

# Nitriding modelling in nanoscale

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**Abstract.** Modelling on Plasma and gas nitriding of austenitic and low alloy steels have strong influence of interfacial - nanoscale phenomena. Gamma prime and epsilon nitrogen-iron phases evolution during the nitriding process wasn't found explicitly simulated on literature. On present work we simulated nitriding process on low alloy steels - with their precipitation phenomena and nitrides moving interfaces - using diffusional models plus cellular automata. Surface effects and heterogeneities and local transition phenomena considered on our models show that some experimental results considered "errors" on literature are predicted by our simulations. In present work parameters like diffusion coefficient and surface conditions and gradient of nitrogen concentrations between different phases was measured.

## 1. Introduction

Nitriding process is a thermochemical method for increasing wear and corrosion resistance, and surface hardness of metals. Gas and plasma nitriding are commercial process mostly used for low alloy and austenitic steels. Efforts in modeling have either been solving the diffusion equation analytically or by numerical methods in one dimension [1]. But it's not so often have found simulations in two or three dimensions [2]. Because of this, some important effects are missed, mainly surface imperfections effects [18] which have an important effect on global diffusion. Surface effects and nitride layers have a thickness of about a few microns or smaller. So multidimensional simulations on this scale have been done numerically and have necessary grids with nanometer increments. Results of simulations are very close to the experimental results found in most experimental works, but because of the nanometer scale, some unusual numerical effects became important – mainly due to the diffusion process.

Some old concepts are revisited, like “diffusion distance”, stability of numerical methods of partial differential equations solutions, and local equilibrium. So despite this work being a solution of an old technological problem with old mathematical tools, looking at that in a nanometer scale caused some useful conclusions to be made for nanomaterial's and material's diffusional process in this scale, and how it can have an important influence on bigger scales (micrometer or millimeter lengths).

The simulations of present work were made on a computer program, developed by the author in Object Pascal language in a open source compiler (Lazarus), with a visual and user-friendly interface. Results can be saved as raw data and as a visual representation in colored 2D images.

## 2. Theory

### 2.1. Surface phenomena and diffusion:

In general, the process of nitriding is inserted in the reactions between gases and metals [3-5]. This type of reaction has been attracting interest for a long time due to their applications not only to surface treatments, but also in studies related to oxidation and corrosion of metals. Under this generic

approach, is the work of Fromm and Horz [3], which divides this kind of reaction in the following steps:

- I) Transport of the gas molecules to the metal surface.
- II) dissociation of the molecules and chemisorption thereof.
- III) Transfer of gas atoms or ions through the surface.
- IV) Diffusion of atoms, or ions, the lattice of the metal.

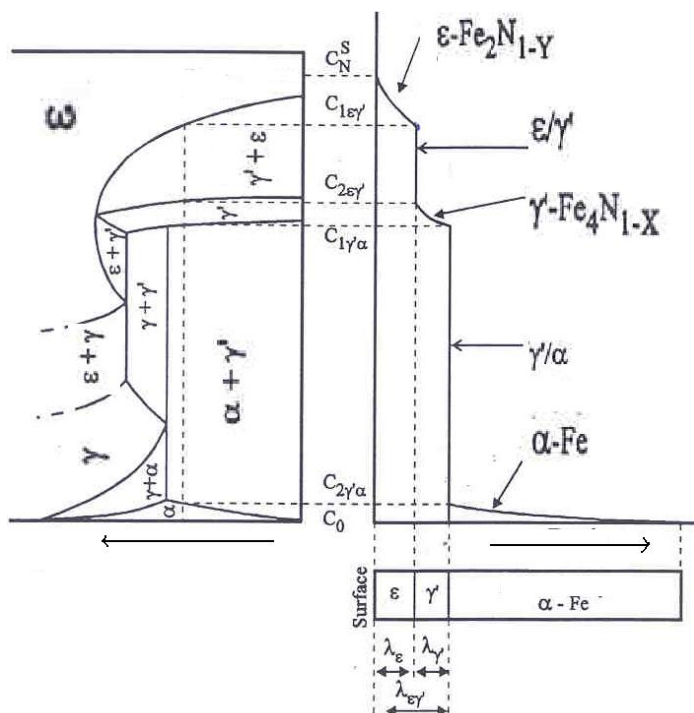
Stages I and II (transport and chemisorption of gas molecules) is strongly influenced by the type of process employed. The gas nitriding, which in most cases uses mixtures-of N<sub>2</sub>, H<sub>2</sub> and NH<sub>3</sub>, where partial pressure will be an important variable, which influences the formation (or not) of the nitrided layer. This is due to the mechanism of interaction between the gaseous atmosphere and the surface, and the number of collisions between molecules of gases. The reaction of nitrogen absorption can be written as:



