kinetics of nitrided layer growth. Another important parameter, also included on T- N_p -N phase equilibrium diagram, is temperature of nitriding process. From T- N_p -N phase equilibrium diagram we can conclude that depending on the process temperature (if nitriding potential of the atmosphere

remains the same), we can obtain layers with different phase structure. For example, if we lower process temperature from 500°C to 450°C (with unchanged nitriding potential of the atmosphere $N_p=3,2$), we get double-phase layer instead of triple-phase layer. Moreover, in multistage processes, higher temperature after the first stage of process lowers the case hardness and simultaneously increases the case depth; it also may lower the core hardness depending on the prior tempering and total nitriding cycle or the apparent effective case depth because of the loss of core hardness, depending on how effective case depth is defined.

It is worth noting that on the basis of T- N_p -N phase equilibrium diagram we cannot draw conclusions about kinetics (speed) of nitrided layer growth and each phase that occurs in it. Phase structure and particular zone thickness depends on time of the process as well. The influence of time has been taken into consideration in phenomenological models of the kinetics of nitrided layer growth, developed by L. Małdziński and his co-workers [1]. Phenomenological description of nitrided layer growth assumes that this growth is caused by diffusion of nitrogen atoms through the interstitial positions of nitrogen atoms subnets; iron atoms participation in diffusion is negligible in comparison with participation of nitrogen in diffusion. Thus, general model of the kinetics of nitrided layer growth can be described using Fick's laws of diffusion. First Fick's law describes diffusion stream of nitrogen atoms j_N^φ in φ phase, in the distance of x from the surface:

$$j_N^\varphi = -D_N^\varphi \frac{\partial c_N^\varphi}{\partial x} \quad (3)$$

In the formula above, c_N^φ means nitrogen concentration in φ phase, and D_N^φ is an actual coefficient of nitrogen diffusion in φ phase, connected with coefficient of self-diffusion $D_N^{*\varphi}$, according to the following formula:

$$D_N^\varphi = D_N^{*\varphi} \frac{d \ln a_N^\varphi}{d \ln c_N^\varphi} \quad (4)$$

$d \ln a_N^\varphi / d \ln c_N^\varphi$ quotient is a thermodynamic factor of nitrogen diffusion in φ phase (where a_N^φ is a nitrogen activity in φ phase, corresponding to concentration c_N^φ), which can be related with nitriding potential of the atmosphere:

$$\frac{\partial \ln a_N^\varphi}{\partial \ln c_N^\varphi} = \frac{\partial \ln N_p}{\partial \ln c_N^\varphi} \quad (5)$$

As mentioned before, nitriding potential of the atmosphere is one of the most important parameters determining kinetics of nitrided layer growth, and its influence on phase structure of layer is shown on T- N_p -N phase equilibrium diagram. Thus, through the nitriding potential of the atmosphere, we can connect a thermodynamic factor of nitrogen diffusion in particular phases of Fe-N phase equilibrium diagram with T- N_p -N phase equilibrium diagram. Distribution of nitrogen concentration as a function of distance from surface in particular phases of Fe-N phase equilibrium diagram can be described by second Fick's law:

$$\frac{\partial c_N^\varphi}{\partial t} = \frac{\partial}{\partial x} \left(D_N^\varphi \frac{\partial c_N^\varphi}{\partial x} \right) = \frac{\partial D_N^\varphi}{\partial c_N^\varphi} \left(\frac{\partial c_N^\varphi}{\partial x} \right)^2 + D_N^\varphi \frac{\partial^2 c_N^\varphi}{\partial x^2} \quad (6)$$

