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# PLASMA NITRIDING OF Fe-Al FERRITIC ALLOYS AT 500 AND 550 ºC

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***Abstract.*** *Low-temperature thermochemical treatments are highlighted due some formed phases particularities. Some of these, known as metastable phases, are obtained by carrying the treatment at specific conditions in which the carbide or nitride formers elements present in solid solution in the alloy has negligible mobility when compared with carbon or nitrogen. This condition of metastability its achieved by its low mobility, low solubility of the aluminum in the iron nitrides and elevated constrains imposed by the ferritic matrix over the stable Al nitride, i.e. hexagonal aluminum nitride. In some conditions this treatment leads to situations of supersaturation which promote a saw layer growth of precipitates. To better understand the change in treated layer morphology, samples of Fe-Al ferritic alloys with 0, 1, 3, 5, 7 and 10 wt. % Al were plasma nitrided at 500 and 550 ºC for 4 hours. Preliminary results reveal, besides the saw-like layer, a homogeneous layer for contents over 5 wt. % at 500 ºC and above 3 wt. % Al at 550 ºC, this layer exhibits a thickness of more than 100 µm with 1500* $HV_{0,1}$ *Vickers hardness, moreover the confocal measurement reveal a surface texture related to the saw-like morphology. XRD indicate the precipitation of a phase similar to Cubic AlN, however at the temperature of 550 ºC the formation of a thin layer of* $Fe_{2\text{-}3}N$ *on the surface is observed, exhibiting a behavior similar to a treatment in thermodynamic equilibrium.*

***Keywords:*** *Plasma Nitriding, Fe-Al Nitriding, Cubic AlN, Nitride Former, Me-N Interaction, Low-temperature Nitriding*

## 1. INTRODUCTION

Low-temperature thermochemical treatments of stainless steels have been presenting notable results in regards of wear, fatigue and corrosion performance (Allenstein, *et al.*, 2014*)*. These stainless steel low temperature treatments distinct themselves by allowing the materials to enhance surface properties without compromising its corrosion resistance, this performance is attained by forming metastable phases without precipitating nitride and carbide of alloying element that are in solid solution.

These nitrides or carbides element formers perform a fundamental role in these treatments (Dalton, 2014), in the case of low-temperature nitriding, which are responsible for retain the iron nitrides precipitation and allowing a nitrogen supersaturation on the iron matrix giving rise to the so-called expanded phases. However, to obtain metastable phases during the nitriding it's necessary to carry out he treatment at low temperatures and duration to avoid the precipitation of the nitride stable phases.

When nitriding is performed at high temperatures - enough for mobility not be a restriction to precipitation - in alloys with nitride formers elements in solid solution, we can expect three different profiles of precipitates of the alloy element according with its interaction and the nitrogen (Biglari, *et al*, 1993), they are:

i) when the interaction is weak, it initially occurs a whole bulk saturation and random precipitation;

ii) when the interaction between nitride element former and nitrogen is strong enough, the precipitation happens in such a way to consume all nitrogen as soon as it's available in the bulk, and the growth of the precipitate layer is given only after all nitride element formers been consumed; and

iii) when intermediate interaction is observed, the process initiates with matrix saturation followed by precipitation due the increase in nitrogen content from the surface.

Aluminum nitride has a highly negative formation energy, thus denoting that in the high mobility conditions the layer growth must be gradual in accord with nitrogen incoming and consumption of aluminum in solid solution, but some factors need to be taken in account on cases with restrict mobility, among these factors stand out the low solubility of aluminum in iron nitride, the high energy necessary to overcome the nucleation barrier due the hexagonal aluminum phase misfit on the body centered cubic crystalline structure of the ferritic matrix(Hussein, 1984).

All these previously mentioned aspects make the layer to grow similarly to an intermediate interaction as follows: at the start of the treatment a nitrogen enrichment of the matrix occur, although the high energy necessary to precipitate the hexagonal stable phase in the ferritic matrix suppress this phase. Then nitrogen saturation on the ferritic matrix develops, however due to the low solubility of the aluminum in the iron nitrides its precipitation is retained, ensuing a solubility limit extrapolation - also known as supersaturation - that happens until at a certain depth where an increase in supersaturation promotes the sudden precipitation of a metastable phase of cubic aluminum nitride with a plane coherent with the ferritic matrix, considerably reducing the energy required for nucleation, which develops to depths where supersaturation conditions are favorable by encompassing the iron atoms in the precipitated volume. Thus, the layer develops from the surface with precipitation imposed by the nitrogen entry, similarly to the elements that have intermediate interaction.

