Application of Computational Thermodynamics to Steel Processing and Alloy Design

André Costa e Silva
EEIMVR-UFF
Volta Redonda Brazil

Outline

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- **Where did we come from?**
  - Empiricism, theories, models, diagrams, data...

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- **Where are we (what can we do)?**
  - CALPHAD and “related techniques”
- **Where do we want to go?**
  - Using CALPHAD to solve practical applications and gain insight on complex problems.

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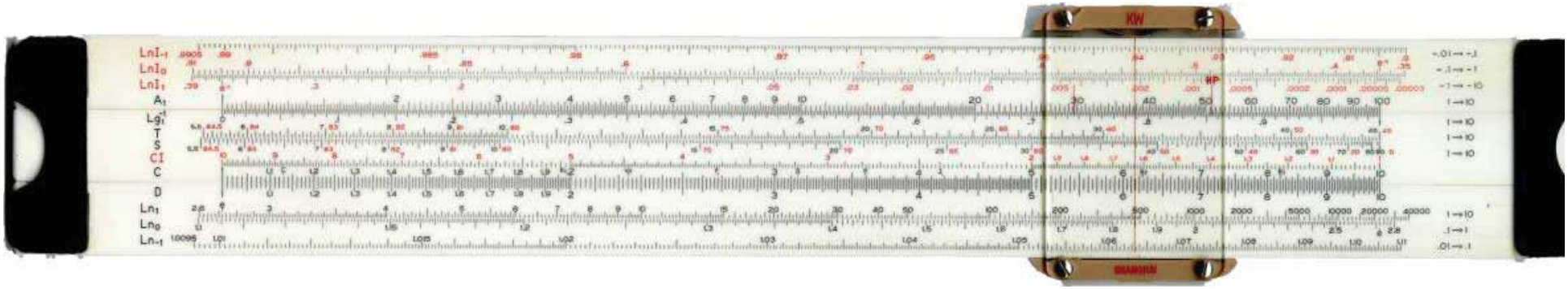

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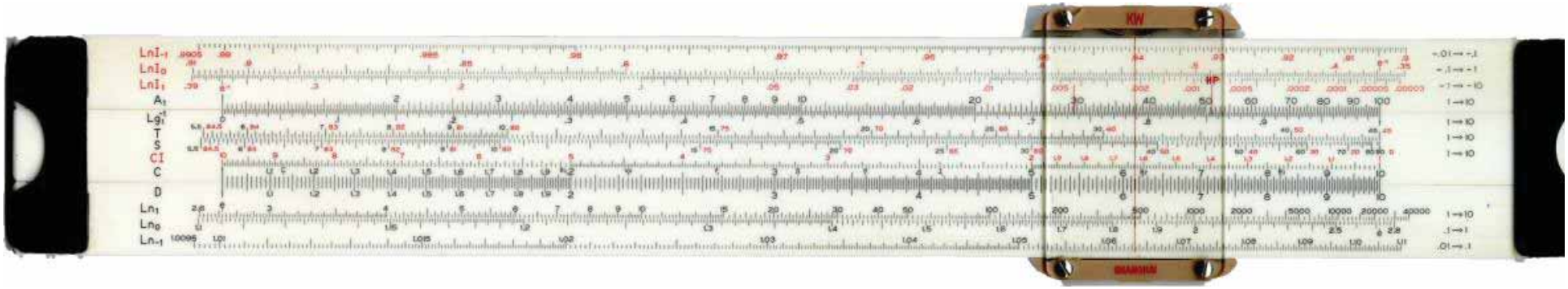

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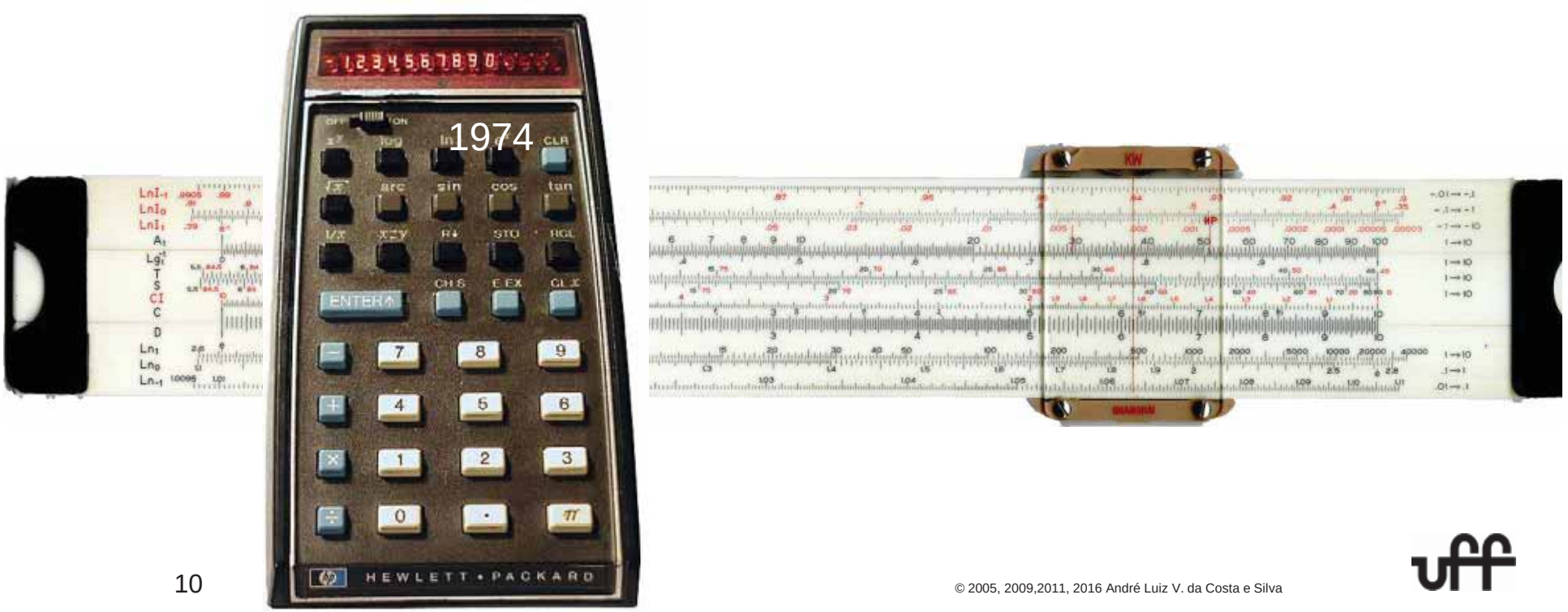