Models developed on the basis of this relations together with determined experimental data describe the growth of nitrided layer in the field controlled by nitrogen diffusion in nitrided layer phases on iron. They are used in the simulations of nitriding processes, where through the adjusting process parameters they enable forming phase structure of nitrided layer, i.e. types of formed phases and their thicknesses, nitrogen concentrations at the surface, profiles of nitrogen concentration in particular phases. Moreover, they allow watching the growth of ϵ and γ' phases as a function of temperature and nitriding potential

of the atmosphere not only in single-stage processes, but also in multistage processes. Unfortunately, they have also some limitations, resulting from complicated physico-chemical nature of nitriding. In industrial practice the biggest limitation is that this models can be used only for pure iron, whereas in fact the carbon and alloy steels are nitrided. The last one are the most problematic, because kinetics of nitrided layer growth on alloy steels is determined by many factors, sometimes contrary interacting, which is a major obstacle in the development of a satisfactory mathematical models and the determination of the necessary physico-chemical data. L. Małdziński proved that T-N_p-N phase equilibrium diagram can be used only for alloy steels containing Cr, Mn, Mo, V, because content of this elements does not change its shape [1,4].

L. Małdziński with collaboration with E. Mittemeijer and M. Sommers attempted to describe quantitatively the kinetics of γ' and $\epsilon+\gamma'$ phases on steels. They used the growth models of this phases on pure iron, and then modified them using correction factors k_{jN} , which take into account the cumulative effect of alloying elements and carbon on diffusion streams of nitrogen atoms in ϵ , γ' and α phases, and as a result – on speed of growth of this phases. Thus, improved models has been received, which are supported by experimental verification; they are based on the phenomenological models of mass flow (nitrogen flow) and diffusion laws mentioned before [4]. Further research of L. Małdziński and his co-workers allows development models of the kinetics of nitrided layer growth. On the basis of this models, which enable precise forming of nitriding layer phase structure, simulator of the kinetics of nitrided layer growth has been created.

3. Simulator of the kinetics of nitrided layer growth

Simulator of the kinetics of nitrided layer growth (figure 6) is a computer programme which enables graphical and computational prediction of the growth of nitrided layer thickness and particular phases that will occur in it (ϵ , γ' , $\epsilon+\gamma'$, α), effective case depth and hardness distribution as a function of process parameters: time, temperature and nitriding potential of the atmosphere. In practice it means that by using a simulator of the kinetics of nitrided layer growth, it is possible to form the nitrided layer precisely, and as a result – to obtain nitrided layer with strictly defined, required properties.

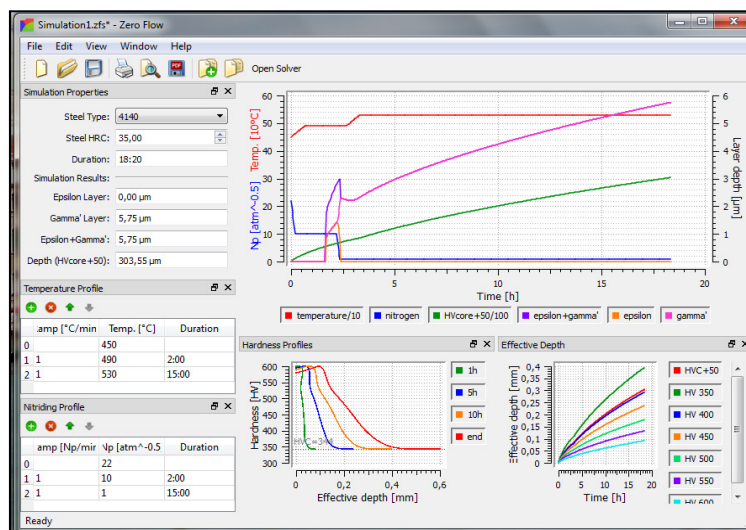


Figure 6. Simulator of the kinetics of nitrided layer growth.

Main simulator window consists of two major parts; on the left side we can recognize a number of cells, which are intended for nitriding parameters input (figure 7), and on the right side – graphs showing the results of conducted simulation (figure 8). Simulation is carried out automatically after entering data about the simulated process, such as simulation properties, temperature profile or nitriding profile. Simulation properties allows choosing the type of steel or determining core hardness (steel HRC). Currently simulator contains models for Armco iron and 12 types of steel, including: 1020 and 1050, low-alloy steels 4140, 5140, 4340, N135M, 18HGT, 8620, medium-alloy steels 32CVD13, H11, H13

and D2. Range of core hardness was based on hardness of steels used in experimental research and it is about 10HRC, however the minimum and maximum values are different for each type of steel. Moreover, in simulation properties we have also “Duration” cell, which shows overall time of nitriding process, computed on the basis of temperature and nitriding profiles defined by user.