Studies have been carried out based on the aluminum nitrides precipitation for a long time (Darken, *et al*, 1951), but they are mainly based on high mobility conditions – high temperatures – where growth or precipitation occurs in equilibrium. However, with the advent of the low temperature thermochemical treatments in stainless steels, studies were also performed on low temperature treatment of alloys containing this element (Jung, *et al,* 2010). Still, there are few records in treatments at intermediate temperatures where a transition between layer growth of the intermediate and high interaction form exists. Thus, this study aims to better understand where this layer growth transition takes place, and what factors influence on this transition, allowing the use of such phenomena in a controlled way.

## 2. EXPERIMENTAL PROCEDURE

Samples of pure Iron and Fe-Al ferritic alloys with content of 1, 3, 5, 7 and 10 wt. % Al in solid solution were produced by deposition of high purity powder by plasma transferred arc (Zanetti, *et al., 2015)* the resulting rod was homogenized in vacuum furnace at 1000 ºC for 10 h then sectioned in samples with 6 mm height. The samples presented the hardness of approximately 90, 93, 120, 145, 165 and 225 $HV_{0,1}$ for samples from 0 wt. % to 10 wt. % Al. Moreover, the samples presented strong crystallographic orientation with grains of the more than 600 μm diameter.

After grinding and polishing the samples where plasma nitrided at 500 ºC and 550 ºC for 4 hours at 3 Torr with an atmosphere composed by 70 % $N_2$, 20 % $H_2$ and 10 % Ar. Subsequently the samples were analyzed by XRD with Cu target ($\lambda$=1,54 Å), surface hardness measurements with Vickers indenter, surface profile by confocal microscopy and the transversal section metallography was analyzed by optical microscopy with Nital etch.

## 3. RESULTS AND DISCUSSION

### 3.1 Metallography

Both samples of pure iron (Figure 1, a) and b)) exhibits similar morphology, composed by two layers (ε and ɣ') and beneath a region with $Fe_{16}N_2$ precipitate due the solubility reduction during the cooling.

When aluminum is added in solid solution to the samples, a saw-like morphology develops due the restrain of the iron nitrides precipitation promoted by the aluminum's low solubility in these phases and its low mobility at this temperature which leads to supersaturation before the sudden transformation to depths in which conditions are favorable.

However, when aluminum content is increased (Figure 1. e)) or temperature raised enough (Figure 1. d) and f)) the conditions are favorable to a different growth mechanism, and a layer analogous to those related to elements with strong interaction takes place, in this case the development occurs with the precipitation of the solid solution element before further growth and a layer with homogeneous thickness takes place.

