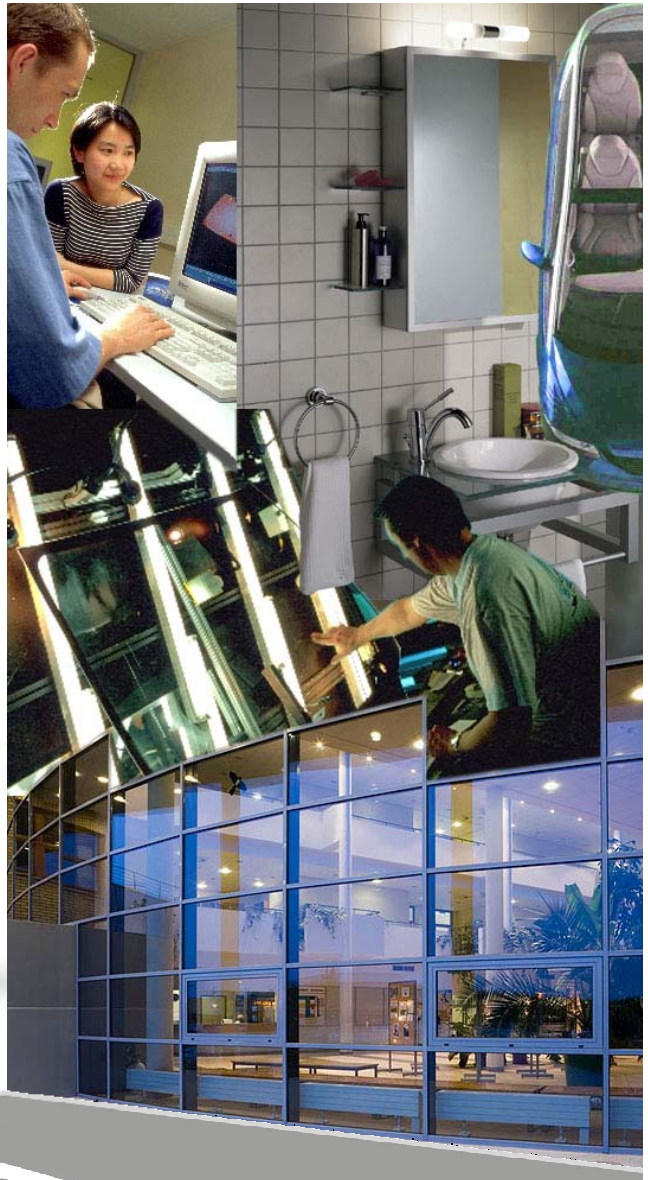
# Phase Transformations of NiS in Tempered Glass.

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SAINT-GOBAIN

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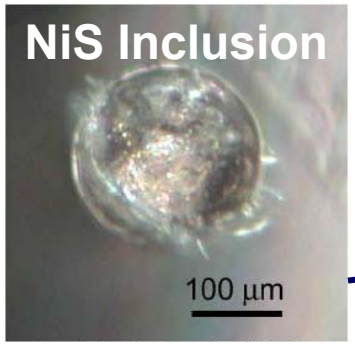
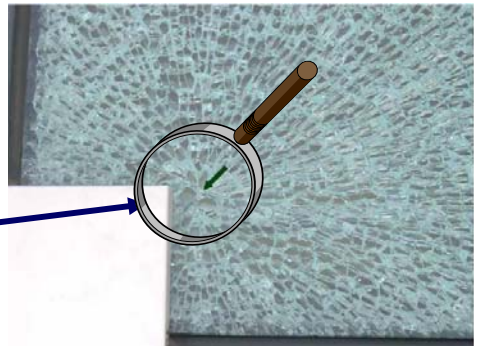
# Industrial issue : Nickel Sulfides & delayed fracture of tempered glass



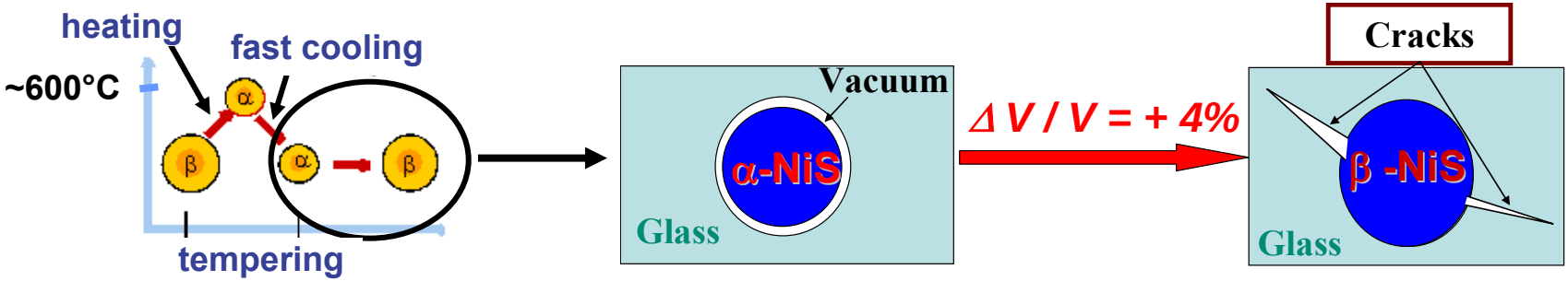



## ➢Inclusion in glass:

- ➢Non soluble in the vitreous matrix
- ➢Origin: Nickel and Sulfur impurities (raw materials, handling and transport)
- ➢Rare: 1inclusion/300m$^2$ (size : 50-600µm)

## ➢Metastable

- **Mechanism : In tempered glass NiS inclusion + phase transformation➔ fracture!!**

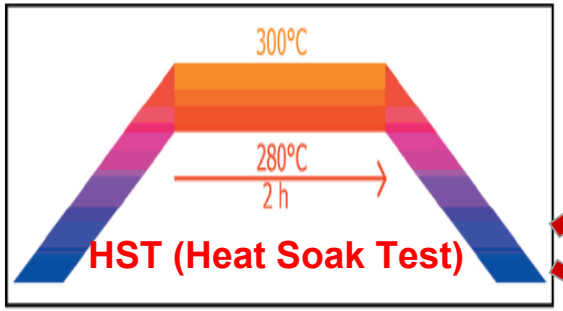


## ➤ Delayed fracture ➔ dangerous on site:

➔ **Strategy:** provoke the α➔β-NiS transformation by accelerating heat treatment before mounting

## ➤ Industrial solution: destructive test to eliminate defective glasses

Tempered glass with NiS inclusion??? ➔




Fractured glasses

Glasses 'without' NiS

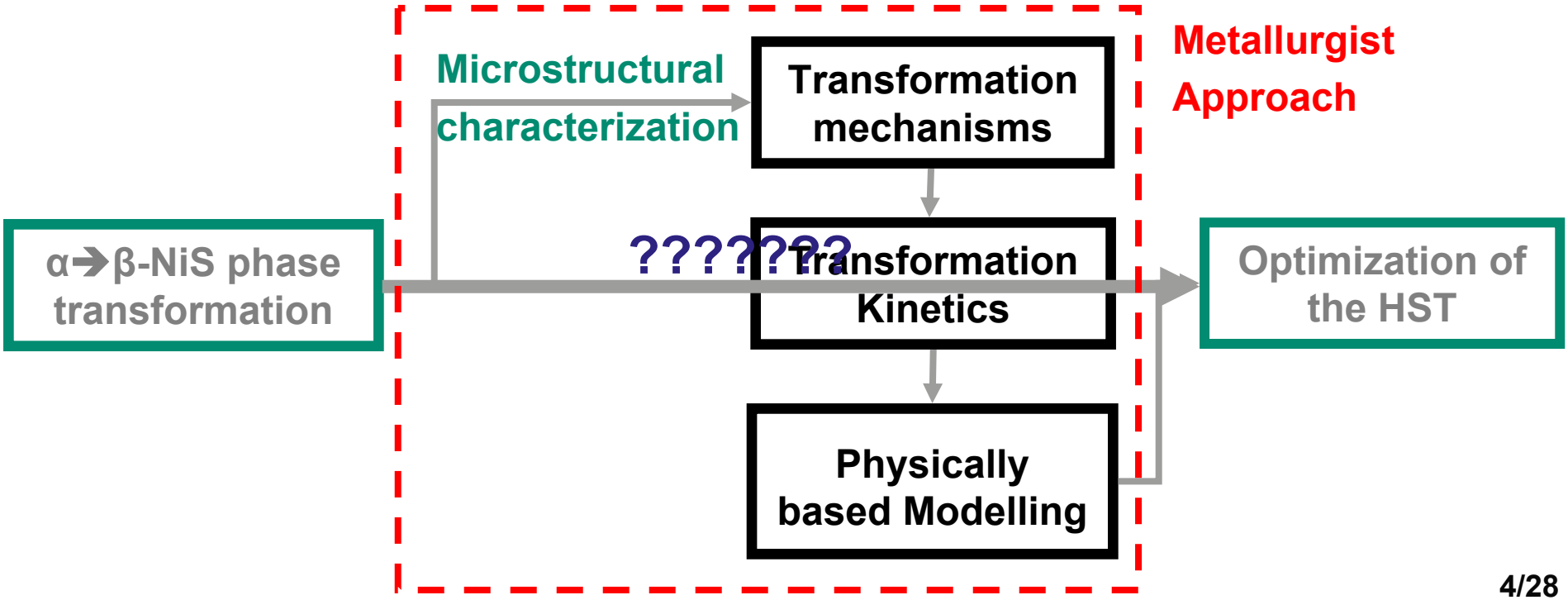
**Thesis: study of the α➔β-NiS phase transformation**

Applicative goal: optimize the HST for better efficiency and lower cost

## Today's industrial approach:

- Global information (DSC-RX)
  used to define the HST
- Limits: range of the inclusion composition
  what is the relation composition/Temperature/kinetics??
- Goals: a better, safer, cheaper HST

