The Nitriding of Ferrous Powder Alloys - Mathematical Modelling and Simulation

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Abstract. Mathematical modelling has been developed to improve processes control and has helped theories about complex systems to be written. Nitriding is a multivariable system that needs the convergence of efforts to allow its improvement. Computer simulation is an important tool to give a simultaneous evaluation of all variables and respective effects in the result of the process. Surface conditions have an important effect in the interaction between gases and metals. Its influence can only be studied under two-dimensional and 3-D simulations. The presence of oxides and other barrier have a critical influence on the kinetic and on the result of the process. Secondary reactions such as precipitation and nitride layer formation also affect the process. Particularly, porosities can have an important effect by enhancing the gas permeation inside the sintered material. Depending on the variables that might be deleterious to the process, the simulations give some indications how to proceed and how to control these process variables. This work show, through simulation tools, how variables such as gas atmosphere, temperature, powder surface conditions, porosity and alloy composition will affect the final result of the nitriding process of sintered and non-sintered powders. A methodology was developed using numerical methods and systemic algorithms.

Introduction

Nitriding is an important process to improve steel surface properties. There are many nitriding process variations that would be difficult to find a general approach for mathematical models. In fact, nitriding is a typical metal / gas reaction where does exist surface reaction phenomena, phase transformations, mass transport through the bulk material and so one. The systematisation of these processes can allow to an effective and helpful simulation tool.

Theoretical concepts of the nitriding process were based upon joining of Fe-N phase diagram and diffusion process [1-5]. This approach is useful for a theoretical treatment of experimental data arising from the nitriding of pure iron. Besides mathematical modelling from this approach are feasible, for the nitriding of steels, the simulations "a priori" either does not fit the experimental data or make difficult to foresee results.

Typical diffusion curves obtained from solutions of Fick's equations [6] does not give good fittings to experimental curves, as schematically showed in fig 1. This lack between experimental works and theory shows that more complex phenomena are present on nitriding. Some conceptual efforts were made by Jack and co-workers [7] in earlier works. Basically, this author pay attention to microstructural effects such as, precipitation of nitrides, solid solution and diffusion questions, on results of nitrogen diffusion patterns. But there was nothing in the mathematical approaches to be used as simulation tools.
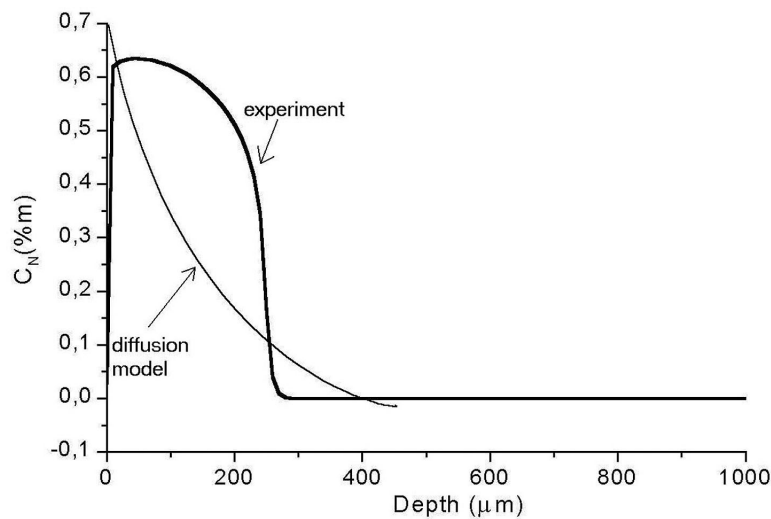
Fig. 1. Typical profiles for nitrogen diffusion model and experimental data [6].

The motivation to undertake this work was: all published models and simulations (as referenced) are one-dimensional; effects of surface condition, such as oxide layer, cleanliness and so one are neglected; mostly of models are restricted to diffusion kinetics, without taking into account phase transformation effects. These concepts were systematised through a mathematical model and a simulation computer program was developed. The model and results applied to sintered steels will be showed below.

Nitriding model - surface phenomena

The initial stage of sintered steels nitriding begin with surface phenomena [8-11] which can be divided in the follow steps:

1- Gas molecules or ionic species transport from atmosphere to the surface of the steel.

The step 1 depends on furnace atmosphere condition; process type and positioning of parts which will be nitrided inside furnace.

2- Physical adsorption.

3- Chemical adsorption.

The steps 2 and 3 depend on physical and chemical interactions between surface and gas molecules and ions. This interaction is affected by surface conditions such as, presence of oxide layers or other compounds. Finally, step 4.

