Phase transformation in Fe-N system : towards the development of HSS

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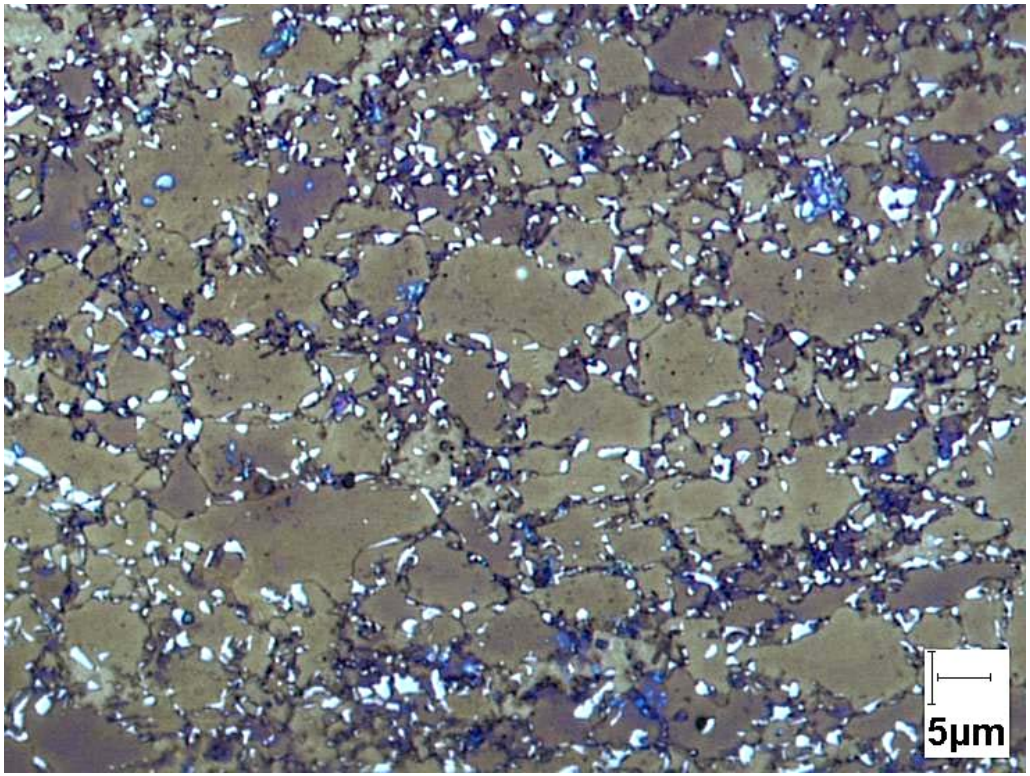
Introduction

C High Strength Steels (C around 0.2 wt%)



- Ferrite formation during cooling
- Bainite formation
- martensite formation
- precipitation in ferrite

Introduction

Interests of Nitrogen metallurgy ?

- Same phases as the C metallurgy

N ferrite, N_austenite, nitride precipitation

- N is able to stabilize austenite at room temperature

The nitrogen solubility limit in austenite higher than that of C (2.4wt% vs 0.8%C)

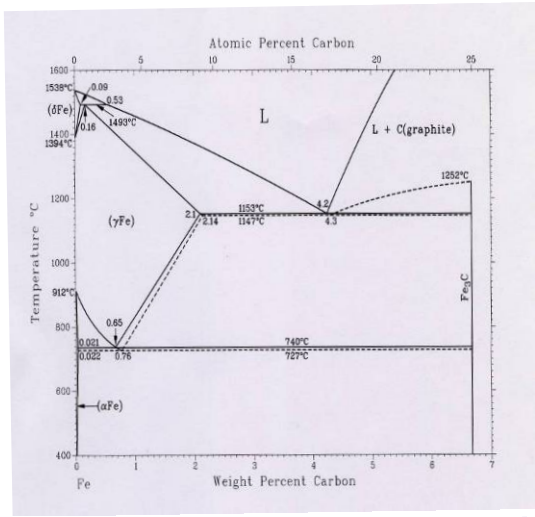
- The obtained microstructure may be finer and harder

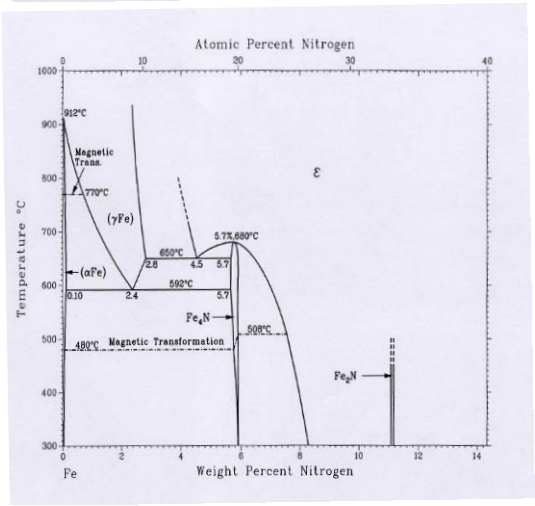
Role on resulting mechanical properties ?

- Energetically more favourable

The eutectoid temperature is lower : 592°C in Fe-N vs 723°C in Fe-C

- High power of hardening precipitation
- Same kind of phase transformation





Main barrier

Impossible to introduce high amount of nitrogen in the steel by the Classical way as the nitrogen solubility in iron liquid is very low

Introduction

Goal of the study

- To introduce high amount of nitrogen in steels (> 0. 1wt%) homogeneously distributed in the matrix
- To study the various phase transformations in Fe-N system and the resulting microstructure

Elaboration of the samples

Very low solubility of N in liquid

At 1600°C and PN_2=1atm : 400 ppm

Solution to elaborate the samples ?

- Nitriding : based on the dissociation of ammonia

$$2NH_3 \leftrightarrows 2N + 3H_2$$

if T<500°C the dissociation is too low

if T>Tc the dissociation is too rapid N →N_2

➔Range of temperature is limited

$$LnK_{eq} = \frac{-6769}{T} + 14.251\,(\text{atm}^{\frac{1}{2}})$$

$$\Delta G_T = \Delta G_T^0 + RTLn\left(\frac{a_N . P_{H_2}^{\frac{3}{2}}}{P_{NH_3}}\right) \Rightarrow \Delta G_T^0 = -RTLn\left(\frac{a_N . P_{H_2}^{\frac{3}{2}}}{P_{NH_3}}\right) = -RTLnK_{éq}$$