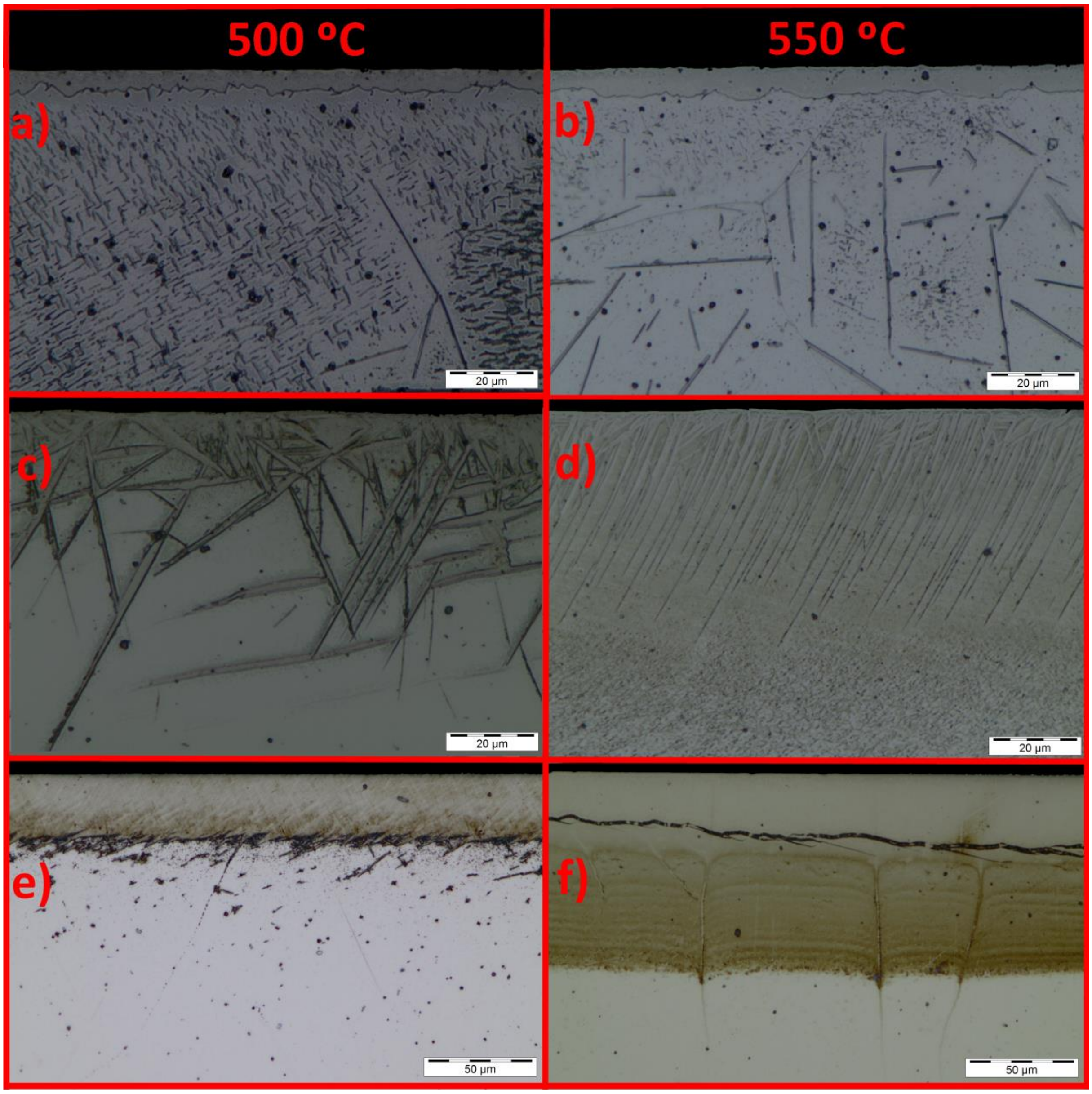

Figure 1. Layer of samples nitrided for 4 h. a) 0 wt. % Al at 500 ºC; b) 0 wt. % Al 550 ºC; c) 3 wt. % Al 500 ºC; d) 3 wt. % Al 550 ºC; e) 7 wt. % Al 500 ºC; f) 7 wt. % Al 550 ºC.

Although the layer growth transition is not well defined, how can be seen due to the temperature raise comparing the layer metallography in figure 1. c) and d); e) and f) and more evident in figure 2 due to the Al content increase. When the conditions are favorable to the precipitation, despite the homogeneous thickness, it begins in a diffuse way (Pinedo and Magnabosco, 2015) and gradually evolves to a layer with a well-defined interface.

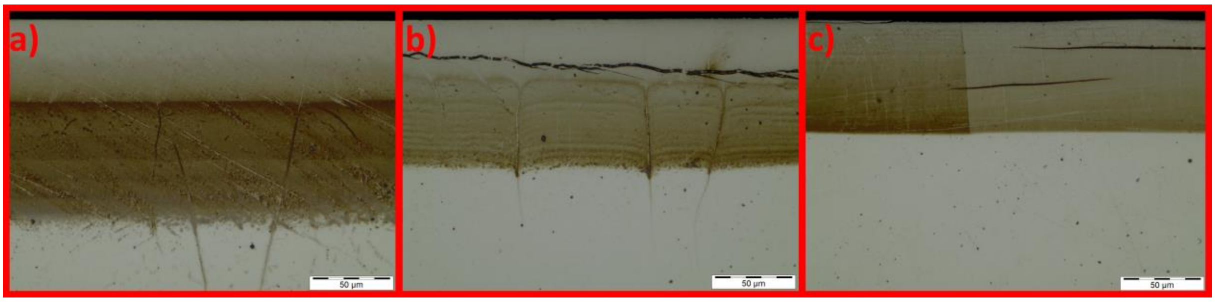

Figure 2. Layer of the samples nitrided for 4 h at 550 C with a) 5 wt. % Al; b) 7 wt. % Al and c) 10 wt. % Al.