The potential of nitrogen in gas nitriding is given by:

$$K_N = \frac{p_{NH_3}}{p_{H_2}^{3/2}} \quad (2.2)$$

The formation of the nitride layer depends on the nitrogen potential in the surface (Eq. 2.2) , it's condition, and the presence of stable non-metallic compounds like oxides. The nitrides of Fe-N system are the phases  $\gamma'$  (Fe<sub>4</sub>N) and  $\epsilon$  (Fe<sub>2</sub>N<sub>1-z</sub>). Finally, the nitrogen atom diffuses into the material - Step IV.



**Figure 1:** Relationship between Fe-N phase diagram and diffusion profile.[6]

The relationship between the phase diagram, diffusion, formation of nitrides, and their respective growth is shown in Figure 1[6]. In this figure the limits for concentrations of each phase and their

respective profiles are schematized. The advancement of each layer depends on the diffusion process between them. It's possible to determine the speed in which each of these layers will advance. Using the symbols of Figure 1 we have that the advancement of the layers and their interfaces are determined by the total flow of nitrogen through the interfaces and the mass balance[6]:

Interface  $\varepsilon / \gamma'$ :

$$(C_{1\varepsilon\gamma} - C_{2\varepsilon\gamma}) \frac{\partial \lambda_{\varepsilon}}{\partial t} = \left( -D^{\varepsilon} \nabla_{x=\lambda_{\varepsilon}} C_{\varepsilon} \right) - \left( -D^{\gamma'} \nabla_{x=\lambda_{\varepsilon}} C_{\gamma'} \right) \quad (2.3)$$

Interface  $\gamma' / \alpha$ :

$$(C_{1\gamma'\alpha} - C_{2\gamma'\alpha}) \frac{\partial \lambda_{\gamma'}}{\partial t} = \left( -D^{\gamma'} \nabla_{x=\lambda_{\gamma'}} C_{\gamma'} \right) - \left( -D^{\alpha} \nabla_{x=\lambda_{\gamma'}} C_{\alpha} \right) \quad (2.4)$$

By means of such equations it is possible to determine the speed of advancement of the layers and their respective positions by numerical procedures which are discussed below. The diffusion on each layer obey the Fick's 2 Law

$$\frac{\partial C}{\partial t} = D \nabla^2 C \quad (2.5)$$

## 2.2. Precipitation of alloy elements nitrides:

In the case of steels containing alloying elements, they can be influenced during the process in three ways: by changing (in some cases dramatically) the boundaries of the phase diagrams, by changing the diffusion coefficient of nitrogen present in phases - mainly in the ferrite, or by reacting with nitrogen to form their nitrides. The last point refers to the presence or absence of the precipitation of nitrides of alloying elements (forming the "strong" are nitrides of Al, Ti, V, Cr, Mo, Nb, W and Mn [1]). The formation of these precipitates influences in the diffusion of nitrogen along the matrix phase, and it's behavior is studied extensively by some authors [7-10], the resulting microstructures were analyzed [11], showing the formation of precipitated coherent or semi-coherent finely distributed through the matrix. It is precisely these precipitates which confer the positive effects of increased strength resulting from treatment. This precipitation occurs already in the initial stage. Even when it is expected a formation of the nitride layer, the formation of nitrides occurs, delaying thus the kinetics of the process. The formation of nitrides obeys the following reaction:



whose equilibrium constant is given by

$$K_e = \frac{1}{[a_N]^y [a_M]^x} \quad (2.7)$$

Assuming that Henry's Law is obeyed, and the solubility product using NMR, it follows that:

$$K_{M_x N_y} = 1/K_e = [N(x, t)]^y [M(x, t)]^x \quad (2.8)$$

where M and N concentrations of alloying and nitrogen in solution, respectively. Occurs when the precipitation in a given region and at any given time:

$$[N(x, t)]^y [M(x, t)]^x > K_{MN} \quad (2.9)$$

All these assumptions are valid if one takes into account the local equilibrium in each time interval analyzed, what will be conceptually and mathematically proved later on.

