

# Linear stability analysis of a $\gamma'$ -Fe<sub>4</sub>N nitride layer growing in pure iron

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## Abstract

In nitriding processes of steels, corrugations are commonly observed at the interface between nitride layers and the ferritic matrix. These corrugations have been explained as the consequence of the destabilization of the interface. We have performed a linear stability analysis in the flavour of the Mullins–Sekerka analysis on the interface separating a growing nitride layer in pure iron. This analysis shows that the corrugations cannot be due to a Mullins–Sekerka type instability, because the interface is absolutely stable, the composition field and the interfacial energy being both stabilizing. We conclude by a discussion on the role of the stress fields in the appearance of the corrugations.

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## 1. Introduction

Nitriding is a thermochemical surface treatment of great importance in practice because it improves the surface quality, especially the mechanical and the anticorrosion properties [1]. Generally, in the case of gaseous nitriding, the reactive nitrogen atoms at the solid surface results from the decomposition of the gas phase NH<sub>3</sub> in the presence of a H<sub>2</sub>–N<sub>2</sub> gas mixture [2]. Then, the diffusion of nitrogen atoms through the surface and into the solid can occur. In the case of nitriding of pure iron at 570 °C, the diffusing nitrogen interacts with the iron matrix to form:

(i) A compound layer at the surface that is mainly composed of the iron nitrides  $\epsilon$ -Fe<sub>2</sub>N<sub>1-x</sub> and  $\gamma'$ -Fe<sub>4</sub>N<sub>1-x</sub>. The presence of these iron nitrides depends mainly on the nitrogen composition imposed at the surface. (ii) A diffusion zone underneath the compound layer that consists of nitrogen atoms interstitially dissolved in the  $\alpha$  ferrite lattice.

The trend for process automation, particularly in gaseous treatments, requires developing some physical based models describing the growth kinetics of the compound layer ( $\epsilon + \gamma'$ ) and of the diffusion zone. Their main goal is to determine the influence of process parameters such as gas composition and temperature, on the formation of compound layer. These last years, several attempts [3–6] have been made to describe nitrogen diffusion in pure iron, relying on the Fick's laws solved in one-dimensional geometry, and on the nitrogen mass balance equations at the  $\epsilon/\gamma'$  and  $\gamma'/\alpha$  interfaces. Recently, some improvements have been proposed by using thermodynamic and diffusion approaches and by taken into account the concentration dependence of the nitrogen diffusivity in  $\epsilon$  and  $\gamma'$  [7]. This infatuation for modelling allowed disposing some detailed information on (i) the composition ranges of iron nitrides ( $\epsilon$  and  $\gamma'$ ) that led to the thermodynamic assessments of the binary Fe–N diagram [8,9], and on (ii) the diffusion coefficients in the various phases, mainly  $\epsilon$  and  $\gamma'$  [5–7]. The published data concerns the self-diffusion coefficients as well as the intrinsic diffusion coefficients as required in models treating the growth of compound layer. However, these works as a whole are based on the main assumption that the layer/substrate interfaces are planar although the

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various light-optical micrographs show clearly that this interface is corrugated and unstable [6]. In this paper, we will not discuss the influence of the corrugation on the kinetics of the phase transformations occurring in nitrated iron, but we will focus on the likely origins of the observed instability and especially the  $\gamma'/\alpha$  interface.

The destabilization mechanisms proposed in the literature are: (i) the Mullins–Sekerka destabilization by the diffusion fields [10], and (ii) the Asaro–Tiller–Grinfeld destabilization by the stress fields [11]. In this paper, we address the first mechanism through a linear stability analysis. Its principle relies on the following steps. (i) At first, a perturbation of known shape and small amplitude is applied to an initially plane interface growing by a diffusion controlled process in a semi-infinite medium; (ii) secondly, the perturbed concentration fields are sought by a regular perturbation expansion with the amplitude of the perturbations as the small parameter, which match the boundary conditions: initial flat concentrations, concentrations at infinity taken equal to zero due to the semi-infinite assumption, and local equilibrium at the interface. (iii) Finally, the expanded fields are used to express the solute balance at the interface. The terms of different orders in the amplitude are collected. At zeroth order, the balance at the plane interface is recovered. At first order, the dispersion relation is found.

Despite the extensive application of the linear stability analysis to various domains such as solidification [12], thin film epitaxy [13] or oxidation [14], as far as we know, it has not been performed yet on nitrated layers despite the observed corrugations at the  $\gamma'/\alpha$  interface.