Cracks were observed longitudinally to the layer or on the interface between layer and substract that showed favorable conditions to a homogeneous growth, meanwhile samples in which the layer developed in a saw-like layer (indicating a matrix supersaturation) it occurred grain boundary slip, as it can be seen in figure 3. This behavior can indicate that in the first case (homogeneous growth) fissures happened due a formed phase's bigger volume allied to a different thermal expansion coefficient. On the case of saw-like growth, the supersaturation before the sudden precipitation could had leads to a 'detachment' of grain boundaries.

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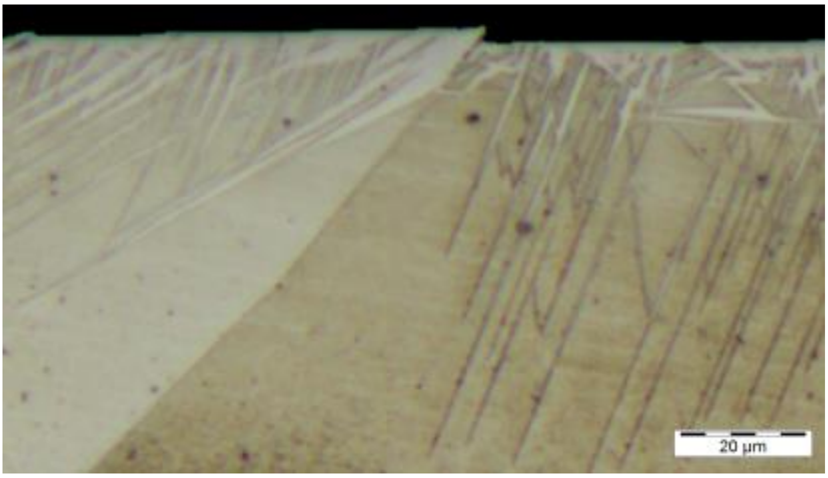

Figure 3. Detached Grain Boundary of the sample nitrided for 4 h at 550 C with a) 3 wt. % Al;

### 3.2 Surface Hardness

Surface hardness measured on the top of the samples after the treatment is presented in the figure 4, it reveals a similar hardness for samples with same aluminum content treated at different temperatures. A similar hardness increases related to the addition of aluminum, reaching 1500 $HV_{0,1}$, is also observed for the different studied temperatures. This result indicates that the hardness is independent of the layer growth mechanism.

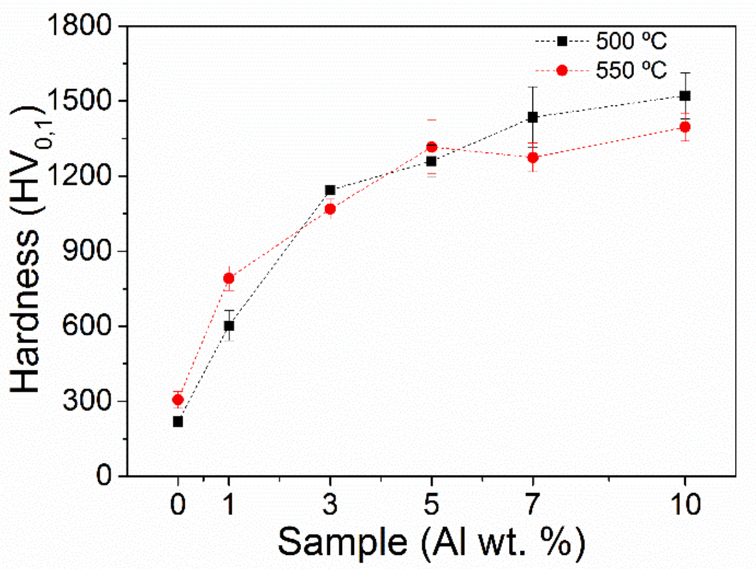

Figure 4. Surface Hardness measured on the samples nitride at 500 and 550 ºC for 4 hours.

