

Mechanism and Kinetic of Layers Growth: Application to Nitriding of 32CrMoV13 Steel

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Abstract—In this work, our goal is to optimize the nitriding treatment at a low-temperature of the steel 32CrMoV13 using gas mixtures of ammonia, nitrogen and hydrogen to improve the mechanical properties of the surface (good wear resistance, friction and corrosion), and of the diffusion layer of the nitrogen (good resistance to fatigue and good tenacity with heart). By limiting our work to the pure iron and to the alloys iron-chromium and iron-chromium-carbon, we have studied the various parameters which manage the nitriding: flow rate and composition of the gaseous phase, the interaction chromium-nitrogen and chromium-carbon by the help of experiments of nitriding realized in the laboratory by thermogravimetry. The acquired knowledge has been applied by the mastery of the growth of the γ' combination layer on the α diffusion layer in the case of the industrial steel 32CrMoV13.

Keywords—Diffusion of nitrogen, Gaseous nitriding, Layer growth kinetic.

I. INTRODUCTION

THE study of the mechanisms of formation and the growth kinetics of nitrided layers from gas mixtures containing ammonia and hydrogen at atmospheric pressure uses the concepts developed in materials science in which the objective is the control of mass transfer in gas-solid interface. The control of the heterogeneous nitriding reaction by the ammonia molecule requires the knowledge of the transfer mechanism of nitrogen between the gas phase and the solid phase. The flow of nitrogen transferred to surface involves mechanisms that depend on the thermodynamic and hydrodynamic behavior of the gaseous medium used. This aims of this text is to explain these concepts from nitriding performed in the laboratory by thermogravimetry on several types of alloys: iron-nitrogen, iron-chromium-nitrogen and iron-chromium-carbon-nitrogen. These alloys are used to describe the basic transfer mechanisms of nitrogen to the gas-solid interface. The 32CrMoV13 steel is an example of industrial application used for the manufacturing of gears.

II. BASIC PRINCIPLE OF A HETEROGENEOUS REACTION GAS-SOLID

The control of heterogeneous nitriding reaction by the ammonia molecule requires the knowledge of the transfer mechanisms of the nitrogen between the gaseous phase and the solid phase. This transfer mechanism can be summarized in four main stages:

- Chemical reaction in gas phase of the ammonia molecule

and catalytic decomposition on the furnace walls.

- Transport of the ammonia molecule on the steel surface.
- Physico-chemical reaction on the steel surface.
- Diffusion and precipitation of nitrogen in the solid state.

Fig. 1 schematically presents the principle of the gas-solid heterogeneous reaction in the case of nitriding by the ammonia molecule.

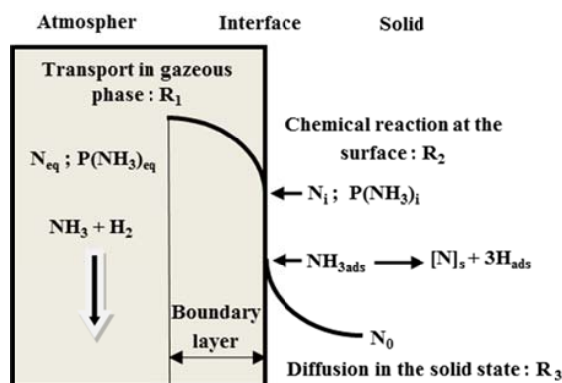


Fig. 1 Schematic representation of a gas-solid reaction of nitriding

The transfer of nitrogen can be described by an equation of the type:

$$\phi = h.(\%N_{eq} - \%N_s) \quad (1)$$

where ϕ the flow in ($\text{mol.m}^{-2}.\text{s}^{-1}$), N_{eq} the nitrogen concentration in the gaseous medium, N_s the nitrogen concentration at the surface of the material and $h = 1/(R_1 + R_2)$ is the coefficient of mass transfer. R_1 and R_2 are respectively the resistances of mass transfer due to the presence of the boundary layer and the chemical reaction [1].

Different analytical expressions can be written to model the flow of nitrogen transferred to surface. The authors can integrate or not the presence of the boundary layer at the surface of the material [2], [3].