## The proposed strategy: mechanism identification and quantitative study of the kinetics



# Outline:

I. Context

II. α → β-NiS transformation mechanisms:

microstructures & mechanisms

III. α → β-NiS kinetic aspect:

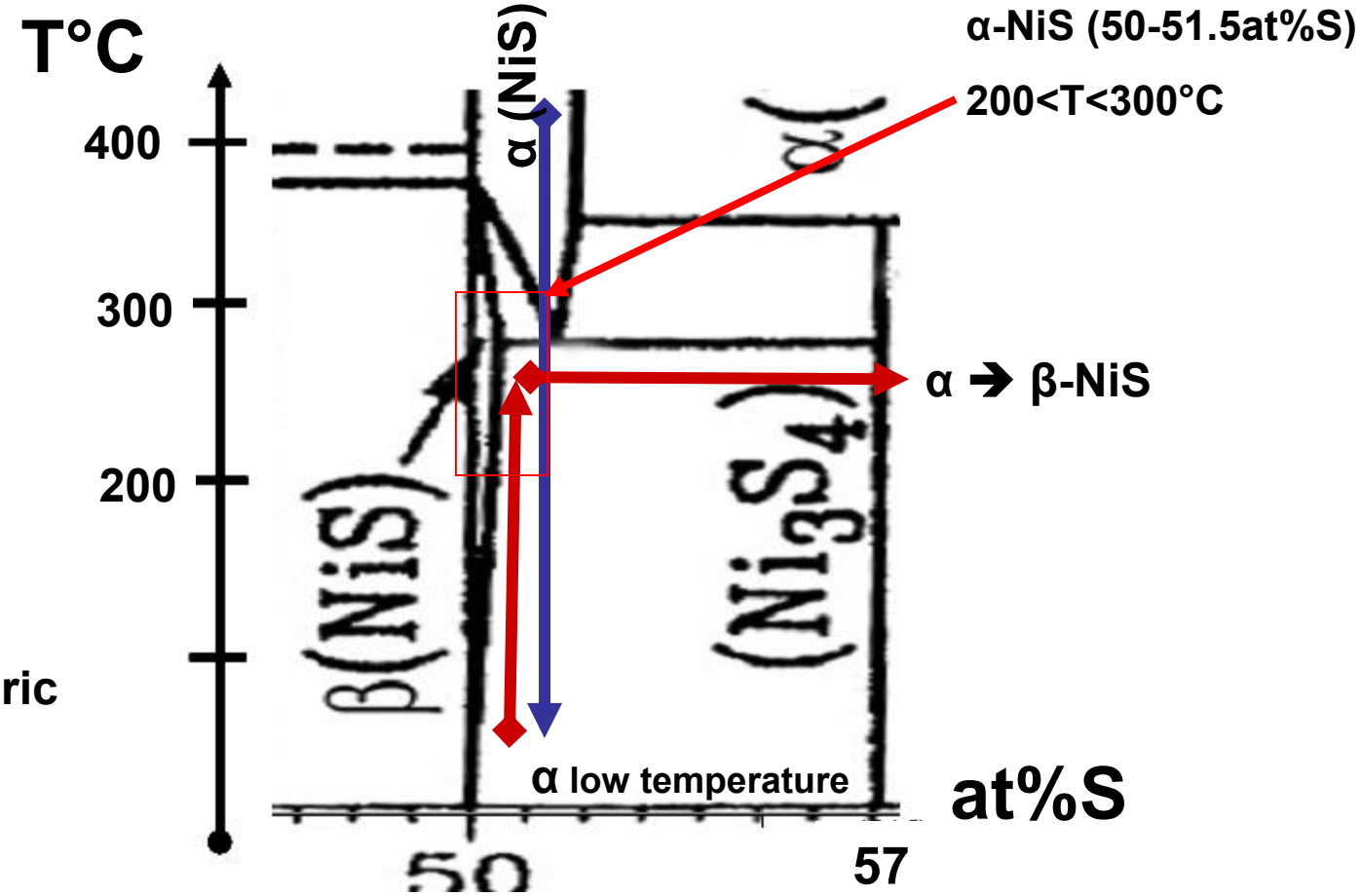
*in situ* observation of phase transformation

IV. α → β-NiS: modelling under isothermal conditions

V. Conclusion and perspectives :

# Mechanisms identification???

**Microstructure=mechanism signature**

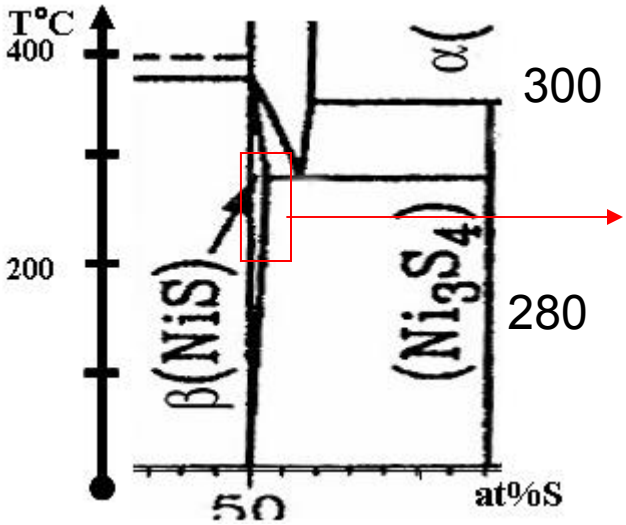



- α: Hexagonal
- β: Rhombohedric
- $Ni_3S_4$: Cubic

Isothermal heat treatment in DSC stopped at various times followed by microscopic (Optical, SEM and TEM) characterization

# Mechanism signature: microstructural aspect

## Effect of temperature and sulfur composition on morphology




Temperature °C

300

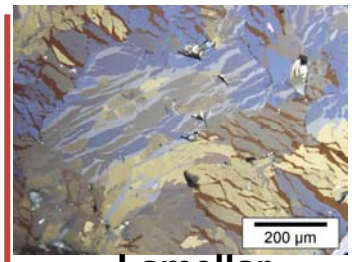
280

200

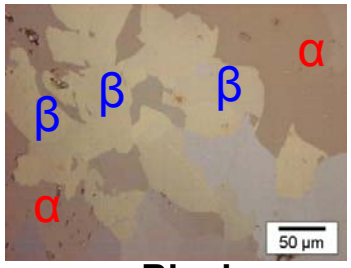
β

β+α

?????

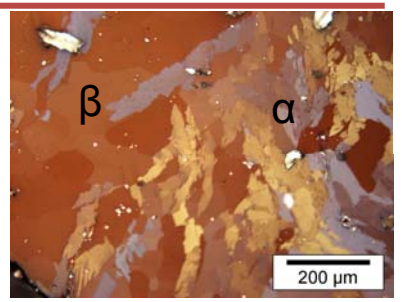



Lamellar



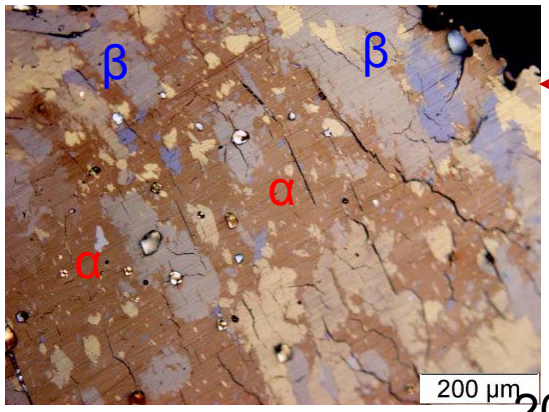

Block

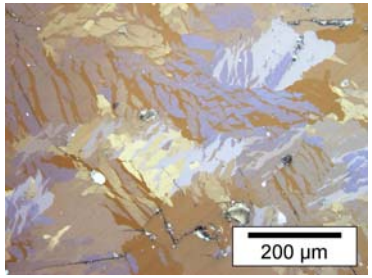
β+$Ni_3S_4$




Coarse lamellar

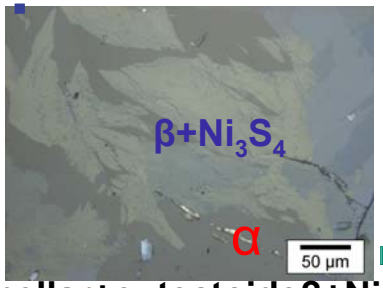
Globular?




Lamellar + $Ni_3S_4$ precipitation at α/β interface

?????