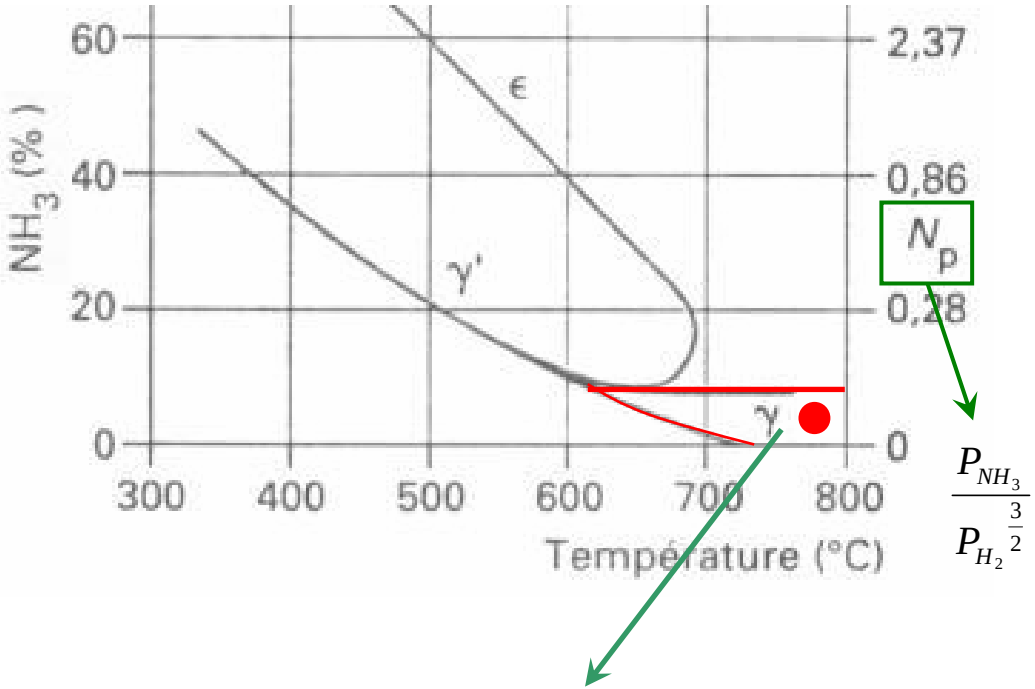
Dissolved nitrogen activity

$$a_N = K_{éq}\frac{P_{NH_3}}{P_{H_2}^{\frac{3}{2}}}$$

Elaboration of the samples

The obtained diagram Lehrer

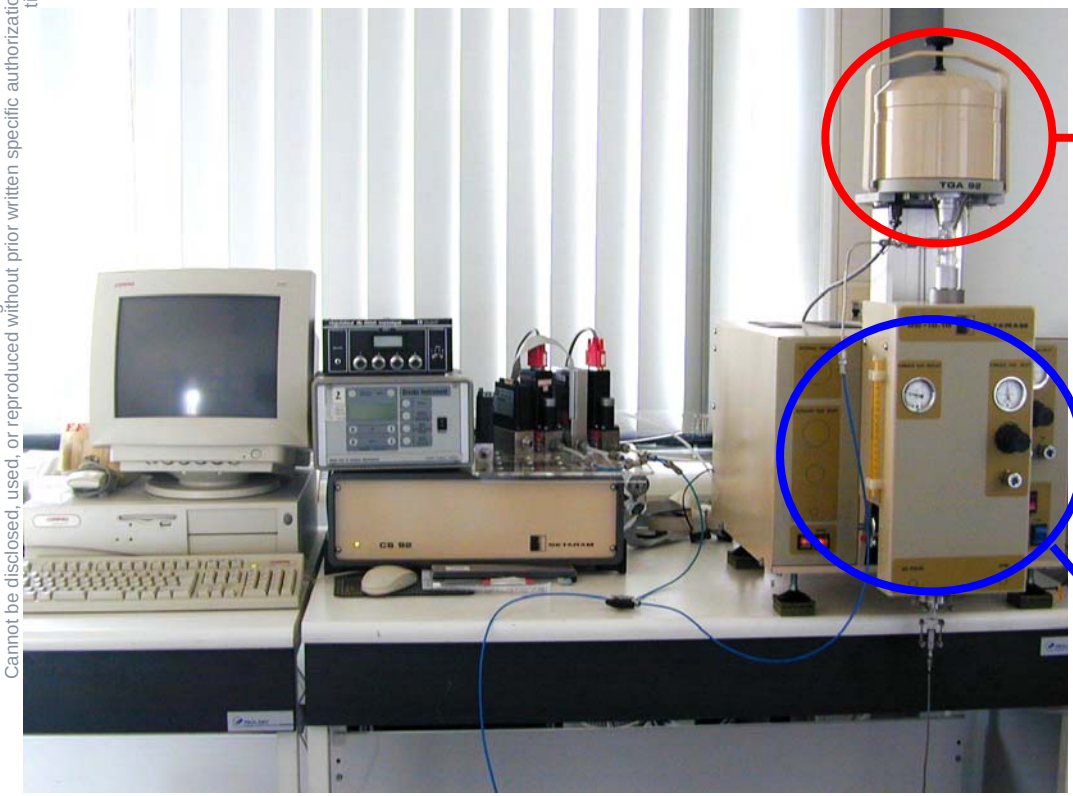
$$a_N = K_{éq} \frac{P_{NH_3}}{P_{H_2}^{\frac{3}{2}}}$$



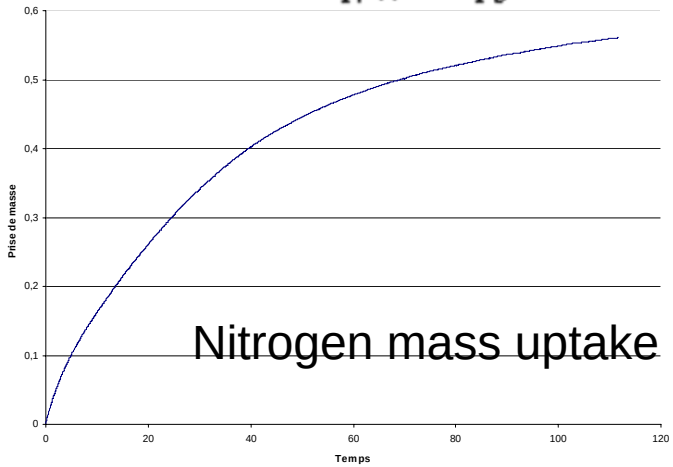
- Nitriding at 840°C in γ region
- Atmosphere NH3-N2-H2
- Np around 0.01-0.05
- NH3 = 4% H2=75% N2=21%

