

# Simultaneous Analysis of the Chemical and Thermal Non-Equilibrium Regimes in Nitriding. Modelling in LabVIEW

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## ABSTRACT

Generally, nitriding regimes are approached at equilibrium. It is thought that the thermal regime is stationary in the diffusion furnaces, and a constant dissociation degree insures, implicitly, the same type of diffusion regime. However, practice shows that we have in fact different zones of temperature in the furnace chamber because of the distribution of the thermal field along different isothermal curves and, consequently, the dissociation conditions are not constant. In addition, there is a certain period of non-stationary regime during the heating of the charge up to the nitriding temperature, characterised by a chemical and thermal non-equilibrium. The paper presents a dynamic model for assessment of chemical non-equilibrium in the diffusion atmosphere at the metal-atmosphere interface as a result of temperature variations with time. In order to become useful in practice, modelling was made using the LabVIEW software, the best software for data acquisition and process control, as the shortest way of linking theory to practice.

**Key words:** thermochemical treatment, electronic noise, diffusion, Gibbs energy, nitriding, thermodynamics

## I. INTRODUCTION

Nitriding is a thermochemical surface treatment during which nitrogen is supplied to a steel surface at a temperature between 480°C and 590°C. The process can be developed in a gaseous mixture of nitrogen and ammonia, in a salt bath, through CVD or in an ionic nitriding process and it results in a nitrides layer with the thickness and composition depending on the type of the process.

Many studies have been dedicated to the surface reactions that occur during gaseous nitriding and corrections have been developed based on the process parameters (nitrogen activity, nitriding potential, etc.). All these studies considered the equilibrium conditions when the process is in a static regime and the

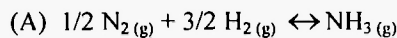
temperature is (almost) constant. But, in the early stages, the nitriding process is a typical non-equilibrium process for two reasons:

- the crude steel is fed into the furnace at room temperature and is heated during a certain time so that the surface possesses a certain and increasing reactivity from the beginning /5/
- during heating, the nitriding atmosphere has a variable composition because the ammonia decomposition equilibrium is strongly dependent on temperature

Taking these factors into consideration, the paper presents a model that describes the transition dynamic regime during the heating period and the products that may influence further evolution of the nitriding.

## 2. THERMODYNAMICS OF THE NITRIDING DYNAMIC PROCESS

1. The ammonia synthesis / decomposition equilibrium is:



The equilibrium constant,  $K$ , can be calculated based on the partial pressure of the gaseous substances involved in the reaction:

$$K = \frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}} \quad (1)$$

The standard Gibbs energy can be related to  $K$ :

$$\Delta G_{NH_3}^0 = -RT \ln K = -RT \ln \frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}} \quad (2)$$

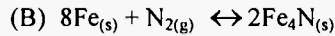
where:  $R = 8\,317 \text{ J/kmole}$  is the gas constant and  $T$  is the absolute temperature, [K]

Based on Equation (2), the nitrogen partial pressure (concentration) can be calculated as a function of temperature and of the nitriding potential  $K_N$ :

$$P_{N_2} = \exp \left[ 2 \left( \frac{\Delta G_{NH_3}^0}{RT} + \ln K_N \right) \right] \quad (3)$$

$$\text{where } K_N = \frac{P_{NH_3}}{P_{H_2}^{3/2}} \quad (4)$$

2. The Fe<sub>4</sub>N formation is represented by:



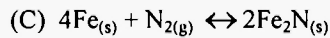
The equilibrium constant, calculated on the basis of the activities of the solid phases ( $a_{Fe_4N}$ ,  $a_{Fe}$ ) and on the partial pressure of nitrogen ( $p_{N_2}$ ), is:

$$K = \frac{a_{Fe_4N}^2}{p_{N_2} a_{Fe}^8} \quad (5)$$

The Gibbs energy can be calculated on the basis of the standard Gibbs energy (previously calculated [1]) and the nitrogen partial pressure:

$$\Delta G_{Fe_4N} = 2\Delta G_{Fe_4N}^0 - 2\Delta G_{NH_3}^0 - 2RT \ln K_N \quad (6)$$

3. The Fe<sub>2</sub>N formation is represented by:



The equilibrium constant of this reaction can be calculated as a function of the partial pressure of nitrogen and the activities of iron and iron nitride:

$$K = \frac{a_{Fe_2N}^2}{p_{N_2} a_{Fe}^4} \quad (7)$$

The Gibbs energy, based on the standard Gibbs energy and on the partial pressure of nitrogen, is:

$$\Delta G_{Fe_2N} = 2\Delta G_{Fe_2N}^0 - 2\Delta G_{NH_3}^0 - 2RT \ln K_N \quad (8)$$

