Durcissement des aciers inoxydables ferritiques : Thermi-SNT

47ème Congrès A3TS - Marseille 2021

High Temperature Nitriding of Ferritic Stainless Steels : Thermi-SNT

THERMI-LYON Groupe

→ THERMI-LYON GROUP

160
EMPLOYEES

+20 M€
CONSACRETED INNOVATION AND INVESTMENT OVER THE LAST 4 YEARS

23 M€
IN TURNOVER

+ 5 000
CUSTOMERS

100 %
QUALITY-CERTIFIED SITES

THERMI-LYON has been able to adapt to changes in its markets by diversifying its scope. Today, the group is a reference in heat treatment and vacuum coatings.

→ 8 national sites
→ 1 international site

→ Outline

- Context and Background
- Key parameters and inputs
- Simulation
- Characterisations
- Conclusion

➔ Context

- Market expectation :
  - Stainless Steel + Abrasive and Adhesive Wear Resistance
- Solutions :
  - Use **martensitic stainless steel** in the hardened state – But corrosion resistance is sometimes not sufficent for some applications
  - Use **austenitic or ferritic stainless steel** in work-hardened state – But wear and adhesive wear resistance is not sufficient for most of applications.
  - Perform a **surface hardening** by a **thermochemical treatment** under conditions preserving the corrosion resistance :
    - For austenitic steels : Low T° Nitrocarburizing = Thermi®-SP
    - For martensitic or ferritic steels : High T° Nitriding = Thermi®-SNT

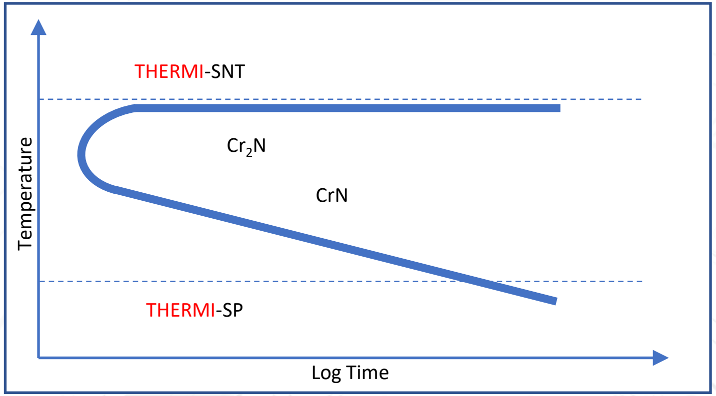
➔ Background

- The first works on the "Solution Nitriding" process was published in 1994 by Hans Berns (Ruhr-Universität, Bochum, D).
- Commercial communications by the furnace supplier Ipsen on this treatment (branded Solnit©) have been found for about 15 years.
- Thermi-Lyon is equipped with IPSEN furnaces incorporating this technology. For the consistency of its treatment range, Thermi-Lyon has named this treatment Thermi©-SNT

- The purpose of this talk today is to describe the approach used to control this process available on the market and the results obtained.

➔ Key Parameters

- The corrosion resistance of stainless steels is based on their ability to form a passive layer based on oxidized chromium.
- The surface enrichment in N requires activating the steel surface by first reducing the passive layer.
- The treatment conditions must then be chosen so as to avoid the precipitation of chromium nitrides which, if they form, consume the free chromium responsible for the passivation.

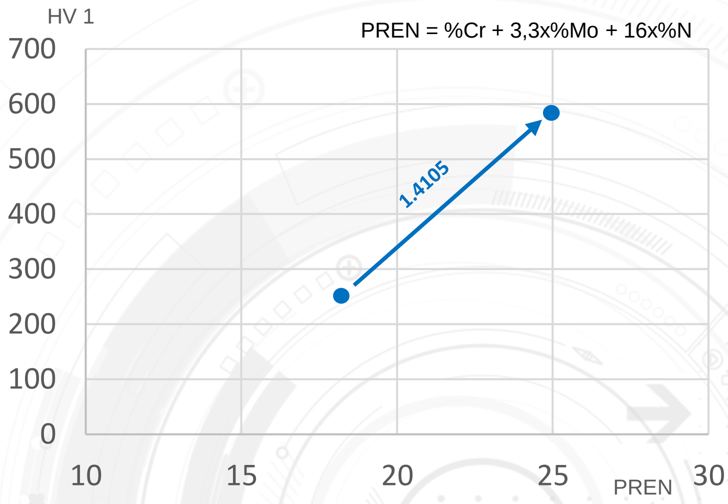


- Once enriched, controlling the cooling conditions and the re-passivation of stainless steel guarantee good corrosion resistance.

