

# Gas-Solid Nitrocarburizing of Steels: Kinetic Modeling and Experimental Validation

L. Torchane

**Abstract**—The study is devoted to define the optimal conditions for the nitriding of pure iron at atmospheric pressure by using  $\text{NH}_3$ - $\text{Ar-C}_3\text{H}_8$  gas mixtures. After studying the mechanisms of phase formation and mass transfer at the gas-solid interface, a mathematical model is developed in order to predict the nitrogen transfer rate in the solid, the  $\epsilon$ -carbonitride layer growth rate and the nitrogen and carbon concentration profiles. In order to validate the model and to show its possibilities, it is compared with thermogravimetric experiments, analyses and metallurgical observations (X-ray diffraction, optical microscopy and electron microprobe analysis). Results obtained allow us to demonstrate the sound correlation between the experimental results and the theoretical predictions.

**Keywords**—Gaseous Nitrocarburizing, Kinetic Model, Diffusion, Layer Growth Kinetic.

## I. INTRODUCTION

THE thermochemical surface treatments of iron and steels called nitriding / nitrocarburizing are of great importance for the practice. These treatments have long been applied in industry to improve the surface quality (fatigue, wear and corrosion resistance). There is a strong desire to process control and automation, then among other things, we should have available accurate models for describing the kinetics and microstructural evolution of the iron nitride / iron carbonitride compound layer. Modeling layer growth due to reaction diffusion is also very interesting from a scientific point of view: Does the local equilibrium concept apply? What about the interaction of layer growth and stress development and relaxation?

For rate control by the inward diffusion of nitrogen and carbon, a mathematical description of the diffusive flux of the interstitially dissolved elements (nitrogen and carbon) through the case produced is sought. This flux can be calculated using Fick's laws if the composition ranges of the phases, as well as the corresponding diffusion coefficients are known. Although some papers have been published, a straightforward prediction of the growth rate and the constitution of the compound layer for nitrocarburizing is still lacking [1]-[3]. The diffusion coefficients of nitrogen in the  $\epsilon$  and  $\gamma'$  phases have been evaluated previously by several authors [4]-[9] from the growth rate of the compound layer formed during the iron nitriding. Moreover, the diffusion coefficients of carbon in the  $\epsilon$  and  $\gamma'$  phases are not available. This can be ascribed to imprecise knowledge of the homogeneity range of these phases [4].

L. Torchane is with the Mechanical Engineering Department, University of Tebessa, Algeria (e-mail: torchanel@yahoo.fr).

The first attempt of drawing up a comprehensive phase diagram of the ternary Fe-N-C system was made several years ago by Naumann and Langenscheid [10] and has frequently been referred to in the nitrocarburizing literature. However, many observations are in disagreement with this diagram. Taking into account the available nitrocarburizing experimental information, Slycke, Sproge and Agren [11] were the first to propose a modified Fe-N-C phase diagram at 570°C. The major difference between the new diagram and the one published by Naumann and Langenscheid is that it allows the frequently observed direct contact between the ferrite  $\alpha$  and the  $\epsilon$  phase such equilibrium has been indicated by frequent observations during nitrocarburizing but was not shown by Naumann and Langenscheid. Kunze [12] also presented a roughly calculated Fe-N phase diagram under different carbon activities and came to a similar conclusion as Slyke and al. [11]; an equilibrium between the  $\alpha$  and  $\epsilon$  exists around 570-590°C.

The thermodynamic properties of the Fe-N and Fe-N-C systems have been reassessed by Du [13]. Under local equilibrium assumption, mathematical model has been developed by Du and Agren [14] for nitrocarburizing of iron. The analytical solution is obtained for the  $\epsilon/\gamma'$  bilayer growth assuming constant diffusion coefficients and taking for the intrinsic diffusivity of carbon in the  $\epsilon$  and  $\gamma'$  the same ratio of carbon to nitrogen diffusivities as in  $\gamma$ -iron. It was found by these authors that the off diagonal diffusivities of the  $\epsilon$  and  $\gamma'$  phases must be taken into account in the analytical solution in order to obtain reasonable results.