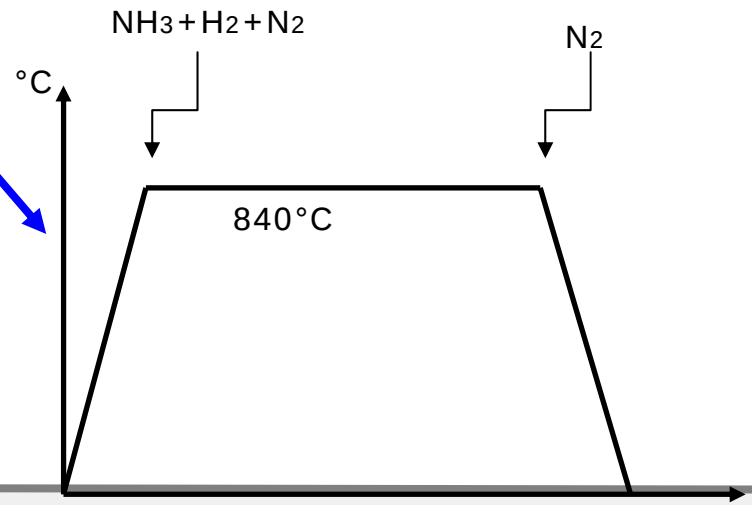
Difficulties to nitride in the γ region
- The Np range of nitriding is low
- The temperature range of nitriding is low

Elaboration of the samples



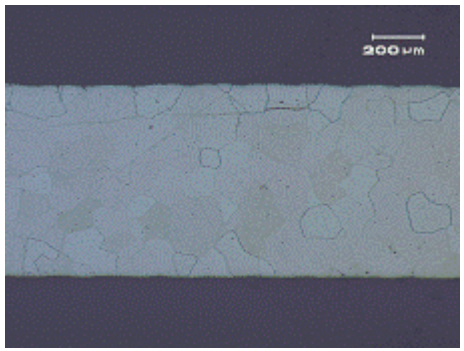
$$[\%N](t) = \frac{M_N(t)}{M_N(t) + M_{Fe}} \times 100\,\%$$