➔ Inputs to treat Ferritic Stainless Steels

- Thermi©-SNT Process T° range is 1050-1200°C
- T° is high enough to dissociate molecular N_2 into atomic nitrogen N
- N diffusion brings about a local ferrite **transformation in austrenite**.
- During the fast cooling, Austenite is transformed to **Nitrogen Martensite** that leads to surface hardening

- Topic today is to adjust treatments parameters to the **steel grade 1.4501 (AISI 430F - X6CrMoS17)**



Thermo-Calc Simulation

All calculations were carried out by the LMI Labs at Claude Bernard University, Lyon

- **CalPhaD Méthod** (Calculation Phase Diagram)
  - Free Gibbs Enegry (G) calculation f (T°, P, steel Composition).
  - Adjusting G to a minimum value to identify the more stable states and to construct the equilibrium diagram
- Databases used are TCFE8 and TCFE10
- Nitrogen activity is calculated for several N_2 partial pressures
- Thermodynamic equilibrium between the gas and the solid is assumed to be obtained
- Diagrams ploted are : %N mass = f(activité) and %N mass = f(P_{N2})

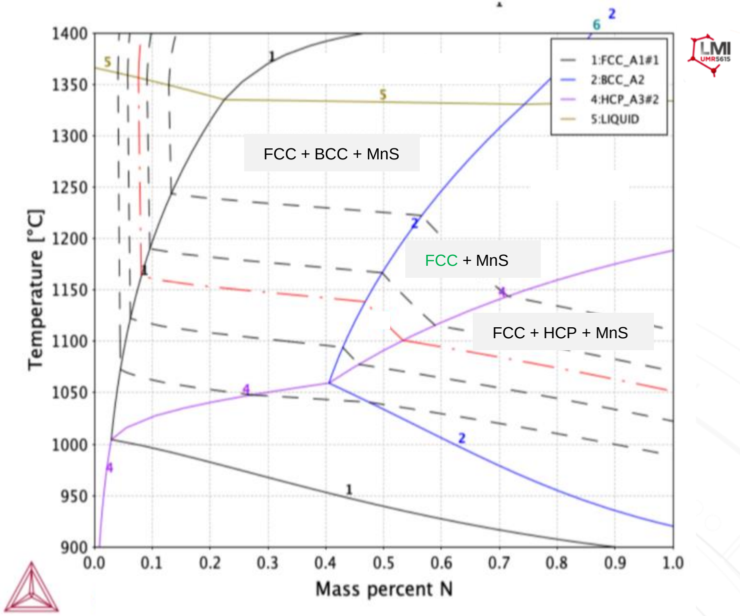
→ Composition and Equilibrium Diagram

Steel batch n°1

1.4105 / AISI 430F	%C	%Si	%Mn	%P	%S	%Cr	%Ni	%Mo	%Fe
X6CrMoS17 **NF EN 10088-3**	0.08 max	1.50 max	1.50 max	0.040 max	0.15-0.35	16.0-18.0	-	0.20-0.60	Bal.
X6CrMoS17 **COMPO 1 étudiée**	0.005	1.214	0.505	0.020	0.278	17.44	-	0.273	Bal.

1.4105 Chemical composition Batch n°1 (mass%)

Both T° and N_2 Pressure must be chosen to be correctly positioned in the diagram in order to obtain 100% FCC and to avoid the precipitation of chromium nitride.



