METALLURGICAL ASPECTS OF THE SOLUBILIZATION OF MICROALLOYING ELEMENTS DURING STEEL SLAB REHEATING

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USIMINAS – Cubatão

INTRODUCTION

- Microalloyed steels must be reheated before hot rolling to a **minimum temperature** that ensures full Nb solubilization – this is a vital requisite for a **successful controlled rolling**.
- There is several equations available for the calculation of this minimum temperature, but the **minimum time** under this temperature that is needed for full Nb solution is generally not known.
- **The detection of Nb precipitates** in microstructure is not exactly easy, requiring transmission electronic microscopy.

INTRODUCTION

- Under practical conditions it is assumed that the full Nb solution demands at least **from 10 to 30 minutes** under temperatures above those calculated by the equilibrium equations.

- However, the demand for minimum dispersion in the final mechanical properties of rolled products requires **a better knowledge about the kinetics of the solubilization** of microalloying elements.

- An industrial continuous cast slab of microalloyed steel presents microalloy precipitates with **several shapes and sizes across its thickness**.

INTRODUCTION

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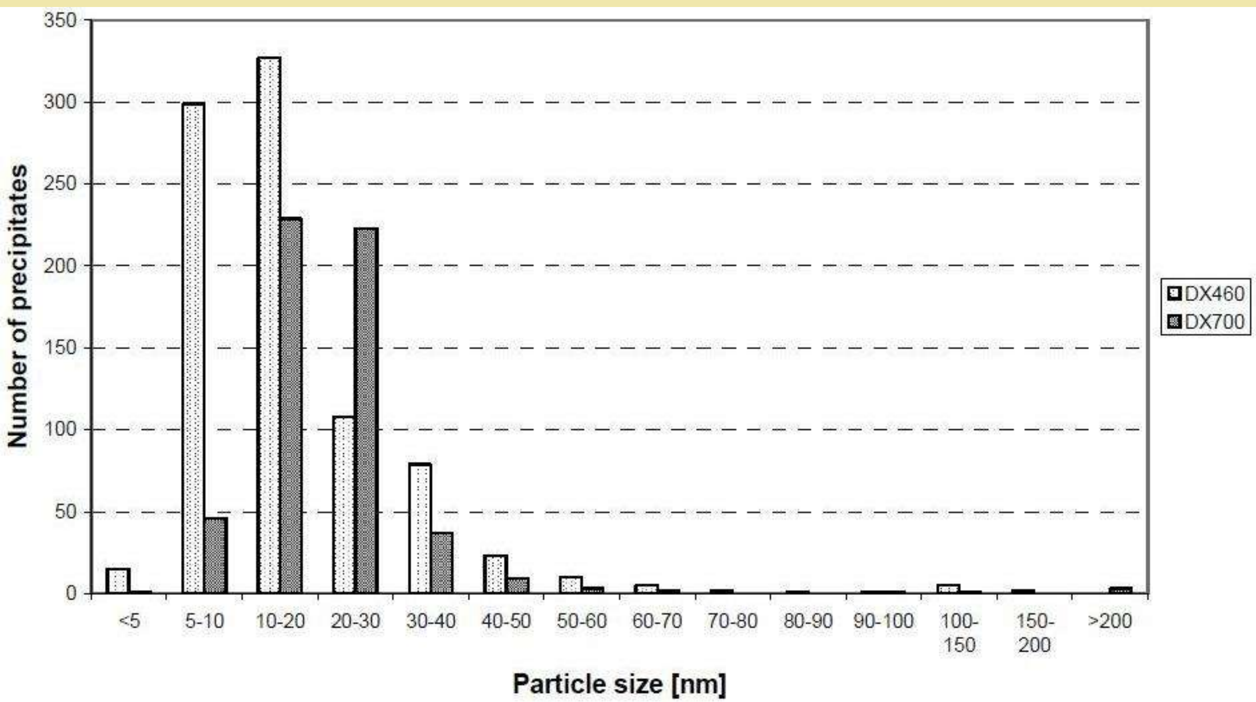
- **Typical slab size distribution** of microalloy precipitates in a NbTiV structural steel:
  - 80%: spherical, 1 to 50 nm;
  - 10%: cubical, 60 to 300 nm;
  - 10%: star/wing, 150 to 600 nm.
- Partition of Nb during solidification is very high: the interdendritic liquid steel has Nb content **7 times higher** than the nominal chemical composition.
- No wonder that the interdendritic region of the slab shows a **higher precipitate concentration**.

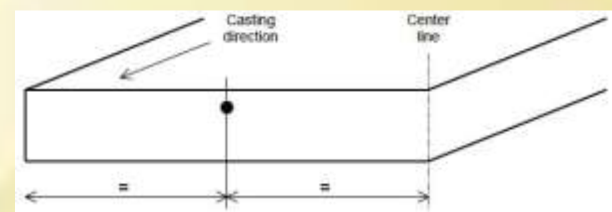
Chakrabarti, Davis & Strangwood, Metallurgical and Materials Transactions A, 39A:8, Aug. 2008, 1963-1977

INTRODUCTION

- **Size precipitate distribution** in microalloyed steel slabs:

Steel	C	Si	Mn	N	Mo	Al	Nb	Ti	V
Domex700	0.061	0.082	1.87	0.0084	0.12	0.041	0.061	0.099	0.007
Domex460	0.064	0.058	1.38	0.0048	0.002	0.037	0.048	0.004	0.005





Borggren, Engberg & Siwecki, Advanced Materials Research, 15-17, 2007, 714-719

INTRODUCTION

- A microstructural analysis of commercial hot coils of microalloyed steels showed that **up to 49% of the microalloy contents are lost** (not solubilized during reheating) as they are present as **coarse eutectic precipitates** (size greater than **500 nm**):

Aço	C	Mn	Si	P	S	Al	Nb	Ti	V	N
NbTi-1	0,05	0,55	0,02	n,d,	n,d,	0,02	0,02	0,06	-	0,006
NbTi-3	0,11	1,54	0,28	0,026	0,007	0,01	0,04	0,11	-	0,008*
NbTiV	0,14	1,38	0,25	0,018	0,007	0,07	0,04	0,04	0,03	0,008