Up to now, the structures produced by nitrocarburizing, where nitrogen and carbon are introduced into the work piece are, even in the case of an initially pure iron specimen, much more complicated than for the case of nitriding [15]. It is then reasonable at this stage, to assume that the growth of the compound layer during nitrocarburizing is controlled by nitrogen and carbon diffusion through the layer itself and that thermodynamic equilibrium prevails locally at moving phase interfaces. Under these conditions, it is possible to establish a diffusion model in the solid state, from the resolution of diffusion equations in a semi-infinite medium and to predict the nitrogen and carbon transfer rate in the solid, as well as the carbonitride layer growth rate and the nitrogen and carbon concentration profiles.

By limiting our study to pure iron and XC38 steel, we are going to show on the one hand, that the analytical solution may be obtained for growth of  $\epsilon$  into a substrate  $\alpha$  using a simple boundary conditions, and on the other hand, that is

possible to control during nitrocarburizing, by means of thermogravimetry and dynamic gas flow rate regulation, the thickness, composition and structure of the  $\varepsilon$  compound layer.

## II. MATHEMATICAL MODEL OF IRON CARBONITRIDE LAYER GROWTH

The formation of the compound layer and the diffusion zone during nitrocarburizing is provided by the new ternary Fe-N-C phase diagram proposed by Slycke and al. [11]. The  $\varepsilon$  carbonitride layer can exist at a lower nitrogen content (~5.5 Wt. pct). Compared to pure iron, the presence of carbon during nitrocarburizing stabilizes the  $\varepsilon$  phase so that it will form at much lower nitrogen activities than in absence of carbon. The kinetic of diffusion-controlled growth of the monolayer  $\varepsilon$  can be described by the shift of the  $\varepsilon/\alpha$  interface between  $\varepsilon$  and  $\alpha$  phases because of a difference in the fluxes of nitrogen and carbon arriving at the interface and the fluxes of these species being removed from the interface [5], [16]-[19]. Fig. 1 represents schematically the qualitative relation between the ternary Fe-N-C phase diagram and the nitrogen and carbon concentration profiles for growth of a monolayer  $\varepsilon$  into a substrate  $\alpha$ -Fe.

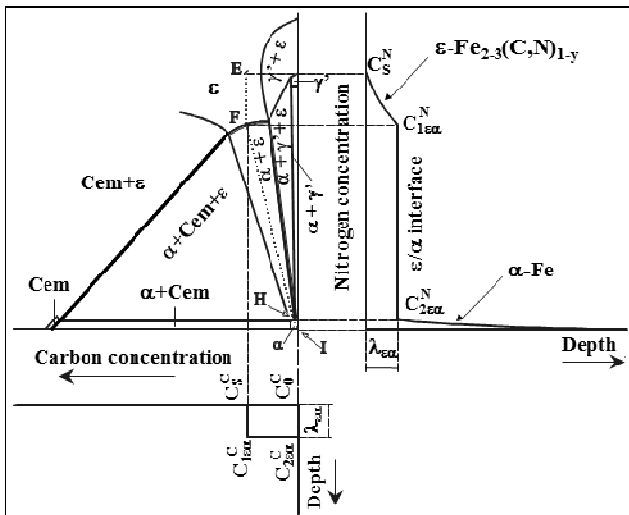


Fig. 1 Relation between the Fe-N-C equilibrium diagram and concentration/depth for growth of a monolayer  $\varepsilon$  into substrate  $\alpha$  [16]

The mass per unit area balance at the  $\varepsilon/\alpha$  interface can be written as:

$$(C_{1\varepsilon}^k - C_{2\varepsilon}^k) \frac{d\lambda_{\varepsilon\alpha}}{dt} = [J_{\varepsilon}^k(t) - J_{\alpha}^k(t)]_{x=\lambda_{\varepsilon\alpha}} \quad (1)$$

where  $k$  denotes (N or C),  $\lambda_{\varepsilon\alpha}$  is the abscissa of the  $\varepsilon/\alpha$  interface,  $d\lambda_{\varepsilon\alpha}/dt$  is the rate of interface advance,  $C_{1\varepsilon}^k$  and  $C_{2\varepsilon}^k$  are respectively the equilibrium concentrations of component  $k$  on the  $\varepsilon$  and  $\alpha$  side of the interface at temperature  $T$  and  $J_{\varepsilon}^k(t)$  and  $J_{\alpha}^k(t)$  are the corresponding

diffusion fluxes at the  $\varepsilon/\alpha$  interface.