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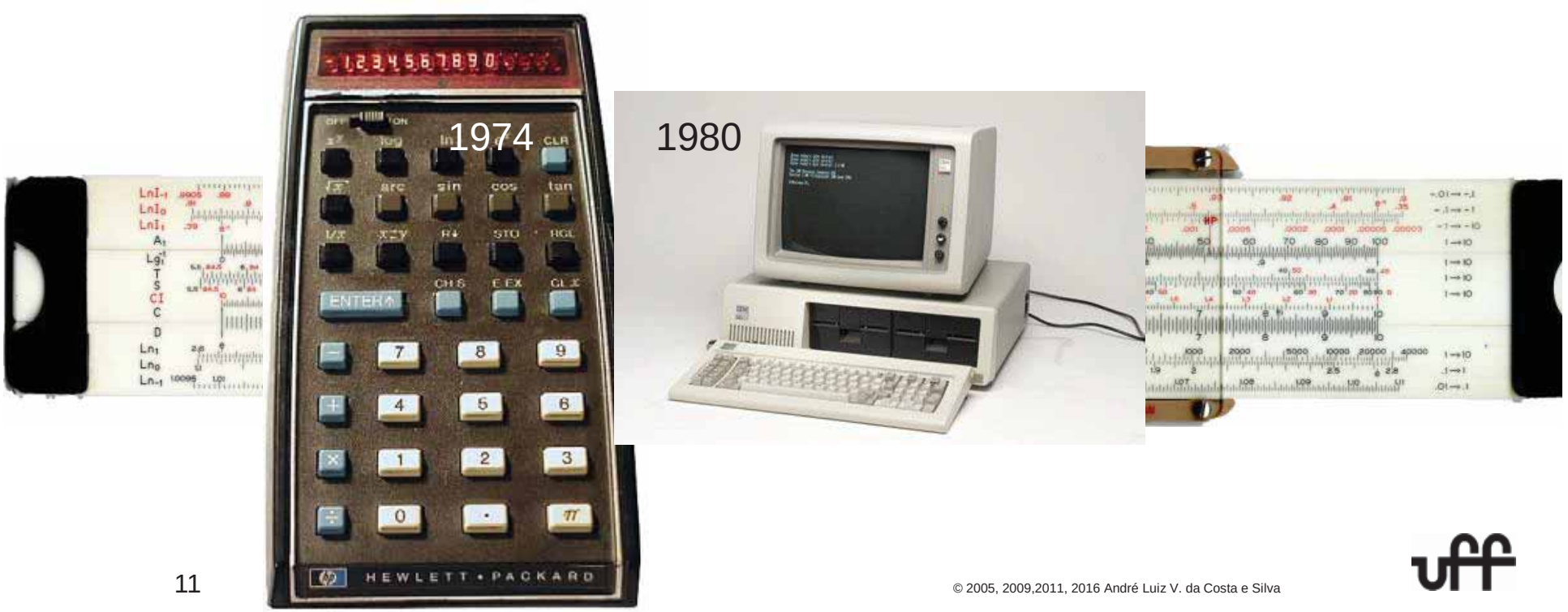

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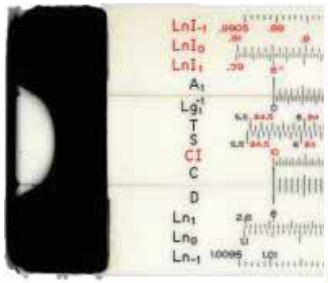

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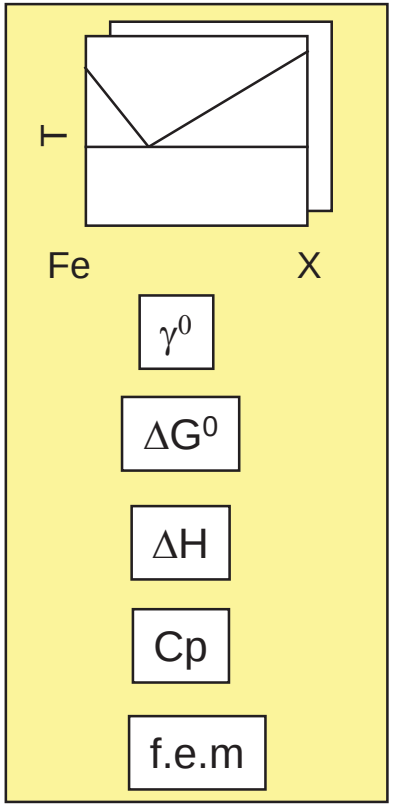

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Binaries, ternaries,…
Isoactivities,
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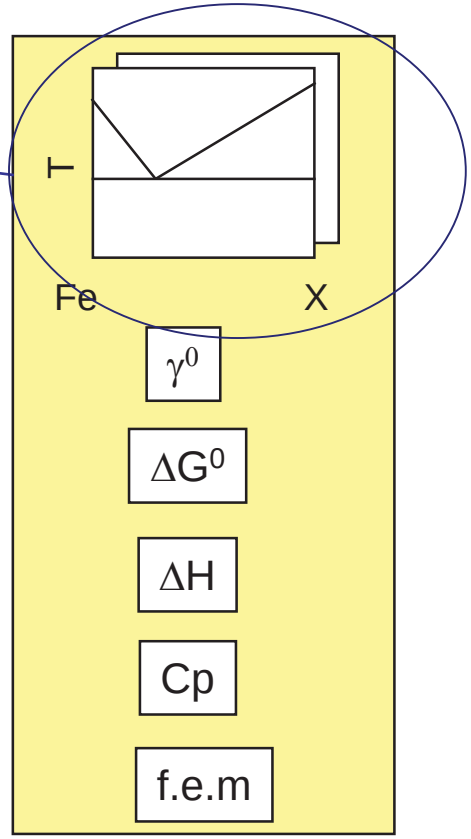

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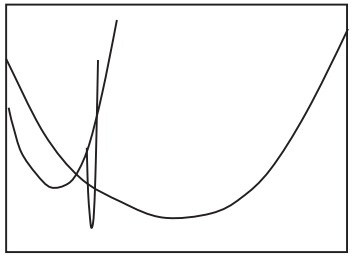

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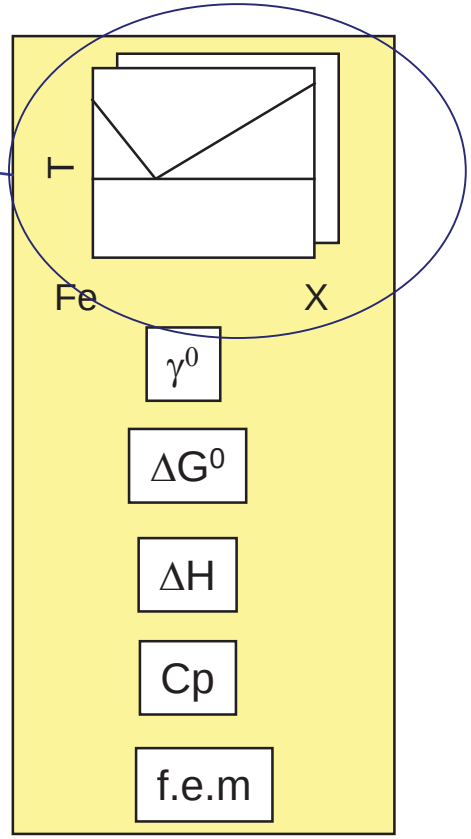