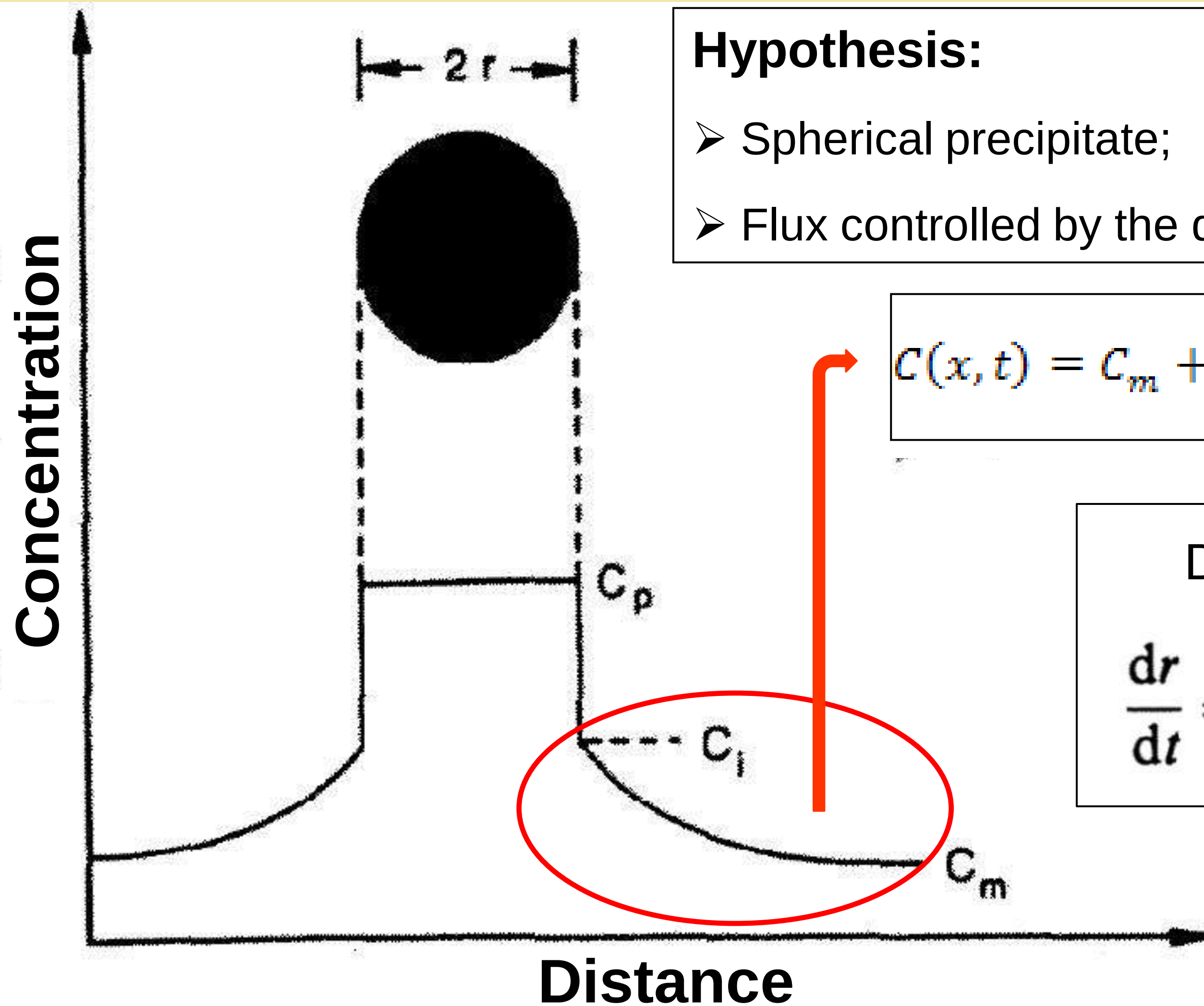
Aço	$V_{f\,max}$ teórico	carbonitretos eutéticos	carbonitretos insolúveis	Perda total de microligantes	TiN_{max} teórico	perda adicional devido segregação
NbTi-1	13.1×10^{-4}	5.6×10^{-4}	0.8×10^{-4}	49 %	4.01×10^{-4}	60 %
NbTi-3	26.1×10^{-4}	8.5×10^{-4}	desconhecido	> 33 %	5.35×10^{-4}	> 59 %
NbTiV	17.4×10^{-4}	5.0×10^{-4}	1.6×10^{-4}	38 %	5.35×10^{-4}	23 %

Gallego, Campos & Kestenbach, CBECIMAT, 2002, 2380-2386

INTRODUCTION

- All these facts led to the development of this work, whose aims were:
  - The development of a mathematical model for the calculation of the **solubilization kinetics of microalloy precipitates** under the typical industrial slab reheating conditions;
  - A better knowledge about the possible effects of variations in the **precipitate size, chemical composition and temperature** in the austenite solubilization of microalloyed steels.

DISSOLUTION



Hypothesis:

- Spherical precipitate;
- Flux controlled by the diffusion of the slowest atom.

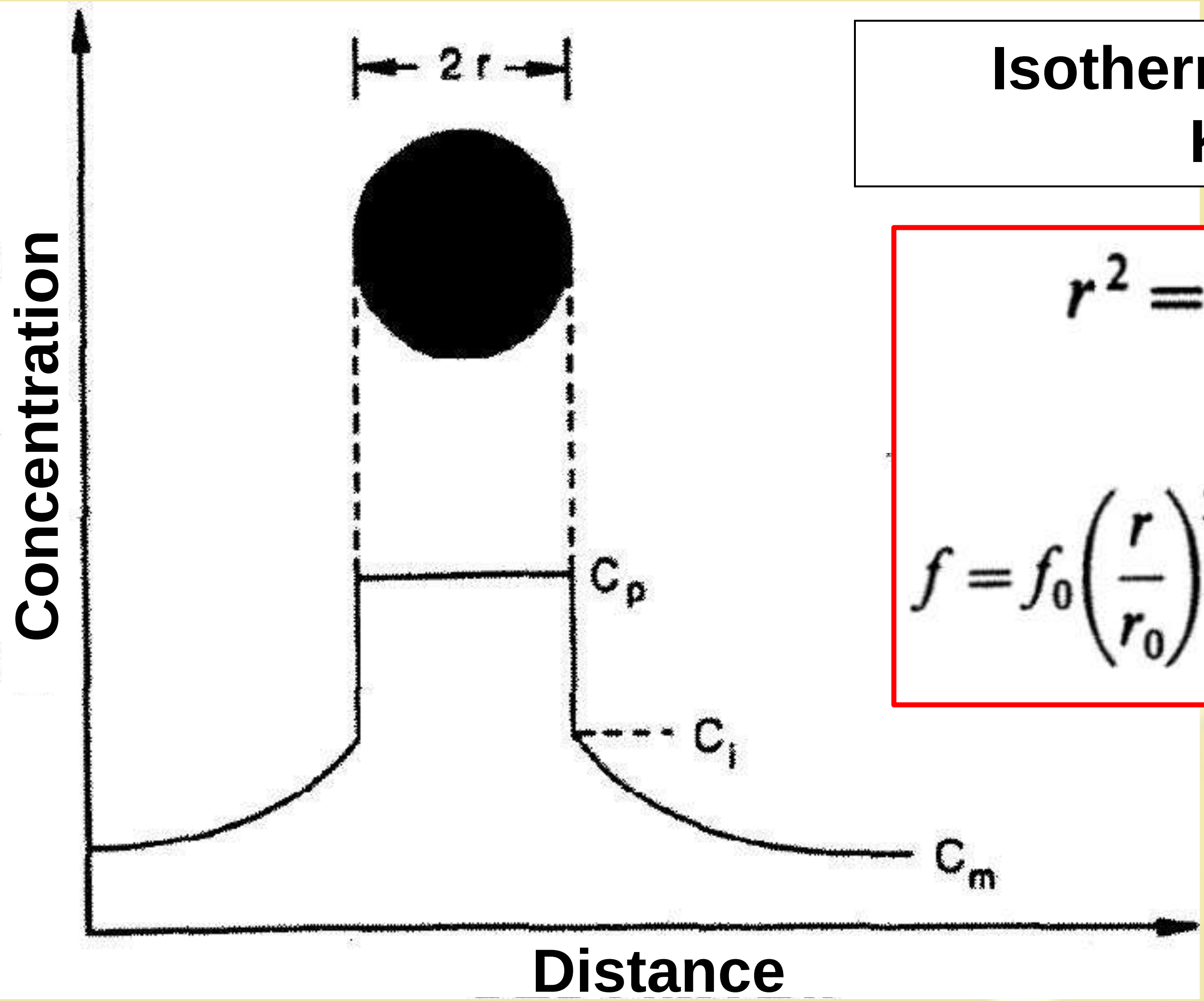
$$C(x,t) = C_m + (C_p - C_m)\ erfc\left(\frac{x-r}{2\sqrt{D_m t}}\right)$$