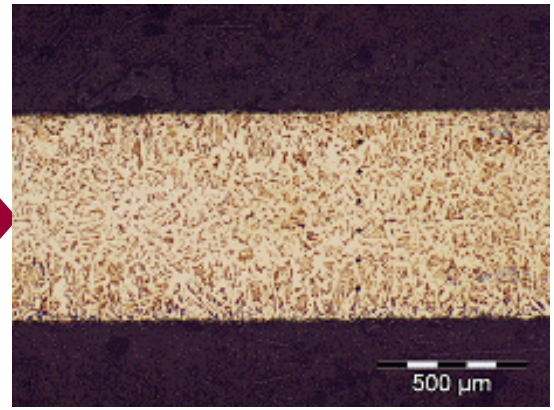


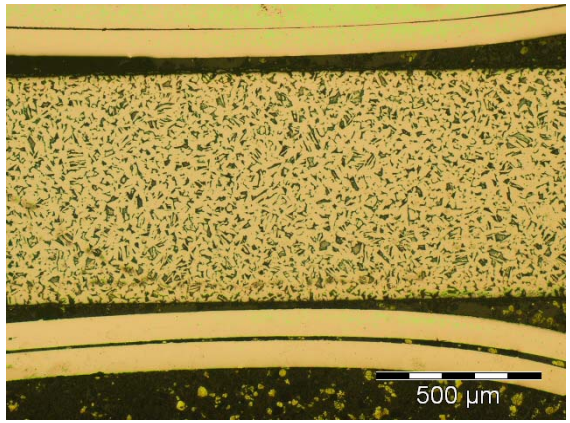


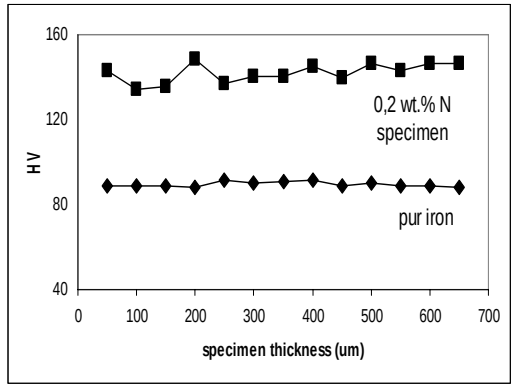
Elaboration of the samples

- Thermobalance : N=0. 17 wt%
- Chemical analysis : N=0.16 wt%



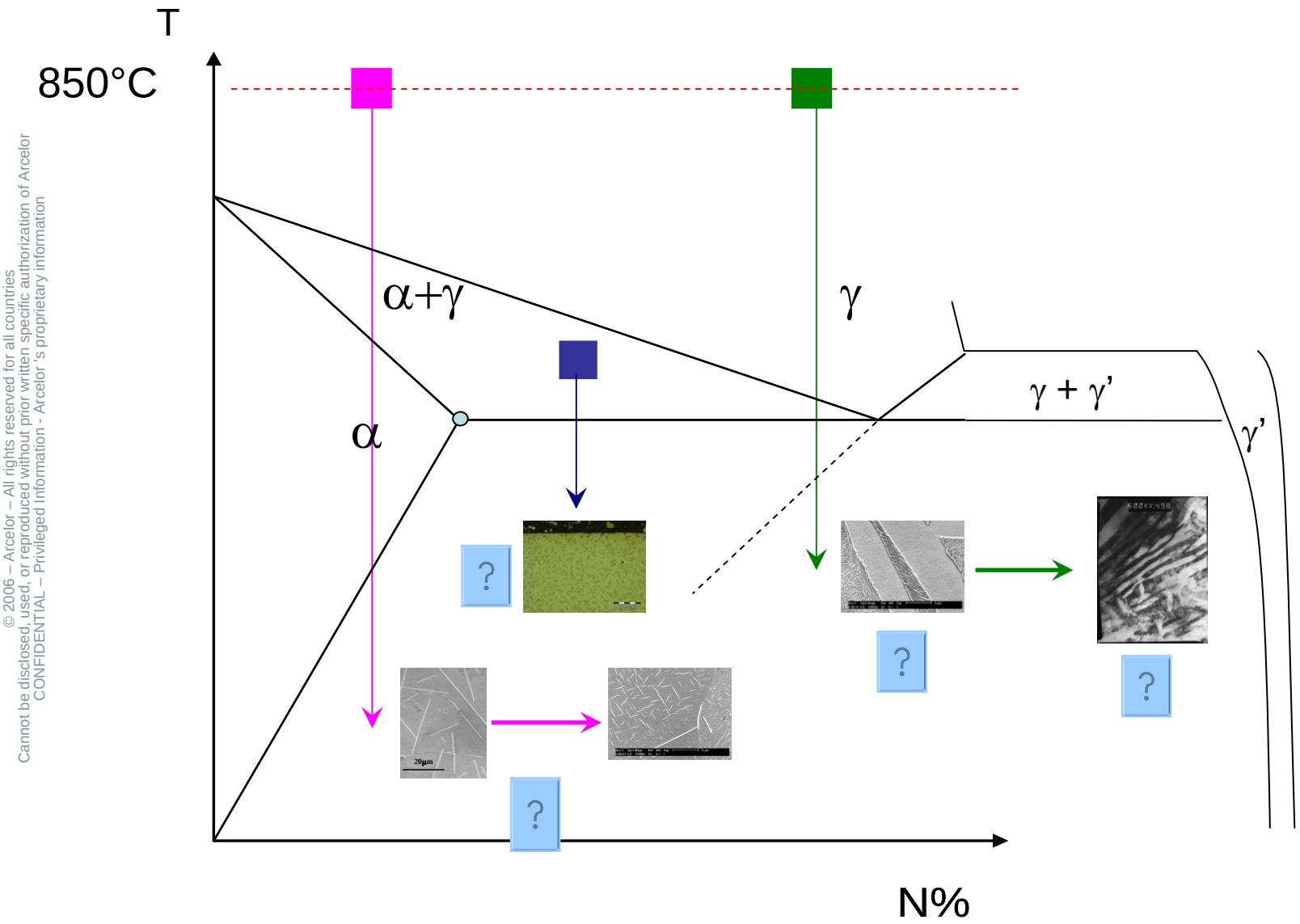




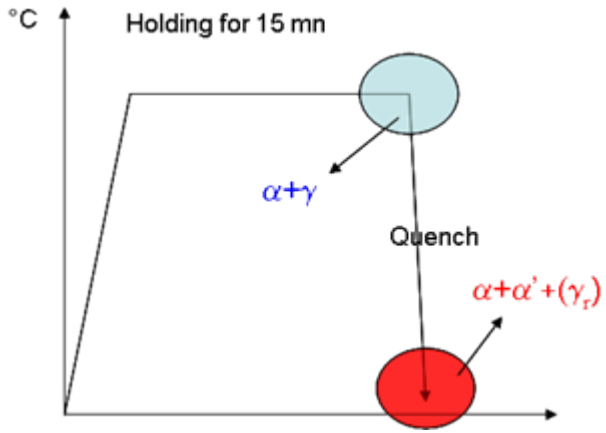


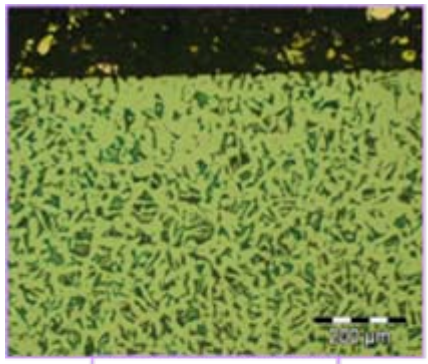
- Thermobalance : N=0. 57 wt%
- Chemical analysis : N=0.54 wt%