## 3. Numerical schemas and simulations.

### 3.1. Numerical procedures:

Discrete mathematics and the finite difference method for the manipulation of variables and solving differential equation, which are present in the theoretical model, were used. As the mathematical approach will be done in a space of three dimensions - x, y and t, using the notation:  $x = i \Delta x$  ;  $y = j \Delta y$  and  $t = k \Delta t$

So is the space (x, y) for discrete mesh M x N, where M and N are the total numbers of points in x and y, respectively. Concentrations are represented by:

CFN (i, j, k): concentration of nitrogen in f phase

CM (i, j, k): concentration of alloying element M

lf (i, j, k) position of the interface nitride f

Df: diffusion coefficient of nitrogen in phase f

The usual operators for the finite difference method are defined from the differential diffusion process used in [12-17] have applied to the solution of equation 2.5 for the two-dimensional case:

$$\frac{c_{i,j,k+1} - c_{i,j,k}}{\Delta t} = \frac{D}{(\Delta x)^2} (c_{i-1,j,k} - 2c_{i,j,k} + c_{i+1,j,k}) + \frac{D}{(\Delta y)^2} (c_{i,j-1,k} - 2c_{i,j,k} + c_{i,j+1,k}) \quad (3.1)$$

Where the stability condition for the solution is:

$$D \left( \frac{1}{\Delta x^2} + \frac{1}{\Delta y^2} \right) \Delta t \leq \frac{1}{2} \quad (3.2)$$

The boundary conditions can be expressed in the same way:

For the plasma nitriding to  $\alpha$  CN (0, j, k)  $< \gamma$  C2 'α:

(CN α represented by c)

$$c_{0,j,k+1} = \frac{2\Delta t}{\Delta x^2} \left[ \frac{A\Delta x}{\rho} + D c_{1,j,k} \right] + \left[ 1 - \frac{D\Delta t}{\Delta x^2} \right] c_{0,j,k} \quad (3.3)$$

where A and ρ are process parameters of plasma treatment (total surface area and density of current, respectively). For the gas nitriding:

$$c_{0,j,k+1} = c_{0,j,k} + \frac{2\Delta t}{(\Delta x)^2} D (c_{1,j,k} - c_{0,j} - k\Delta x (c_{0,j,k} - c_{eq})) \quad (3.4)$$

where  $C_{eq}$  is indicated by Lehrer diagram for the respective nitriding potential, and k is given by:

$$k = 9 \times 10^{-4} p_{H_2} \exp(-64220/RT) \quad (3.5)$$

where R is gas constant and T is the temperature in K). At the opposite end surface, the concentration gradient will be zero. Hence the boundary condition for  $j = N$ :

$$c_{i,N,k+1} = c_{i,N,k} + \frac{2D\Delta t}{\Delta x^2} (c_{i,N-1,k} - c_{i,N,k}) \quad (3.6)$$

Implicit Cranck-Nickolson method or alternating direction implicit method can also be used for bi-dimensional schema solution where the constant of tridiagonal matrix of the linear equations set is:

$$\alpha = \frac{\Delta t D}{2\Delta x^2} \quad \beta = \frac{\Delta t D}{2\Delta y^2} \quad (3.7)$$

Theoretically these methods are stable in most cases.

Finally, the diffusivity D of interstitial nitrogen in  $\alpha$ -iron (diffusion layer) is given by[6]:

$$D_N^\alpha = 6.6 \times 10^{-7} \exp\left(\frac{-77900}{RT}\right) m^2 s^{-1} \quad (3.8)$$

### 3.2 Simulations:

Initial conditions are set, such as:

- surface conditions (proportion of surface barriers and their fragmentation/relative size);

- alloying composition;
- atmosphere conditions of treatment (partial pressures of molecular gases)
- time and temperature of treatment.
- size of region to be simulated, number of points in the mesh (M and N) and  $\Delta x$ . The time increment  $\Delta t$  is calculated from stability condition from equation 3.2.