The diffusive flux  $J_{\phi}^k(t)$  of component  $k$  in phase  $\phi$  ( $\varepsilon$  or  $\alpha$ ) at depth  $x$  beneath the surface is related to the corresponding concentration gradient  $\partial C_{\phi}^k(x, t)/\partial x$  by Fick's first law:

$$J_{\phi}^k(t) = D_{\phi}^k \frac{\partial C_{\phi}^k(x, t)}{\partial x} \quad (2)$$

where  $\phi$  denotes  $\varepsilon$  or  $\alpha$  phase,  $C_{\phi}^k(x, t)$  and  $D_{\phi}^k$  are respectively the concentration and the intrinsic diffusion coefficient of component  $k$  in phase  $\phi$ .

The evolution of concentration-depth profiles, for nitrogen and carbon in the carbonitride resulting from nitrocarburizing, is obtained by solving the Fick's second law [20] subject to the relevant boundary conditions indicated in Fig. 1:

$$\frac{\partial C_{\phi}^k(x, t)}{\partial t} = D_{\phi}^k \frac{\partial^2 C_{\phi}^k(x, t)}{\partial x^2} \quad (3)$$

Concentration profiles in each phase  $\varepsilon$  and  $\alpha$  can be expressed by means of the error function [20]:

$$\text{for } 0 \leq x < \lambda_{\varepsilon\alpha}; \quad C_{\varepsilon}^k(x, t) = A + B \cdot \text{erf}\left(\frac{x}{2\sqrt{D_{\varepsilon}^k \cdot t}}\right) \quad (4)$$

$$\text{and for } \lambda_{\varepsilon\alpha} \leq x < \infty; \quad C_{\alpha}^k(x, t) = A' + B' \cdot \text{erfc}\left(\frac{x}{2\sqrt{D_{\alpha}^k \cdot t}}\right) \quad (5)$$

Constants  $A$ ,  $B$ ,  $A'$  and  $B'$  of (4) and (5) can be determined by introducing the following hypothesis:

- The model is applied for the nitrocarburizing of pure iron, the interface between  $\varepsilon$  and  $\alpha$  is planar and parallel to the surface and the substrate  $\alpha$ -Fe is semi-infinite. The local equilibrium at phase interface  $\varepsilon/\alpha$  is maintained during nitrocarburizing. This assumption implies that the growth rate is given by the rate of diffusion through the various layers and the compositions at the  $\varepsilon/\alpha$  interface are constant and independent of the treatment time:

$$C_{\varepsilon}^k(x = \lambda_{\varepsilon\alpha}) = C_{1\varepsilon}^k \quad \text{and} \quad C_{\alpha}^k(x = \lambda_{\varepsilon\alpha}) = C_{2\varepsilon}^k$$

- The surfaces concentrations of nitrogen  $C_S^N$  and carbon  $C_S^C$  are constant and controlled from the beginning of the treatment (this hypothesis requires that the  $\varepsilon$  phase is formed instantaneously at  $t = 0$ ):

$$\text{for } t \geq 0; \quad C_{\varepsilon}^k(x = 0) = C_S^k$$

- The carbon concentration is constant in the  $\varepsilon$  phase and there is no carbon transfer in the  $\alpha$  phase

$$\text{for } 0 \leq x < \lambda_{\varepsilon\alpha}; \quad C_{\varepsilon}^C(x, t) = C_S^C = C_{1\varepsilon}^C = 1 \text{ (Wt. pct)}$$

$$\text{and for } \lambda_{\varepsilon\alpha} \leq x < \infty; \quad C_{\alpha}^C(x, t) = C_{2\varepsilon}^C = 0$$

- The interaction between nitrogen and carbon is negligible and concentration profiles of nitrogen and carbon in the  $\varepsilon$  carbonitride layer can be calculated as:

$$\text{for } 0 \leq x < \lambda_{\varepsilon\alpha} \quad C_{\varepsilon}^{N+C}(x, t) = C_{\varepsilon}^N(x, t) + C_{\varepsilon}^C(x, t)$$

$$C_{\varepsilon}^{N+C}(x = 0) = C_S^{N+C} = C_S^N + C_S^C$$

$$\text{and} \quad C_{\varepsilon}^{N+C}(x = \lambda_{\varepsilon\alpha}) = C_{1\varepsilon\alpha}^{N+C} = C_{1\varepsilon\alpha}^N + C_{1\varepsilon\alpha}^C$$