III. NITRIDING IN THE BINARY Fe-N SYSTEM

The equilibrium diagram iron – nitrogen from Fig. 2 and the diagram of Lehrer (Fig. 3) [4] predict the nature of the susceptibility phases to be formed during a gas-solid reaction between iron and atmosphere partially dissociated of ammonia. The gas mixture in steady state is then characterized by a K_N parameter whose value determines the pseudo-equilibrium between the gas mixture and the various phases of the diagram iron – nitrogen. The nitrogen concentration $\%N_{eq}$,

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results from this pseudo- equilibrium between the gas phase and the solid. This size is fixed by the value of K_N which is

defined by $P_{\text{NH}_3}/P_{\text{H}_2}^{3/2}$ report called nitriding potential noted K_N .

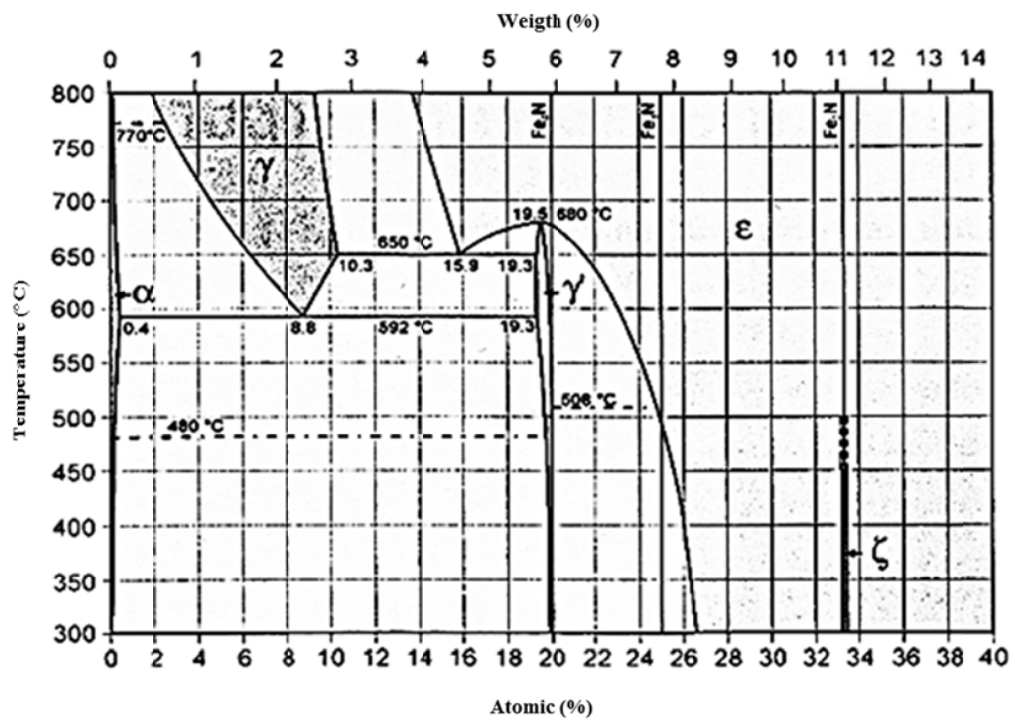


Fig 2 Mapping Binary Fe-N diagram [4]