4- Transport from surface to inner material.

Thermodynamics and surface crystallography will affect step 4, which have influence on nitride formation and on nitrogen flux towards the material. For modelling purposes, a flux equation is necessary as contour condition. This equation can be determined for all factors mentioned above. There are different flux equations for each nitriding process - gas, ionic, plasma and so one. The presence of a surface barrier determine a locally zero flux - that's the convenience of a two or three-dimensional simulation. An example of a flux equation for gas nitriding is eq. 1, where k is a coefficient, C_{eq} is the nitrogen equilibrium concentration under the experimental

condition and Cs is the actual surface concentration.

$$J = k(Ceq - Cs) \tag{1}$$

Nitriding model - bulk phenomena

Three basic phenomena are possible in bulk material: nitride layer growing, diffusion and formation of precipitates. The latter is seldom presented in modelling literature. But these processes form a system, which determine the result of every nitriding experiment. So, joining all of them is necessary to have a good simulation. These basic processes are included in the developed simulation program through systemic algorithm that can be summarised as follow: diffusion is computed through finite difference equations in a two-dimensional mesh. Each node is verified (in each time step) if a nitride formation or precipitation is thermodynamically necessary. The amount of nitrogen reacted is computed from overall concentration for each kind of precipitates. Then, the next time step is executed.

Eq. 2 describe the second Fick's law for pure diffusion:

$$\frac{\partial C}{\partial t} = D\nabla^2 C \tag{2}$$

where C is nitrogen concentration and D is the nitrogen diffusion coefficient in the diffusing media.

The presence of grain boundaries, microstructural discontinuities (as pores, low nitrogen soluble second phase) is computed using alternative equations. Eq. 3 and 4 represents the diffusion near and inside of a grain boundary:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right) - V\frac{\partial c}{\partial x}, \quad |x| > \frac{\delta}{2} \tag{3}$$

for the neighbours nodes of the interface, where V is the velocity of grain boundary migration and δ is the grain boundary thickness and:

$$\frac{\partial c_{cg}}{\partial t} = D_{cg}\left(\frac{\partial^2 c_{cg}}{\partial y^2}\right) + \frac{D}{\delta}\left(\frac{\partial c}{\partial x}\right)_{x=+\delta/2} - \frac{D}{\delta}\left(\frac{\partial c}{\partial x}\right)_{x=-\delta/2}, |x| < \frac{\delta}{2} \tag{4}$$

for inside diffusion of grain boundary, where D_{cg} is the diffusion coefficient for this region.

These eq. 3 and 4, can be used to simulate sintered materials where δ and D_{cg} are greater than conventional steels. Simulations based on this mathematical approach, using finite difference method in a two-dimensional grid were made using a personal computer.

For this approach, a discrete tree-dimensional space x, y, t were used in the standard form: x = i Δx ; y = j Δy and t = k Δt. The space (x, y) is used in a grid M x N where M and N are total numbers of grid points in x and y, respectively. Concentrations are represented by: $C^f_N(i, j, k)$ nitrogen concentration in a f phase; $C_M(i, j, k)$ M - alloy element concentration; D_f diffusion coefficient of nitrogen in a f phase.

The finite difference method follows these discrete functions, eq. 5 to 8:

$$\left(\frac{\partial C}{\partial t}\right)_{i,j,k} = \frac{c_{i,j,k+1} - c_{i,j,k}}{\Delta t} \tag{5}$$

$$\left(\frac{\partial C}{\partial x}\right)_{i,j,k} = \frac{c_{i+1,j,k} - c_{i-1,j,k}}{2\Delta x} \tag{6}$$

$$\left(\frac{\partial C}{\partial y}\right)_{i,j,k} = \frac{c_{i,j+1,k} - c_{i,j-1,k}}{2\Delta y} \tag{7}$$

$$\left(\frac{\partial^2 C}{\partial x^2}\right)_{i,j,k} = \frac{c_{i+1,j,k} - 2c_{i,j,k} + c_{i-1,j,k}}{\Delta x^2} \tag{8}$$

Solving eq. (2) using eq. (5) to (8) allows, for a two-dimensional approach, eq. 9:

$$\frac{c_{i,j,k+1} - c_{i,j,k}}{\Delta t} = \frac{D}{(\Delta x)^2}\left(c_{i-1,j,k} - 2c_{i,j,k} + c_{i+1,j,k}\right) + \frac{D}{(\Delta y)^2}\left(c_{i,j-1,k} - 2c_{i,j,k} + c_{i,j+1,k}\right) \tag{9}$$