- The growth of the  $\varepsilon$  layer obeys a parabolic law

$$\text{for } 0 \leq x < \lambda_{\varepsilon\alpha}; \quad \lambda_{\varepsilon\alpha} = b_{\varepsilon\alpha} \cdot \sqrt{t} \quad (6)$$

where  $b_{\varepsilon\alpha}$  is the constant of the parabolic rate dependent on the surface nitrogen and carbon concentration imposed during the treatment, the phase composition at  $\varepsilon/\alpha$  interface at a given temperature and the effective diffusion coefficients in the  $\varepsilon$  and  $\alpha$  phases.

- The effective diffusion coefficient of nitrogen in the  $\varepsilon$  phase is the same than the one evaluated previously in the binary Fe-N system [5]. It is assumed constant and independent of concentration for a composition of the  $\varepsilon$  carbonitride between 7 and 9.5 (Wt. pct). This coefficient is taken as the average intrinsic diffusion coefficient of nitrogen throughout the thickness of the  $\varepsilon$  layer and is only dependent on temperature [4], [5]

$$\langle D_{\varepsilon}^N \rangle = \frac{1}{(C_S^N - C_{1\varepsilon\alpha}^N)} \int_a^b D_{\varepsilon}^N \cdot dC_{\varepsilon}^N(x, t) \quad (7)$$

with:  $a = C_{1\varepsilon\alpha}^N$  and  $b = C_S^N$

The intrinsic diffusion coefficient of nitrogen is related to the self-diffusion coefficient  $D_{\phi}^{N*}$  by [21], [22]:

$$D_{\varepsilon}^N = D_{\phi}^{N*} \cdot \frac{d \ln a_{\phi}^N}{d \ln C_{\phi}^N} \quad (8)$$

where  $\frac{d \ln a_{\phi}^N}{d \ln C_{\phi}^N}$  is the thermodynamic factor,  $a_{\phi}^N$  being the activity of nitrogen corresponding to concentration  $C_{\phi}^N$ .

With the assumed boundary conditions, the nitrogen and carbon concentration profiles in the  $\varepsilon$  and  $\alpha$  phases can be expressed as follows:

$$\text{for } 0 \leq x < \lambda_{\varepsilon\alpha}; \quad C_{\varepsilon}^{N+C}(x, t) = C_S^{N+C} - (C_S^{N+C} - C_{1\varepsilon\alpha}^{N+C}) \cdot \frac{\left[ \text{erf}\left(\frac{x}{2\sqrt{\langle D_{\varepsilon}^N \rangle \cdot t}}\right) \right]}{\left[ \text{erf}\left(\frac{b_{\varepsilon\alpha}}{2\sqrt{\langle D_{\varepsilon}^N \rangle}}\right) \right]} \quad (9)$$

$$\text{and for } \lambda_{\varepsilon\alpha} \leq x < \infty; \quad C_{\alpha}^{N+C}(x, t) = C_{\alpha}^N(x, t) = C_{2\varepsilon\alpha}^N \cdot \frac{\left[ 1 - \text{erf}\left(\frac{x}{2\sqrt{\langle D_{\alpha}^N \rangle \cdot t}}\right) \right]}{\left[ 1 - \text{erf}\left(\frac{b_{\varepsilon\alpha}}{2\sqrt{\langle D_{\alpha}^N \rangle}}\right) \right]} \quad (10)$$

After differentiating (9) and (10) and substituting into (1), we obtain the following flux balance equation at the  $\varepsilon/\alpha$  interface:

$$(C_S^N - C_{1\varepsilon\alpha}^N) \cdot \frac{\left[ \sqrt{\langle D_{\varepsilon}^N \rangle} \cdot \exp\left(\frac{-b_{\varepsilon\alpha}^2}{4 \langle D_{\varepsilon}^N \rangle}\right) \right]}{\left[ \text{erf}\left(\frac{b_{\varepsilon\alpha}}{2\sqrt{\langle D_{\varepsilon}^N \rangle}}\right) \right]} = \quad (11)$$

$$\frac{\sqrt{\pi}}{2} \left[ (C_{1\varepsilon\alpha}^N + C_{1\varepsilon\alpha}^C) - C_{2\varepsilon\alpha}^N \right] b_{\varepsilon\alpha} + C_{2\varepsilon\alpha}^N \frac{\left[ \sqrt{\langle D_{\alpha}^N \rangle} \cdot \exp\left(\frac{-b_{\varepsilon\alpha}^2}{4 \langle D_{\alpha}^N \rangle}\right) \right]}{\left[ 1 - \text{erf}\left(\frac{b_{\varepsilon\alpha}}{2\sqrt{\langle D_{\alpha}^N \rangle}}\right) \right]}$$