Lamellar+eutectoideβ+$Ni_3S_4$

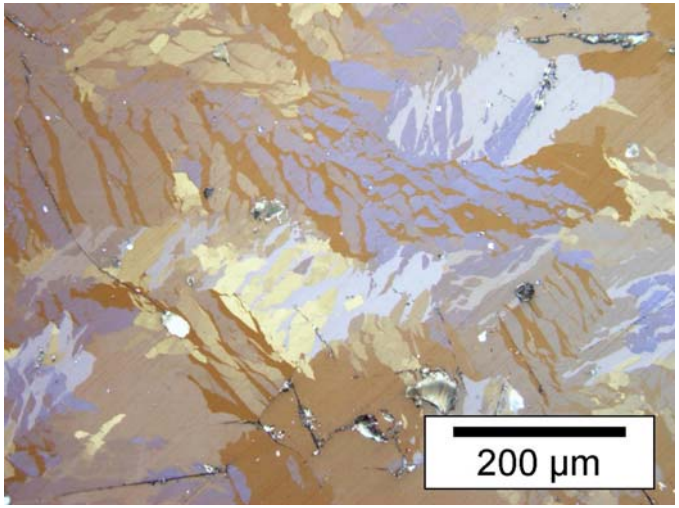
50.3

51.14

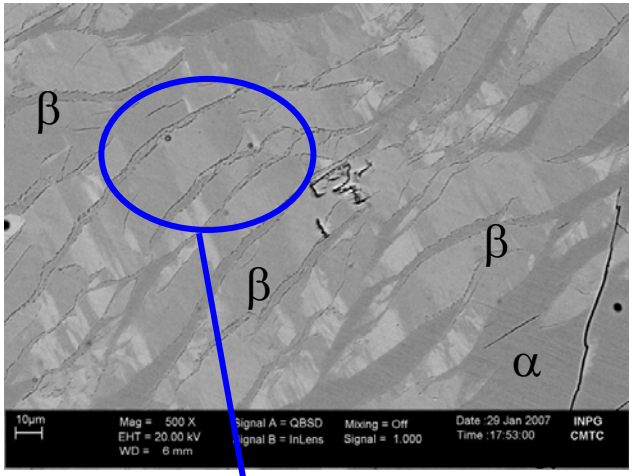
51.28

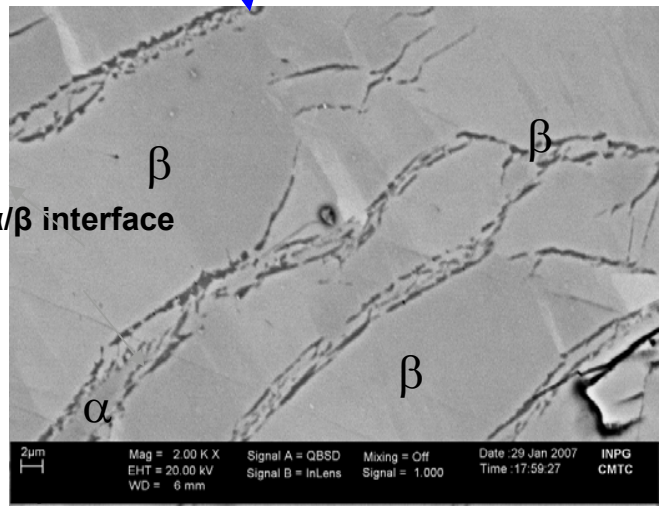
Composition **at%S**

# lamellar morphology:



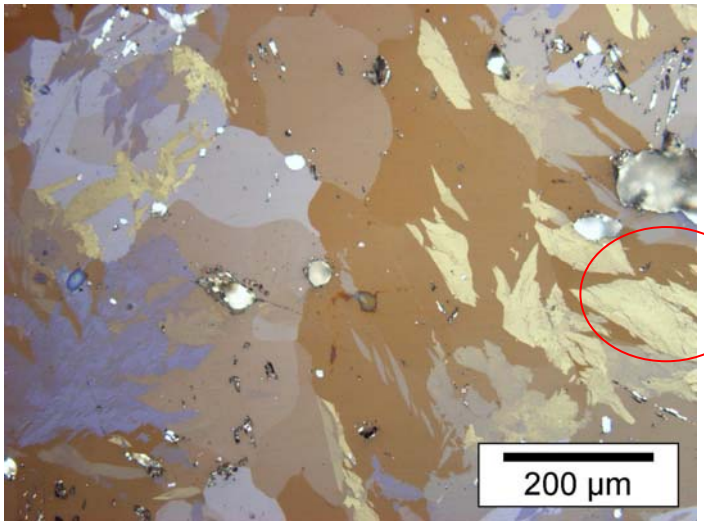

SEM-FEG
**QBSD**

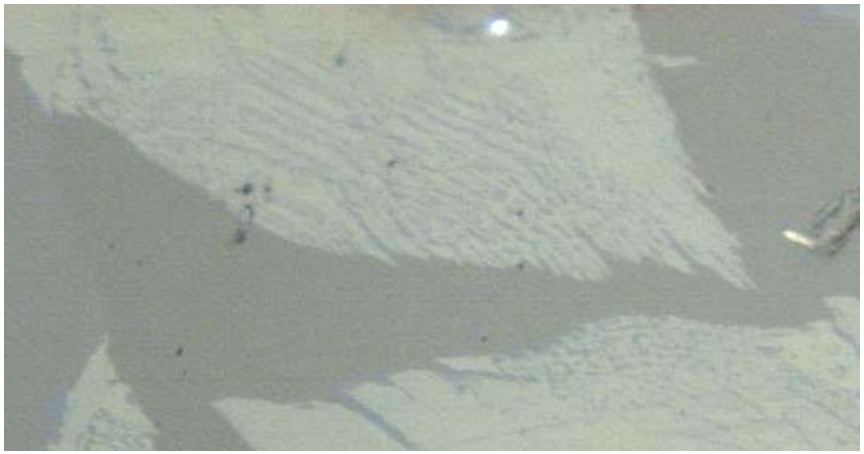


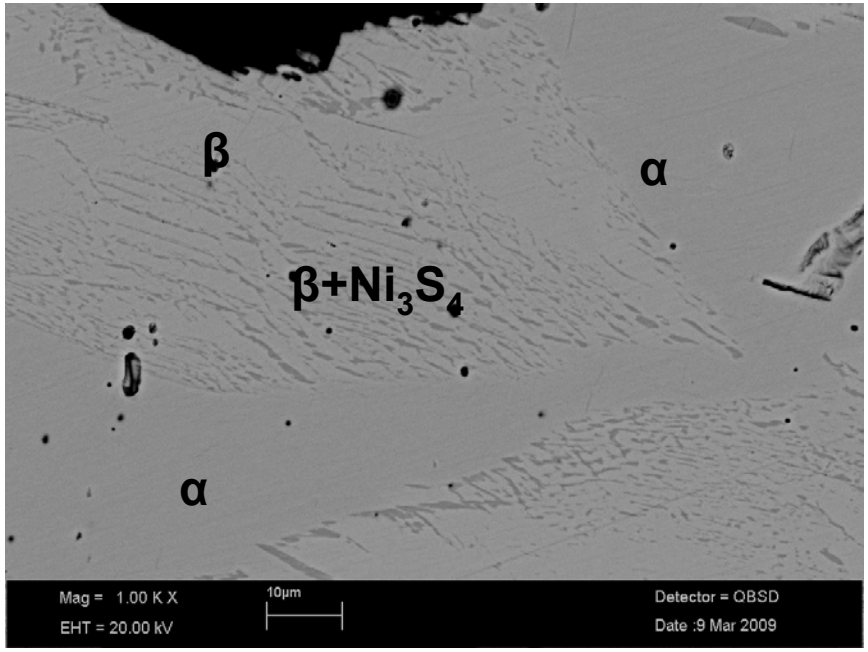

**$Ni_3S_4$ precipitates at α/β interface**

# Eutectoid β+$Ni_3S_4$ for very overstoichiometric sample



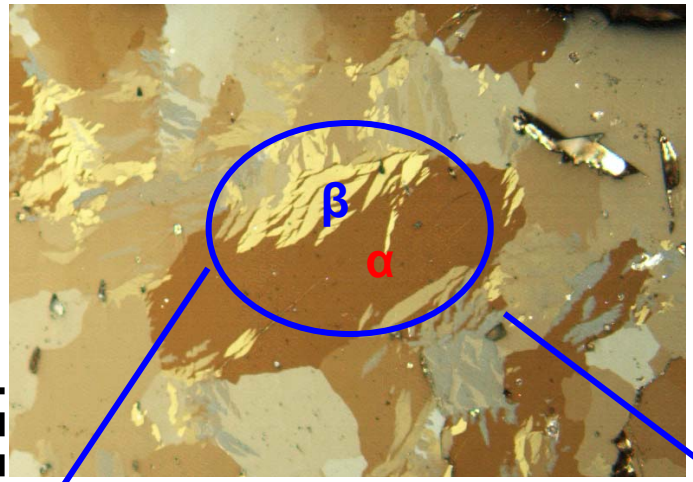



($Ni_{48.72}S_{51.28}$)-200°C-600 min



# Mechanism signature: α-β composition and OR??

**Lamellar morphology**



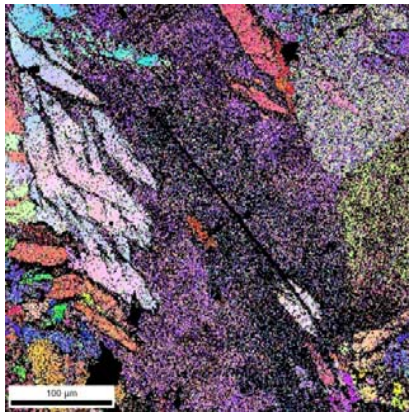

**α/β Composition**

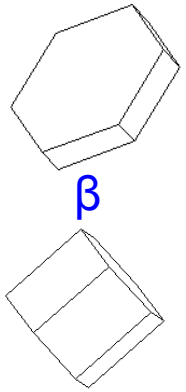
| T (°C) | α | β |
|---|---|---|
| 200 | 50.9 ±0.14 | 50.04 ±0.07 |
| 260 | 50.75±0.08 | 50.07±0.13 |

➢ Cα ≠ Cβ

➢ Long range sulfur diffusion

**α/β Orientation relationship**

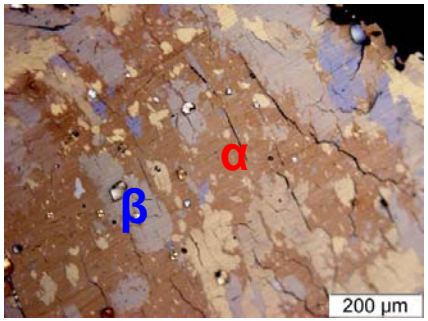




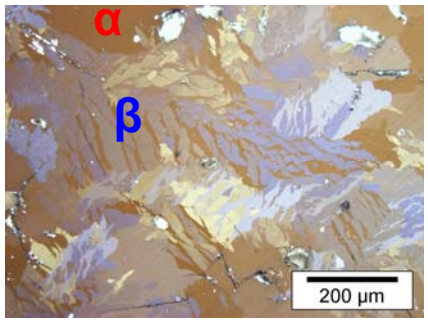

OR: (001)α // (1-10)β; [450]α // [110]β.

➢ β Prismatic plan // α basal plan

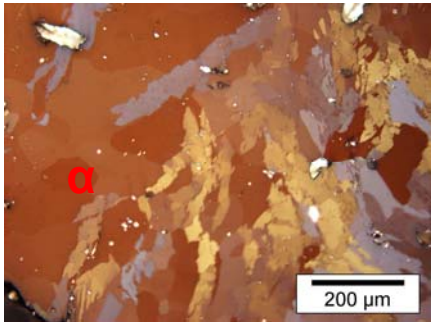
# Mechanism signature: Orientation Relation??