Dissolution Rate:

$$\frac{dr}{dt} = \alpha\left[\frac{D_m}{r} - \sqrt{\frac{D_m}{\pi t}}\right]$$

Andersen & Grong, Acta Metallurgica et Materialia, 43:7, 1995, 2673-2688

ISOTHERMAL DISSOLUTION



Isothermal Dissolution Kinetics:

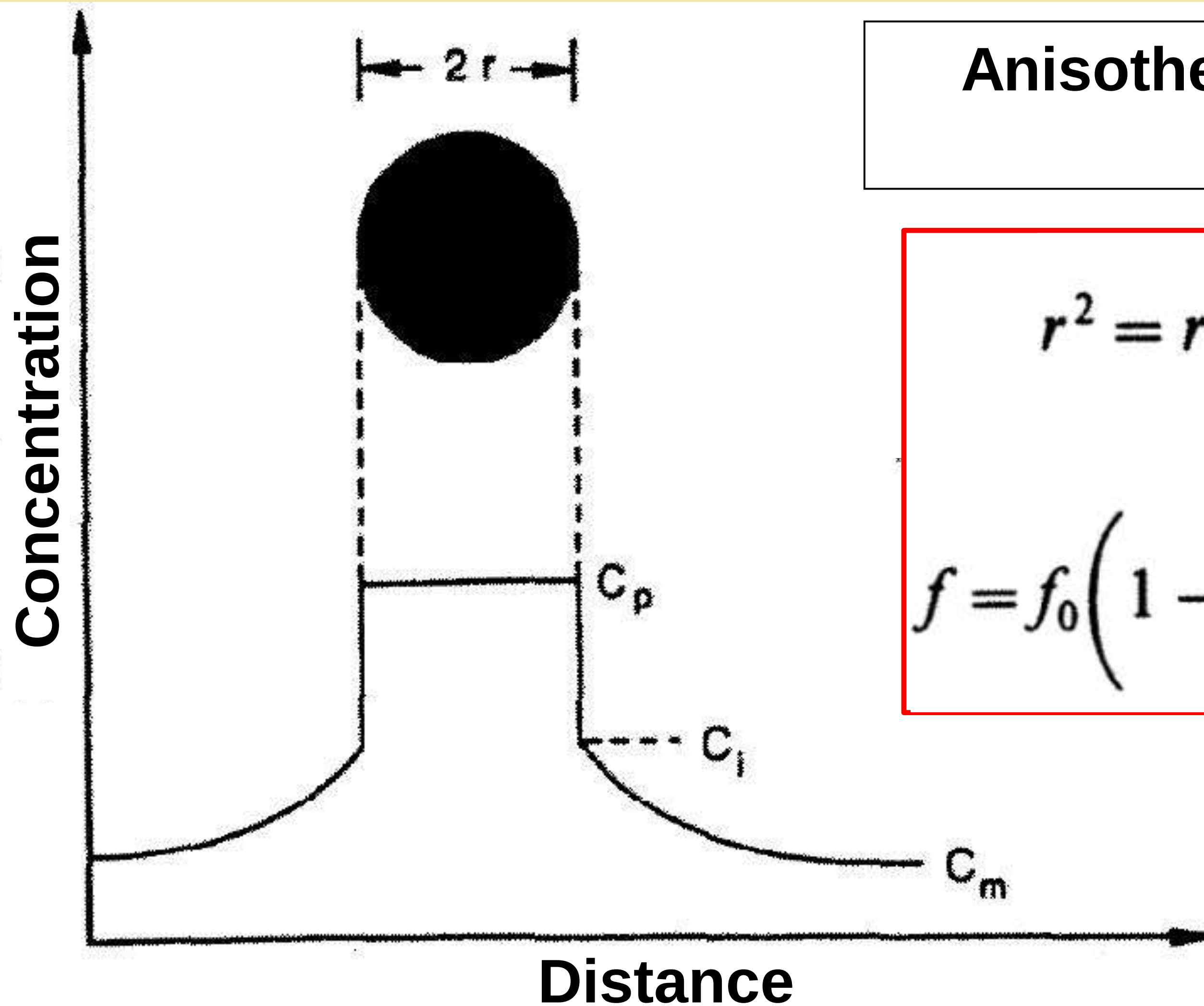
$$r^2 = r_0^2 - 2\alpha D_m t$$

$$f = f_0\left(\frac{r}{r_0}\right)^3 = f_0\left(1 - \frac{2\alpha D_m t}{(r_0)^2}\right)^{3/2}$$

$$\alpha = \frac{C_i - C_m}{C_p - C_i}$$

Andersen & Grong, Acta Metallurgica et Materialia, 43:7, 1995, 2673-2688

ANISOTHERMAL DISSOLUTION



Anisothermal Dissolution Kinetics:

$$r^2 = r_0^2 - 2\int_{t_1}^{t_2} \alpha D_m \, dt$$

$$f = f_0\left(1 - \frac{2}{(r_0)^2}\int_{t_1}^{t_2} \alpha D_m \, dt\right)^{3/2}$$

$$\alpha = \frac{C_i - C_m}{C_p - C_i}$$

Andersen & Grong, Acta Metallurgica et Materialia, 43:7, 1995, 2673-2688

ANISOTHERMAL DISSOLUTION

- The anisothermal dissolution implies in an **additional complication**, as the precipitate fraction and its chemical composition (and, consequentely, the composition of the matrix) are function of the **temperature.**