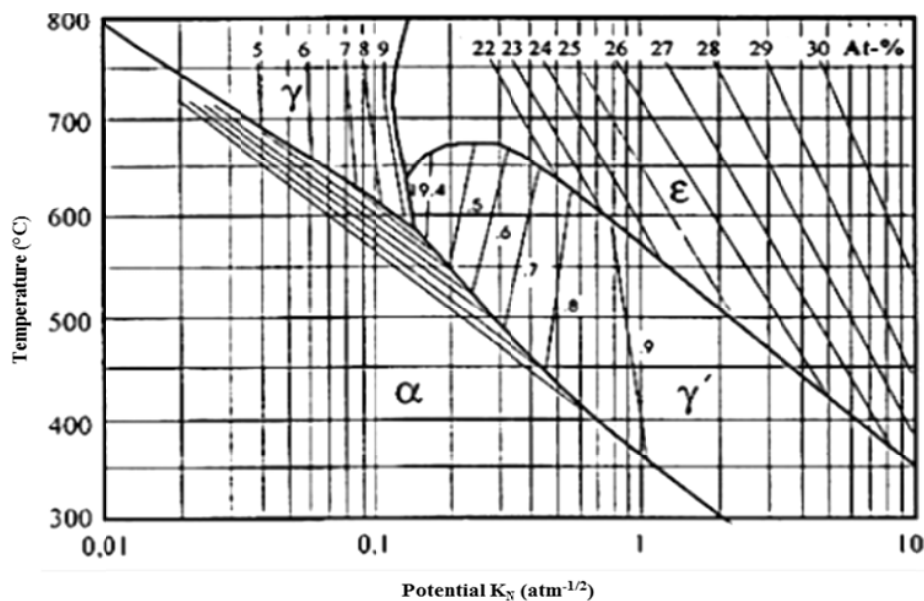


Fig 3 Lehrer diagram [4]

The rate of decomposition of ammonia in the gas phase is sufficiently slow for a steady state corresponding to a gas mixture (NH_3 , H_2 , N_2) of constant composition can be established in the reactor by adjusting the ammonia flow to the rate of its decomposition. The calculation of the nitrogen flow at the gas-solid interface from (1) requires knowledge of mass

transfer coefficient h and the control of the concentration of equilibrium, Neq . The latter depends directly on the value of the potential K_N . Accordingly, at determined temperature, the nature and growth rate of the different phases (solid solution of nitrogen in the iron nitride α , γ - Fe_4N and ϵ - Fe_{2-3}N) can be controlled by parameters potential K_N and flow of ammonia

introduced into the reactor. These two parameters are not independent [2] [5].

Thermogravimetric study associated with a microscopic study has allowed to analyse the mechanisms of germination and growth of γ' phase on pure iron in order to highlight the importance of the transfer coefficient h during the nitriding reaction. Then, we have chosen to show the effect of potential K_N on the growth kinetics of γ' layer for different hydrodynamic conditions [6].

The nitriding treatments are performed in the furnace of a thermobalance with a quenching device in order to fix the structure after treatment. The reactor is a tubular furnace made of alumina which means that the decomposition of ammonia on the walls is negligible. The circulation rate of the gaseous mixtures being sufficiently high (low residence time) and the

gas phase decomposition is negligible. These conditions are optimal to study the chemical surface reaction. The samples used are iron Armco dimension 10x10x50 mm.

In order to control the growth of the γ' layer according to the gradient of nitrogen concentration in phase γ' , we use the theoretical relation giving the evolution of K_N as a function of the nitrogen concentration in the phase γ' at 570°C [2]. For our experimental conditions, three values of K_N are used:

- $K_N = 0,23$: value close to the lower limit α/γ' ,
- $K_N = 0,43$: intermediate value domain γ' ,
- $K_N = 0,88$: value close to the limit γ'/ϵ .

The values of the total flow rate are between 0,05 to 0,6 l/mn.