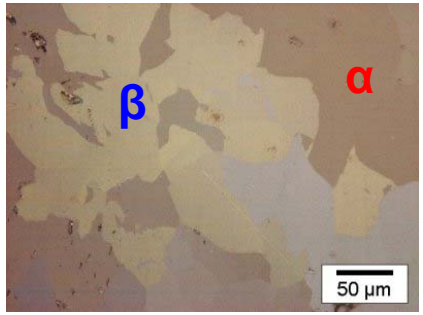

Globular




Lamellar

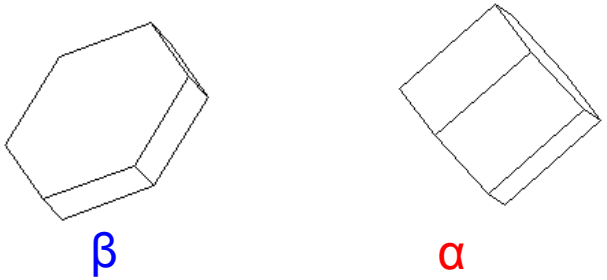



Coarse lamellar

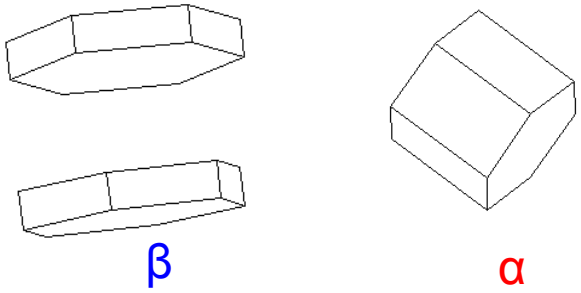



Block

OR: (001)α // (1-10)β; [450]α // [110]β.



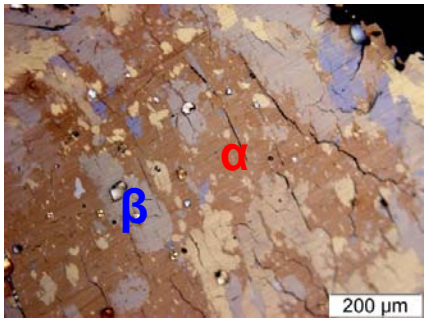

Non similar and undefined OR



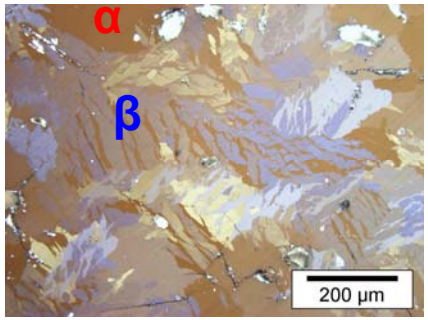

**T and overstoichiometry effect on transformation:**

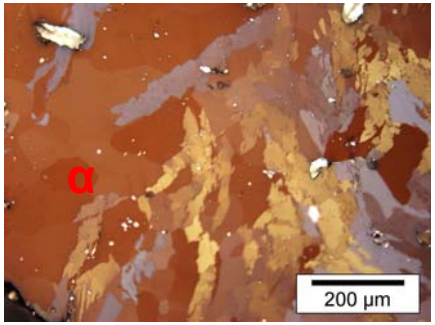
**➔Change of crystallographic aspect**

# Mechanism signature: Composition??



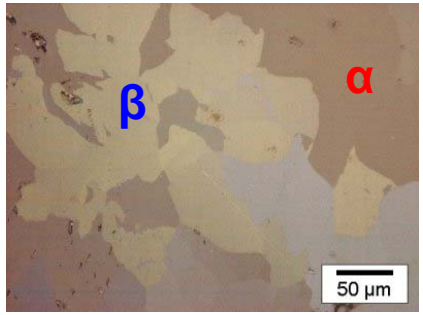

Globular




Lamellar

Coarse lamellar




Block

With no sulfur partition

With sulfur partition

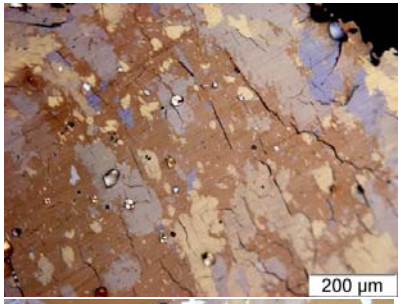
| System | Phase Morphology | T (°C) | α | β | $Ni_3S_4$ |
|---|---|---|---|---|---|
| NiS | Globular | 300 | 49.97±0.09 | 50.09 ±0.09 | - |
| | Lamellar | 200 | 50.9 ±0.14 | 50.04 ±0.07 | |
| | | 260 | 50.75±0.08 | 50.07±0.13 | |
| | Block | 300 | 51.46 ±0.37<br>50.63±0.15 | 50.19 ±0.16 | - |

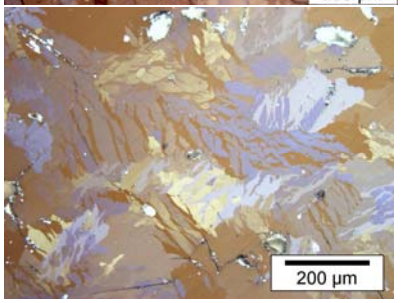
✓ Composition of the β phases varies with T and composition of the mother phase

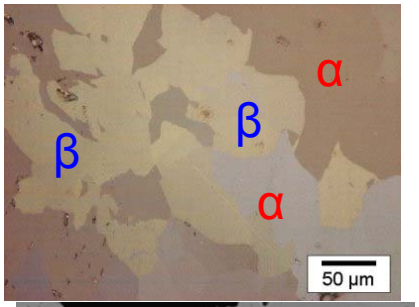
✓ Only for globular morphology β and α phase have the one composition

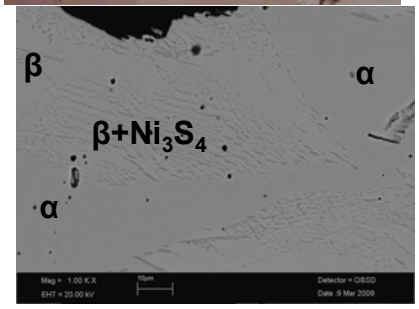
✓ In all other cases long range sulfur diffusion is involved

# Parallel with Fe-C system




| Ni-S | Fe-C |
|---|---|
| **Globular**<br>•no sulfur partition<br>•Relatively rapid<br>•R~t??? | **Massive**<br>•no Carbon partition<br>•Rapid kinetics<br>•R~t |
| **Lamellar**<br>•sulfur partition<br>•Relatively rapid<br>•e~$t^{1/2}$???; L~t??? | **Upper bainite**<br>•Carbon partition<br>•Relatively rapid<br>•e~$t^{1/2}$; L~t |
| **Block &coarse lamellar**<br>•sulfur partition<br>•Slow kinetics<br>•R~$t^{1/2}$??? | **Allotriomorphe ferrite**<br>•Carbon partition<br>•Slow kinetics<br>•R~$t^{1/2}$ |
| **Lamellar β+$Ni_3S_4$**<br>•sulfur partition<br>•slow<br>•L~t??? | **Pearlite**<br>•Carbon partition<br>•Slow kinetics<br>•L~t |

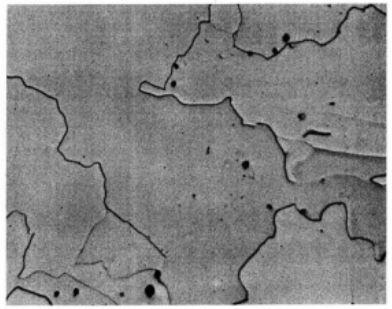
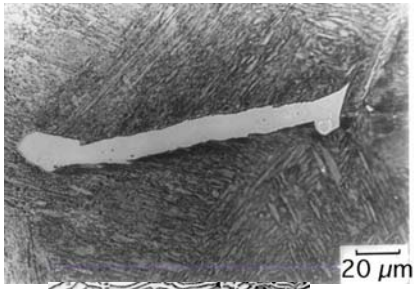
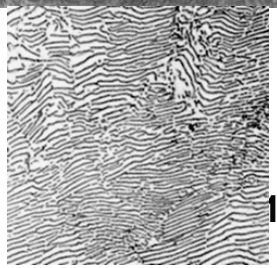


Fig. 5.80 Massive α in an Fe–0.002 wt% C quenched into iced brine from 1000 °C. Note the irregular α/α boundaries. (After T.B. Massalski in *Metals Handbook*, 8th edn., Vol. 8, American Society for Metals, 1973, p. 186.)

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microstructural aspect & mechanisms

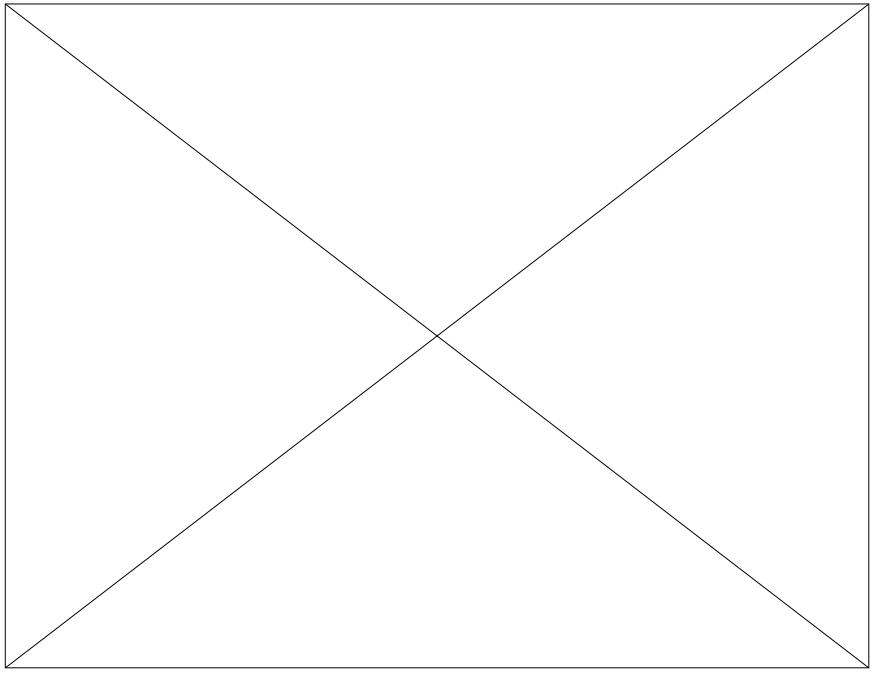
III. α → β-NiS kinetic aspect:

*in situ* observation of phase transformation

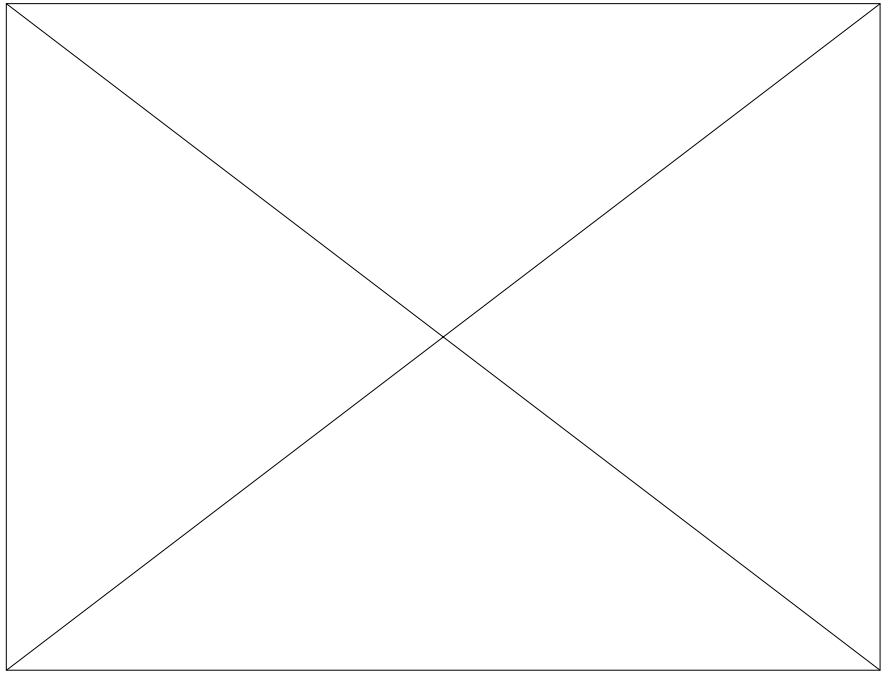
IV. α → β-NiS: modelling under isothermal conditions

V. Conclusion and perspectives :

# In situ observation in optical microscopy

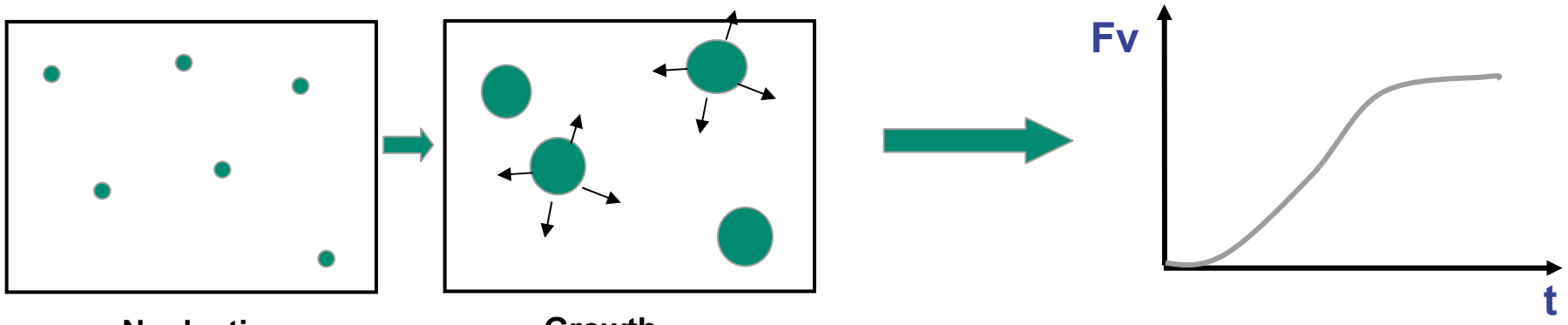


Lamellar morphology



Globular morphology

# Kinetic aspect :




Nucleation

(N(t)

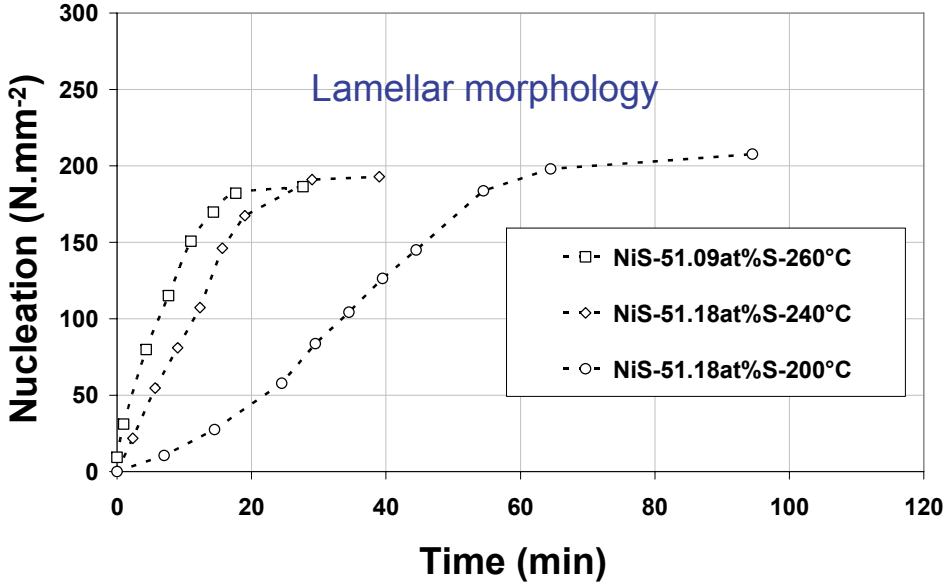
Growth

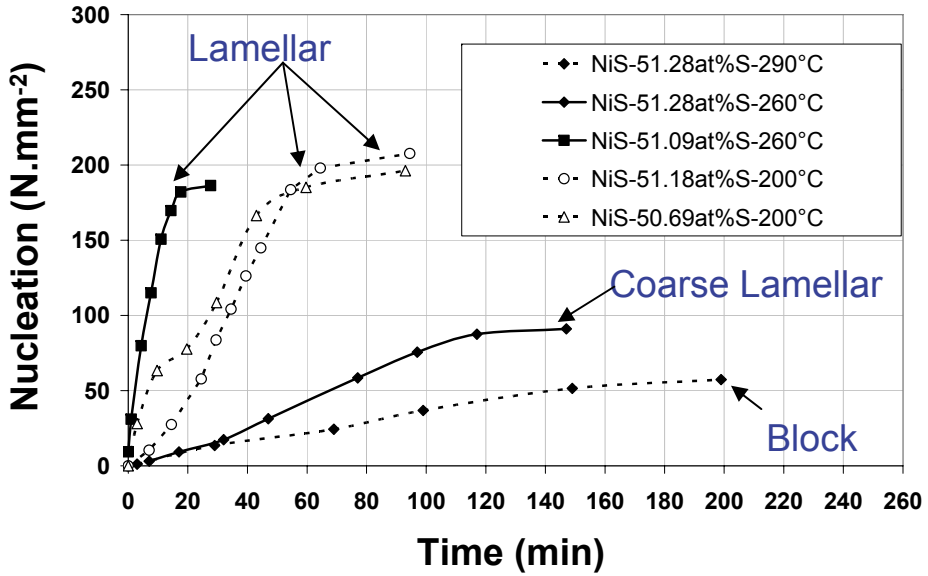
L(t)

e(t)