### 3.3 Topography

Confocal microscope was used to verify the surface profile as function of Al content and the formed layer. As on the metallography, the images presented in figure 5 a) and d) refer to pure iron samples and were utilized as reference treatments without influences of aluminum in solid solution. In these samples is possible to observe topography without defined pattern, basically formed of peaks and valleys distributed in a random way. However, on the layers that was seen a saw-like growth, attached to the supersaturation and sudden precipitation, this topography is formed by a pattern that resembles a mesh (Figure 5 b) and e)), probably caused by the expansion caused by the 'saw-teeth' base. In figure 5 e), this effect isn't as pronounced because it's a transition condition, which can be verified since in favorable growth conditions - higher aluminum content or higher temperatures – the topography doesn't show patterns and has lower peaks and valleys (figure 5. c) and f)).

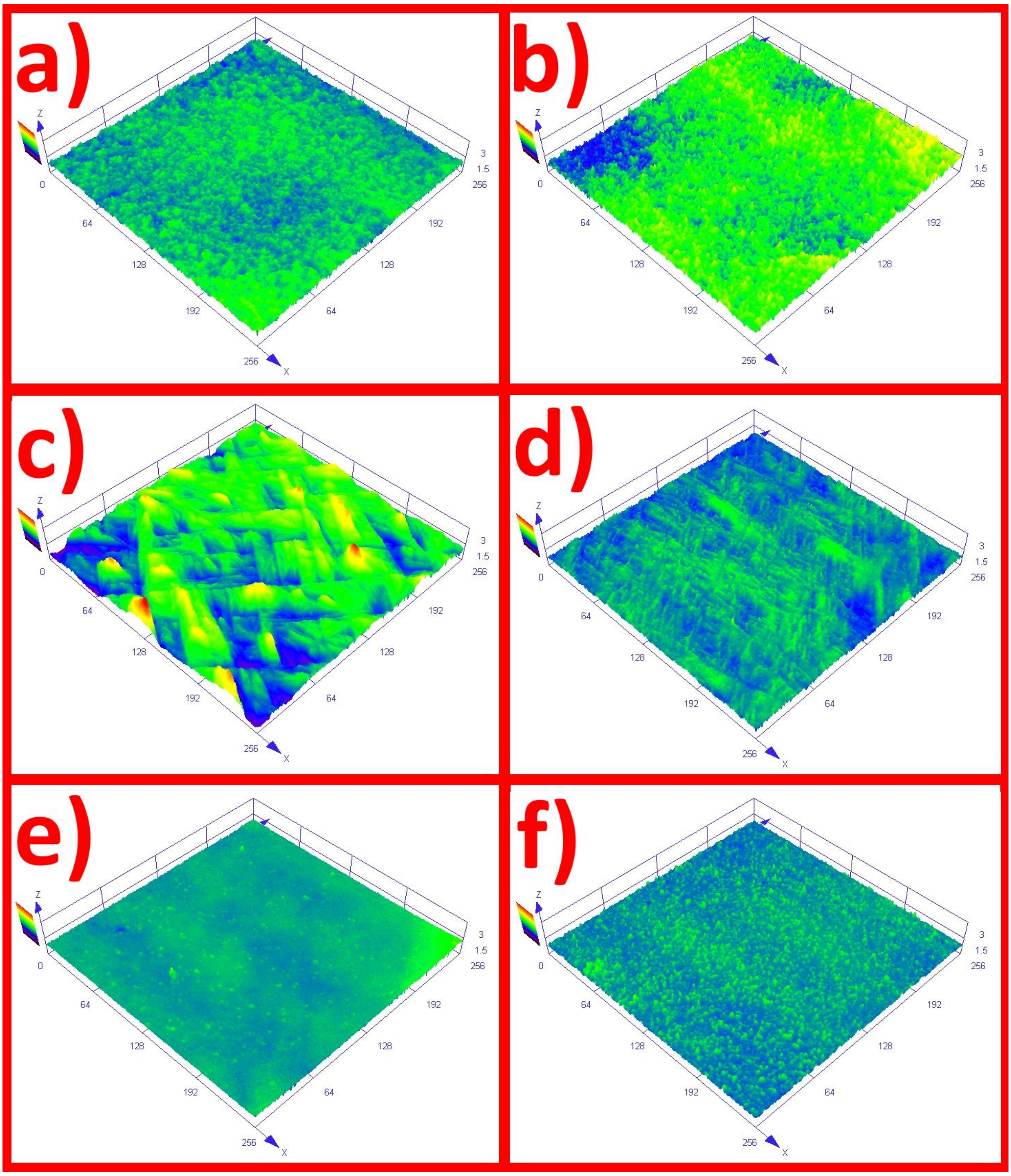

Figure 5. Surface topography of the samples nitride for 4 h a) 0 wt. % Al at 500 ºC; b) 0 wt. % Al 550 ºC; c) 3 wt. % Al 500 ºC; d) 3 wt. % Al 550 ºC; e) 7 wt. % Al 500 ºC; f) 7 wt. % Al 550 ºC.

### 3.4 X-Ray Diffraction

XRD reveals the presence of a phase identified in other studies as cubic $FeAl_xN$ (Meka, *et al.