Vertical section (T, %m N, pN2) 1.4105 – Batch n°1

FCC = austenite / HCP = CrN / BCC = ferrite / MnS = Manganese Sulphide

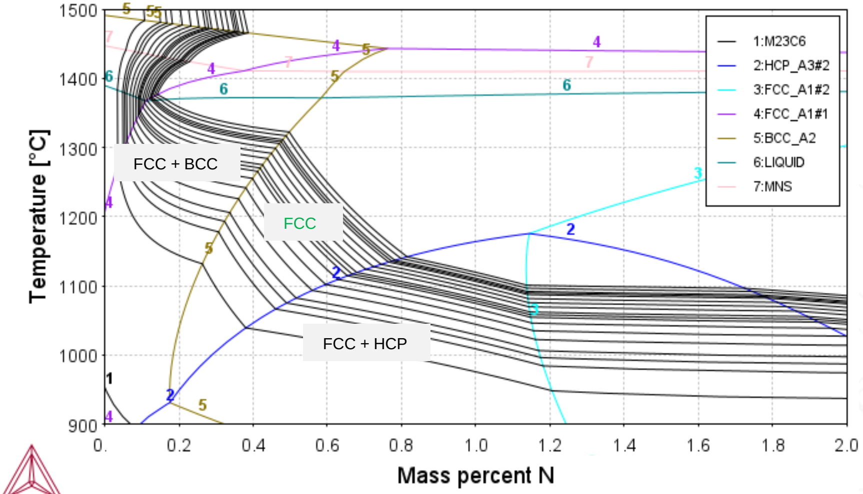
➔ Composition and Equilibrium Diagram

Steel batch n°2

1.4105 / AISI 430F	%C	%Si	%Mn	%P	%S	%Cr	%Ni	%Mo	%Fe
X6CrMoS17 **NF EN 10088-3**	0.08 max	1.50 max	1.50 max	0.040 max	0.15-0.35	16.0-18.0	-	0.20-0.60	Bal.
X6CrMoS17 **COMPO 1 étudiée**	0.005	1.214	0.505	0.020	0.278	17.44	-	0.273	Bal.
X6CrMoS17 **COMPO 2 étudiée**	0.064	0,523	0,684	0,020	0,280	16,17	0,183	0,226	Bal.

1.4105 Chemical composition Batch n°2 (mass%)

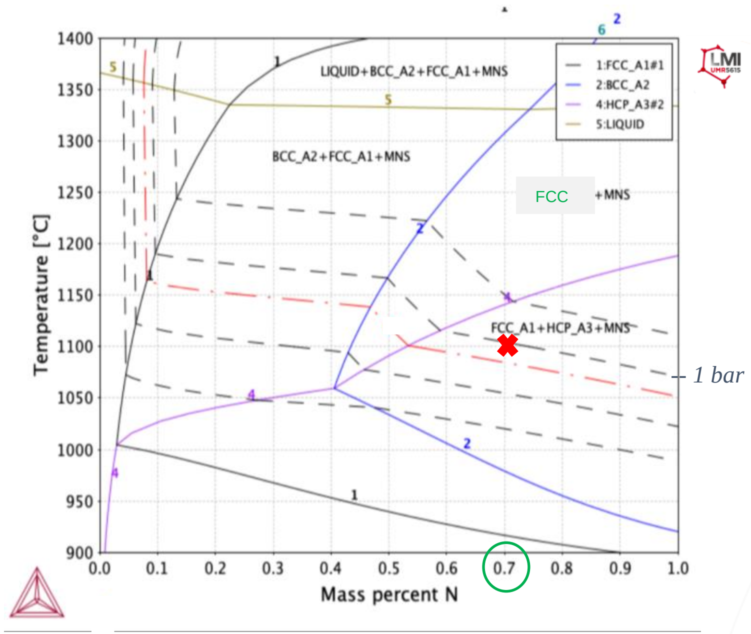
The difference in composition leads in a significant shift in the bondaries between domains.



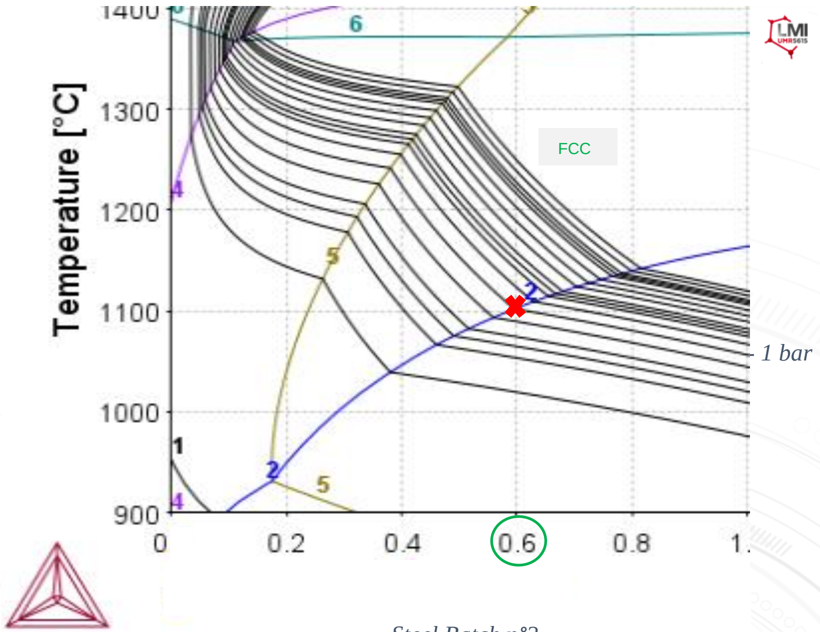
Vertical section (T, %m N, pN2) 1.4105 – Batch n°2