This paper is organized as follow. First, by means of suitable experiments, we show clearly the presence of corrugations at the  $\gamma'/\alpha$  interface even if the chemical reaction on the surface is not the limiting process of the nitrating. In this case, the nitrating process is completely controlled by the nitrogen diffusion in the solid state. Then, we present the system that have been studied and the main simplifications of the analysis. A linear stability analysis is performed in the case of constant diffusion coefficients in both phases  $\gamma'$  and  $\alpha$ , before taking into account the concentration dependence of the nitrogen diffusion coefficient in the nitride. From the results, the possible mechanism is discussed that could explain the observed corrugations in experiments.

## 2. Experiments

An equilibrium state of  $\gamma'$  cannot be achieved with pure nitrogen gas at atmospheric pressure. Ammonia/hydrogen gas mixtures at atmospheric pressure are suitable to study the formation of  $\gamma'$  on  $\alpha$ -Fe. In this case, the chemical potential of nitrogen in a gas phase, consisting of a  $\text{NH}_3/\text{H}_2$  mixture can be defined on the basis of the hypothetical equilibrium  $\text{NH}_3 \rightleftharpoons \frac{3}{2}\text{H}_2 + \frac{1}{2}\text{N}_2$ , described by

$$\mu_{\text{N}}^{\text{g}} = \frac{1}{2}G_{\text{N}_2}^0 + \frac{1}{2}RT \ln p_{\text{N}_2} = G_{\text{NH}_3}^0 - \frac{3}{2}G_{\text{H}_2}^0 + RT \ln r \quad (1)$$

where  $p$  refers to the partial pressure, the superscript 0 indicates the standard state, and  $r = p_{\text{NH}_3}/p_{\text{H}_2}^{3/2}$  is the so-called nitrating potential. The chemical potential of nitrogen in  $\gamma'$ - $\text{Fe}_4\text{N}$  will be equal that in the gas ( $\mu_{\text{N}}^{\text{g}} = \mu_{\text{N}}^{\gamma'}$ ), if equilibrium is reached between an imposed  $\text{NH}_3/\text{H}_2$  mixture and  $\gamma'$ - $\text{Fe}_4\text{N}$ . Then, from (1), the nitrogen activity in  $\gamma'$  can be defined as

$$a_{\text{N}}^{\gamma'} \propto r \quad (2)$$

The previous relation allows defining a pseudo-phase diagram temperature versus  $r$ . This diagram, often called “Lehrer diagram” [15] is given in Fig. 1.

Fig. 1 defines the temperature and ratio  $r$  where the various phases are formed. Therefore, to obtain the desired nitride layer it is a prime of necessity to adjust  $r$  from the ammonia and hydrogen partial pressures. For example, to form a  $\gamma'$  layer into iron at 570 °C,  $r$  has to be in a range of 0.16 up to 1.62. Then, we have performed nitrating experiments at 570 °C of pure iron for 4 h. The high purity iron has been prepared by Goodfellow Laboratory (Cambridge). The chemical composition in impurities are given in Table 1.

The composition of the gas mixtures was adjusted with mass-flow controllers. The ammonia–hydrogen gas mixtures contained 0.4 volume fraction of  $\text{NH}_3$  and 0.6 volume fraction of  $\text{H}_2$  ( $r = 1.13$ , Fig. 1) for the forming of  $\gamma'$  layer above the  $\alpha$  diffusion zone. The surfaces of the samples have been very carefully polished until 1  $\mu\text{m}$  diamond paste and cleaned by subsequent ultrasound and ethanol, in order to dismiss the hypothetical effect of an unplanar surface on the appearance of corrugations, as it is

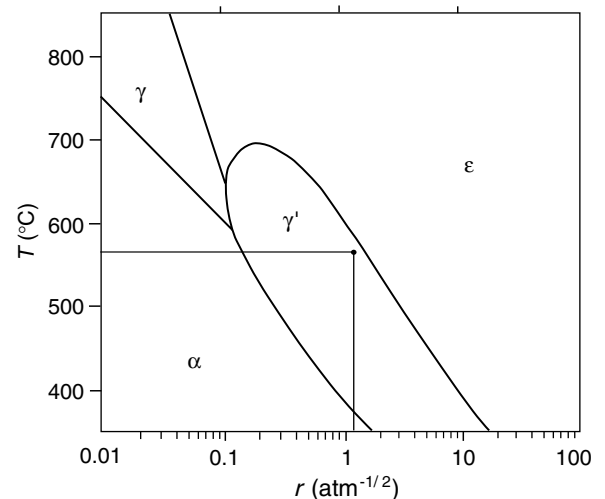


Fig. 1. Fe–N binary phase diagram as a function of the nitrating potential. The dot indicates the condition of the experiments.

Table 1  
Concentration in impurities of the high purity iron used

Impurity	C	O	N	Al
Concentration (ppm)	82	520	4	6

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