If the surface nitrogen and carbon concentration is assumed constant during nitrocarburizing, then the constant  $b_{\varepsilon\alpha}$  of (11) can be determined. From (6), (9) and (10) we deduce the nitrogen concentration profiles in the  $\varepsilon$  and  $\alpha$  phases and the  $\varepsilon$  layer thickness.

According to Fick's first law, the total nitrogen mass that crosses the carbonitrided surface  $S_L$  of the sample at the instant  $t$  of treatment is:

$$M_{\varepsilon,\alpha}^{N+C}(t) = S_L \int_0^t \left[ - \langle D_{\varepsilon}^N \rangle \cdot \frac{\partial C_{\varepsilon}^{N+C}(x, t)}{\partial x} \right]_{x=0} \cdot dt$$

$$M_{\varepsilon,\alpha}^{N+C}(t) = \left[ \frac{2 S_L (C_S^{N+C} - C_{1\varepsilon\alpha}^{N+C})}{\text{erf}\left(\frac{b_{\varepsilon\alpha}}{2\sqrt{\langle D_{\varepsilon}^N \rangle}}\right)} \right] \cdot \sqrt{\frac{\langle D_{\varepsilon}^N \rangle \cdot t}{\pi}} \quad (12)$$

In order to limit the growth rate of the  $\varepsilon$  carbonitride layer during nitrocarburizing treatment, we choose to vary over time the surface concentration of carbon and nitrogen. The theoretical curve of the sample mass variation can be calculated from (12) and the following relation:

$$b_{\varepsilon\alpha} = \sqrt{\ln(0.9510 + 0.0074 \cdot C_S^{N+C}(t))} \quad (13)$$

By using the same value of the effective diffusion coefficient of nitrogen in the  $\varepsilon$  phase evaluated previously in the binary Fe-N system, the constant of parabolic rate (13) is determined by simulation and validated experimentally after many experiments of nitrocarburizing performed at 843K on pure iron specimens. The results obtained show that the effective diffusion coefficient of nitrogen in the  $\varepsilon$  carbonitride is constant and remains valid in the (carbon + nitrogen) concentration range 7 to 9.5 Wt. pct. [16].

### III. EXPERIMENTAL APPROACH

The mathematical model is developed in order to calculate and to predict the weight gain of sample and thickness of  $\varepsilon$  layer as a function of time and surface nitrogen and carbon

concentration. Nitrocarburizing treatments are performed in a thermobalance furnace on pure iron specimens (13x13x49mm) at a temperature 843K and atmospheric pressure. We conducted the treatment by adjusting the gas flow rate ( $\text{NH}_3\text{-Ar-C}_3\text{H}_8$ ) at the inlet of the reactor in order to follow the theoretical curve of mass variation calculated by (12) for a constant or variable surface nitrogen and carbon concentration. After treatment, the samples are quenched in water in order to avoid the transformation of  $\epsilon$  phase during cooling. The experimental results, determined by X-ray diffraction, light microscopy and electron microprobe analysis are compared with theoretical prediction given in Table I.

TABLE I

THE CALCULATED THICKNESS OF  $\epsilon$  LAYER AS A FUNCTION OF TREATMENT TIME AND SURFACE NITROGEN AND CARBON CONCENTRATION

Times (hours)	0.5	0.5 - 1.5	4	10
Surface Concentration (N+C)	9	9 - 7	7	7
Variable (Wt. pct)				
$\epsilon$ Layer Thickness ( $\mu\text{m}$ )	5.6	5.6 - 8.5	11	14.7
Surface (N+C) Concentration		9		
Constant (Wt. pct)				
$\epsilon$ Layer Thickness ( $\mu\text{m}$ )	5.6	5.6 - 9.7	15.8	25

#### IV. EXPERIMENTAL RESULTS

The model is validated after many experiments of nitrocarburizing performed at 843K for several times between 0.5 to 10 hours and for nitrogen and carbon concentrations between 7 to 9 Wt. pct. Fig. 2 shows the experimental and theoretical weight gain of the sample per unit area ( $\Delta M/S$ ) as a function of nitrocarburizing time ( $t$ ) for growth of the  $\epsilon$  carbonitride layer into a substrate  $\alpha$  with: a constant surface nitrogen and carbon concentration 9 Wt.pct. (curve 1), and a variable surface nitrogen and carbon concentration 9 to 7 Wt. pct. (curve 2).