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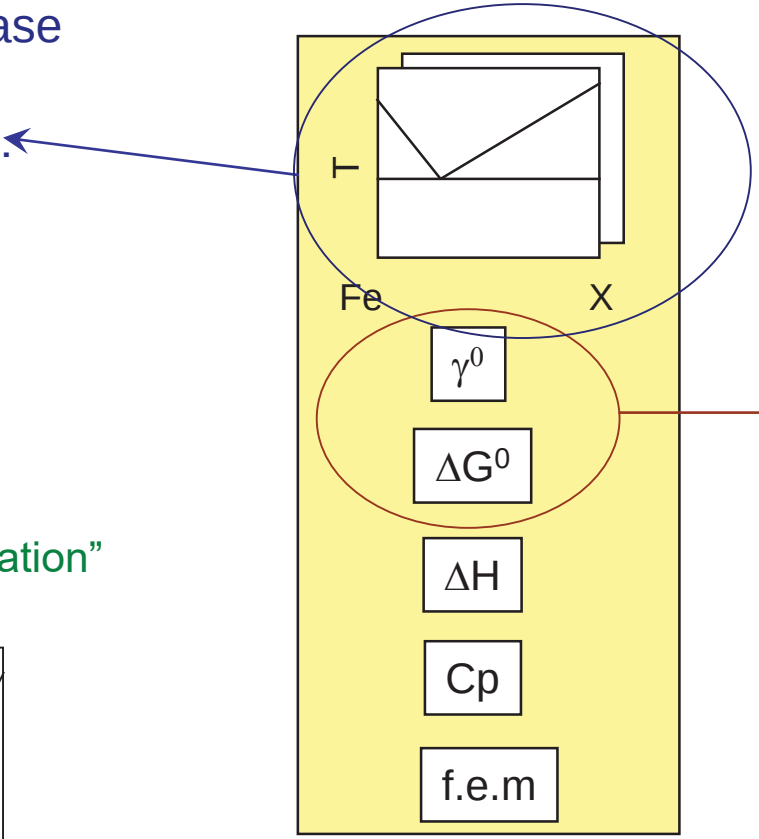

Calculations for dilute solutions:
Equilibria,
Solubility products,
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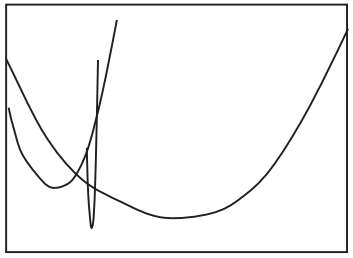

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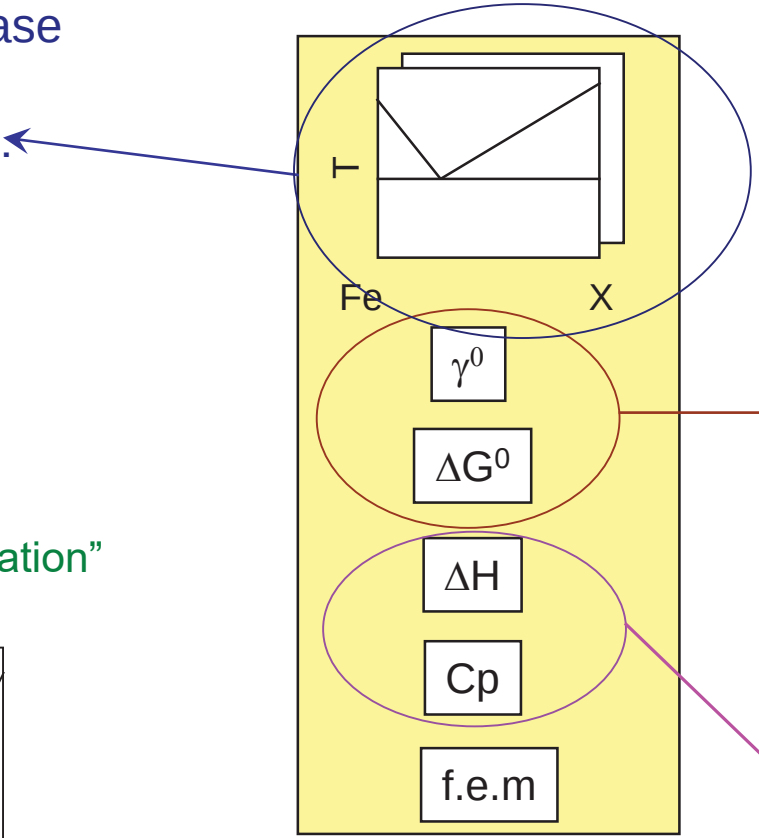