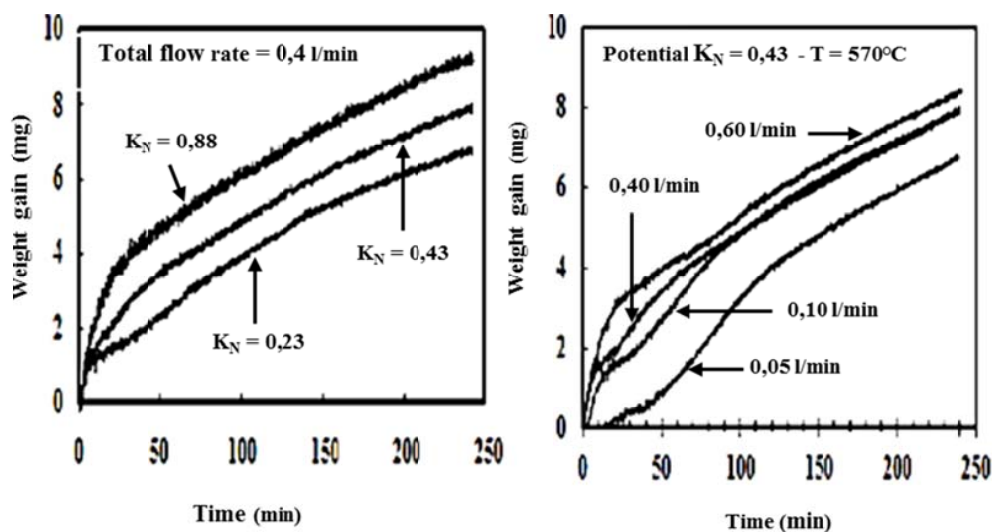


Fig. 4 Augmentation of weight gain as a function of time at constant total gas flow rate 0,4l/min and $K_N = 0,43$ ($T = 570^\circ\text{C}$)

Fig. 4 shows the influence of the total flow and K_N on the evolution of the weight gain of the samples as a function of nitriding time. It notes in particular, that:

At constant flow rate, the weight gain increases with increasing K_N :

- For $K_N = 0,88$, the transfer of nitrogen at the interface is essentially limited by diffusion in the solid state, the germination rate is very fast and curve of weight gain does not highlight the germination stage γ' .
- For $K_N = 0,43$, the transfer of nitrogen at the interface is limited by the chemical reaction and diffusion in the solid state (mixed diet).
- For $K_N = 0,23$, the transfer of nitrogen at the interface is limited primarily by the chemical reaction (resistance R_2).

At $K_N = 0,43$ constant, the weight gain increases with increasing total flow rate.

- For a low flow rate of 0,05 l/mn, the transfer of nitrogen to gas-solid interface is limited by the rate of transport of ammonia in the gas phase (the resistance R_1 is important) which implies that the transfer of the nitrogen in the solid state is low and therefore the rate of germination of the γ'

phase is very slow. The curve of weight gain of Fig. 4 highlights three stages which are clearly marked: nitrogen enrichment of phase α , germination and growth of nitride γ' .

- For a high flow rate of 0,6 l/mn, the transfer of nitrogen at the interface is limited primarily by the diffusion in the solid state because of rate of germination which is fast. Curve of weight gain of Fig. 4 does not show the step of germination of phase γ' .

These tests show that the flow of nitrogen transferred to the gas-solid interface depends on both hydrodynamics behavior (total flow rate) and thermodynamics (potential K_N) of the gas mixture used. Therefore, thickness and morphology of γ' layer depend directly on the flow of nitrogen transferred. Morphology of γ' layer varies as a function of values of couple (K_N – total flow rate).

The micrographs of Fig. 5 show that when the rate of germination is low ($K_N = 0,23$ – flow rate 0,1 l/mn), the interface γ'/α is indented.

In contrast, when the rate of germination is high ($K_N = 0,88$

– flow rate 0,6 l/mn), the interface γ'/α is planar. The growth rate of γ' layer depends on the nitrogen diffusion mechanisms in α and γ' phases. These results have perfected different models by describing the growth of these layers in polyphase systems [7]-[10].