FCC = austenite / HCP = CrN / BCC = ferrite

➔ Diagram comparison



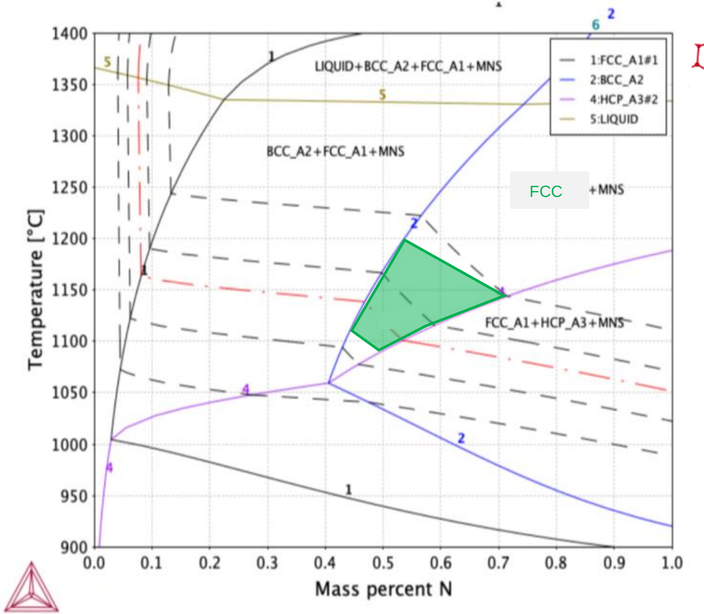
Steel Batch n°1



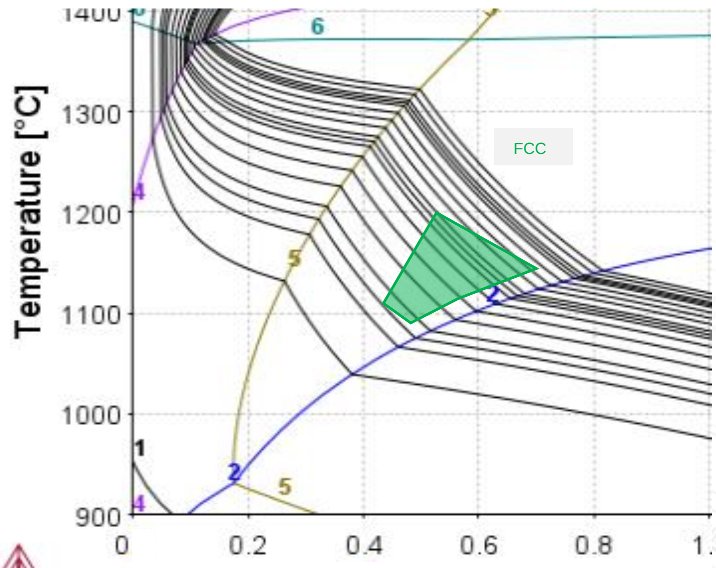
Steel Batch n°2

FCC = austenite / HCP = CrN / BCC = ferrite / MnS = Manganese Sulphide

➔ Thermi©-SNT parameters compatible with both comp.