Volume fraction

# Temperature and composition effect on: nucleation rate

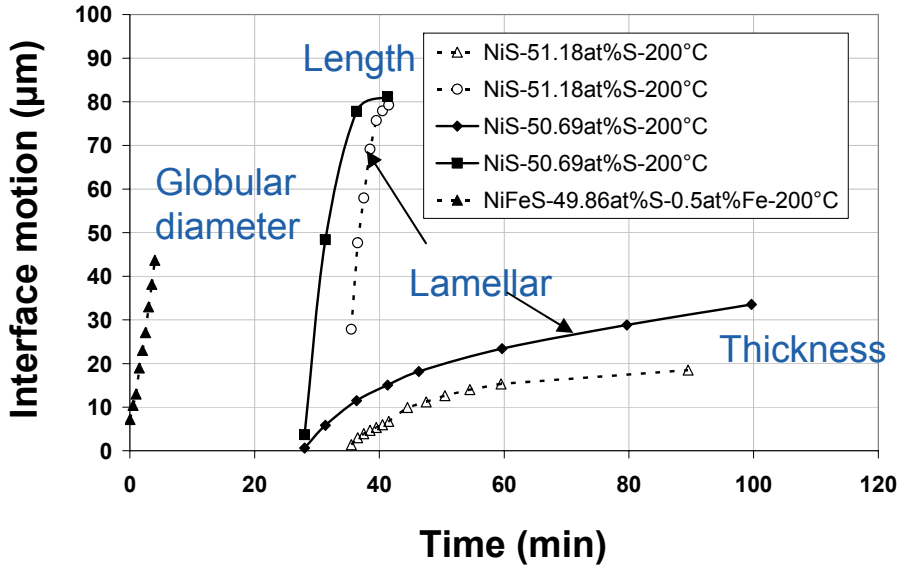


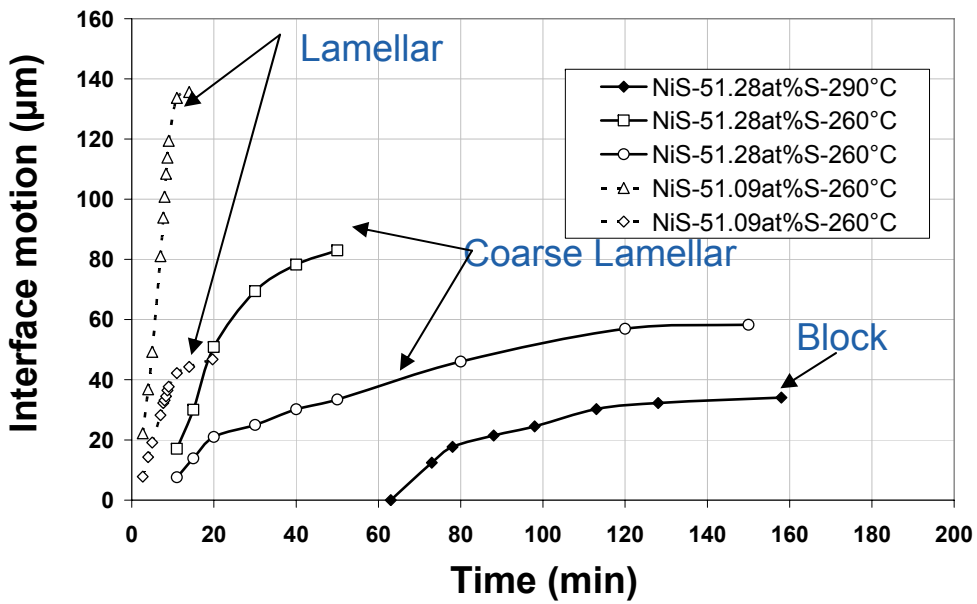




➢ **Nucleation rate**

- **Increase when T increases**
- **Decrease when Cs increases**

# Temperature and composition effect on: interface velocity

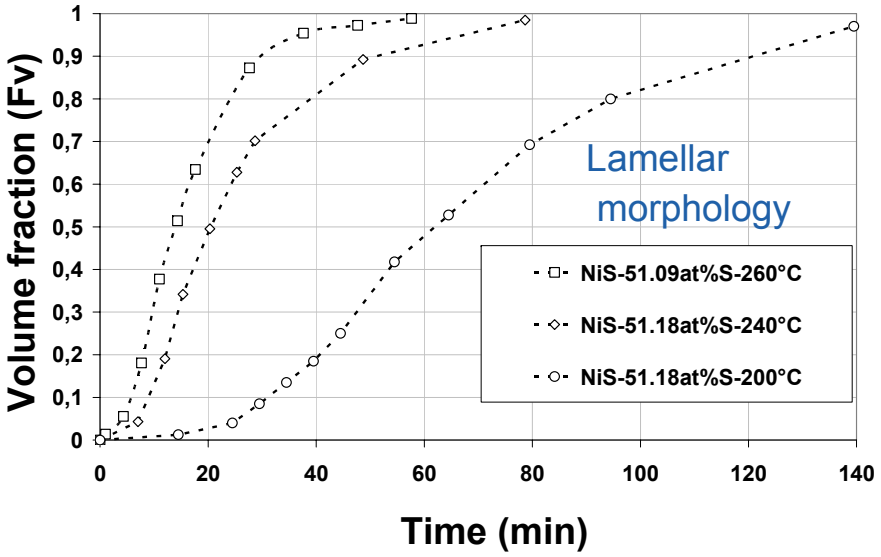


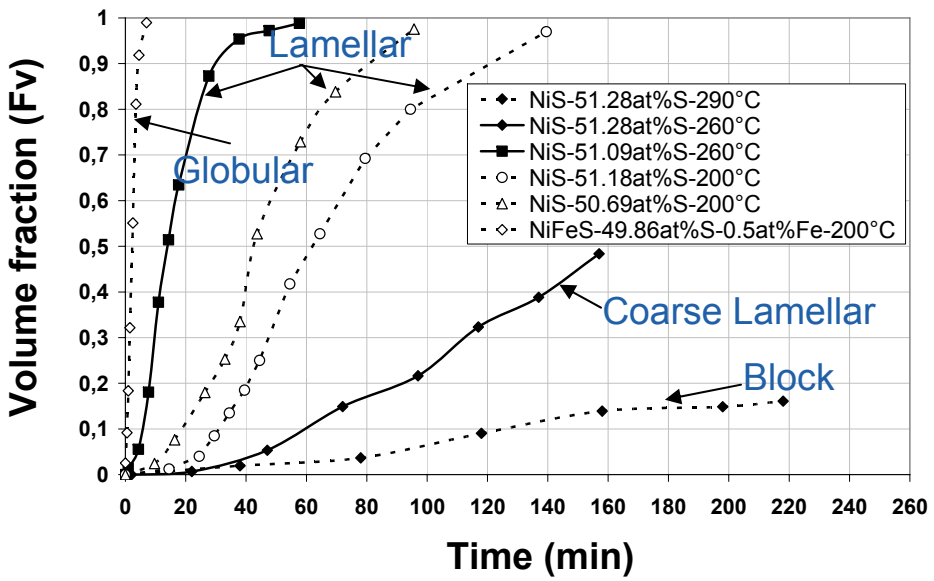




➢ **Growth rate**

- **Increase when T increases**
- **Decrease when Cs increases**

# Temperature and composition effect on: volume fraction,




➢ **Volume fraction**
- **Increase when T increases**
- **Decrease when Cs increases**

# Outline:

I. Context

II. α → β-NiS transformation mechanisms:

microstructural aspect & mechanisms

III. α → β-NiS kinetic aspect:

*in situ* observation of phase transformation

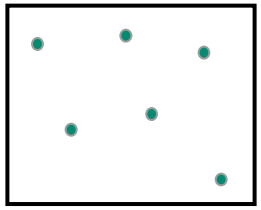
**IV. α → β-NiS: modelling under isothermal conditions**

**V. Conclusion and perspectives:**

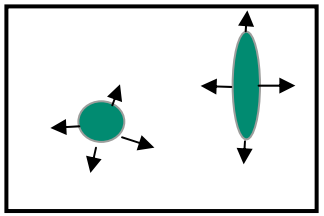
# Physically based modelling of isotherms transformation