Main results on phase transformation

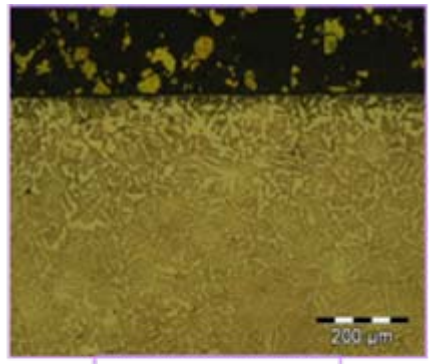


Some results : in the α+γ phase region

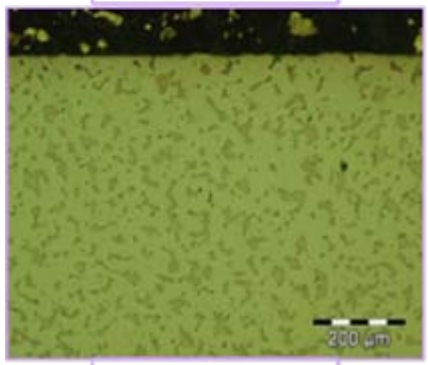




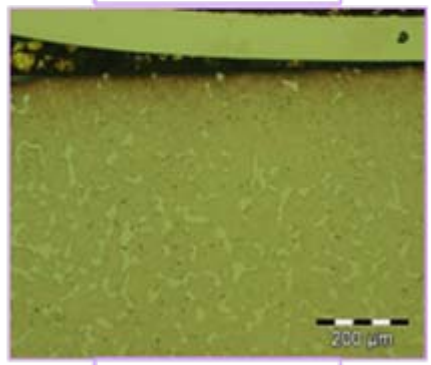
0.5%N, 600°C



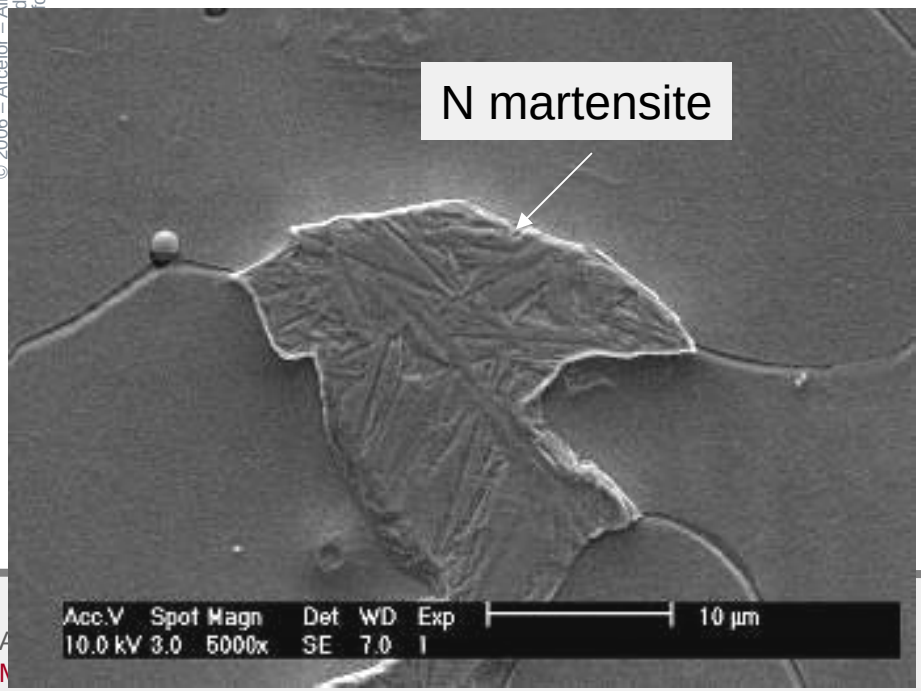
0.5%N, 640°C



0.2%N, 750°C

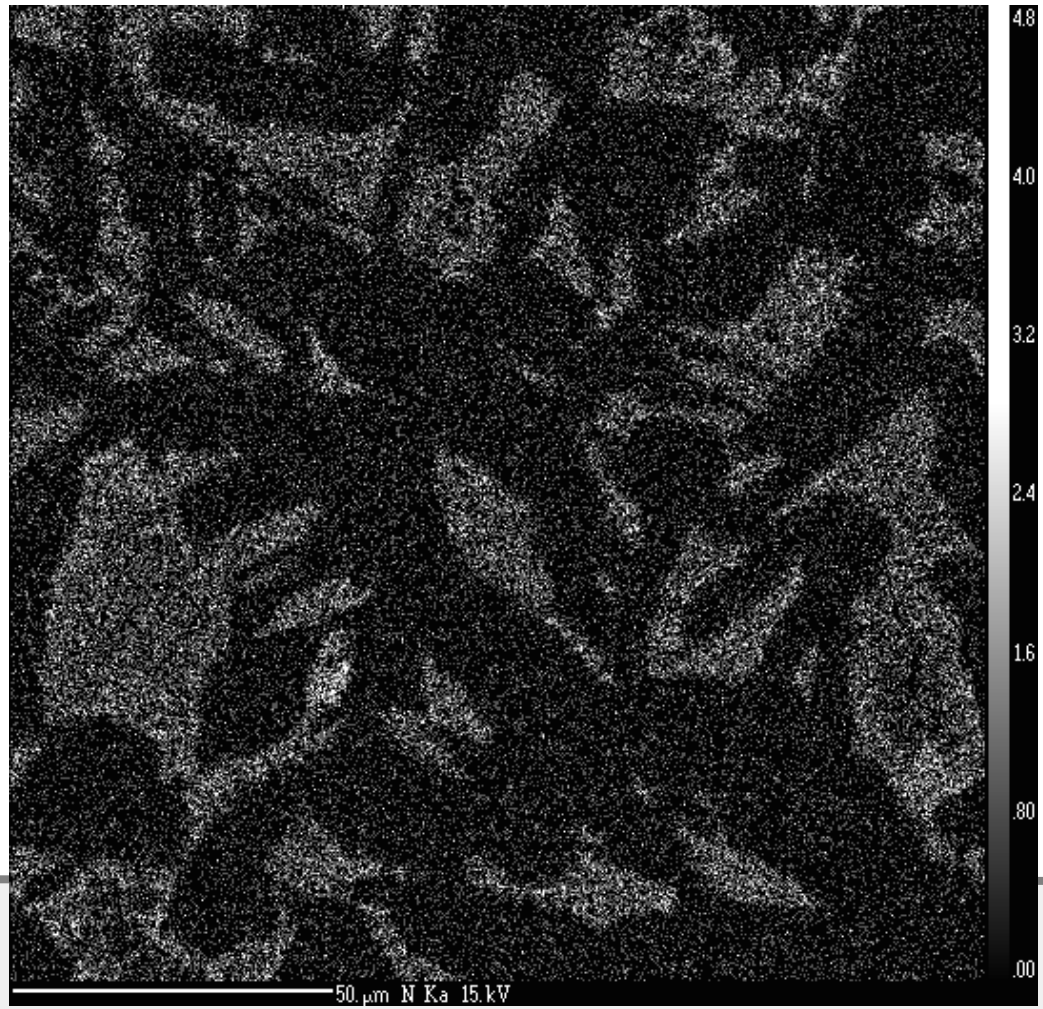


0.2%N, 800°C