Steel Batch n°1



Steel Batch n°2

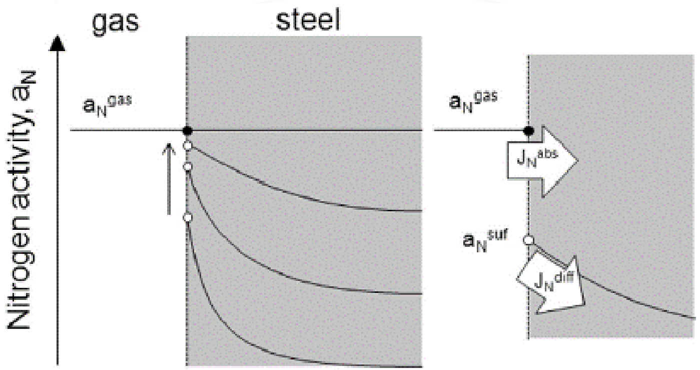
FCC = austenite / HCP = CrN / BCC = ferrite / MnS = Manganese Sulphide

→ Prediction of Diffusion Profils vs Time

- N diffusion is driven by Fick's Laws

- Activity as a flux function is a more accurate approach than a fixed activity. (Ref. Nakada, Kyushu University, Japan - 2014)

→ $J_N^{abs} = k\rho(a_N^{gaz} - a_N^{sur}) = f(a_N^{gaz} - a_N^{sur})$



Avec $f = k\rho = 1.10\text{-}8\ mol/m^2\ s$

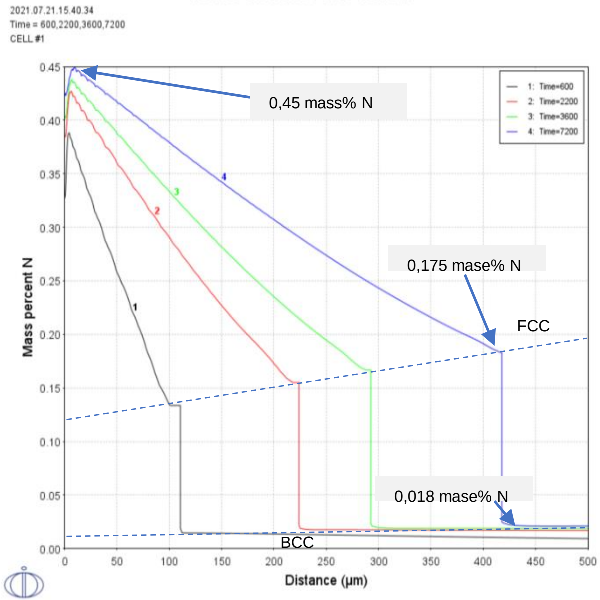
K = mass transfert coefficient (m/s) and ρ = the density of the steel (mol/m^3)

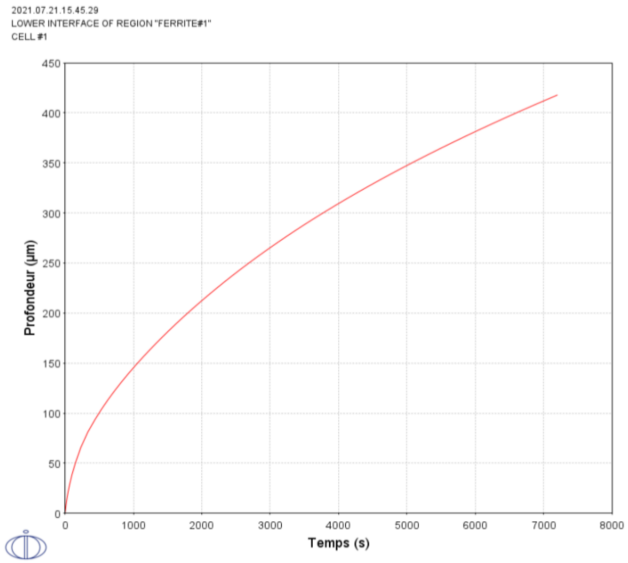
To predic the diffusion depth as a function of Thermi©-SNT conditions, calculation is performed using DICTRA software and the Database MODFE2