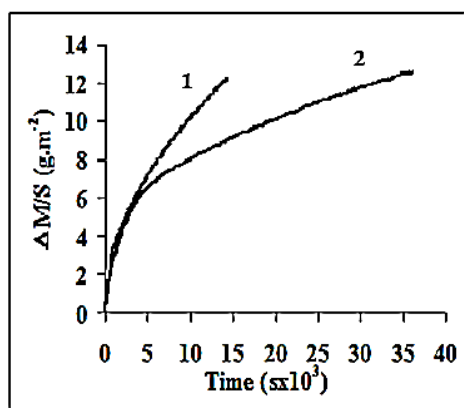


Fig. 2 Experimental and theoretical curves of weight gain of the sample per unit area ( $\Delta M/S$ )

During the treatments, we have chosen the operating conditions so that the transport of species in the gaseous phase and the chemical reactions on the surface of the specimens do not impose a limitation on the reaction of nitrocarburizing. For this case, a surface nitrogen and carbon concentration can be fixed and controlled from the beginning of the treatment and

the  $\epsilon$  phase is formed instantaneously.

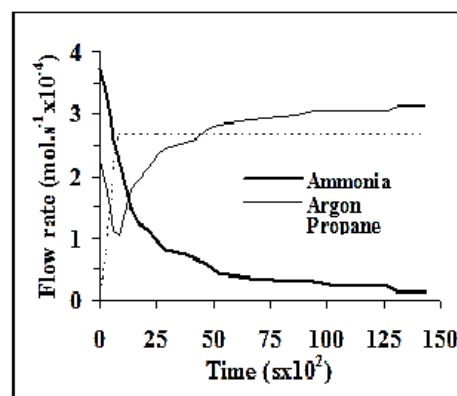


Fig. 3 Gas flow rate variation as a function of nitrocarburizing time for growth  $\epsilon$  into  $\alpha$  (surface of specimen  $S_L = 28.60 \times 10^{-4} \text{ m}^2$  - total gas flow rate  $\text{NH}_3\text{-Ar-C}_3\text{H}_8$  constant 5.95 mol/s)

We can see (Fig. 3) that the ammonia gas flow rate introduced in the reactor decreases regularly: very high at the beginning of the treatment to allow the immediate formation of the  $\epsilon$  carbonitride and it rapidly decreases to become very low at the end of the treatment. The carbon concentration is fixed by addition of the propane in the gas mixtures (for  $t > 5\text{mn}$ , the propane partial pressure is equal to 0.25atm). The characteristics results of micrographic measures of  $\epsilon$  layer thickness and quantitative analysis of the surface nitrogen and carbon concentration (Table II) allow us to confirm on the one hand, that the different tests were performed at constant and variable surface nitrogen and carbon concentration and on the other hand, the good correspondence between experimental and theoretical thickness of  $\epsilon$  carbonitride layer.

TABLE II

COMPARISON BETWEEN EXPERIMENTAL (EX) AND THEORETICAL (IN BOLD) VALUES OF SURFACE NITROGEN AND CARBON CONCENTRATION AND LAYER THICKNESS AS A FUNCTION OF NITROCARBURIZING TIME AND SURFACE NITROGEN AND CARBON CONCENTRATION: (PURE IRON SPECIMENS CARBONITRIDED AT  $T = 843\text{K}$ )