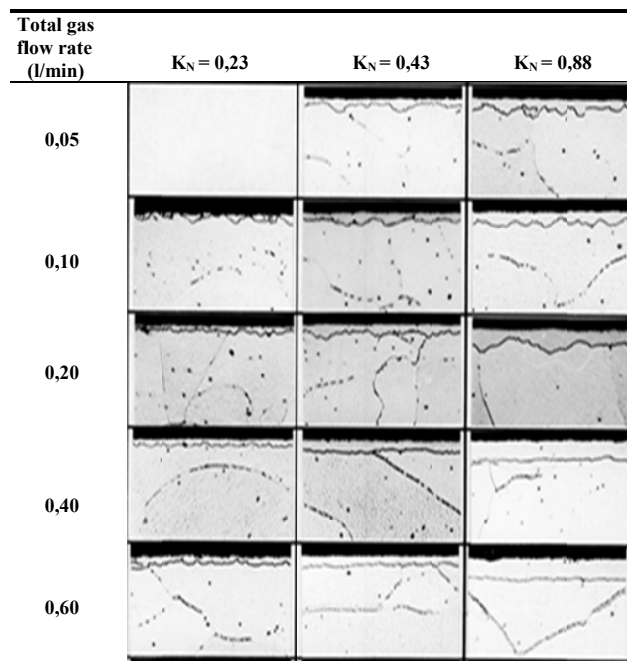


Fig. 5 Influence of K_N and total gas flow rate on the morphology of γ' phase: nitriding of pure iron 4 hours at 570°C

After establishing the basic principles of nitriding layer formation, we present some experimental results of nitriding conducted on iron-chromium alloys and iron-chromium-carbon in order to identify the mechanisms of interaction between the carbon and chromium as well as their influence on the nitrogen diffusion kinetics.

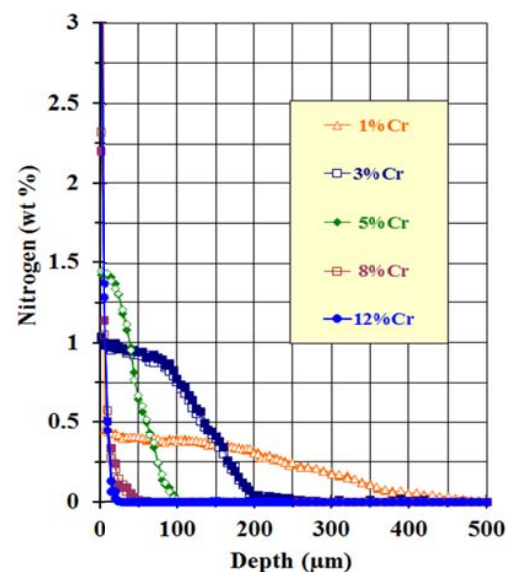
IV. NITRIDING IN THE TERNARY Fe-Cr-N SYSTEM

The ternary system iron-chromium-nitrogen has perfected the subject of numerous studies on the particular, precipitation phenomena of chromium nitride CrN [11]. In order to demonstrate the interaction existing between chromium and nitrogen, different nitriding tests are performed on alloys of iron-chromium composition (1%Cr, 3%Cr, 5%Cr, 8%Cr and 12%Cr) and treated in a temperature of 520°C for 24 hours with a nitriding potential ($K_N = 1$ and $K_N = 9$).

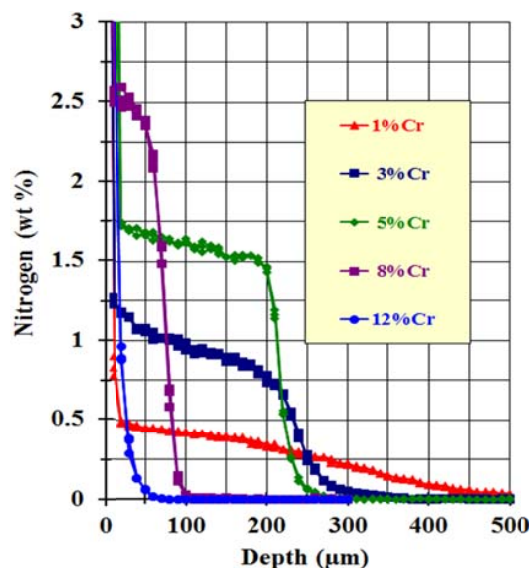
Fig. 6 presents the profiles of nitrogen concentration obtained by electron microprobe. It is found that:

- The depth of the diffusion layer of nitrogen is as much as low as than the concentration of the highest chromium.
- More the chromium concentration increases, more the value of nitrogen near to the surface is important (nitrogen combined + nitrogen in solid solution).
- When the value of K_N increases, the diffusion depth of nitrogen becomes important and the total nitrogen

concentration increases.