→ Dictra Predictions

Thermi©-SNT parameters (T° and N_2 pressure) optimised for 1.4105

The vertical line = interface between FCC and BCC phases





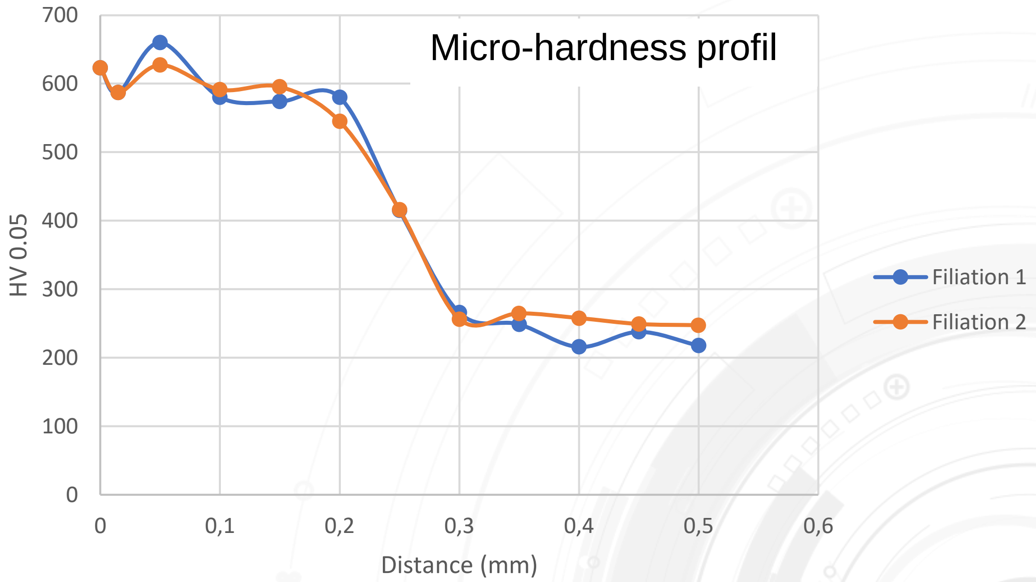
→ Characterisation after Thermi©-SNT

- Samples were caracterised by
  - Hardness measurment (Superficial and Core)
  - Microhardness profils
  - Optical Microscopy observations
  - X-Ray Diffraction

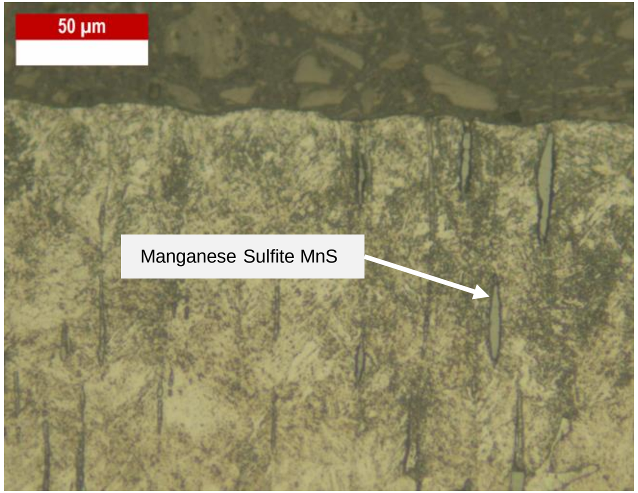
- Properties were evaluated by
  - Cyclic Voltametry for the corrosion behavior
  - ASTM G196 for the adhesive wear

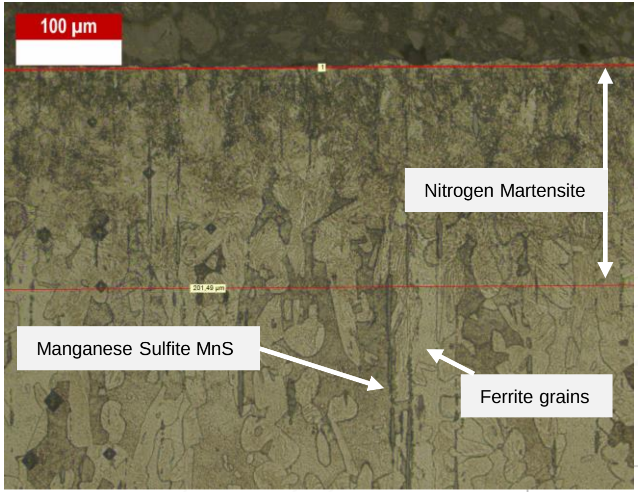
➔ Hardness and Thickness

HV0,05 sup	HV1 sup	HV10 cœur	Profondeur de filiation (µm)	Profondeur théorique par Dictra (µm)
623	588	261	277	226