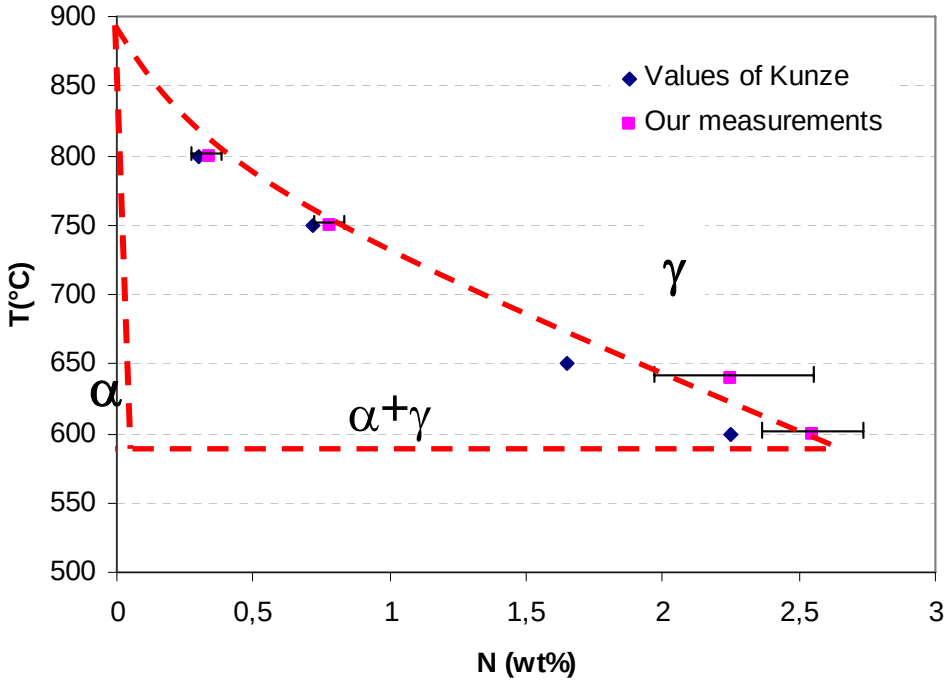


Some results : in the $\alpha+\gamma$ phase region

Micro probe
X image ($K\alpha$)
N=0.5 wt%
T=600°C



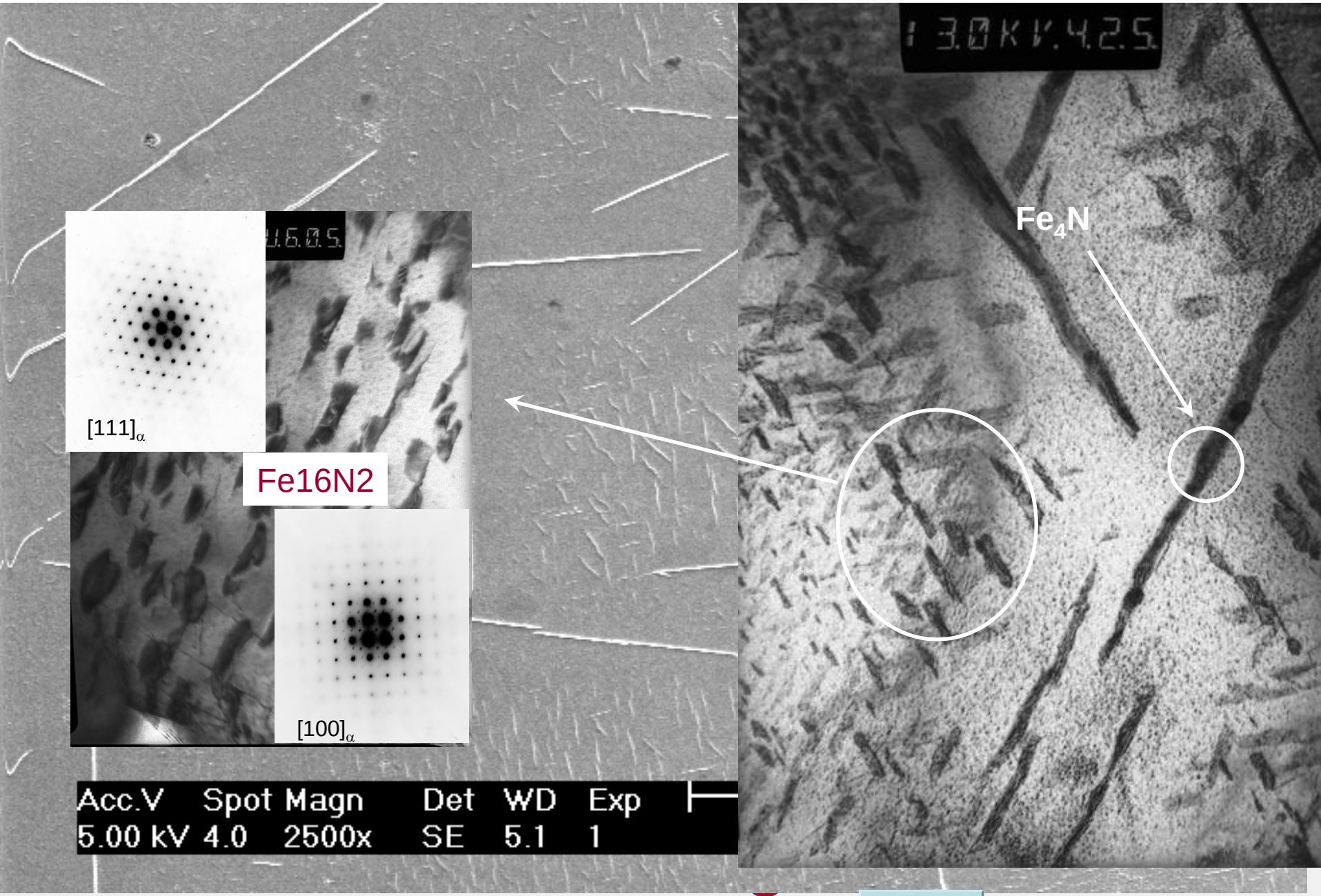
Some results : in the α+γ phase region

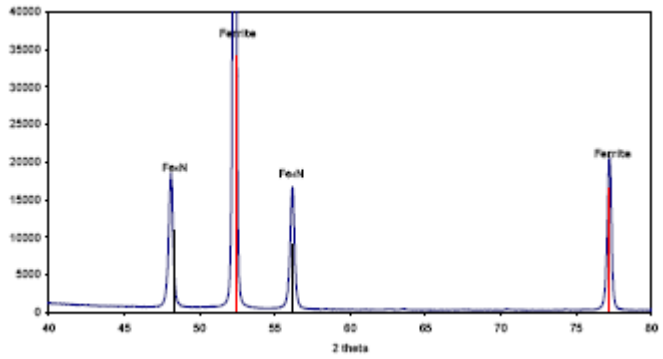


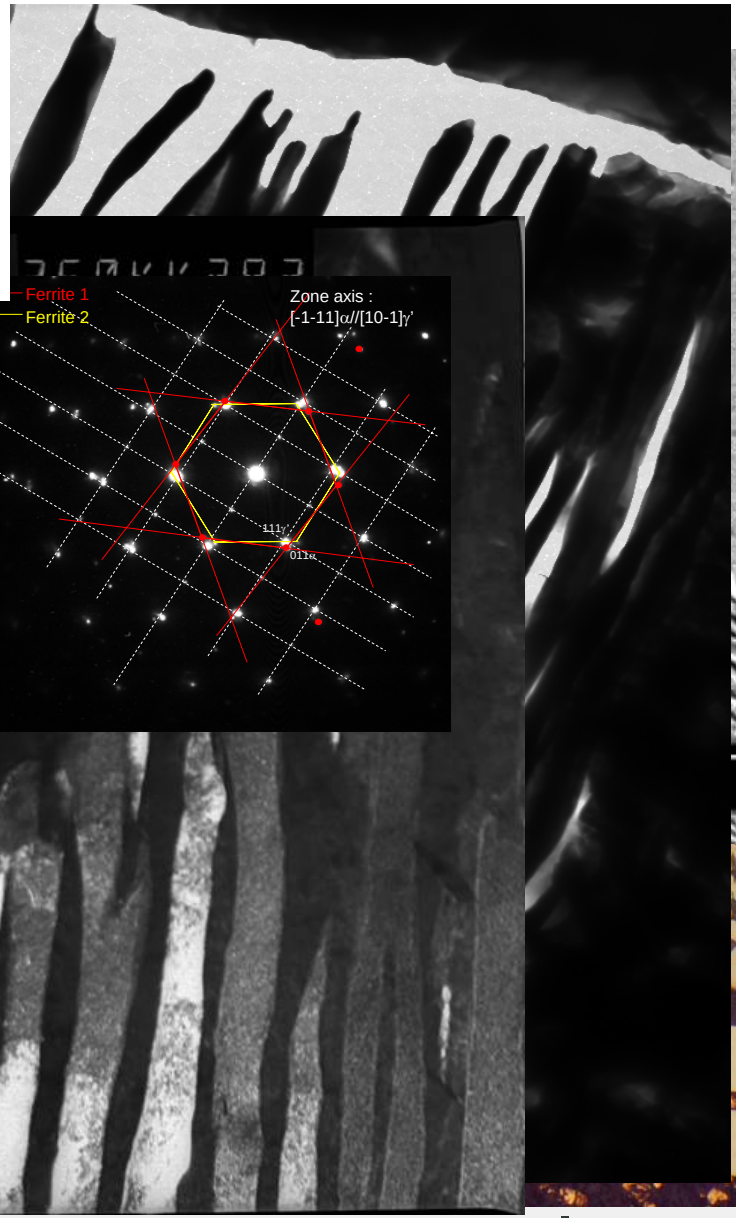
$$G_m = \Sigma X_i^0 G_i - TS_m^{ideal} + {}^E G_m$$