## Objective : Transformed fraction = F(t,T,C)

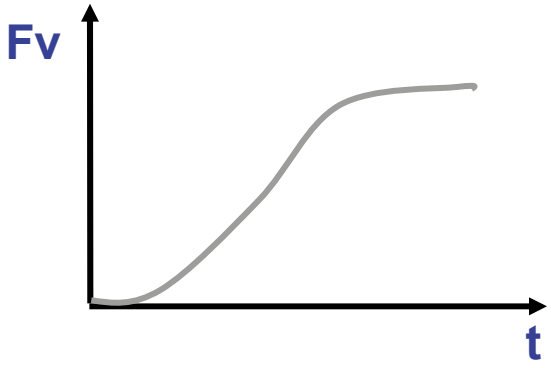
Nucleation



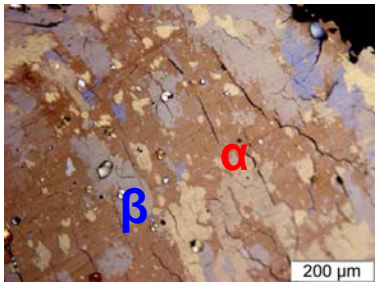
Growth



Experimental measurement + phenomenological description

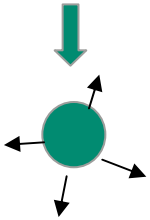


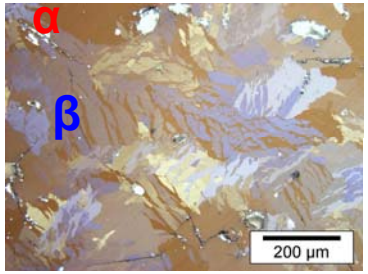

Experimental measurement + diffusion kinetic modelling



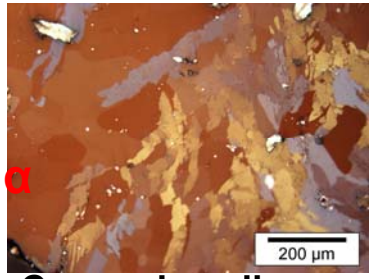

Globular

With no sulfur partition

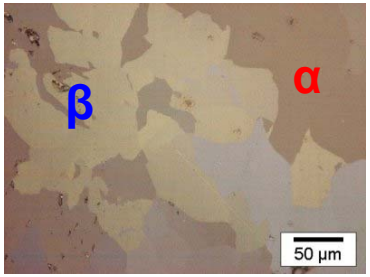



Lamellar

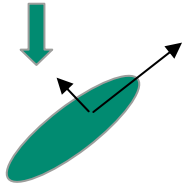


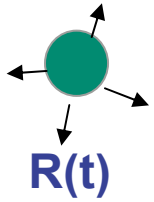

Coarse lamellar



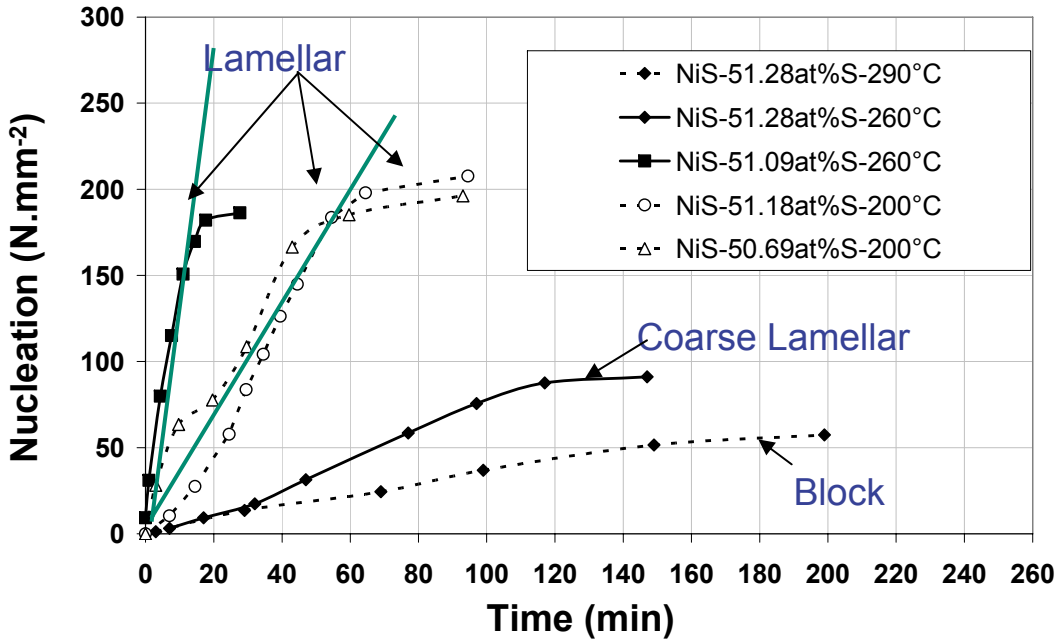

Block

With sulfur partition



# Nucleation : empirical description




$$Ns = Nv \cdot L$$

**measured**

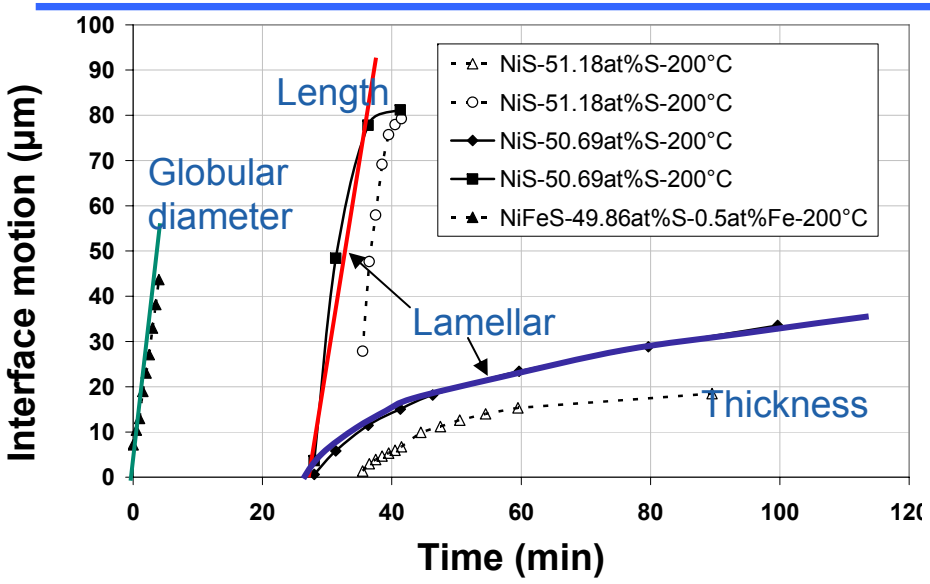
$Ns(t) \sim a.t$

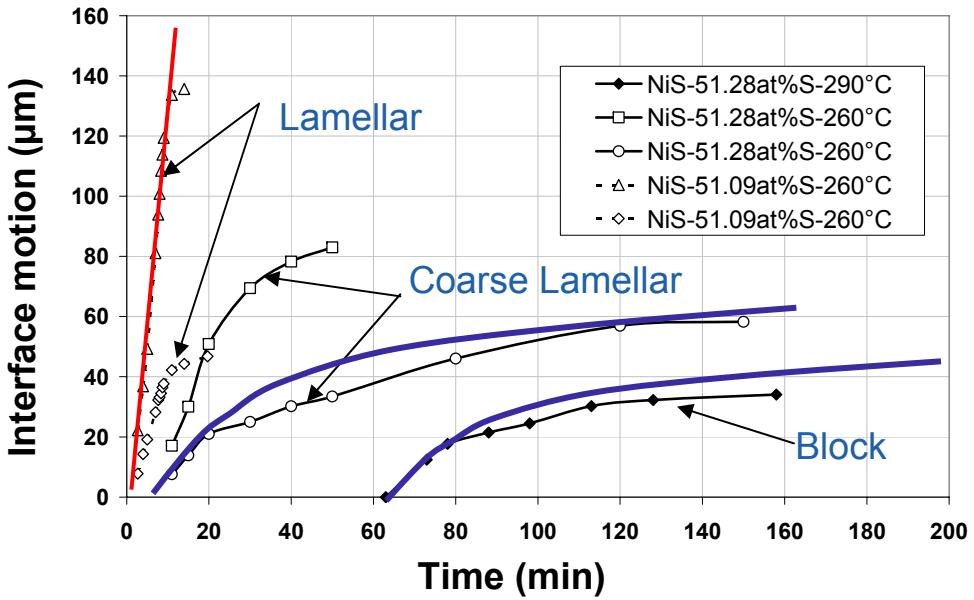
**Computed**

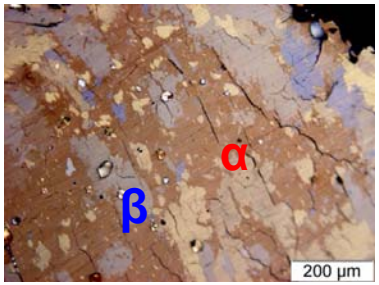
$$Nv = \frac{a(T,Cs).t}{L}$$

**Cst**

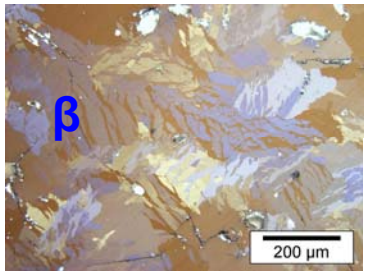
# Interface velocity modelling:



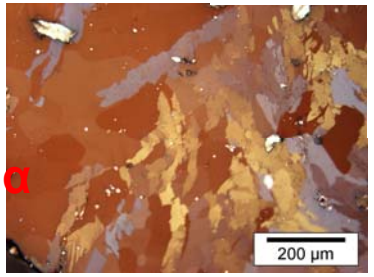



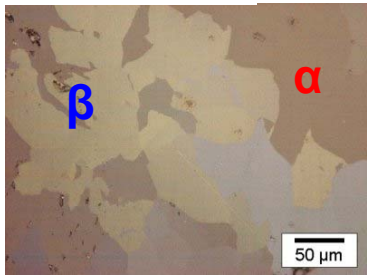

Globular: R(t)




Lamellar: L(t), e(t)




Coarse lamellar R(t)




Block: R(t)

**Massive growth**

**V=cst**

**Lamellar thickening : Zener**

$$e^2 = \frac{D(C_{\alpha\beta} - C_\alpha^0)^2}{(C_{\alpha\beta} - C_\beta)(C_\alpha^0 - C_\beta)} \cdot (t - t_1)$$

**Lamellar lengthening: Zener-Hillert**

$$V = \frac{D}{2 \cdot r} \cdot \frac{(C_{\alpha\beta} - C_\alpha^0)}{(C_{\alpha\beta} - C_\alpha^0)}$$

**Block and coarse lamellar size R(t): Zener**

$$R^2 = \frac{D(C_{\alpha\beta} - C_\alpha^0)^2}{(C_{\alpha\beta} - C_\beta)(C_\alpha^0 - C_\beta)} \cdot (t - t_1)$$

# Parameters of the model

**Nucleation:**

**Ns(t)~a.t**
**measured**

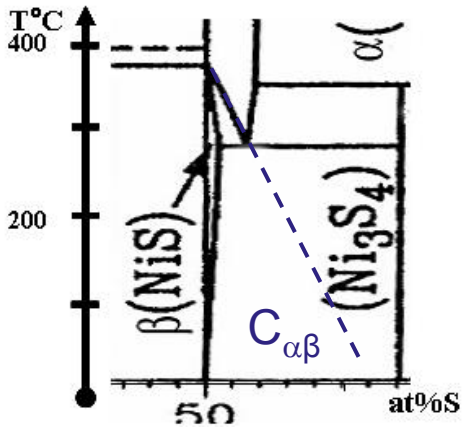
**Nv(t)**

L depth value (morphology)

**"Adjustable" parameters**

**Growth:**

| **Available in literature** | **Measured for the thesis** | **"Adjustable" parameters** |
|---|---|---|
| ✓ $C_{\alpha\beta}$, $C_{\beta}$, $C_{\alpha}^{0}$: phase diagram | ✓ D : sulfur diffusion coefficient diffusion couple | ✓ r (Tip radius): morphology |

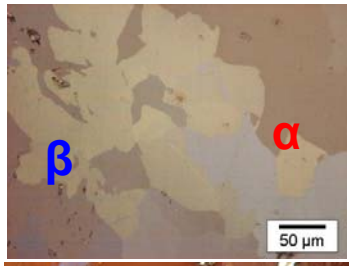


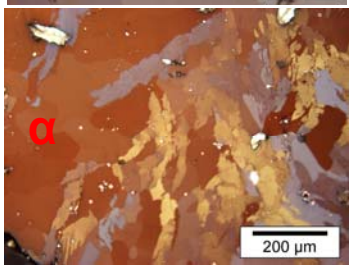

**But having physical signification**

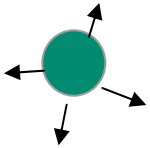
→ **L(t)**, **e(t)**, **R(t)**

# Interface velocity: Comparison model and experimental results

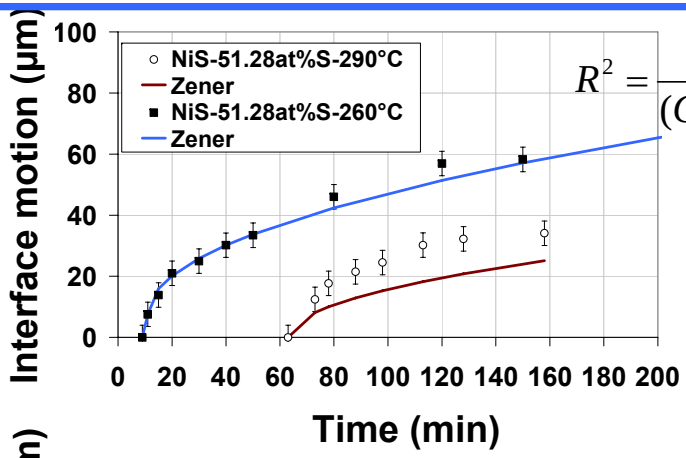
## Coarse lamellar Block R(t)



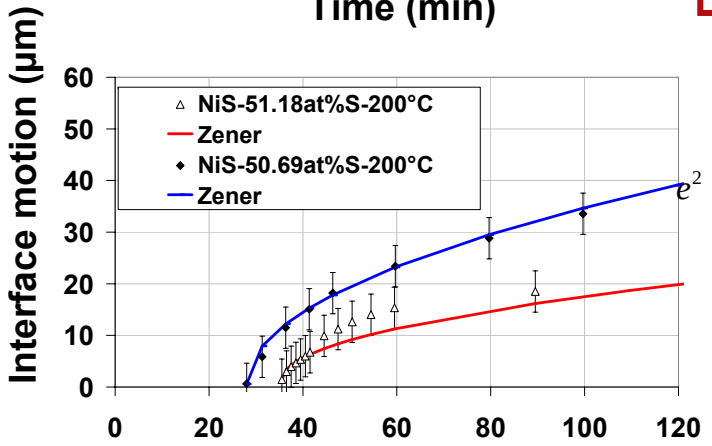



R(t)



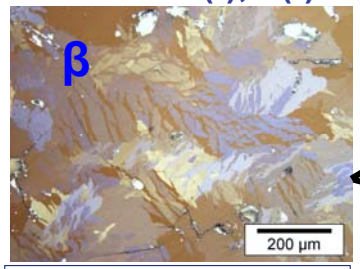

$$R^2 = \frac{D(C_{\alpha\beta} - C_\alpha^0)^2}{(C_{\alpha\beta} - C_\beta)(C_\alpha^0 - C_\beta)} \cdot (t - t_1)$$