Temperature and nitriding profile have the form of tables, where each row represents one section of the profile. Every section can be edited, moved or added/deleted. One section corresponds to one stage of process and it is described by the following quantities: the duration of the section, its target value and a ramp (speed at which the target value is reached). Ramp is connected with actual conditions of heating and nitriding potential reduction, resulting, among others, from the size of the furnace (or more precisely – from the size of its retort) or batch size. Each of these values are entered into another column.

The screenshot shows a software window titled "Simulation Properties" with several input fields and two tables. The "Simulation Results" section displays calculated values for layer thicknesses and depth. The "Temperature Profile" and "Nitriding Profile" sections contain tables with columns for ramp, temperature/potential, and duration.

Simulation Properties			
Steel Type:	4140		
Steel HRC:	35,00		
Duration:	18:20		
Simulation Results:			
Epsilon Layer:	0,00 μm		
Gamma' Layer:	5,75 μm		
Epsilon+Gamma':	5,75 μm		
Depth (+Hvcore+50):	303,55 μm		
Temperature Profile			
Ramp	Temp. [$^{\circ}\text{C}$]	Duration	
0	450		
1 1	490	2:00	
2 1	530	15:00	
Nitriding Profile			
Ramp	Np [atm $^{-0.5}$]	Duration	
0	22		
1 1	10	2:00	
2 1	1	15:00	

Figure 7. Simulator of the kinetics of nitrated layer growth – cells intended for nitriding parameters input.

Any change in parameters (time, temperature, nitriding potential of the atmosphere, as well as the properties of the steel) will restart the simulation and automatically perform calculations for the new input parameters. Results of the simulation are presented both in numerical and graphical form. Selected results in numerical form are presented under simulation properties and they contain the following values:

- epsilon layer thickness,
- gamma' layer thickness,
- compound zone thickness (epsilon + gamma' layer), also known as a white layer,
- layer effective thickness with core hardness of +50HV (HVC+50).

As well as values in numerical form show only the final result of simulated nitriding process, graphs allow following the whole course of process and determining on its basis specific values during the process. Main part of simulator window contains graph of ϵ , γ' , $\epsilon+\gamma'$ layers thickness and effective case depth HVC+50 growth as a function of nitriding time, which also includes curves presenting changes of temperature and nitriding potential during nitriding process. Below are another two graphs. First of them shows hardness profiles on the cross-section of nitrated layer after different times of nitriding. Second graph shows growth of the effective case depth for specific values of hardness (e.g. HVC+50, HVC400, HVC500, HVC600) as a function of nitriding time.