(a) Fe-Cr-N system: $K_N = 1$



(b) Fe-Cr-N system: $K_N = 9$

Fig. 6 Nitrogen concentration profiles after nitriding 24 hours at 520°C

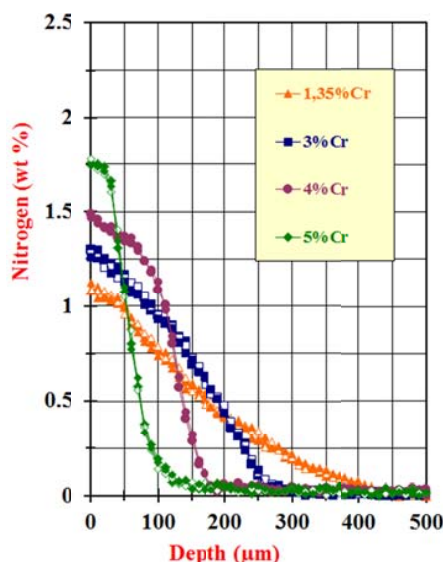
V. NITRIDING IN Fe-Cr-C-N SYSTEM

In order to demonstrate the interaction between the carbon and nitrogen in the presence of chromium, we have carried out four types alloys (1,35%Cr, 3%Cr, 4%Cr, 5%Cr and 0,35%C) of nitriding treatments at a temperature of 520°C during 24 hours for two potential values ($K_N = 1$ and $K_N = 9$). The nitrogen and carbon concentration profiles in Fig. 7 show that:

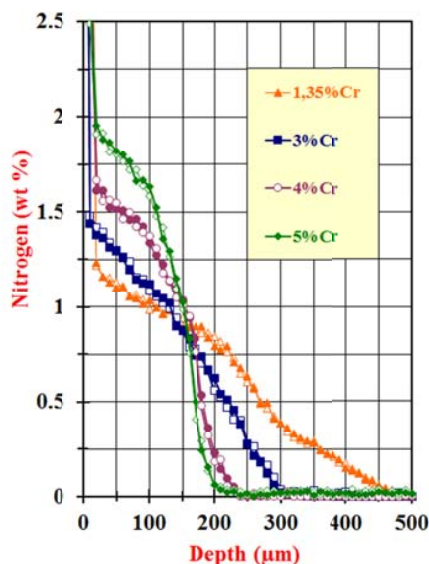
- The diffusion depth is as much as low than the highest of chromium content.
- The increasing of the chromium content increases the

nitrogen total value and the interaction nitrogen-chromium becomes stronger ; the nitrogen diffusion profiles has a steep gradient of nitrogen in the case of alloys with 4% and 5%Cr.

- When the potential value of K_N is high, the total nitrogen concentration increases and the diffusion depth of nitrogen became important.
- For a low $K_N = 1$, the layer configuration obtained is the type γ'/α , however, for a high $K_N = 9$, the layer configuration is the type $\varepsilon/\gamma'/\alpha$.



(a) Fe-0,35%C-Cr-N system: $K_N = 1$



(b) Fe-0,35%C-Cr-N system: $K_N = 9$

Fig. 7 Nitrogen concentration profiles after nitriding 24 hours at 520°C

VI. INDUSTRIAL APPLICATION OF NITRIDING STEEL 32CrMoV13

To illustrate the control growth of the γ' layer on an industrial steel, we present some experimental results obtained during the nitriding steel 32CrMoV13 at 520°C for a treatment duration between 4 and 55 hours.

Unlike the case of iron-nitrogen binary system, where the solubility limit of nitrogen at the interface γ'/α is fixed (constant temperature). The nitrogen concentration profiles of Fig. 8 show that the concentration at the γ'/α interface is not constant; it ranges from 1,4 to 1,86% for the nitriding treatment of 4 hours at 520°C and for the potential values of K_N ranging between 0,4 and 1,62. The thickness of the γ' layer and the nitriding depth increases with increasing K_N . Thus, the thickness of the diffusion layer is about 150μm after 4 hours for $K_N = 1,62$.