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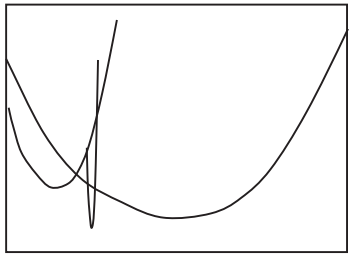
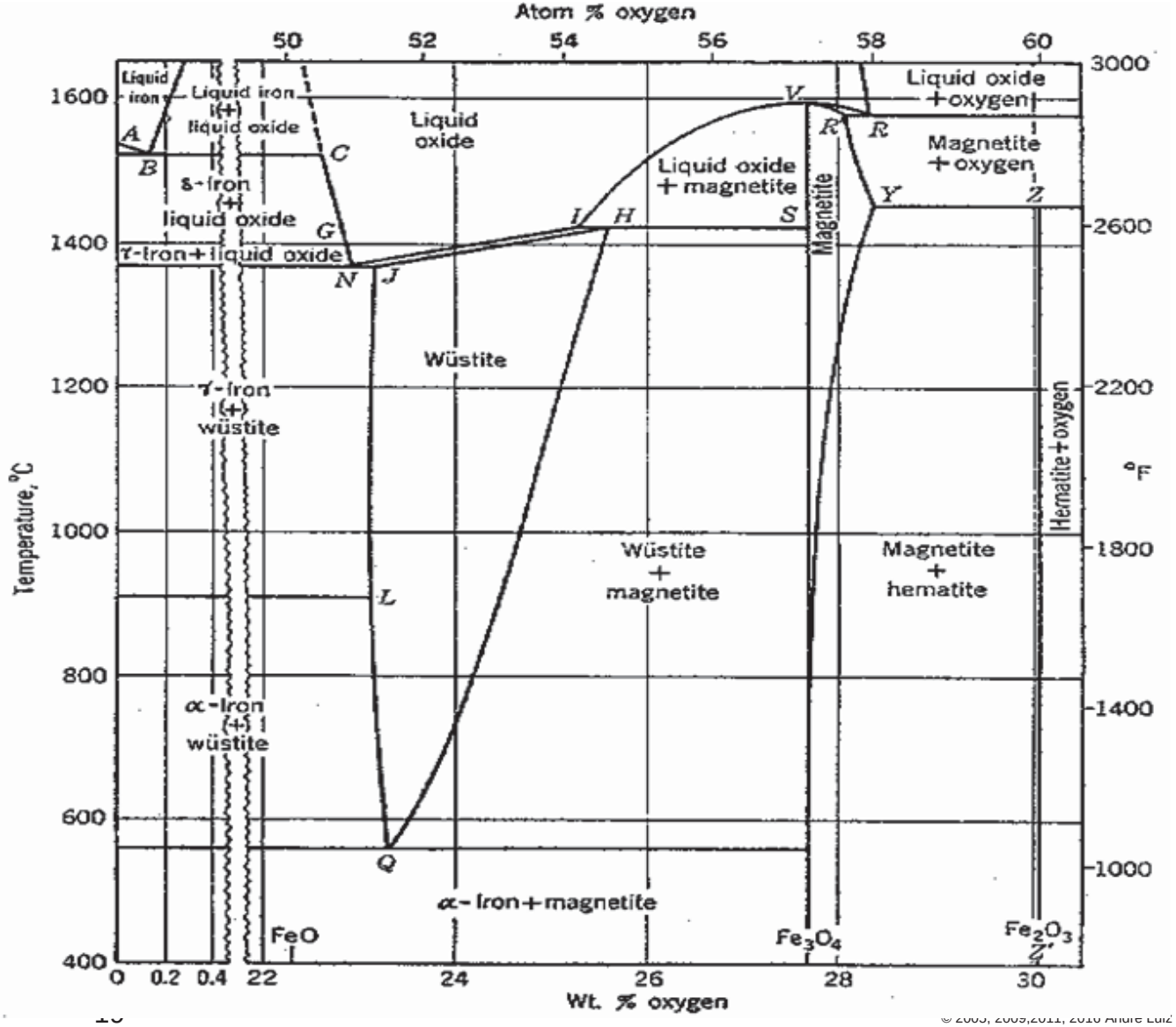


Heat balances using EXTERNAL information about the state of the system.

Example: O solubilty in Liquid Fe



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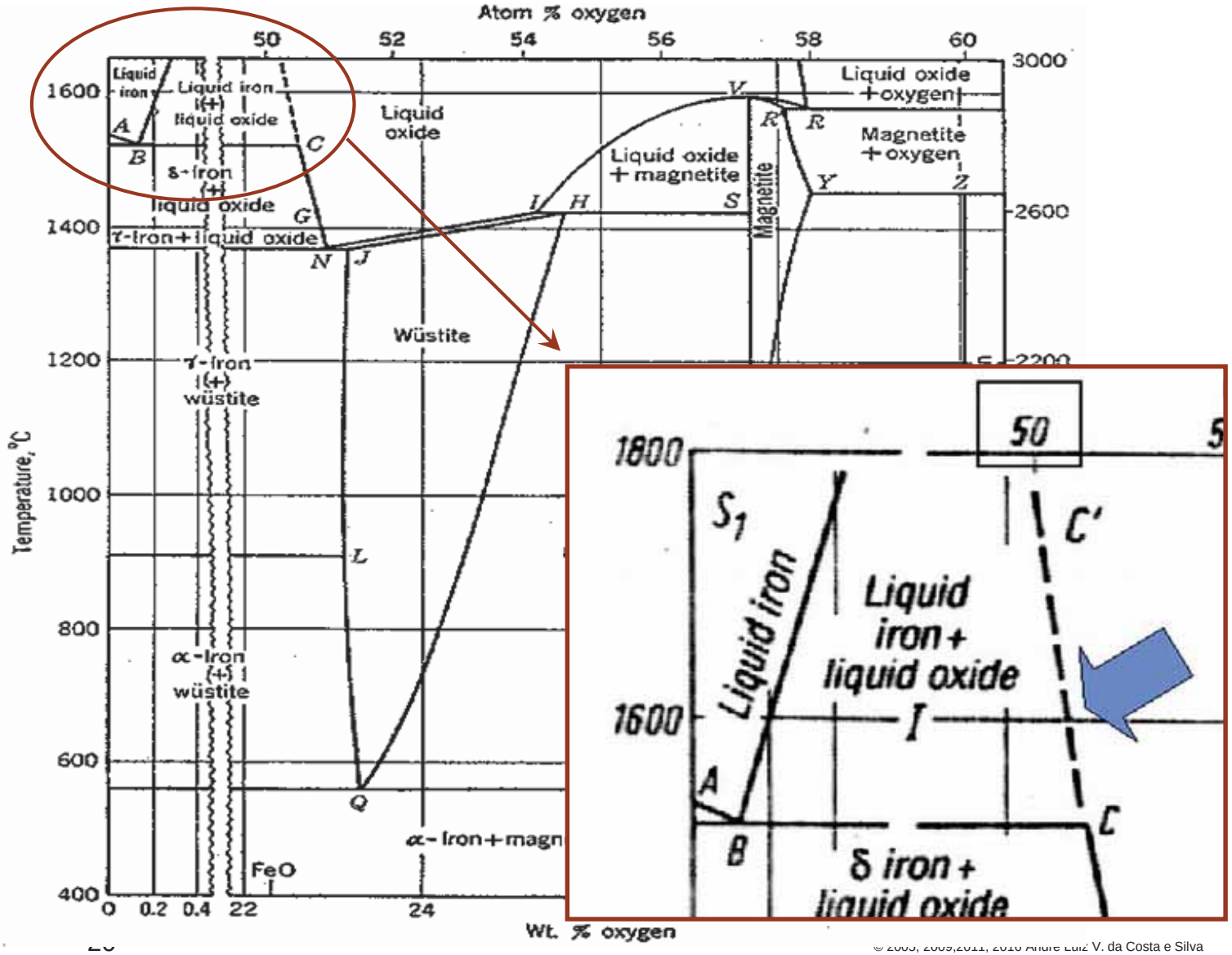