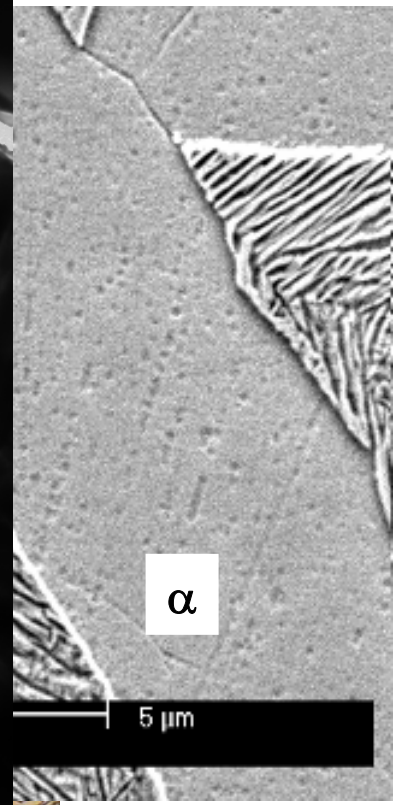
$$G_m^\varphi = y_N^\varphi G_{Fe:N}^0 + y_{Va}^\varphi G_{Fe:Va}^0 + cRT(y_N^\varphi \ln y_N^\varphi + y_{Va}^\varphi \ln y_{Va}^\varphi) + y_N^\varphi y_N^\varphi {}^0L_{Fe:N,Va}$$

→ -20000-6,1×T (J/mol)

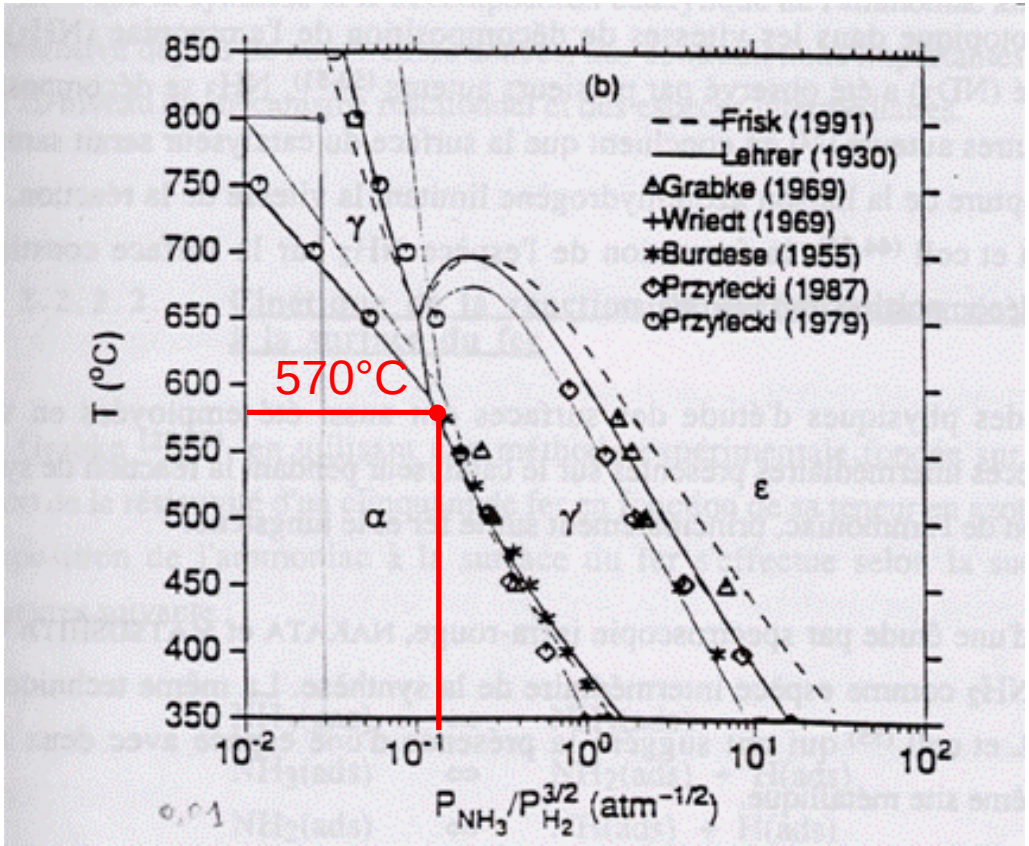

[111]α
Fe16N2
[100]α
Acc.V Spot Magn Det WD Exp
5.00 kV 4.0 2500x SE 5.1 1
Fe4N





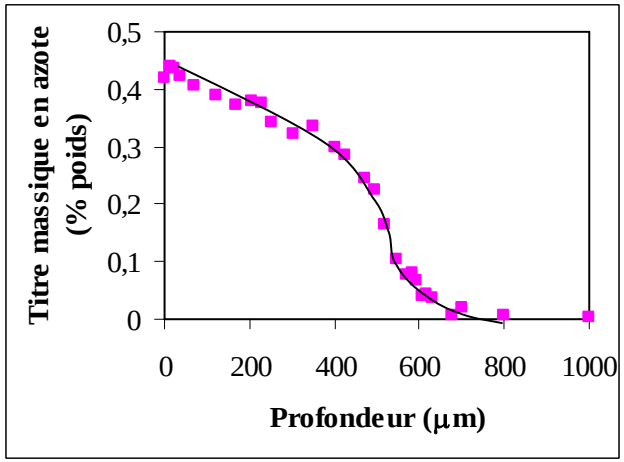


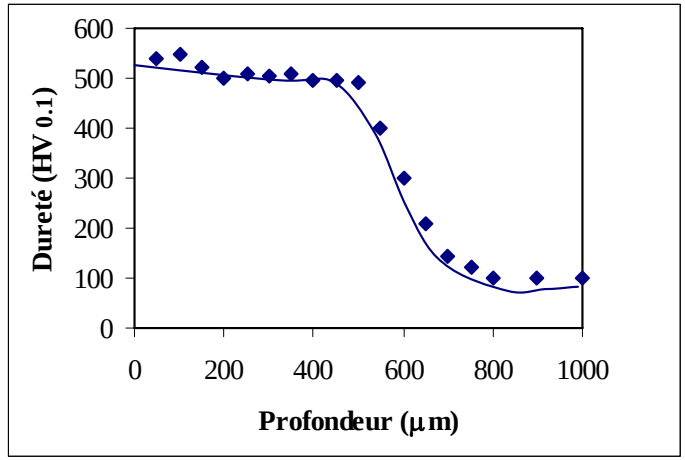
On precipitation in ferrite



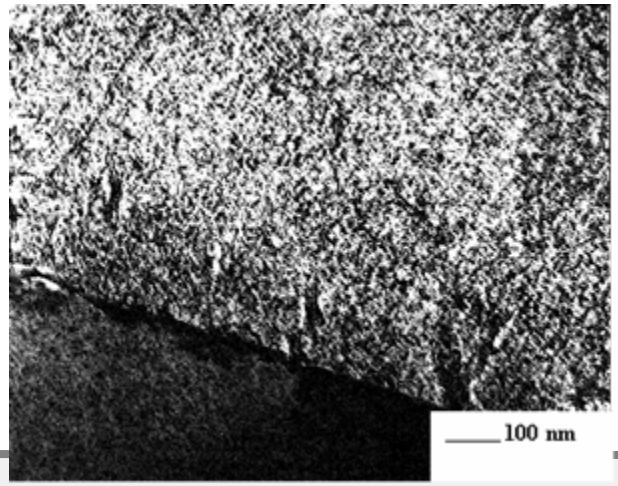
On precipitation in ferrite : Fe-0.5wt%V-N