The steps of calculations can be summarized as:

- 1) surface calculations: length of nitride layers (eqs 2.3 and 2.4). Concentration on diffusion layer boundaries (eqs 3.3 or 3.4 and 3.5)
- 2) diffusion calculations (eq. 3.1)
- 3) precipitation calculation from 2.9 condition. Decrement on nitrogen and alloy elements solution concentrations  $CFN(i,j,k)$  and  $CM(i,j,k)$ .

## 4. Results and discussions

### 4.1 Choosing parameters for nanometer scale simulations.

A useful concept for diffusive phenomena is "diffusion distance" or "diffusion length":

$$\langle x \rangle = (Dt)^{1/2} \quad (4.1)$$

For a temperature of 823K,  $D=7,6 \times 10^{-12} \text{m}^2 \text{s}^{-1}$ . In one hour (3600 s)  $\langle x \rangle$  would be  $1,65 \times 10^{-4} \text{m}$ , or  $165 \mu\text{m}$  - three orders of magnitude greater than a nanometer scale. So, is necessary determine how many time is involved in one nanometer distance of diffusion:

$$t = \frac{\Delta x^2}{D} \quad (4.2)$$

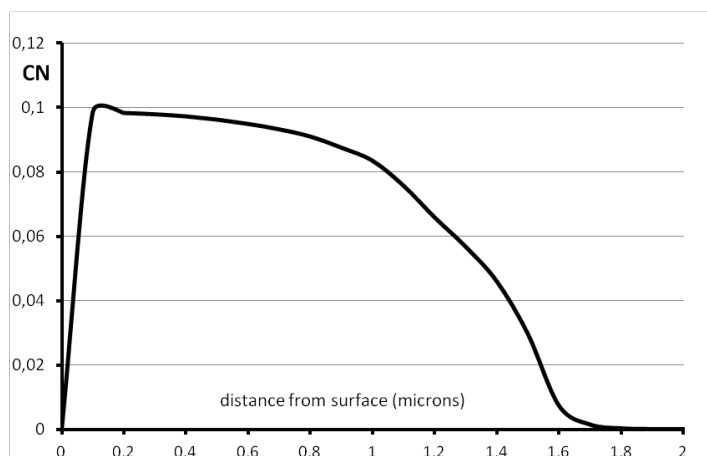
for  $\Delta x=1 \text{nm}$ ,  $t=1,3 \times 10^{-7} \text{s}$ ,  $10 \text{nm}$  would be  $t=1,3 \times 10^{-5} \text{s}$ ! So, times to be choose must be very short to not cover transient phenomena on this scales. Indeed, the mathematical condition for stability of explicit numerical solutions (eq. 3.6), when rearranged for  $\Delta x=\Delta y$  allows :

$\Delta t \leq \frac{\Delta x^2}{4D}$  what means that with this time interval transients are not mathematically covered, but local equilibrium is reached in 4 steps (eq 4.2). These results, which are almost obvious, are important for the assumptions used on the modelling as a whole, mainly about the precipitation of nitrides and reactions on the surface, when considerate on nanoscale. A general remark is that when talking about nanomaterials, there is a high surface and interface proportioned material but also a material with very high diffusional processes.

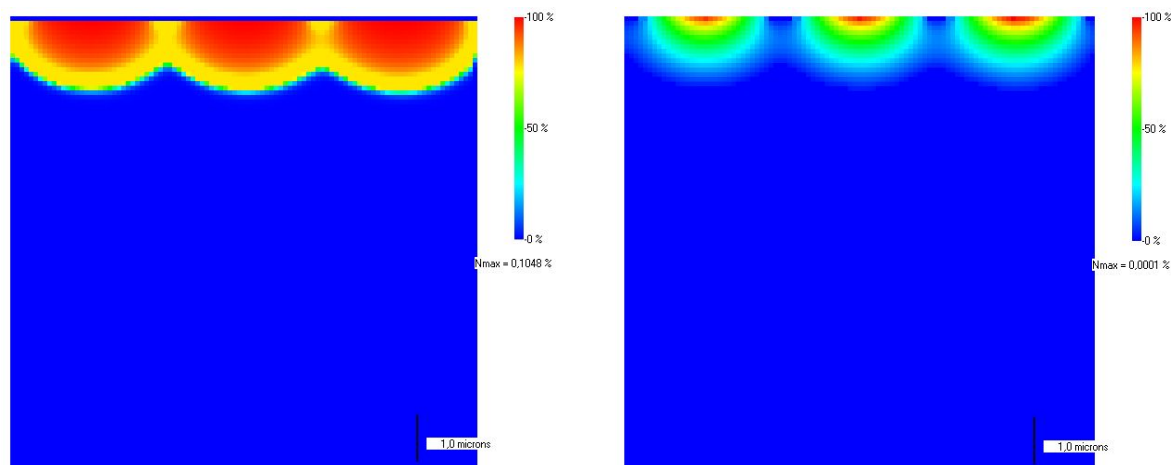
Even though literature says that alternating direction implicit methods in 2 dimensions are always stable, instable behaviour of solutions with this method was found for  $\alpha$  and  $\beta$  of 3.11 greater than 0.5. Therefore, explicit method - with clear stability criteria - was chosen.