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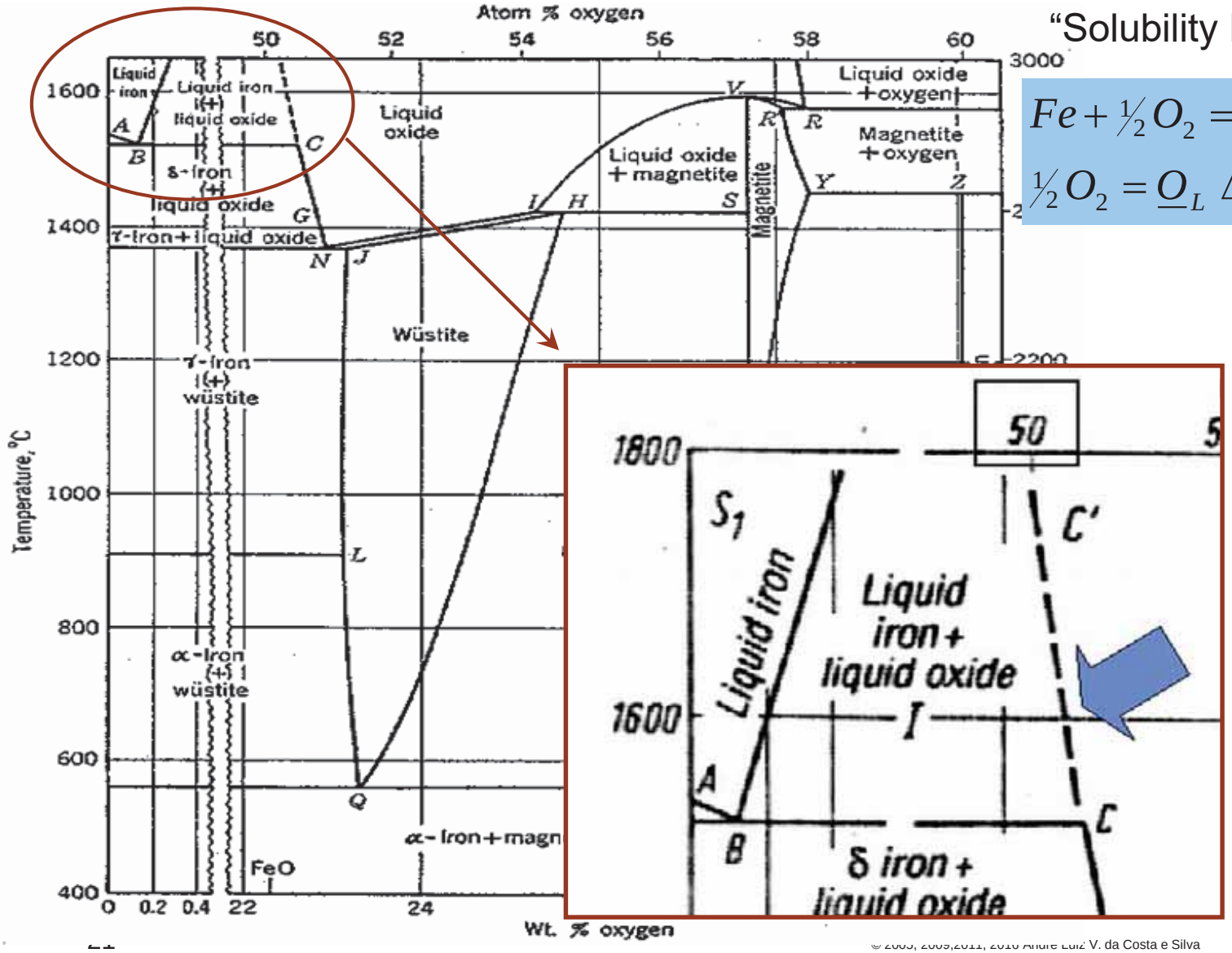

"Solubility limit"

$$Fe + \tfrac{1}{2}O_2 = "FeO" \quad \Delta G^0$$

$$\tfrac{1}{2}O_2 = \underline{O}_L \quad \Delta G^{M,1\%}_{O,L}$$

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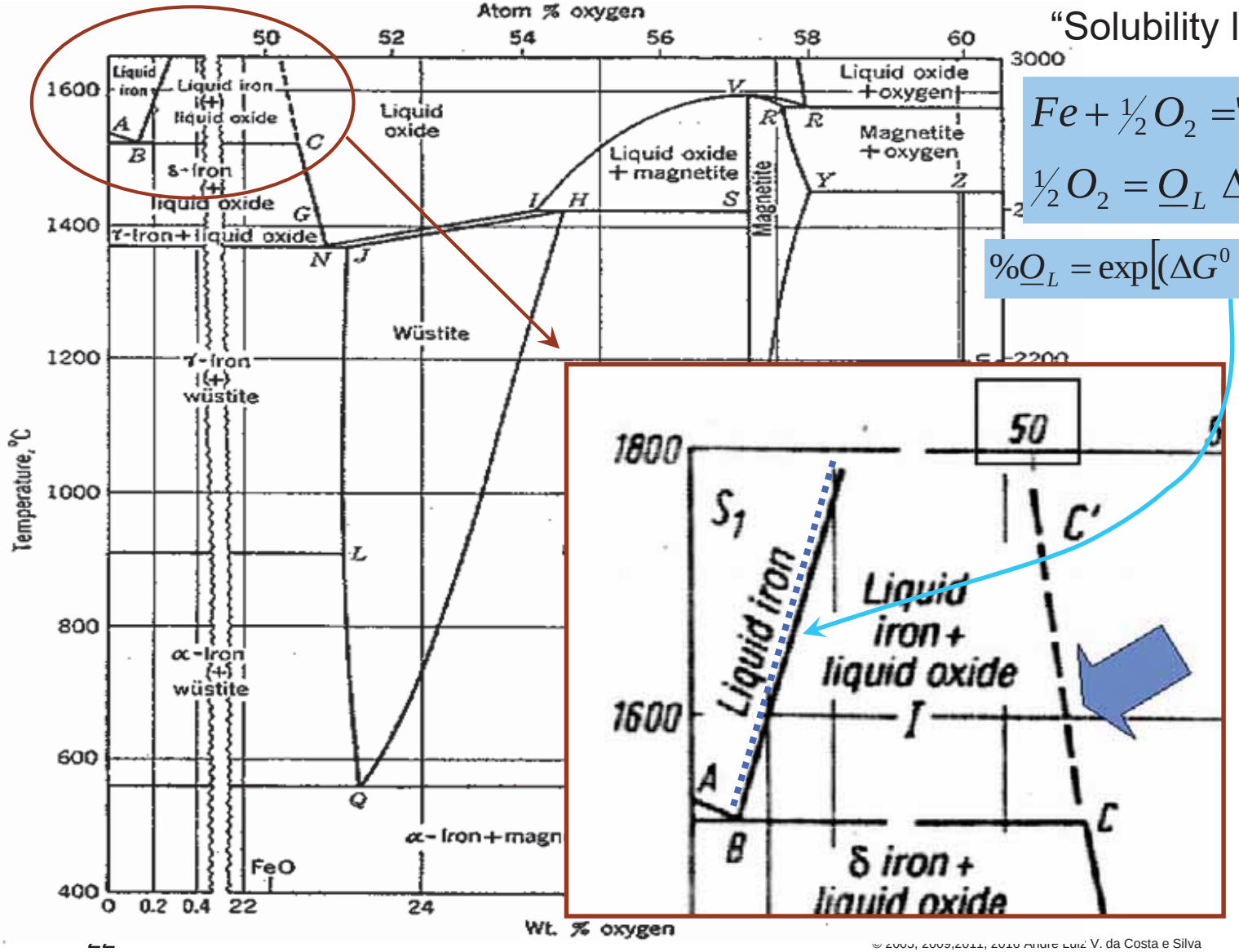