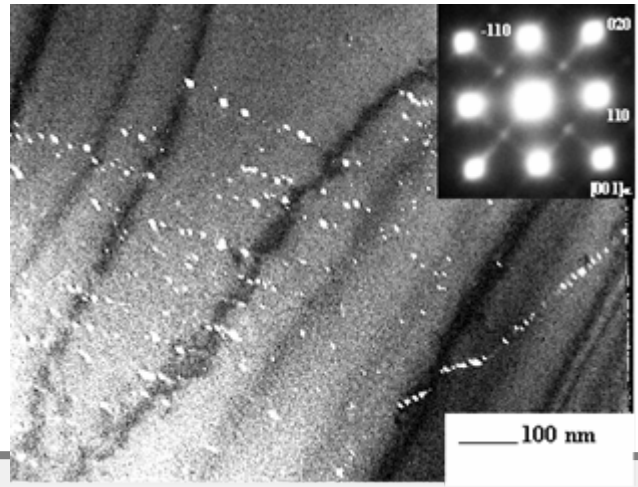
T=843K, t=4h





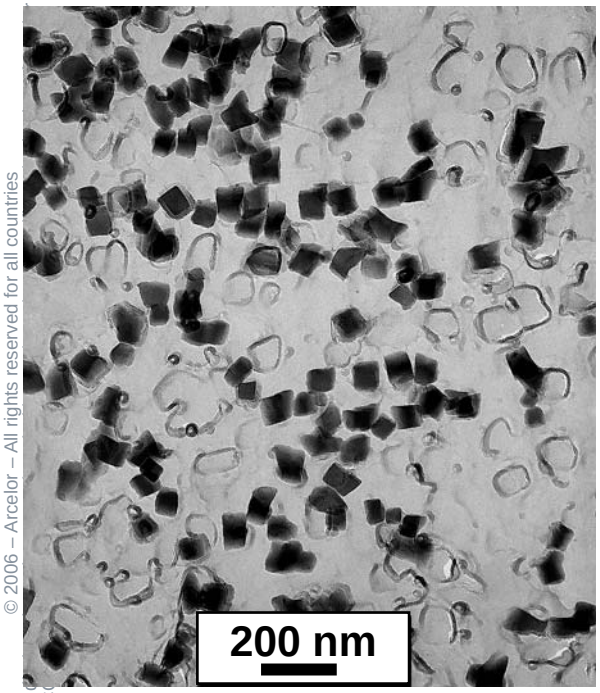
Nano precipitation of VN

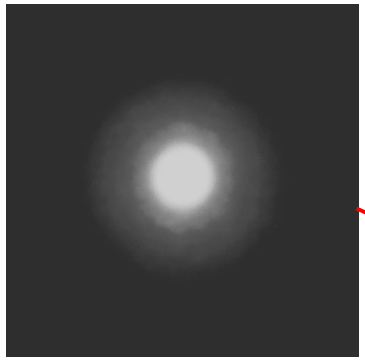


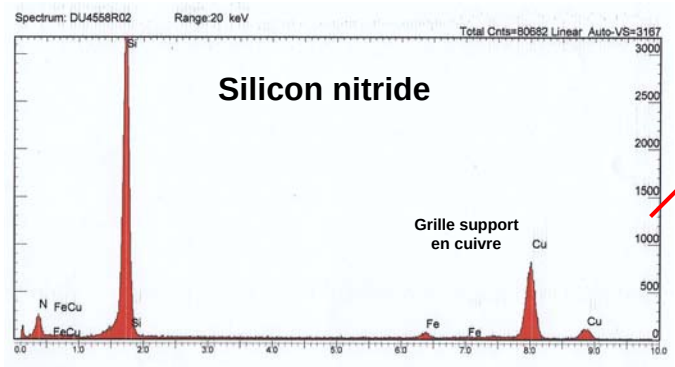


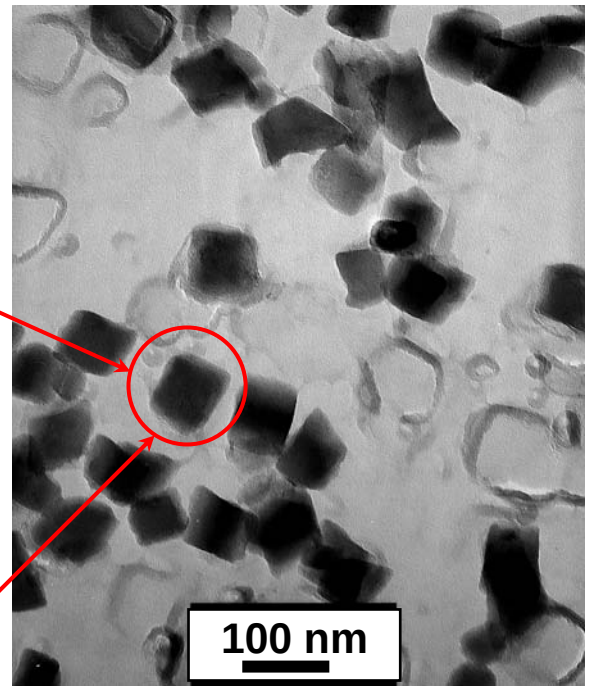
On precipitation in ferrite : Fe-1wt%Si-N

HV=320









Amorphous nitride with a cubic geometry !!!!

CONCLUSION

- High amount of nitrogen (>0.2 mass%) has been introduced in pur iron and homogenously distributed in the matrix
- Richness of the phase transformations in the Fe-N system :

  → Formation of Fe4N and Fe16N2 from supersaturated ferrite

  → Eutectoid type transformation (« nitrogen pearlite » = α + Fe4N)

  → Formation of ferrite into lamellar Fe4N during cooling

  → Formation of a Dual Phase microstructure (ferrite + martensite)

  → Precipitation phenomenon lead to a high power of strengthening
- To be done :

Kinetics of phase transformation

Resulting mechanical properties