*, 2012), this phase is very similar to the cubic AlN, however the low mobility of aluminum prevents the precipitation of a stoichiometry phase composed only by aluminum and nitrogen. Then the iron atoms are “dragged” to precipitate in the AlN crystal structure causing the lattice parameter of this to vary according to the aluminum content in solid solution, which doesn’t happen to the iron nitride $Fe_{2\text{-}3}N$ (ε). At the studied temperatures, there are not peaks identified as hexagonal aluminum nitride stable phase.

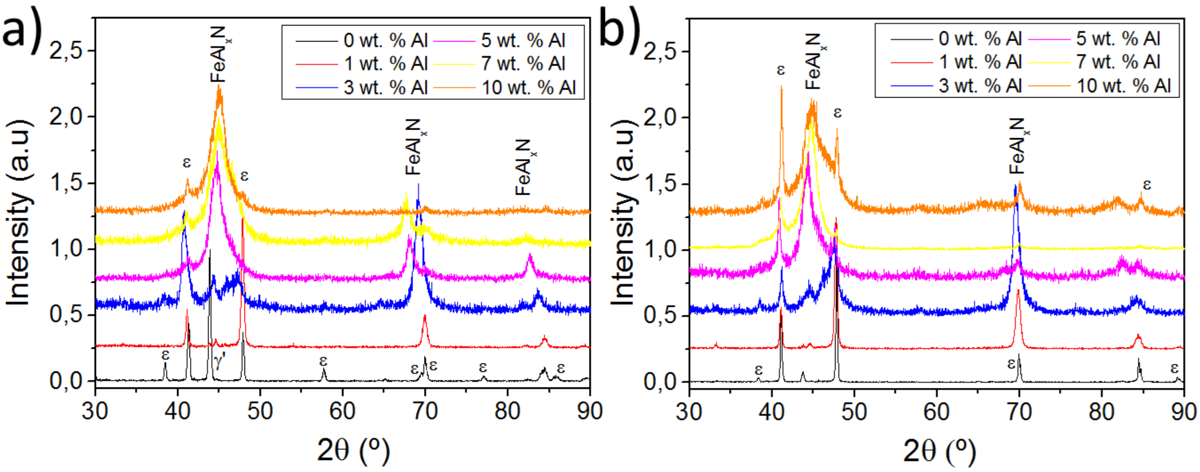

Figure 6: XRD patterns of the samples nitrided for 4 hours at: a) 500 ºC; b) 550 ºC

## 4. CONCLUSIONS

Analyzing the formed layers by nitriding Fe-Al ferritic alloys at 500 and 550 ºC for 4 hours it‘s possible to conclude:

Two diferent layer morphology can be distinguished as function of temperature and aluminum content.

The transition between both growths is not well defined.

Hardness of 1500 $HV_{0,1}$ can be achieve nitriding Fe-Al ferritic alloys and the hardness is mainly influenced by the aluminum content;

Saw-like layer is associated to surface texture due expansion of precipitation;

Aluminum content and its difusion plays a important role in the layer morphology of the Fe-Al ferritic nitriding;

High temperature leads to the precipitation of a thin $Fe_{2\text{-}3}N$ layer, decharacterizing it as a metastable treatment , however not enough to allow the aluminum nitride stable phase (Hexagonal AlN).

## 5. ACKNOWLEDGEMENTS

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