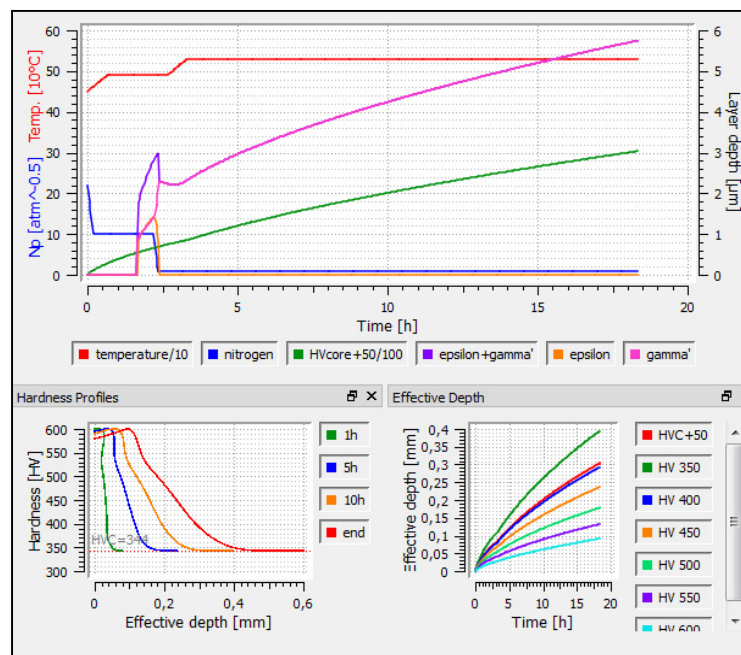


Figure 8. Simulator of the kinetics of nitrated layer growth – graphs showing the results of conducted simulation.

To sum up, simulator of the kinetics of nitrated layer growth enables precise simulations of nitriding process as a function of process parameters: time, temperature and nitriding potential of the atmosphere. Parameters can be adjusted to suit actual conditions of nitriding process, which delivers detailed information about the growth of nitrated layer. Thus, simulator can function both as a regulatory and control. By regulatory is understood the ability to determine the process parameters in order to obtain specific properties of the layer; by control – the ability to compare layers obtained after nitriding process with simulation results. However, the most important advantage of simulator is the ability to optimize process parameters, and as a result – forming required nitrated layer in the shortest possible time and with the lowest energy and gases consumption. It is possible by using a simulation solver (figure 9).

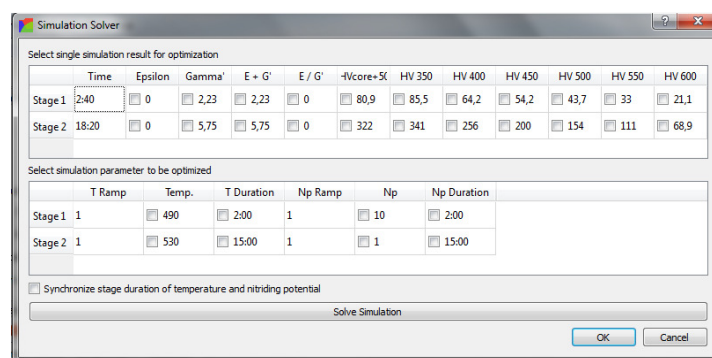


Figure 9. Simulator of the kinetics of nitrated layer growth – simulation solver.

Main solver window consist of two groups of cells. First of them, described as a “Select single simulation result for optimization”, contains results of simulation which is currently carried out. Among them we can distinguish: total duration of each stage of the process, ϵ , γ' , $\epsilon + \gamma'$ layers thickness, ϵ / γ' ratio, effective case depth HVC+50 and others. In second group, described as a “Select simulation parameter to be optimized”, we have process parameters – time, temperature, nitriding potential of the atmosphere – which are optimized in order to obtain required layer structure and properties. To optimize

the parameters, we have to select single cell from the first group and set its target value, and then select parameter from the second group, which will be changed. After pressing the button “Solve simulation”, new value of selected parameter will be shown instead of previous one. Without no doubt, solver is one of the most important functions of simulator of the kinetics of nitrided layer growth, because it is an essential factor determining economical and environmentally friendly character of nitriding using ZeroFlow method.

Gathered industrial experience not only confirmed the effectiveness of ZeroFlow method, but they also confirmed the effectiveness of using a simulator of the kinetics of nitrided layer growth as an application that supports precise forming of nitrided layer with respect to the required phase structure, zone thicknesses and hardness distribution.

4. Summary

The simulator of the kinetics of nitrided layer growth is an application which supports nitriding using ZeroFlow method. Despite of many advantages and proven effectiveness it still requires further development and research – like verification and modification of the existing models or development of models for new types of steel. However, it should be noted that limitations of the simulator does not preclude from using them, both in experimental and industrial scale. Gathered experience has shown that simulator of the kinetics of nitrided layer growth allows precise forming of nitrided layers with respect to the required phase structure, zone thicknesses and hardness distribution. Furthermore, through the use of mathematical models these layers are produced in the shortest possible time and with the lowest energy and gases consumption.

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