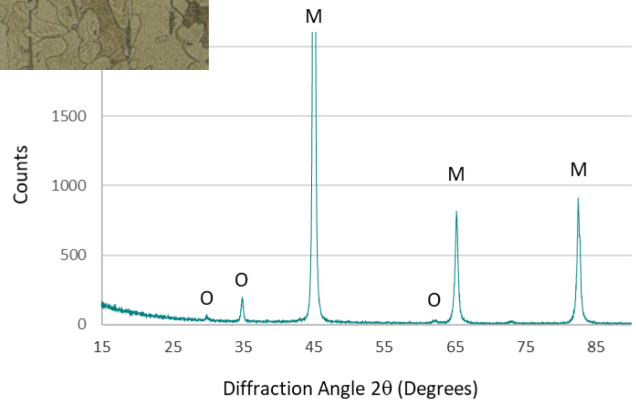


➔ Typical Surface Microstructure





Etching : Aqua Regia.



No Chromium Nitrides observed

→ Core Microstructure

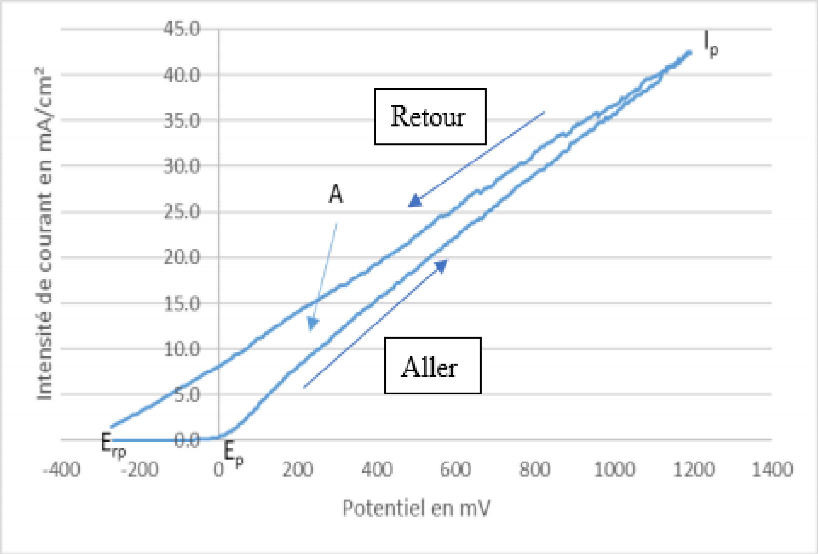
Comparison of core microstructures before and after treatment :

→no grain growth observed

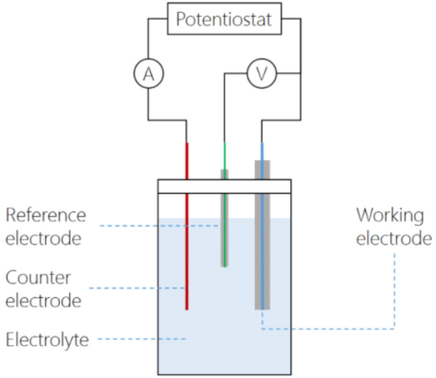
Core microstructure before treatment

Core microstructure after treatment

➔ Cyclic Voltametry



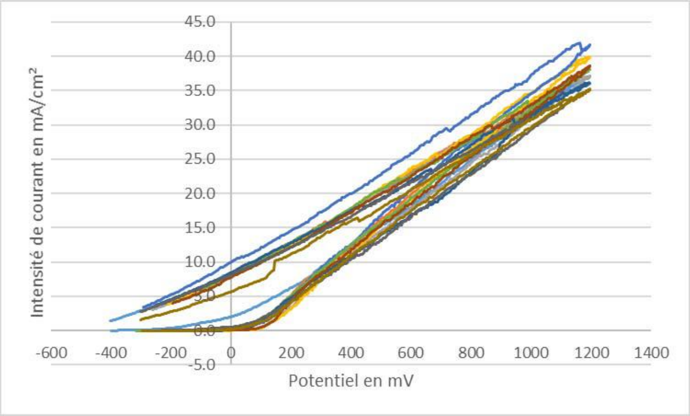
Exemple of curves obtained by cyclic voltametry