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- **“Brave” applications**
  - Alloy design
  - Process design
  - Forecasting

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- **Steelmaking Alloy and Processing design**
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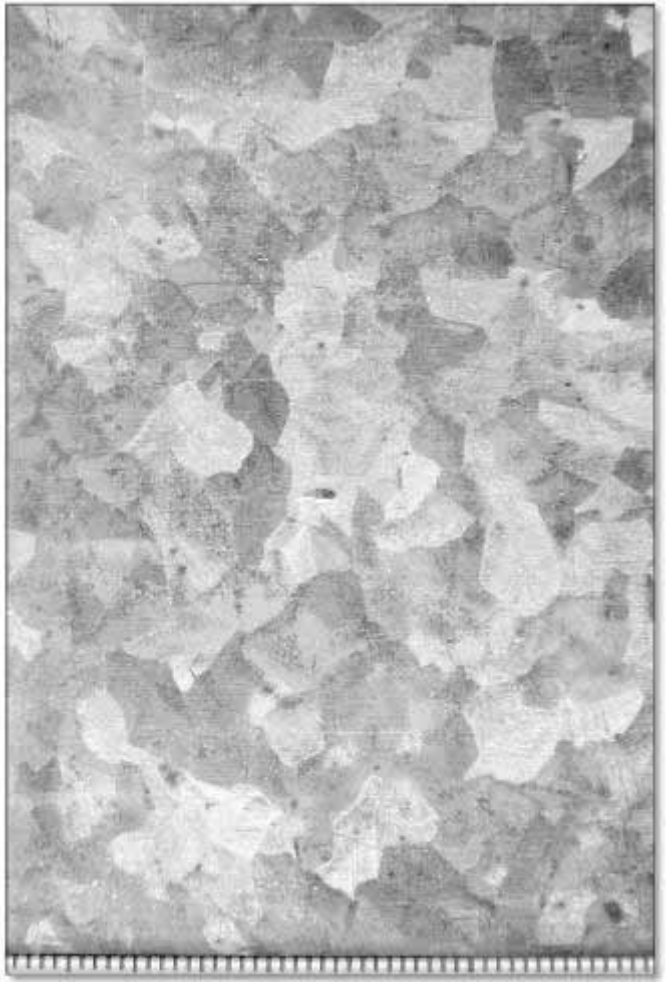
- **Steelmaking Alloy and Processing design**
  - 6 elements at least (besides Fe), some in ppm quantities, high temperatures, need to be “very, very” close to reality or lose your job!
- **Forecasting Alloy behavior**
  - Component ageing (innaccessible experiments...)
  - Understanding oxidation...

Understanding galvanizing- small additions to Zn bath have large effects...



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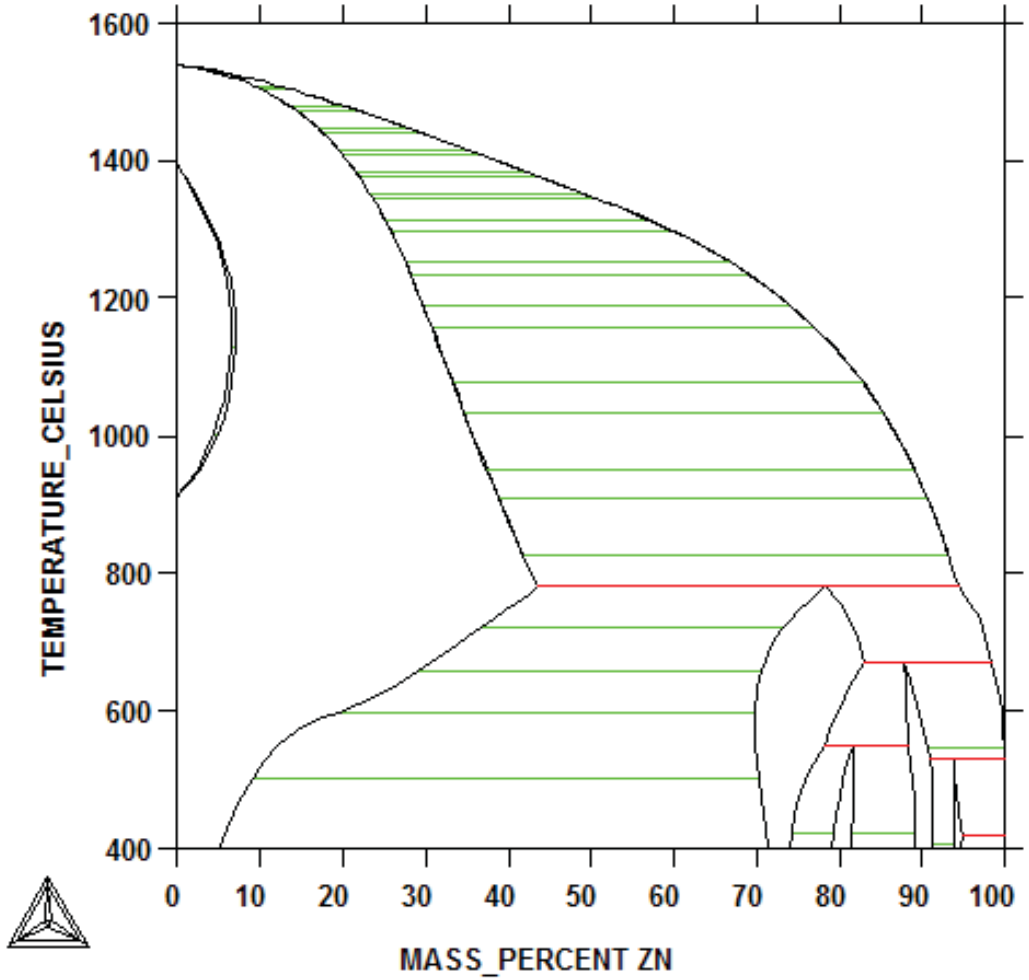