The condition for a stable numeric solution is, eq. 10:

$$D\left(\frac{1}{\Delta x^2} + \frac{1}{\Delta y^2}\right)\Delta t \le \frac{1}{2} \tag{10}$$

Boundary conditions are transformed in the same way, solving eq. (1) using eq. (5) to (8), for gas nitriding in the surface of grains, eq. 11:

$$c_{0,j,k+1} = c_{0,j,k} + \frac{2\Delta t}{(\Delta x)^2} D\left(c_{1,j,k} - c_{0,j} - k\Delta x\left(c_{0,j,k} - c_{eq}\right)\right) \tag{11}$$

where C_{eq} is obtained by Lehrer Diagram for a nitriding potential and k is calculated by eq. 12:

$$k = 9\text{x}10^{-4}\ p_{H2}\ \exp(-64220/RT) \tag{12}$$

Using finite operators on eq. (3) it is possible calculate the effect of grain boundary and/or porosity diffusion effects.

Results

Some general simulations were made to analyse the effects of each input parameter, type of surface and alloying elements. The fig. 2 shows the effect of a discontinuous oxide layer (or other type of barrier) on the net process. A sintered steel part is a good example of a material containing such kind of heterogeneity. It's clear how this can affect the result. As the barriers on the surface increase, less nitrogen flux and nitrogen amount on the surface and inside the material is available.

Fig. 3 shows the effect of an oxide layer partitioning into smaller or lager parts. This kind of effect is neglected in most of the works published on the subject and the graph shows how much this is important. The nitrogen profiles are calculated by averaging each dimensional layer.
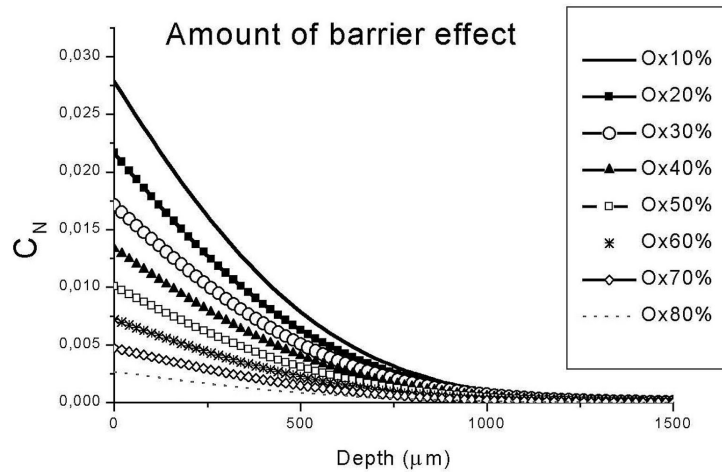
Fig. 2. Effect of the amount of barriers on pure iron nitriding at 450 ˚C for 2 h; each line corresponds to a percentage of the surface covered.
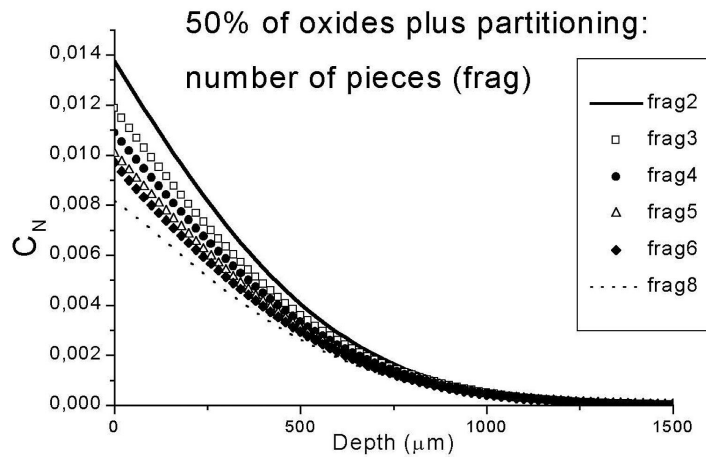

Fig. 3. Effect of barriers partitioning on the nitriding thickness layer.