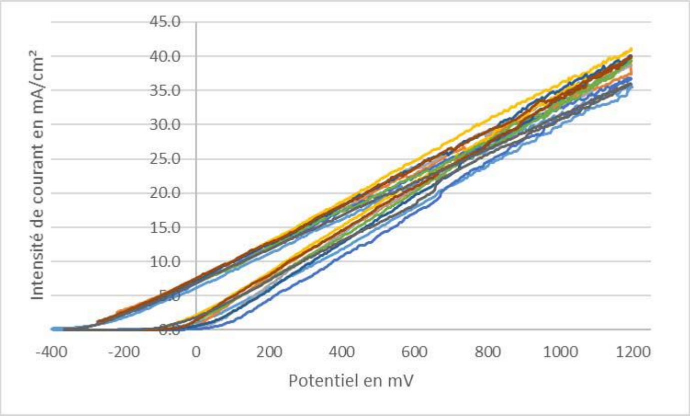
- *Potential Ep : Start of pitting*
- *Intensity Ip : proportional to the number of pits or their severity*
- *Potential Erp : when pits are neutralized*
- *Area A : the weaker A, the stronger pitting resistance*
- *Slope Ep - Ip represents the corrosion kinetics*

→ Cyclic Voltametry

- Thermi©-SNT samples are slightly more resistant to pitting than untreated ones
- Pitting Potential Ep is similar but with half less extensive values
- The corrosion kinetics is slightly lower after treatment



Before treatment



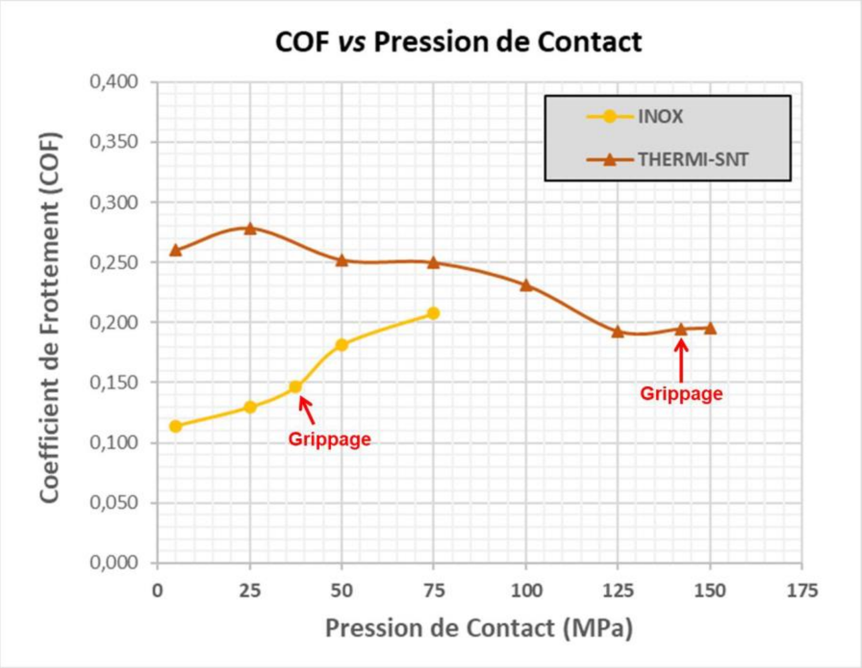
After treatment

→ Adhesive Wear Evaluation

- ASTM G196 Conditions

	Valeur / Description
Contact	Plan / Plan (Pion /Disque) Pion en INOX non revêtu Disque à tester en INOX, sans et avec Traitement de surface
Mouvement	Rotatif continu (1 Tour)
Pression de contact	De 5 MPa à 400 MPa
Vitesse de rotation	6 RPM
Durée de l'essai	10 s
Température	Ambiante (23 °C)
Lubrification	Contact sec

Palier de Grippage				
	Essai – 1	Essai – 2	Essai – 3	Moyenne
Inox non traité	25 MPa	50 MPa	-	37,5 MPa
Thermi-SNT	150 MPa	125 MPa	150 MPa	142 MPa



→ Conclusions

- There is a good constistency between simulation and observation
- Simulation saves time and is guaranteed in terms of safe treatment parameters
- Improvement of the steel grade 1.4105 observed after Thermi©-SNT treatment :
  - Superficial hardness is 2,5 time higher than untreated parts
  - Corrosion resistance is sligtly improved
  - Adhesive wear resistance is improved by a factor of 4
  - Core microstructure is preserved from grain growth

Merci pour votre attention

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