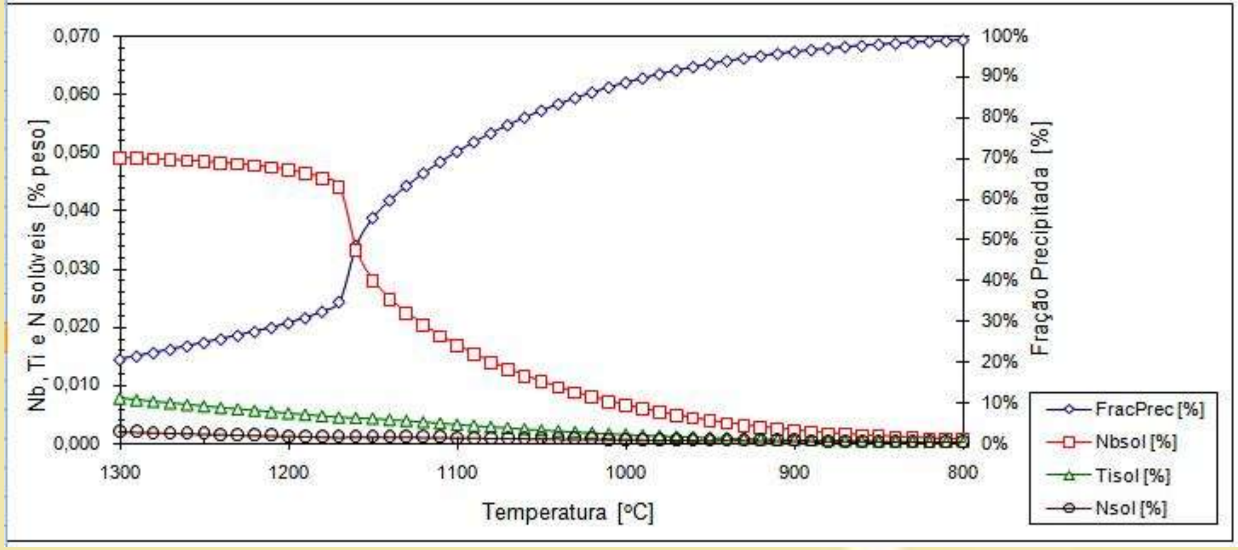
- The solution of this problem requires the use of a mathematical model to calculate the **thermodynamical equilibrium between precipitates and austenite**, which was already developed.

AUSTENITE EQUILIBRIUM

Amostra	Aço NbTi Genérico				
Composição Química [% peso]	C	Mn	Nb	Ti	N
	0,11	1,53	0,050	0,016	0,0043

11/03/2009
15:40

T [°C]	f	FracPrec [%]	Carbonitreto $Nb_x Ti_{(1-x)} C_y N_{(1-y)}$ x	(1-x)	y	(1-y)	Nb_{sol} [%]	Ti_{sol} [%]	C_{sol} [%]	N_{sol} [%]
1300	0,00020	21%	0,05	0,95	0,08	0,92	0,0490	0,0078	0,1094	0,0020
1250	0,00024	25%	0,07	0,93	0,10	0,90	0,0484	0,0064	0,1093	0,0016
1200	0,00029	30%	0,12	0,88	0,15	0,85	0,0469	0,0051	0,1091	0,0012
1150	0,00054	55%	0,49	0,51	0,53	0,47	0,0278	0,0042	0,1065	0,0011
1100	0,00069	72%	0,57	0,43	0,62	0,38	0,0167	0,0032	0,1050	0,0010
1050	0,00079	82%	0,60	0,40	0,65	0,35	0,0105	0,0022	0,1041	0,0008
1000	0,00086	88%	0,61	0,39	0,66	0,34	0,0064	0,0015	0,1035	0,0007
950	0,00090	93%	0,61	0,39	0,67	0,33	0,0038	0,0009	0,1031	0,0006
900	0,00093	96%	0,61	0,39	0,67	0,33	0,0022	0,0005	0,1029	0,0004
850	0,00095	98%	0,62	0,38	0,67	0,33	0,0012	0,0003	0,1028	0,0004
800	0,00096	99%	0,62	0,38	0,67	0,33	0,0006	0,0002	0,1027	0,0003



Gorni, in: Spreadsheets in Science and Engineering, Springer-Verlag, Berlin, 1998, 229-260

MODEL APPLICATIONS

- Dissolution kinetic studies generally have a **microstructural approach**, analysing precipitate diameter and fraction evolution along time.

- In this work dissolution was expressed in terms of **dissolved Nb in austenite**, a parameter much more relevant for industrial objectives.

- The heating curve used as input for the model was measured under **industrial conditions**, using a thermocouple placed at **half slab thickness**, just above the water cooled skid/slab interface. This point has the **worst thermal soaking condition**.