Composition of steel has a large influence when including nitride-forming elements. Fig. 4 shows this effect for some alloying elements. For the summation of barrier effect plus alloying elements, fig. 5 shows how would general experimental curves look like.
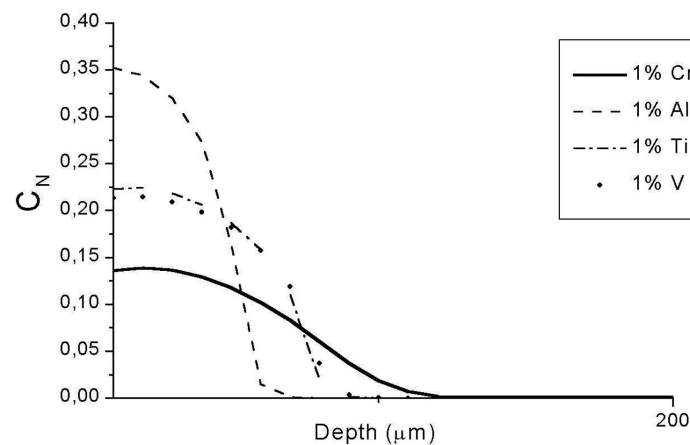

Fig. 4. Effect of alloying elements on the shape of simulated curves for steel nitriding at 450 ˚C for 2 h.
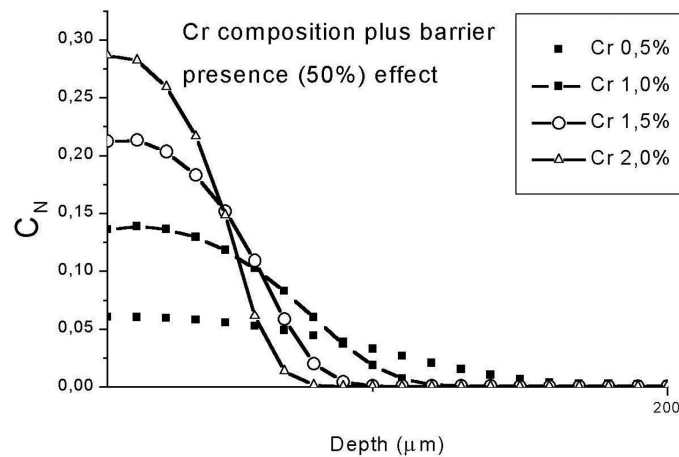
Fig. 5. Effect of alloying elements plus barriers on simulated curves shape for nitriding steel at 450 ˚C for 2h.

Discussion

As described in the last section, the showed results present strong effects on surface conditions of nitrided samples. In sintered steel these phenomena are important because in powder metallurgy processes the surface of the particles are exposed to reactive atmospheres, which can form compound layers or barriers. Despite how the nitrogen move inside of sintered part - surface / bulk, surface / pore / bulk or surface / pore / grain boundary / bulk - which depends on the used nitriding process, the presence of barriers and their partitioning may strongly affect the final result.

For good nitriding results, the chemical condition of the surface of the steels powder is important and also the control of the sintering atmospheres. A monolayer [8-11] of a barrier compound is enough to allow some of effects showed in the last section to occur. A dramatic decrease of nitrogen amount as the barrier area increase is significant and show how sensitive is the nitriding process to an uncontrolled variable such as oxides percentile on the surface. This is a good explanation about results spreading, found in literature. But using indirect methods, such as electric resistivity of the sample to determine percentile of barriers, and working with this number on simulations it is possible a decrease in that uncertainty.

The steel composition is another important variable noticed in the simulations and determines the amount and depth of nitrogen penetration. This effect plus barriers allows protuberances in the simulated curves, which correspond to "experimental error" found in the references.

The accuracy of the simulations depends on quality of experimental parameters like diffusion coefficients, amount and fragmentation of barriers, partial pressures of nitriding gas and so one. The mathematical method is based on a phenomenological approach, so more sensitive disturbances or hidden variables could be analysed if more accurate experimental data are find. So, the importance of the presented method is to help a more precise experimental analysis and, on other side, to make a preview of actual factors in the nitring practical results.

Conclusions

Modelling of nitriding processes are important to prevent some unexpected or unexplained results. All encountered literature is restricted to one dimension simulation and only diffusion /

phase diagram models are published. This work showed how important is a detailed modelling concerning at least two-dimensional simulation and regarding the surface condition as an input for the model.

The presence of alloying elements has also a strong influence on the depth of nitrided layer and diffusion layer.

Efforts undertaken in order to produce more accurate simulation must take into account the grain boundary diffusion, as a tool to preview the nitriding through a sintered sample. In a barrier free sample, this effect is clearer. But in the presence of barriers, high-path diffusion is shaded below the surface phenomena. So, it will appear only as difference on the apparent diffusion coefficient.

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