Time	Surface Nitrogen and Carbon Concentration (Constant)			$\epsilon$ Layer Thickness ( $\mu\text{m}$ )	
t (h)	$C_S^C$ (EX)	$C_S^N$ (EX)	$C_S^{N+C}$ (Th)	$\lambda_{\epsilon\alpha}$ (EX)	$\lambda_{\epsilon\alpha}$ (Th)
0.5	1.00	8.15	9	5.40	<b>5.60</b>
1.5	1.15	8.10	9	9.70	<b>9.70</b>
4.0	1.30	8.05	9	15.70	<b>15.80</b>
Time	Surface Nitrogen and Carbon Concentration (Variable)			$\epsilon$ Layer Thickness ( $\mu\text{m}$ )	
t (h)	$C_S^C$ (EX)	$C_S^N$ (EX)	$C_S^{N+C}$ (Th)	$\lambda_{\epsilon\alpha}$ (EX)	$\lambda_{\epsilon\alpha}$ (Th)
0.5	1.00	8.15	9	5.40	<b>5.60</b>
1.5	1.05	6.15	7	8.60	<b>8.50</b>
4	1.15	6.10	7	10.90	<b>11.00</b>
10	1.20	6.00	7	14.80	<b>14.70</b>

The evolution of the  $\epsilon$  carbonitride layer thickness as a function of the square root of diffusion time shows (Fig. 4) that the  $\epsilon$  layer growth is parabolic. Therefore, from the present experiments it seems that the thermodynamic

equilibrium prevails locally at the  $\varepsilon/\alpha$  interface and the growth kinetic of the  $\varepsilon$  compound layer is controlled during nitrocarburizing by nitrogen and carbon diffusion.

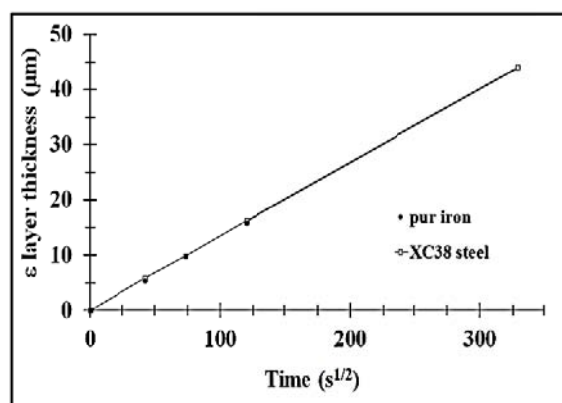


Fig. 4 Evolution of  $\varepsilon$  layer thickness as a function of square root of diffusion time for growth  $\varepsilon$  into substrate  $\alpha$  with surface nitrogen and carbon concentration 9 (Wt. pct)

After 30 hours of nitrocarburizing and water cooling, the  $\varepsilon$  compound layer formed on XC38 substrate does not show the presence of  $\gamma'$  and cementite. Moreover, the nitrogen and carbon depth profiles obtained by quantitative electron microprobe analysis show (Fig. 5) that:

- In the zone immediately below the compound layer, a carbon is depleted demonstrating that a minor part of carbon in the compound layer originates from the substrate.
- The carbon content appears to be highest near the bottom of the  $\varepsilon$  compound layer. This occurrence is not singular because during nitrocarburizing, the carbon atoms in the near surface region of the  $\varepsilon$  compound layer are pushed away by nitrogen atoms being taken up, leading to an increase of carbon atoms content at larger depths [23].

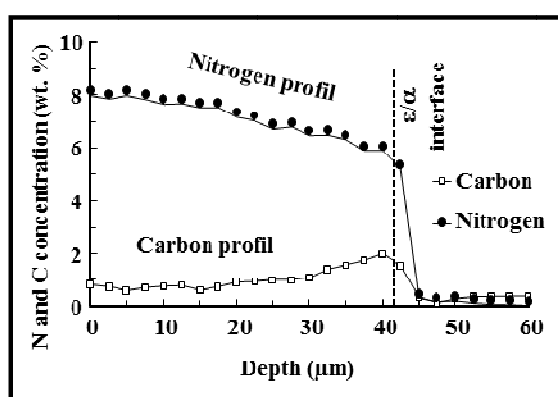


Fig. 5 Nitrogen and carbon contents as a function of depth below the surface determined by electron microprobe analysis in a cross section of  $\varepsilon$  carbonitride layer obtained after nitrocarburizing XC38 at 843K for 30 hours and water cooling

## V.CONCLUSION

**Kinetic model:** A model is developed for the growth of  $\varepsilon$  compound layer into  $\alpha$ -Fe during gaseous nitrocarburizing using  $\text{NH}_3\text{-C}_3\text{H}_8\text{-Ar}$  gas mixtures. The analytical solution has been obtained assuming a simple boundary conditions : (1) the local equilibrium between  $\varepsilon$  and  $\alpha$  phases is maintained at the moving interface (2) the carbon concentration is constant in the  $\varepsilon$  phase and there is no carbon transfer in the  $\alpha$  phase, (3) the interaction between carbon and nitrogen is negligible, (4) the growth of  $\varepsilon$  layer obeys a parabolic law, (5) the effective diffusion coefficient of nitrogen in the  $\varepsilon$  phase is the same than the one evaluated previously in the Fe-N system. It is assumed constant and independent of concentration.