Table 1 presents the values of the thermodynamic parameters of the reactions described so far:

**Table1**  
Thermodynamic parameters of the reactions

Reaction	$\Delta H_{298K}^0$ [kJ/mole]/1,2,3/	$\Delta G^0$ [J/mole] /4/	T [K]
(A)	-46.19	-52090 + 113.9 T	300.....900
(B)	-10.2	-17250 + 58.6 T	
(C)	-5.58	-6230 + 44.e6 T	

#### 4. Other reactions.

The steel samples can have the surface covered with spots of rust (oxides) or grease (hydrocarbons).

a) Considering the reaction conditions, the metal oxides do not decompose and, because of the lack of oxygen, they do not form products in a superior oxidation state:

the reaction  $\text{Fe}_x\text{O}_y \rightarrow x \text{Fe} + y/2 \text{O}_2$  is impossible, because  $\Delta G > 0$ ;

the reactions  $3\text{FeO} + 3/2\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4$  and  $2\text{Fe}_3\text{O}_4 + 1/2 \text{O}_2 \rightarrow 3\text{Fe}_2\text{O}_3$  are impossible at very low oxygen partial pressures.

b) The reaction of the iron oxides with hydrogen is possible only at temperatures higher than 700K (for  $\text{Fe}_2\text{O}_3$  and even higher for the other two oxides):

$\text{FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O}$  ( $\Delta G > 0$  in the considered temperature domain)

$\text{Fe}_3\text{O}_4 + 4 \text{H}_2 \rightarrow 3\text{Fe} + 4\text{H}_2\text{O}$  ( $\Delta G > 0$  in the considered temperature domain)

$\text{Fe}_2\text{O}_3 + 3 \text{H}_2 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O}$  ( $\Delta G < 0$  if  $T > 700\text{K}$ )

c) In an atmosphere that does contain only nitrogen and hydrogen the hydrocarbons are inert.

#### 5. The Model

Based on the previous observations, the model developed to describe the non-equilibrium conditions represents the Gibbs energy as function of temperature and the nitriding potential.

Using Equations (4) and (6) and the parameters presented in Table 1, the form of this equation for  $\text{Fe}_4\text{N}$  is as follows:

$$\Delta G_{\text{Fe}_4\text{N}} = 69680 - 110.6T - 16.62T \ln K_N \quad [\text{J/mole}] \quad (9)$$

A similar equation was developed for  $\text{Fe}_2\text{N}$ , based on Equations (4) and (8) and on the data from Table 1:

$$\Delta G_{\text{Fe}_2\text{N}} = 91720 - 138.6T - 16.62T \ln K_N \quad [\text{J/mole}] \quad (10)$$

#### 6. Software developed in LabVIEW

We developed the software using the graphic programming language LabVIEW ("G" programming) from National Instruments - USA. This software offers the flexibility to develop modular applications and has a powerful graphic interface. At any time we can develop our software and models and we can even add any new models. LabVIEW software was developed initially for Data Acquisition and has powerful tools for acquisition and data processing /6/. The development is at this moment many times faster than for other comparable softwares.

Our software SURFACE.VI permits the display of a curve family and its interpolation in a continuous surface. In this “Diagram” the user can select the desired ranges and steps (Fig.1). In the soft interface we also introduced two 2D graphics, built for selected constant temperatures.

### 3. RESULTS AND DISCUSSION

Fig. 1 presents the graphical results based on Equations (9) and (10).

The calculation covers a temperature domain from 300K to 900K. It considers the evolution of the nitriding potential decreasing to zero from a high value (30), when ammonia starts to decompose and the partial pressure of hydrogen is very low, conditions that might be found in the beginning of the process.

The graphs in the first column present the results for the process of obtaining Fe<sub>4</sub>N. The negative values of the Gibbs energy - and the formation of the nitride – appear only at temperatures higher than 400K, and at this temperature it is possible to run the reaction even at average values of  $K_N$  (above 5). This confirms the possibility of Fe<sub>4</sub>N formation before the process reaches the recommended temperature. The necessary  $K_N$  value for achieving a reaction decreases when the temperature increases, so that at the process temperature  $K_N$  has the regular sub-unit values.

The same type of variation characterises the reaction producing Fe<sub>2</sub>N (graphs presented in column 2, Fig. 1). Still, the process requires higher temperatures and  $K_N$  values and the nitride formation is possible at 500K only if  $K_N$  is above 15. Since this condition is rather difficult to achieve, requiring a very large amount of nitrogen in the nitriding mixture, one may say that, in practice, the reaction starts at higher temperatures. Using Eq. (4) this value is estimated at  $p_{N_2} \cong 16bar$  which is completely unrealistic.