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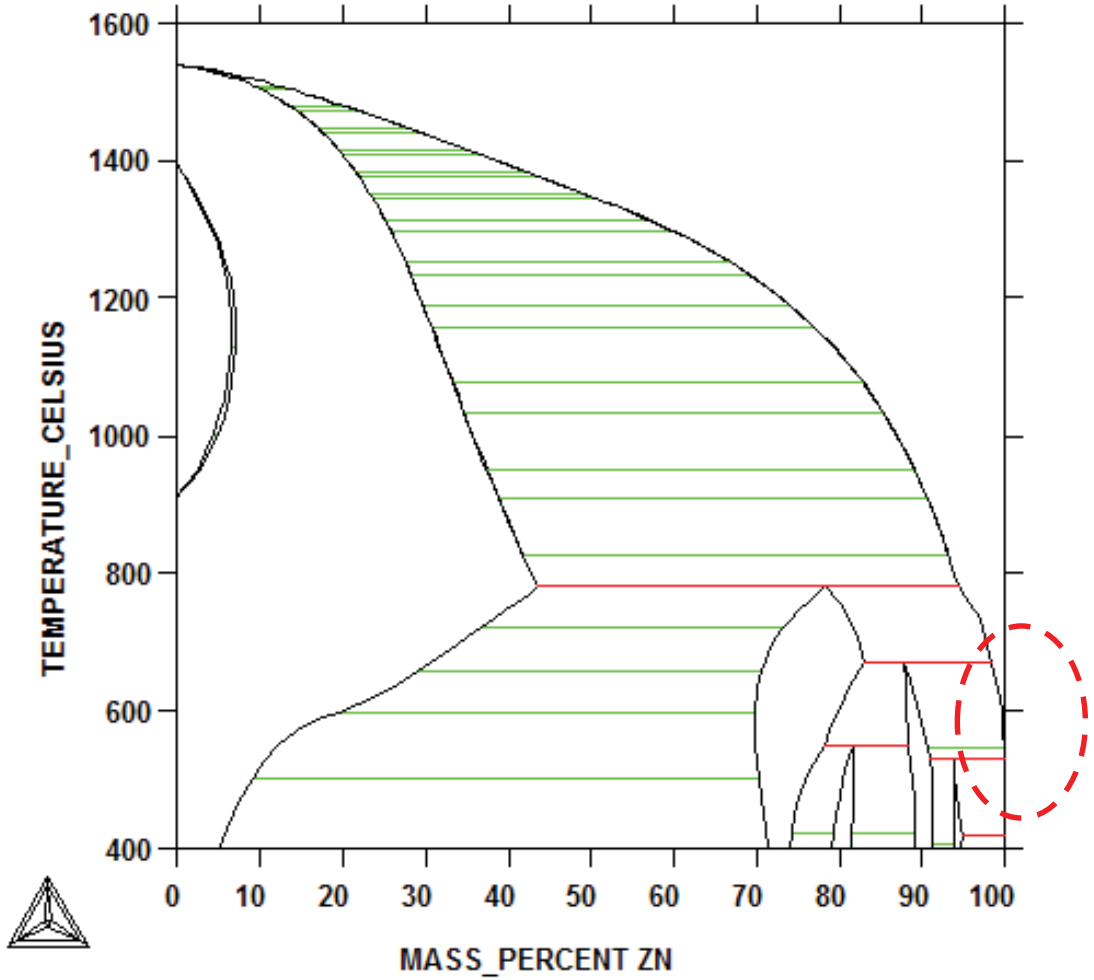