**Validation of the model:** Experimental results (performed at 843K on pure iron and XC38 specimens for several times between 0.5 to 30 hours and for constant and variable surface nitrogen and carbon concentration between 7 to 9.5 (Wt. pct.) are compared with the predictions of the model and the agreement is satisfactory found under the various approximation applied. From the results obtained by EPMA, we have shown that during nitrocarburizing, the carbon content appears to be highest near the bottom of the  $\varepsilon$  compound layer and a minor part of carbon in the compound layer originates from the substrate. Therefore, much more fundamental research is needed in order to find a functional relationship between the rate and parameters of diffusion.

## REFERENCES

- [1] M.A.J. Somers, P.F. Colijn, W.G. Sloof and E.J. Mittemeijer, Z. Metallkd., Vol.81, (1990), p.33-43.
- [2] J. Slycke, and L. Sproge, Surface Engineering, Vol.5 (2), (1989), p.125-140.
- [3] M.A.J. Somers and E.J. Mittemeijer, Surface Engineering, vol.3 (2), (1987), p.123-137.
- [4] M.A.J. Somers, and E.J. Mittemeijer, Metall. Mater. Trans. A, Vol.29A, (1995), p.57-74.
- [5] L. Torchane, Ph. Bilger, J. Dulcy and M. Gantois, Metall. Mater. Trans. A, Vol.27A, (1996), p.1823-1835.
- [6] H. Du and J. Agren, Trita-Mac 0570 (1994), Roy. Inst. of Tech., Stockholm, Sweden.
- [7] B. Prenosil, Konove Mater., Vol.3, (1965), p.69-87.
- [8] Yu.M. Lakhtin and Ya.D. Kogan, Mashinostroenie, Moscow, (1976).
- [9] A. Marciniak, Surface Engineering, Vol.1 (4), (1985), p.283-88.
- [10] F.K. Naumann, G. Langenscheid, Arch. Eisenhüttenwes, Vol.36 (9), (1965), p. 677-682.
- [11] J. Slycke, L. Sproge and J. Agren, Scandinavian Journal of Metallurgy, 17, (1988), p.122-126.
- [12] J. Kunze; Thermodynamics, Physical Research, Vol.16, Akademie Verlag, Berlin, (1990).
- [13] H. Du, J. Phase equilibria, Vol.14 (6), (1993), p.682-693.
- [14] H. Du and J. Agren, Metall. Mater. Trans. A, Vol.27A, (1996), p.1073-1080.
- [15] E.J. Mittemeijer and M.A.J. Somers, Surface Engineering, Vol.13, No.6, (1997), p.483-497.
- [16] L. Torchane: Ph.D. Thesis, I.N.P.L., Nancy, France, (1994).
- [17] L. Torchane, Ph. Bilger, J. Dulcy, and M. Gantois: Mater. Sci. Forum, Vol.163-165, (1994), p.707-712.
- [18] L. Torchane, Ph. Bilger, J. Dulcy and M. Gantois, entropie, No.202/203, (1997), p.45-49.
- [19] M. Gantois, Mater. Sci. Forum, Vol.163-165, (1994), p.37-48.
- [20] Y. Adda, and J. Phillibert, Tome I, Sarclay, France, (1966).
- [21] L.S. Darken, Trans. AIME, Vol.175, (1948), p.184-94.
- [22] K. Schwerdtfeger, P. Grieseson, and E.T. Turkdogan: Trans. AIME, Vol.245, (1969), p.2461-2466.

- [23] H.C.F. Rozendaal, P.F. Colijn and E.J. Mittemeijer, Surface Engineering, Vol.30, No.1, (1985), also published in Heat Treatment '84', The Metal Society, London, (1984), 31.1-31.16.