### 4.2. Simulations results:

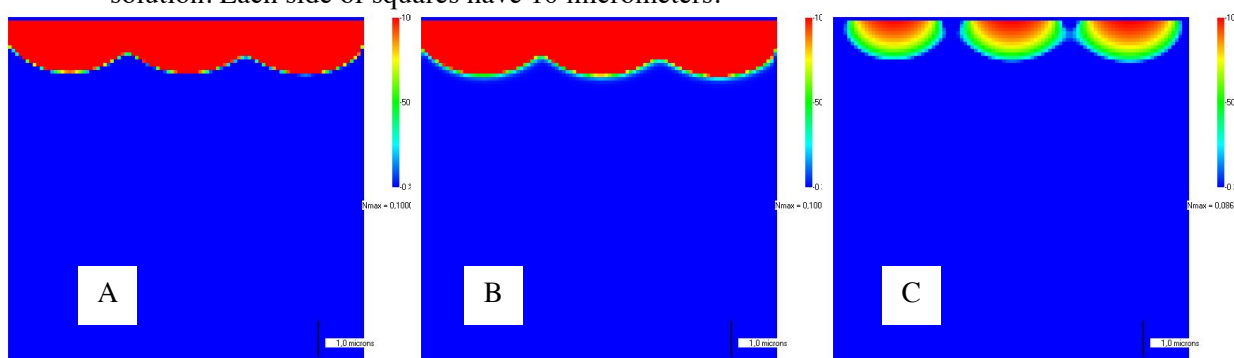
Figures 2, 3 and 4 show a quantitative and semi quantitative simulations for a 0.1%V,0.1%Ti,0.1%Al Fe alloy, nitrated in a 0.1atm $\text{N}_2$  and 0.1atm $\text{H}_2$  atmosphere, for 200s at 823K, with 20% of the surface with some barrier with a size of 700nm and  $\Delta x=\Delta y=10 \text{nm}$ . These bidimensional figures show a typical microstructure with a wavy frontiers of nitrated regions, which traditional simulations don't show, as a result of the presence of proportionally tiny barriers on the surface of the experimental samples. Usually the non-diffusional profile show in Figure 2 found on most of other author's experimental data is considered as an experimental error of the determination on either the local nitrogen concentrations or microhardness measurements. It's clear that it is an effect of the sample surface and their composition [18].



**Figure 2:** result of simulation - average total concentration of nitrogen (CN) in %mass with distance from surface in micrometers and respective.



**Figure 3:** bidimensional image of simulation show in Figure 2, with normalized scale of colors. In the left side, total nitrogen (precipitated and in solid solution), in right side, nitrogen in solid solution. Each side of squares have 10 micrometers.



**Figure 4:** Result of simulation where a) is amount of nitrogen precipitated in AlN, b) TiN and c) VN.

## 5. Conclusions

The present work makes the relationship between nanometer scale and velocity of transformations, especially diffusion controlled process, clear. Some attractive properties of nanomaterials have come from this. But fast reactions in metal surfaces in a nanometer scale make clear the importance to pay attention to that in their planning. It's clear for 2.3 and 2.4 equations, where time scales for reach the local equilibrium in hundred nanometers makes the usual theory approach for gas-solid –specifically nitrogen – iron (steel) reactions inappropriate. Another point is the importance to take account of nanoscale objects in simulations of micro and millimeter scale process. The results of present work showed the importance of computer simulations, a mathematical and phenomenological approach for understanding technological problems.

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