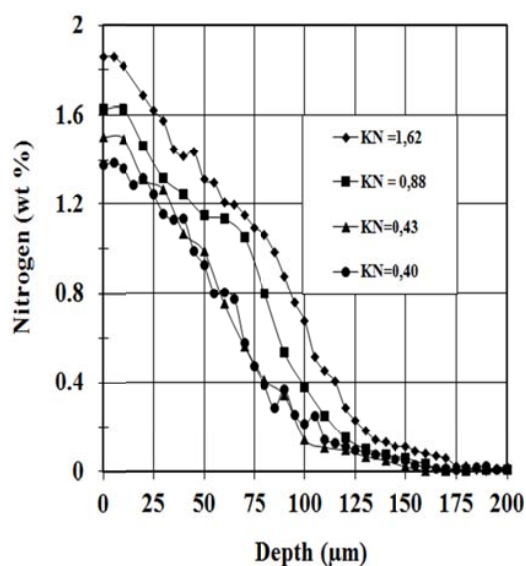


Fig. 8 Nitrogen concentration profiles after nitriding 4 hours at 520°C

The study of the growth kinetics of the diffusion layer in the presence of the compound layer of γ' to a constant of $K_N = 0,88$ shows that the value of the nitrogen concentration at the interface γ'/α is fixed over time to a value of about 1,6%. The control of the composition of the gas phase provides a thin layer combination γ' on an important depth of diffusion layer: (γ' : 5μm and α : 430μm).

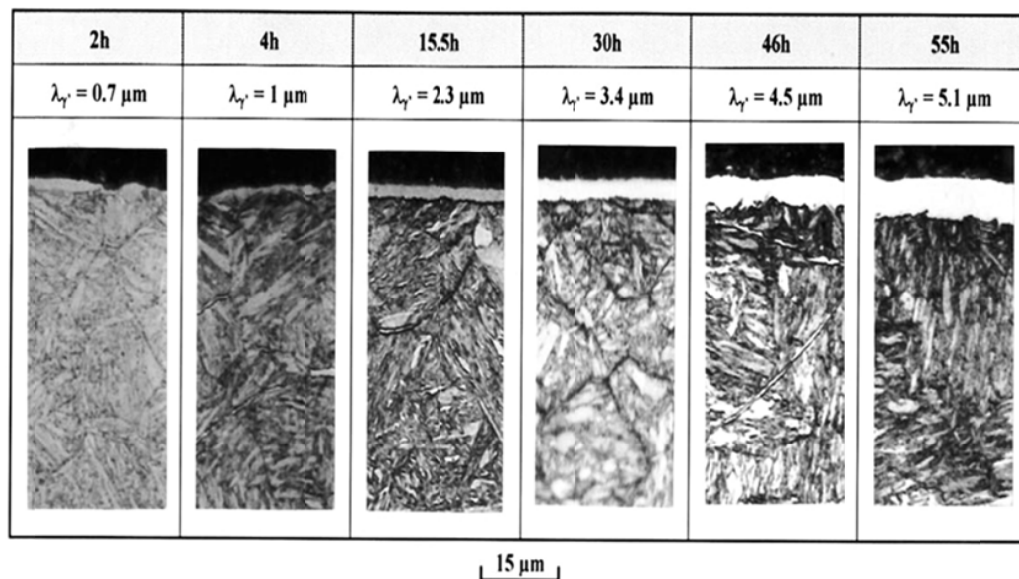


Fig. 9 Kinetic of γ' layer growth after nitriding between 2 and 55 hours at 520°C with $K_N = 0,88$

VII. CONCLUSION

A study of the forming mechanisms and the growth kinetics of nitrided layers from gaseous mixtures, at an atmospheric pressure, containing ammonia and hydrogen require the control of the transfer of the nitrogen gas-solid interface. The flow of nitrogen transferred to the surface depends on the thermodynamic and hydrodynamic behavior of the gas mixture used. In the current state, the growth kinetics of layers in the iron-nitrogen system is generally well controlled as much for the thermodynamic data point of view as for the data of transport phenomena in the solid state. However, for the alloys Fe-Cr-N and Fe-Cr-C-N and a fortiori for industrial steels, the interpretation as much thermodynamic as the forming kinetics of the different phases is much more complex.

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