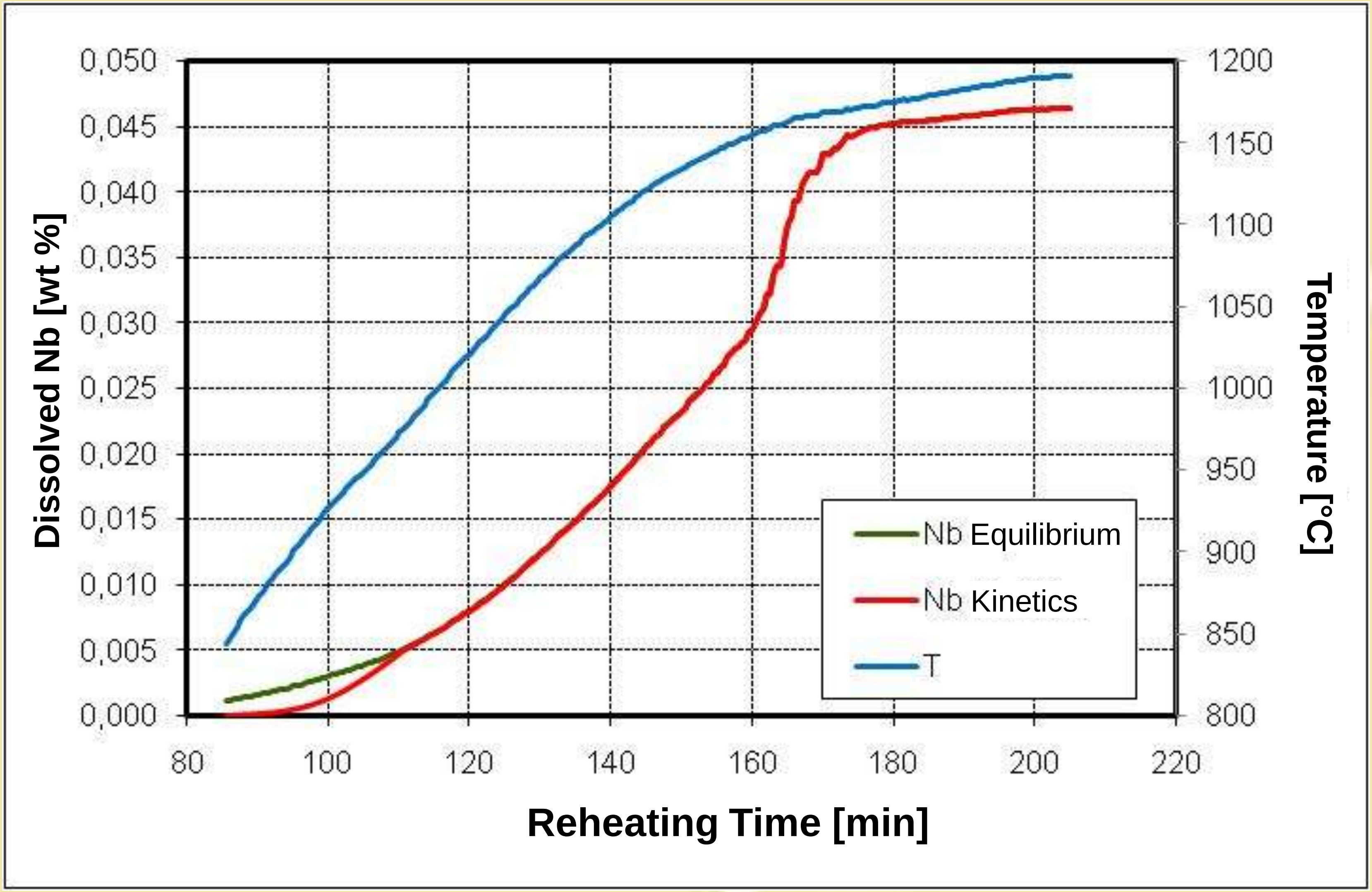
#1: PRECIPITATE SIZE

- Input data:
  - **Chosen steel chemical composition:**
    - 0.11% C
    - 0.050% Nb
    - 0.016% Ti
    - 0.0043% N
  - **Precipitate diameters:**
    - **Average:** 17 nm (according to Borggren, NbTi steel)
    - **Eutectoid:** 250 nm and 500 nm.