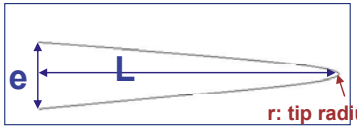
**Without adjustable parameters:**




$$e^2 = \frac{D(C_{\alpha\beta} - C_\alpha^0)^2}{(C_{\alpha\beta} - C_\beta)(C_\alpha^0 - C_\beta)} \cdot (t - t_1)$$

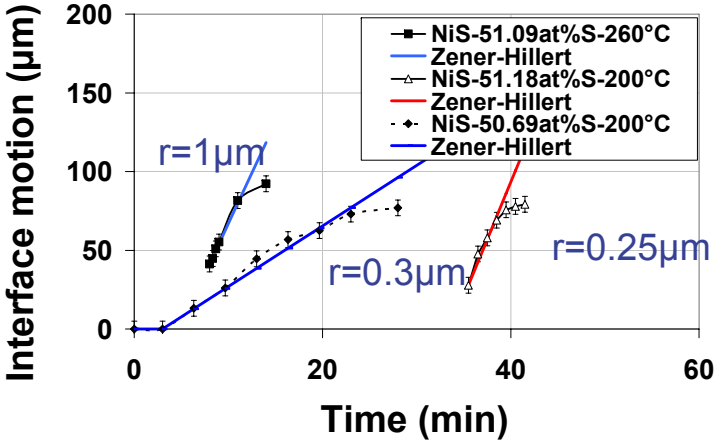
## Lamellar: L(t), e(t)




Lamellar thickening

Lamellar lengthening




$$V = \frac{D}{2 \cdot r} \cdot \frac{(C_{\alpha\beta} - C_\alpha^0)}{(C_{\alpha\beta} - C_\alpha^0)}$$

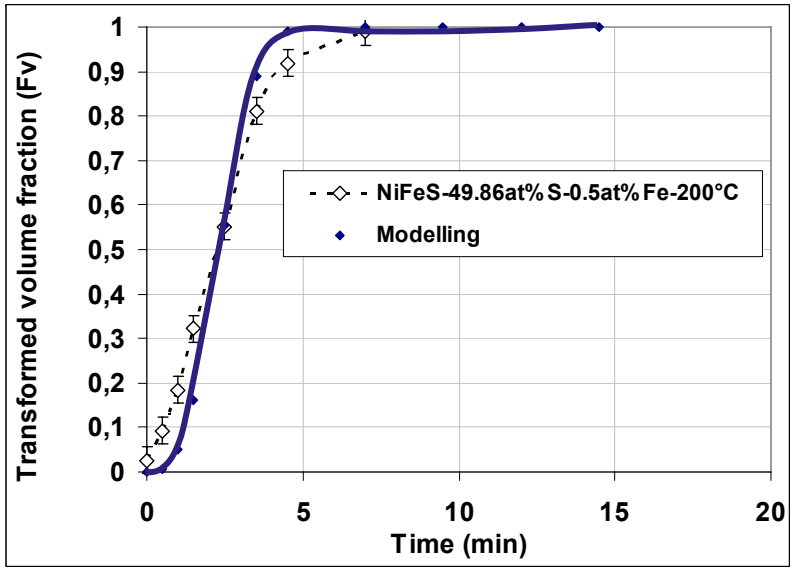
**Adjustable parameters: realistic value for tip radius**

# Global kinetic Modelling : case of the globular and block morphology

## Globular

- Interface velocity law➔Vi=cst
- Nucleation law➔Nv(t)=$N_v$ (cste)

$$f = 1 - \exp\left(-\frac{4}{3} N_v \cdot \Pi \cdot d^2 \cdot t^3\right)$$

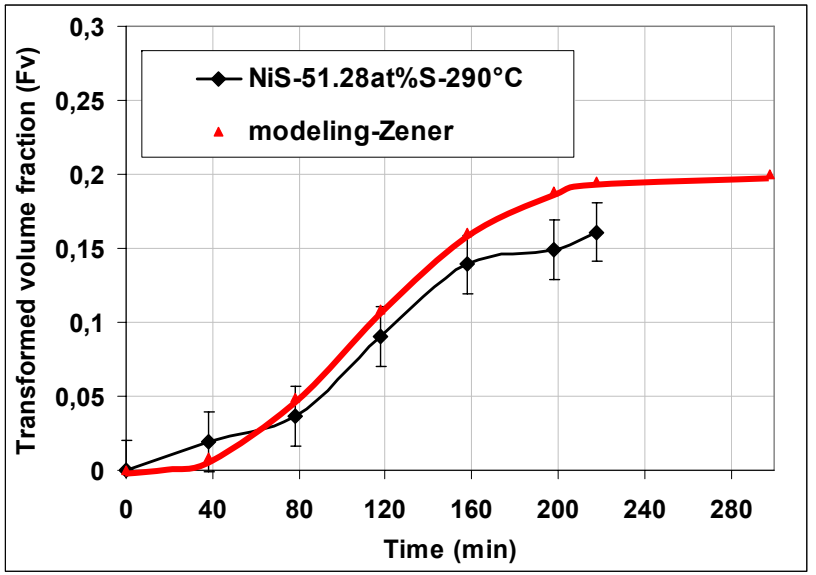



## Block

Interface velocity law➔ $$R^2 = \frac{D(C_{\alpha\beta} - C_\alpha^0)^2}{(C_{\alpha\beta} - C_\beta)(C_\alpha^0 - C_\beta)} \cdot (t - t_1)$$

Nucleation law➔ Nv(t)=$N_v$.t

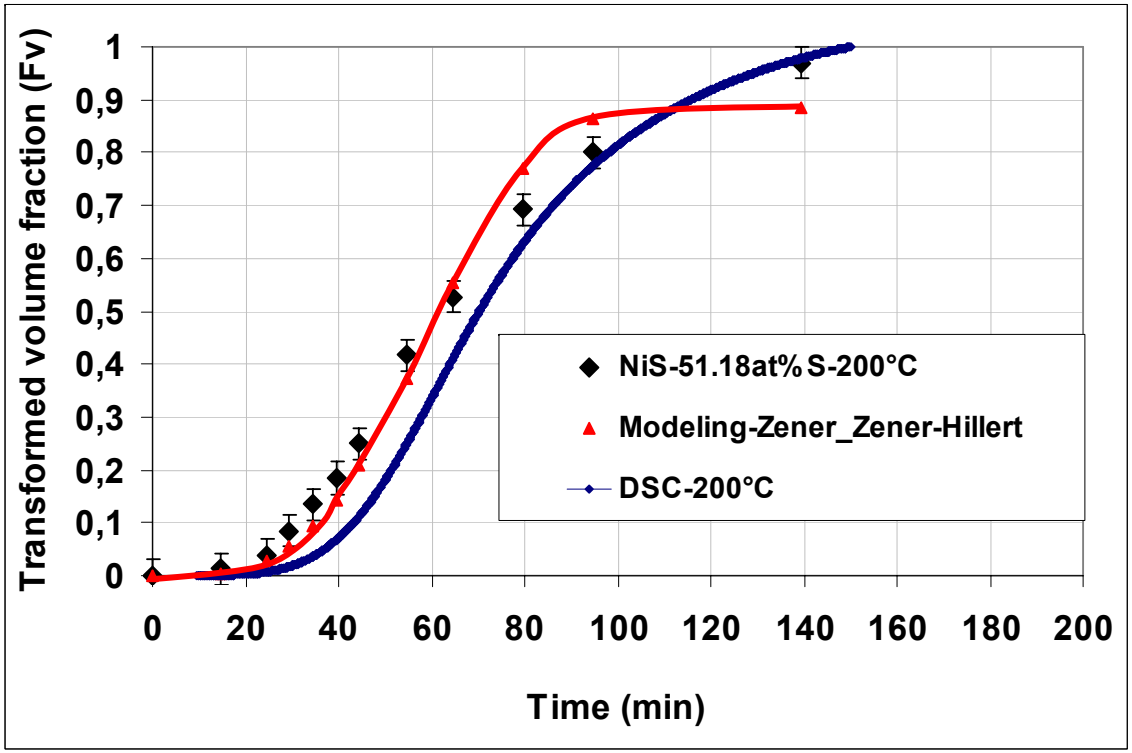
$$f = \frac{1 - \exp - \left[\frac{8}{15} N_v \cdot \Pi \cdot D^{3/2} \cdot \left(\frac{(C_{\alpha\beta} - C_\alpha^0)^2}{(C_{\alpha\beta} - C_\beta)^{3/2}(C_\alpha^0 - C_\beta)^{1/2}}\right) t^{5/2}\right]}{f_{eq}}$$



# Global kinetics for lamellar morphology :

## comparison model and experimental results

$$f = \frac{1 - \exp - \left[ \frac{2}{7} \Pi \cdot N_v \cdot \left( \frac{C_\zeta - C_\beta}{C_\zeta - C_\alpha^0} \right) \cdot \left( \frac{D}{2.r} \cdot \frac{(C_{\alpha\beta} - C_\alpha^0)}{(C_{\alpha\beta} - C_\alpha^0)} \right)^2 \cdot \left( \frac{D(C_{\alpha\beta} - C_\alpha^0)^2}{(C_{\alpha\beta} - C_\beta)(C_\alpha^0 - C_\beta)} \right)^{1/2} .t^{7/2} \right]}{\left( \frac{C_\zeta - C_\alpha^0}{C_\zeta - C_\beta} \right)}$$




Adjustable parameters: realistic value for tip radius

r=0.25µm → r=0.55µm

**Interfaces velocity** **Volume fraction**

# Conclusion

## Transformation mechanism vs (T,Cs)

- ✓ Partitionless (Massive) for low overstoichiometry
- ✓ Partitionned and diffusive controlled mechanism for high overstoichiometry

## Transformation kinetics:

- ✓ Nucleation rate=Cst
- ✓ Growth:
  - Globular → linear
  - Block → quadratic
  - Lamellar: → quadratic thickening
    → linear length

## Modelling under isothermal conditions: physically based modelling

# Perspectives:

## Phase transformation in NiS :

- NiS a simple but rich by the variety of phase transformation mechanism
- *Insitu* observation of phase transformation in easy conditions (low temperature and optical microscopy)
- Similarities with classic systems: Fe-C…

❑ **An adequate system for training:**

- **Study of phase transformation**
- **Initiation on phase transformation in steel**

❑ **An ideal system to study open questions in transformations with diffusion and crystallographic changes (steels, titanium alloys…)**

# Questions…