These results are in good agreement with the practical situation which registers at first the formation of Fe<sub>4</sub>N.

The reaction rate increases with temperature so the nitride formation in the first step is a possible but slow process. This may also have the consequence that the products are strongly bonded to the surface.

### 4. CONCLUSIONS

- The steel that is the subject of the nitriding process hosts surface reactions with nitrogen, but secondary chemical decompositions (of oxides) are not possible.
- The formation of the iron nitride starts on the surface of the steel before the process conditions are attained, at temperatures higher than 500 K and at high values of the nitriding potential.
- The paper presents a model, based on the thermodynamic approach, that describes the non-equilibrium regime leading to the formation of Fe<sub>4</sub>N and Fe<sub>2</sub>N, as a function of temperature and the nitriding potential.

- The results are presented in graphic form using LabVIEW and represent a useful tool for understanding the surface modifications *before* the moment usually considered as the starting point of the process.

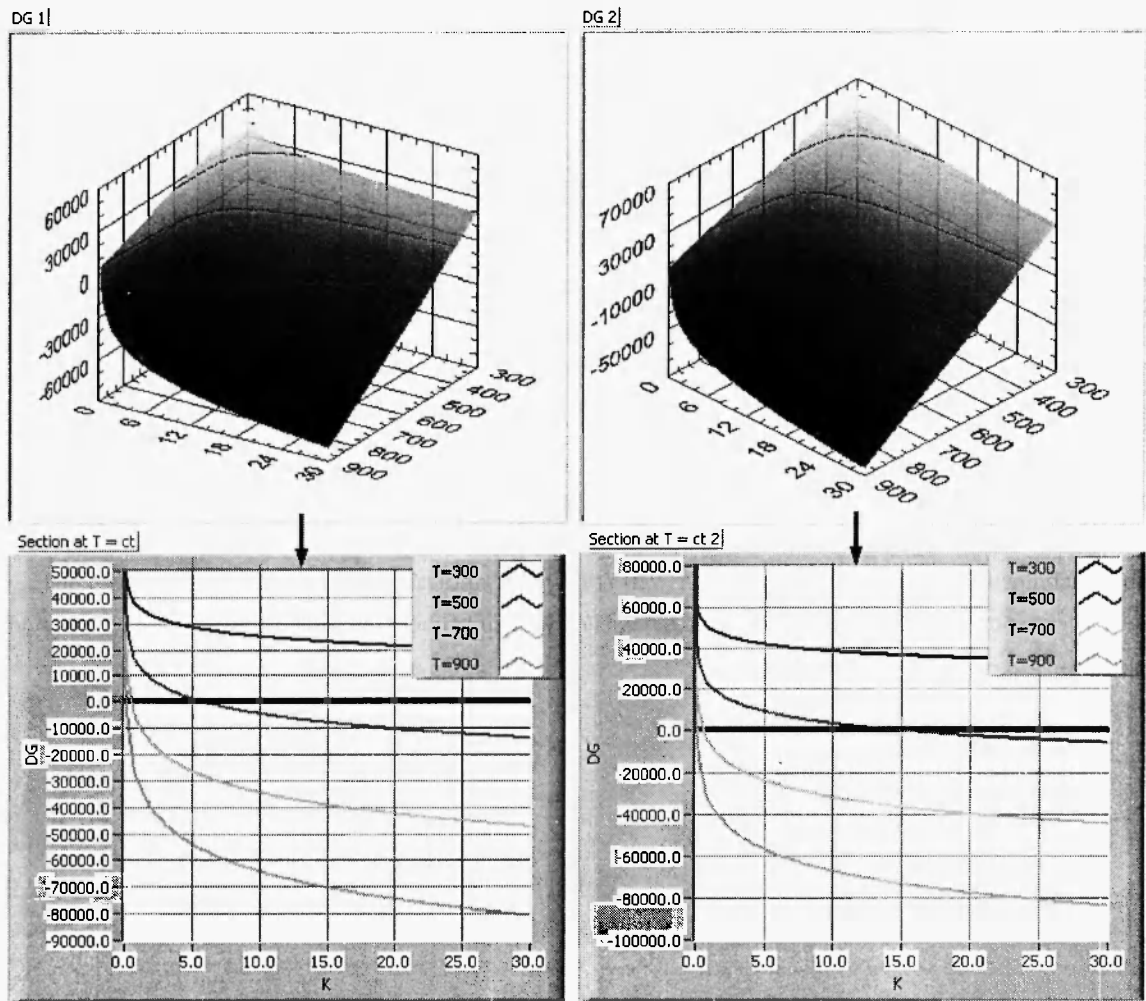


Fig.1: The SURFACE.VI software panel.

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