Borggren, Engberg & Siwecki, Advanced Materials Research, 15-17, 2007, 714-719

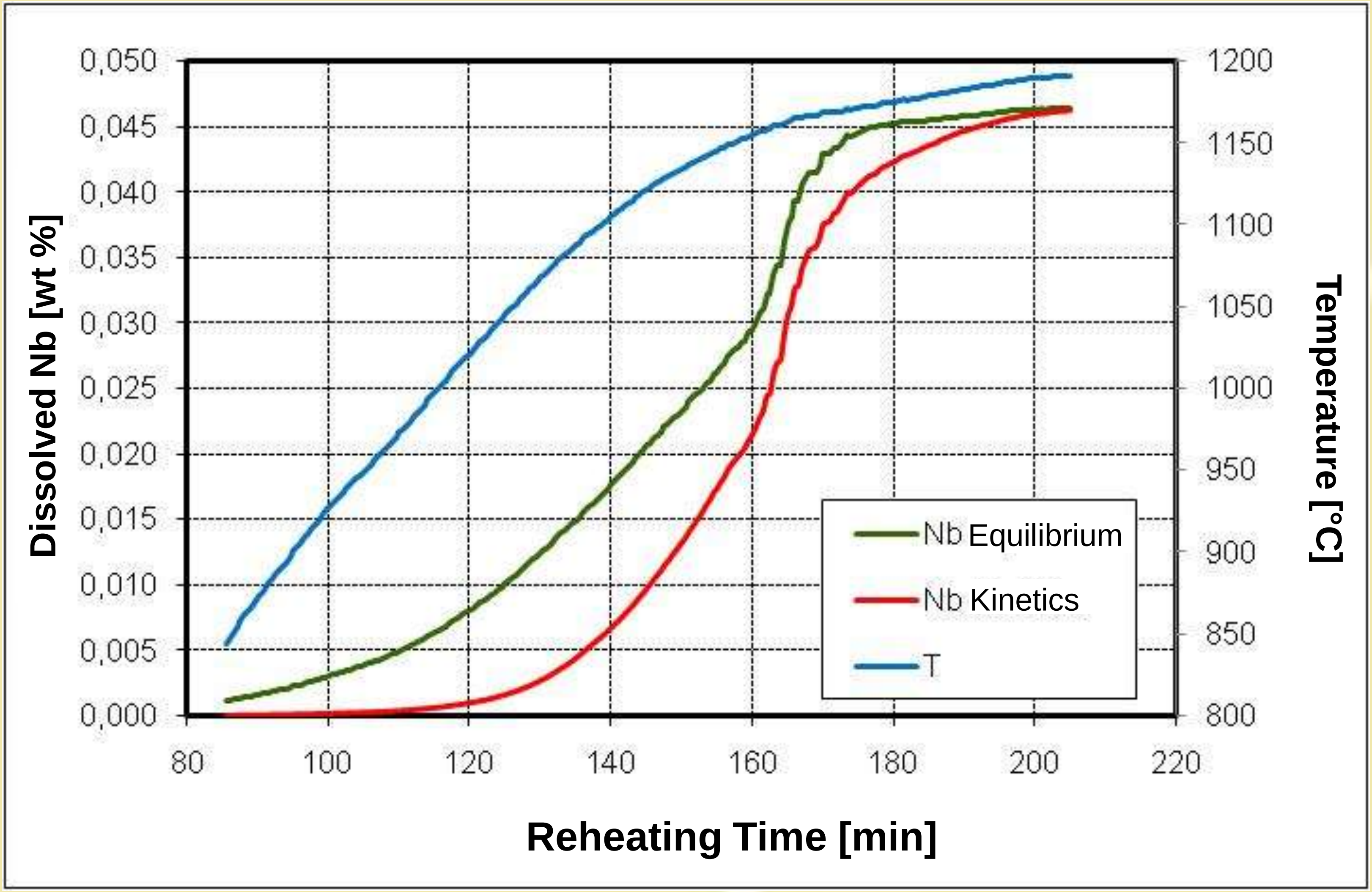
#1: PRECIPITATE SIZE

ø precipitate: 17 nm



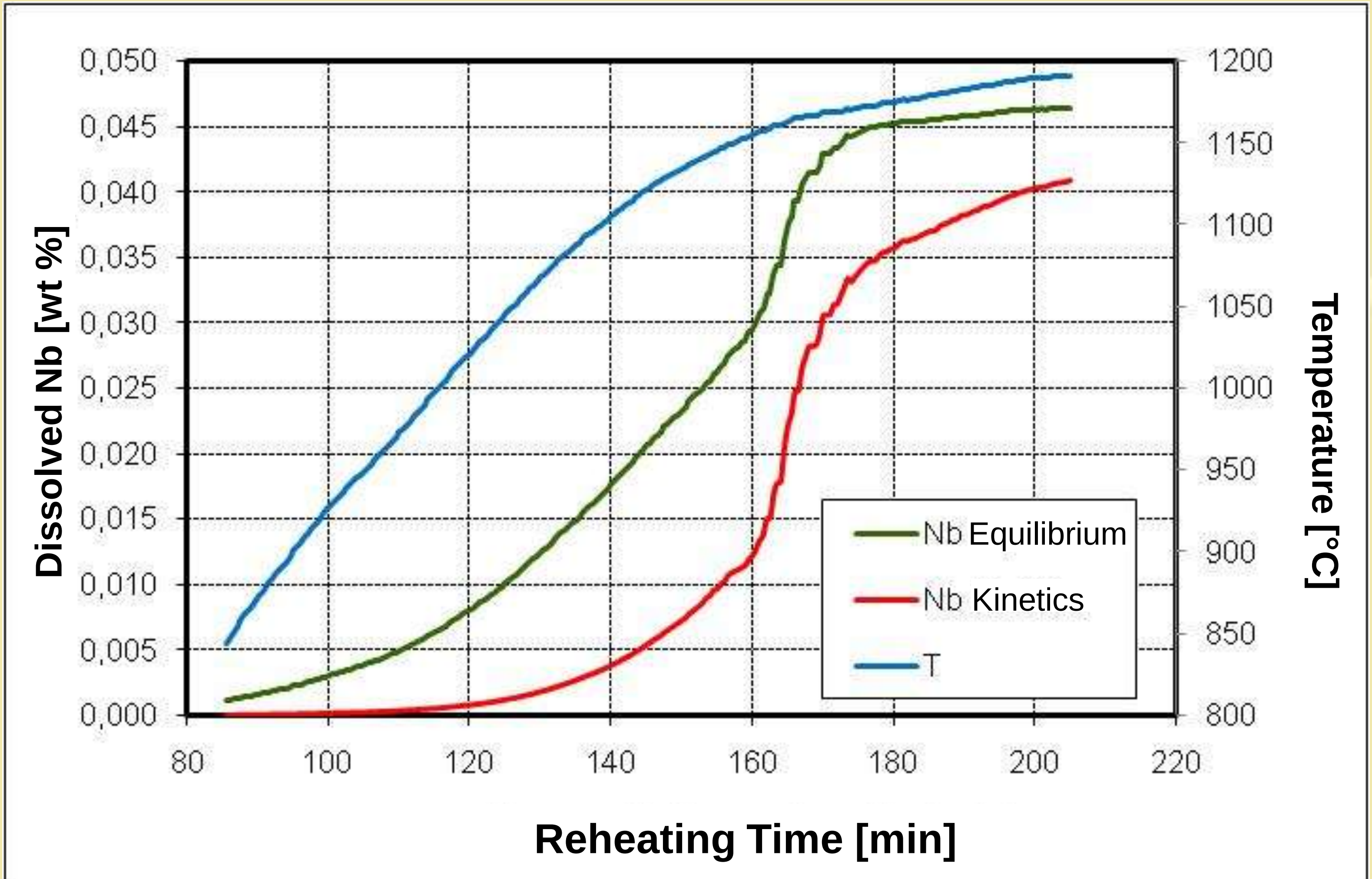
#1: PRECIPITATE SIZE

ø precipitate: 250 nm



#1: PRECIPITATE SIZE

ø precipitate: 500 nm



#1: PRECIPITATE SIZE

- For this specific alloy, and considering the worst slab reheating condition, **full Nb solubilization** is achieved for precipitates with a **maximum diameter of 250 nm** – well above the mean precipitate diameter.

- As a matter of fact, models Structura (IRSID) and TACSI (ArcelorMittal) **disregard kinetic effects** during the calculation of microalloy solubilization of during slab reheating – both consider enough only the use of a **thermodynamical equilibrium model**.

Piette, Materials Science Forum, 284-286, 1998, 361-368

Huin, 3rd Int. Conf. On Thermomechanical Processing of Steels - TMP 2008, Padua, 2008

#2: ALLOY COMPOSITION

- All industrial steel alloys are specified within a **chemical composition tolerance range** due to the normal precision limitations of the elaboration and refining processes.

- The model developed here was used to verify **the effect of such tolerance range** in the Nb solubilization evolution.

- **Base alloy:**
  - 0.11% C
  - 0.050% Nb
  - 0.016% Ti
  - 0.0043% Nb

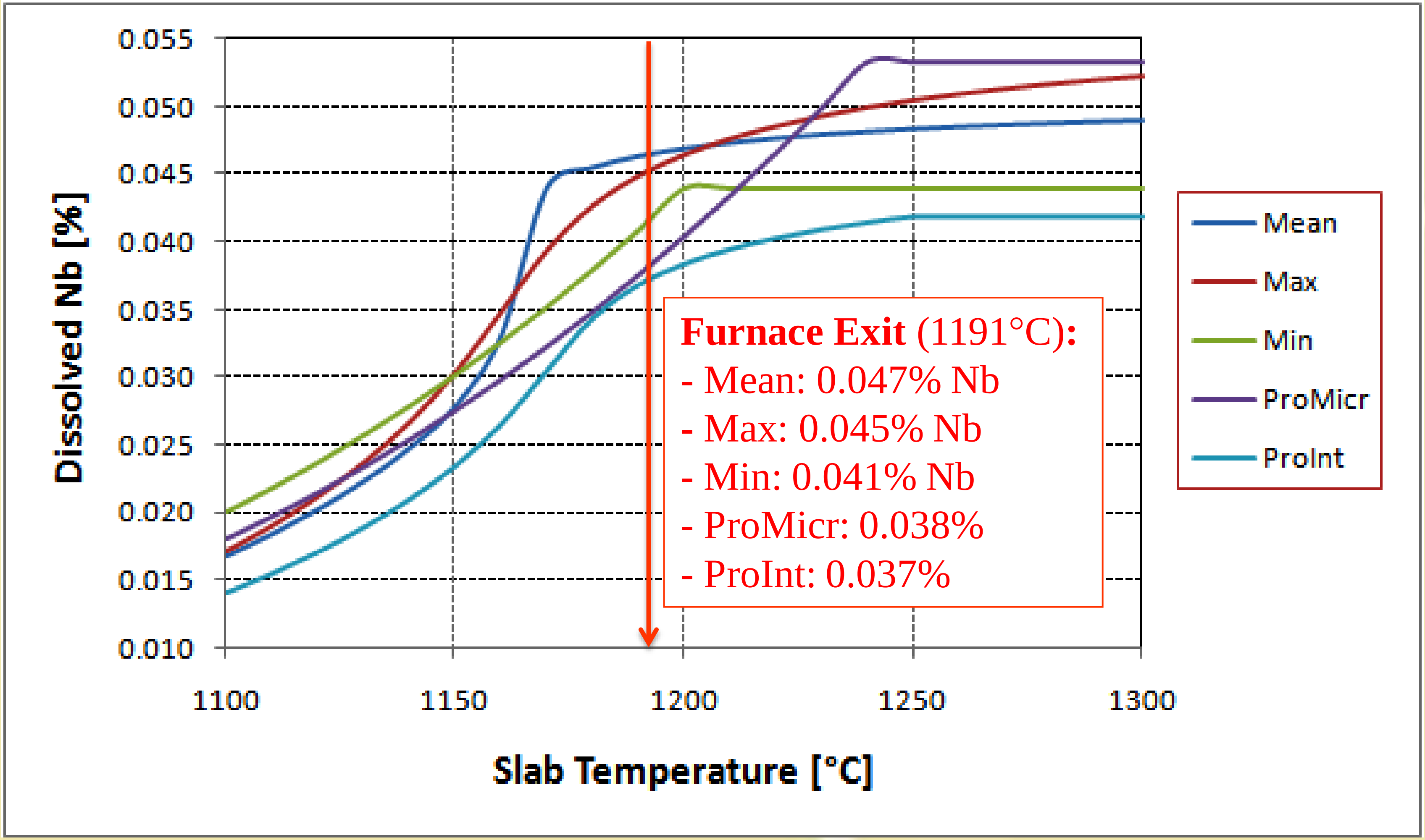
#2: ALLOY COMPOSITION

- Definition of **limit compositions** within the normal specification range of an hypothetical microalloyed steel:

Alloy	C	Nb	Ti	N
Mean	0.11	0.050	0.016	0.0043
Min	0.09	0.045	0.010	0.0005
Max	0.12	0.055	0.022	0.0080
ProMicr	0.09	0.055	0.022	0.0005
ProInt	0.12	0.045	0.010	0.0080

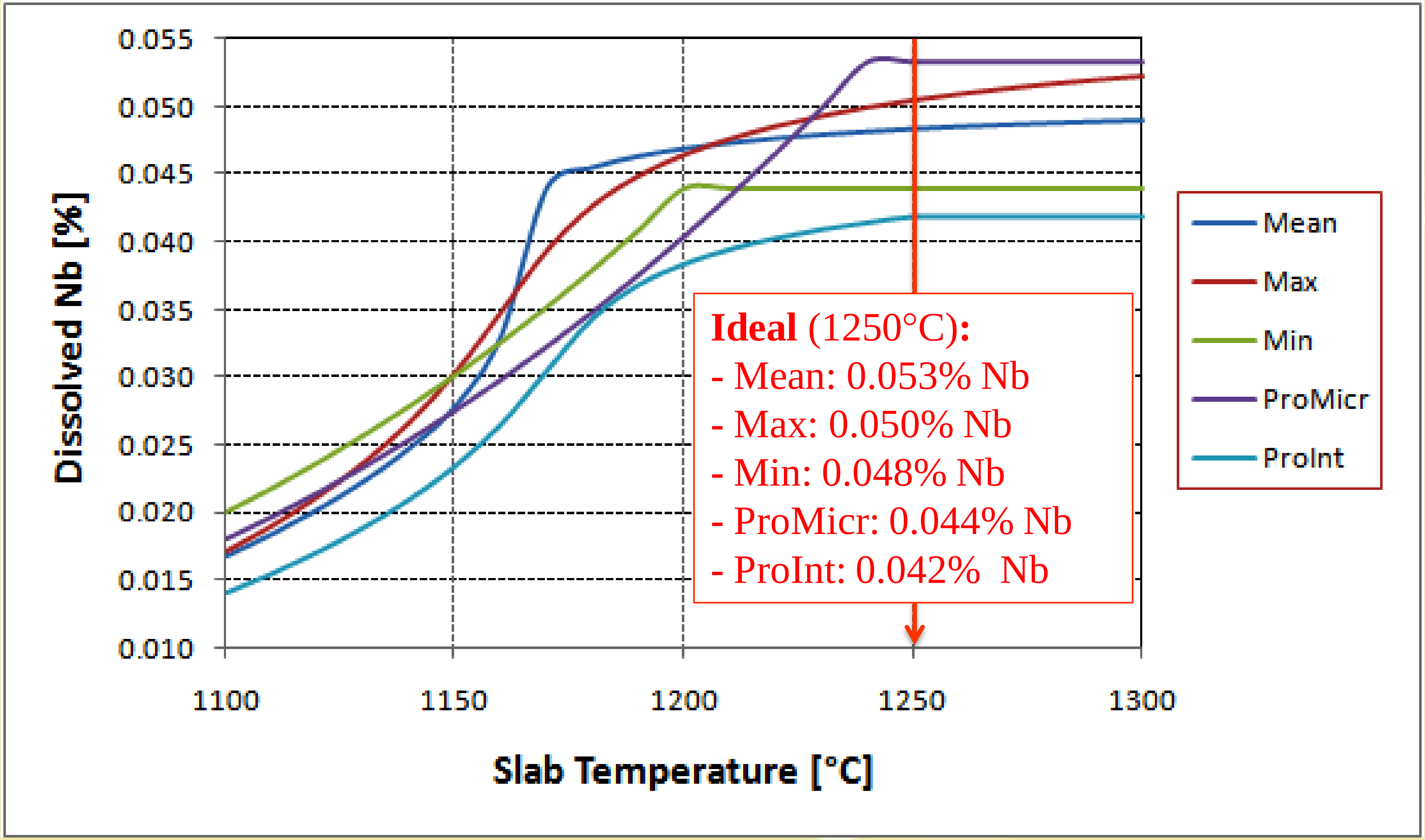
#2: ALLOY COMPOSITION

- **Solubilization evolution** along temperature:



#2: ALLOY COMPOSITION

- **Solubilization evolution** along temperature:

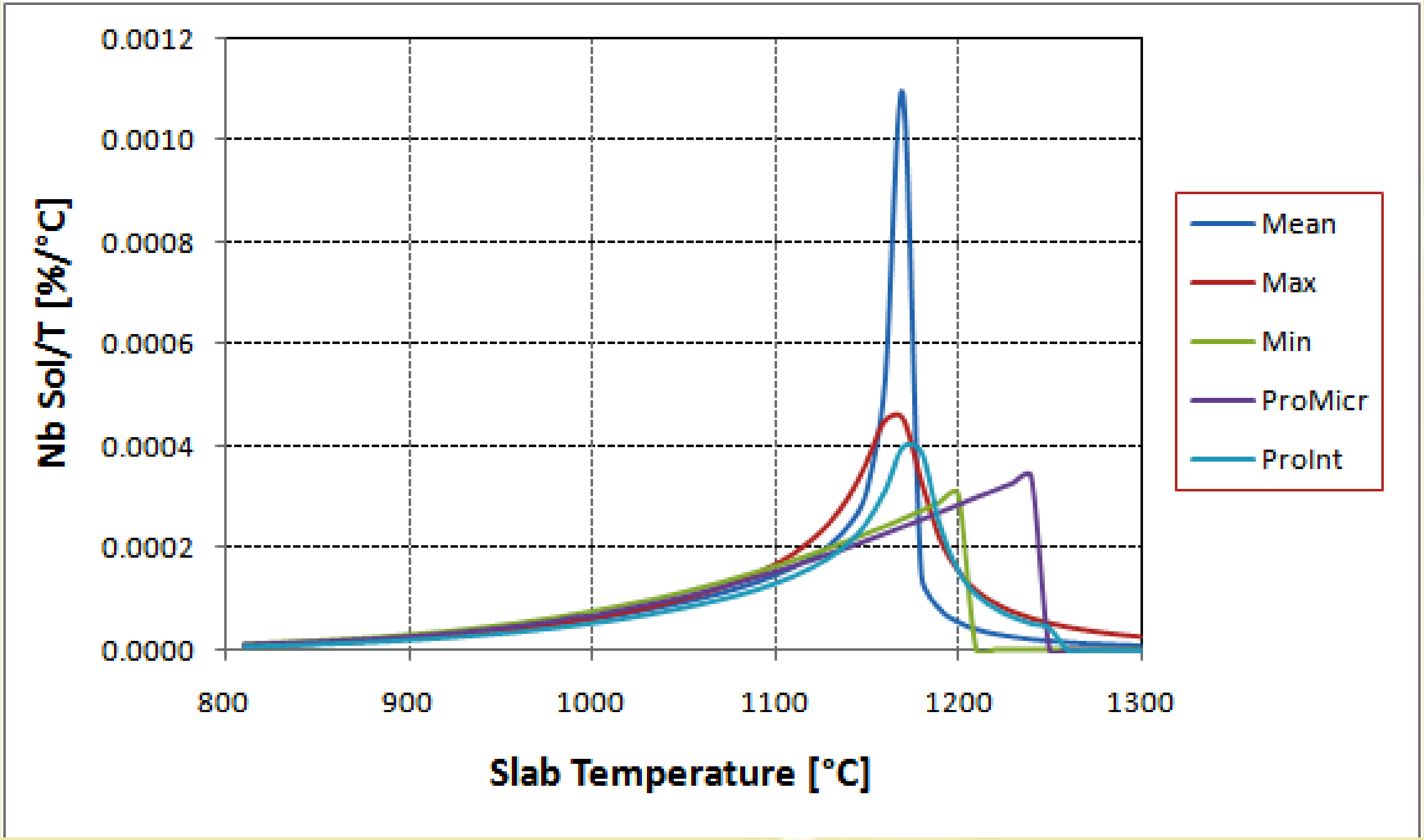


#2: ALLOY COMPOSITION

- **ProInt** alloy showed the worst solubilization evolution along temperature: **slow and limited**.
- **ProMed** alloy is the most convenient: **quick solubilization** at relatively low temperatures (**1150-1170°C**), followed by slight increase for higher temperatures.
- **Max** and **ProMicr** alloys showed **slower solubilization** along temperature, but higher than **ProMed** above 1200°C.
- **Min** alloy had quickest solubilization up to 1150°C and then was surpassed by all others but **ProInt**.

#2: ALLOY COMPOSITION

- **Solubilization rate evolution** along temperature:



#3: SKID MARKS + COMPOSITION

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- As we have just shown, solute Nb levels across the slab depends on **local temperature** and steel **chemical composition**.
- As the slab is supported by water cooled skids during its travel through the reheating furnace, the slab portions near the skids have **significantly lower temperatures** than the remainder of the slab.
- According to real temperature measurements, while slab core temperature at the skid mark location is about **1193°C**, this same region, but away from the skids, is at **1225°C -** that is, a **32°C** difference.

#3: SKID MARKS + COMPOSITION

- Calculated **solubilized Nb** levels:

Alloy	Nb_{sol}		ΔNb_{sol}	ΔNb_{sol}
	1225°C	1193°C	[%]	[%]
Mean	0.048	0.046	-0.002	-4
Min	0.044	0.042	-0.002	-5
Max	0.049	0.045	-0.004	-8
ProInt	0.041	0.037	-0.004	-10
ProMicr	0.050	0.038	-0.012	-24

- It can be seen that **alloys with sluggish solubilization along temperature** tended to show **greater variations** of solute Nb levels across the slab.

#4: COMPOSITION + PRECIPITATE SIZE

- The **maximum size** of the precipitates that can be fully solubilized during slab reheating varies according to the steel **chemical composition**:
  - Mean: 250 nm
  - Max: 225 nm
  - ProMicr: 200 nm
  - Min: 175 nm
  - ProInt: 150 nm

- **Trend:** alloys with **lower and less balanced** levels of Nb, Ti, C and N tend to show **lower diffusion potential**, which makes more difficult the solubilization of their precipitates.

CONCLUSIONS

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- Up to this moment, the understanding about the austenite solubilization kinetics in microalloyed steels is **somewhat incipient** due to the **experimental difficulties** associated with its study.

- However, solubilization control of microalloy elements during slab reheating is of **paramount importance** to the **consistency of the properties** of controlled rolled flat products.

- This work is a **small contribution** to get more knowledge about the **kinetics** of the austenite microalloy solubilization under industrial conditions.

CONCLUSIONS

- The **mathematical model** developed in this work highlighted the following main factors that affect **austenite microalloy solubilization**:
  - **Precise alloy chemical composition**, particularly C, N, Nb and Ti;
  - **Slab continuous casting conditions** that affect **Nb segregation** and, consequentely, the **distribution and size of its precipitates**;
  - **Slab reheating conditions**, including the intensity of the so called **skid marks**.

THANK YOU VERY MUCH FOR YOUR ATTENTION!