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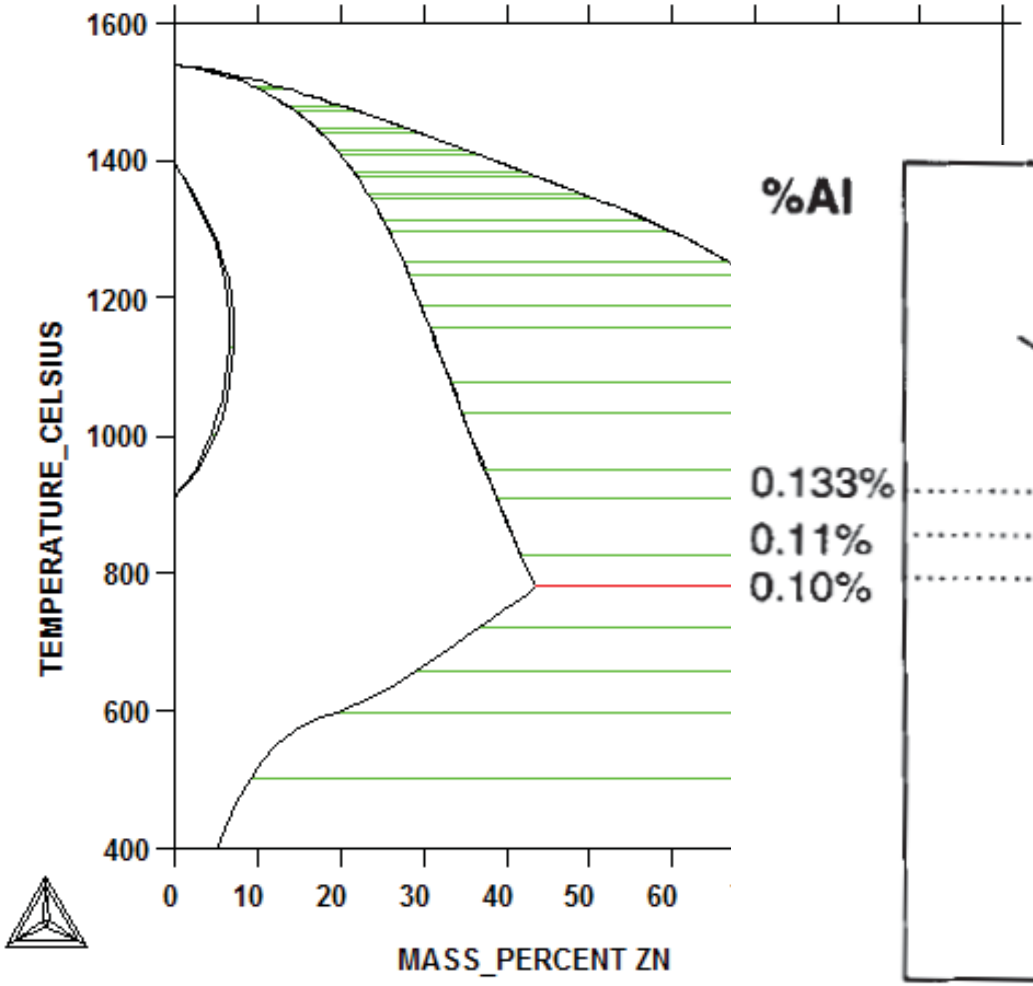
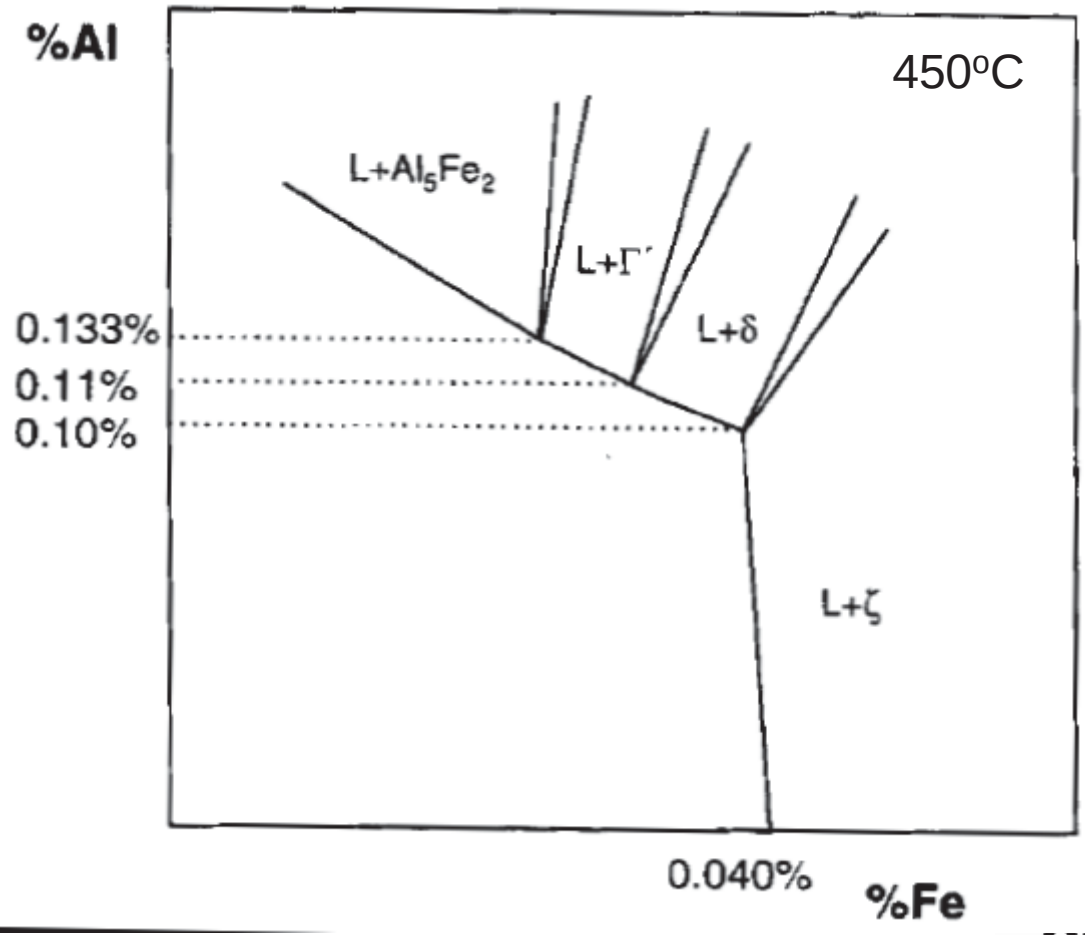
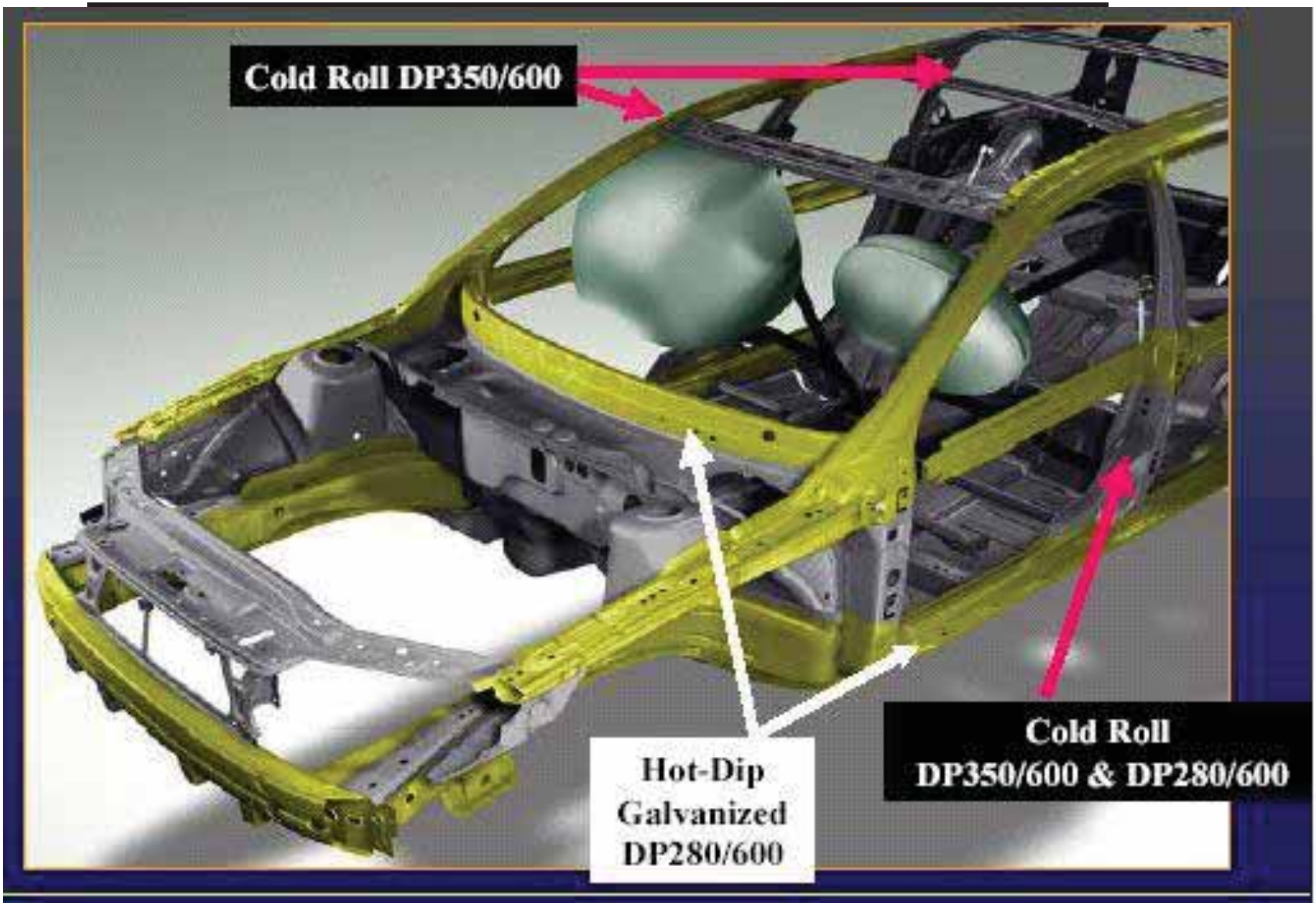


Costa e Silva, Avillez, Marques, 1999



Dual phase steels



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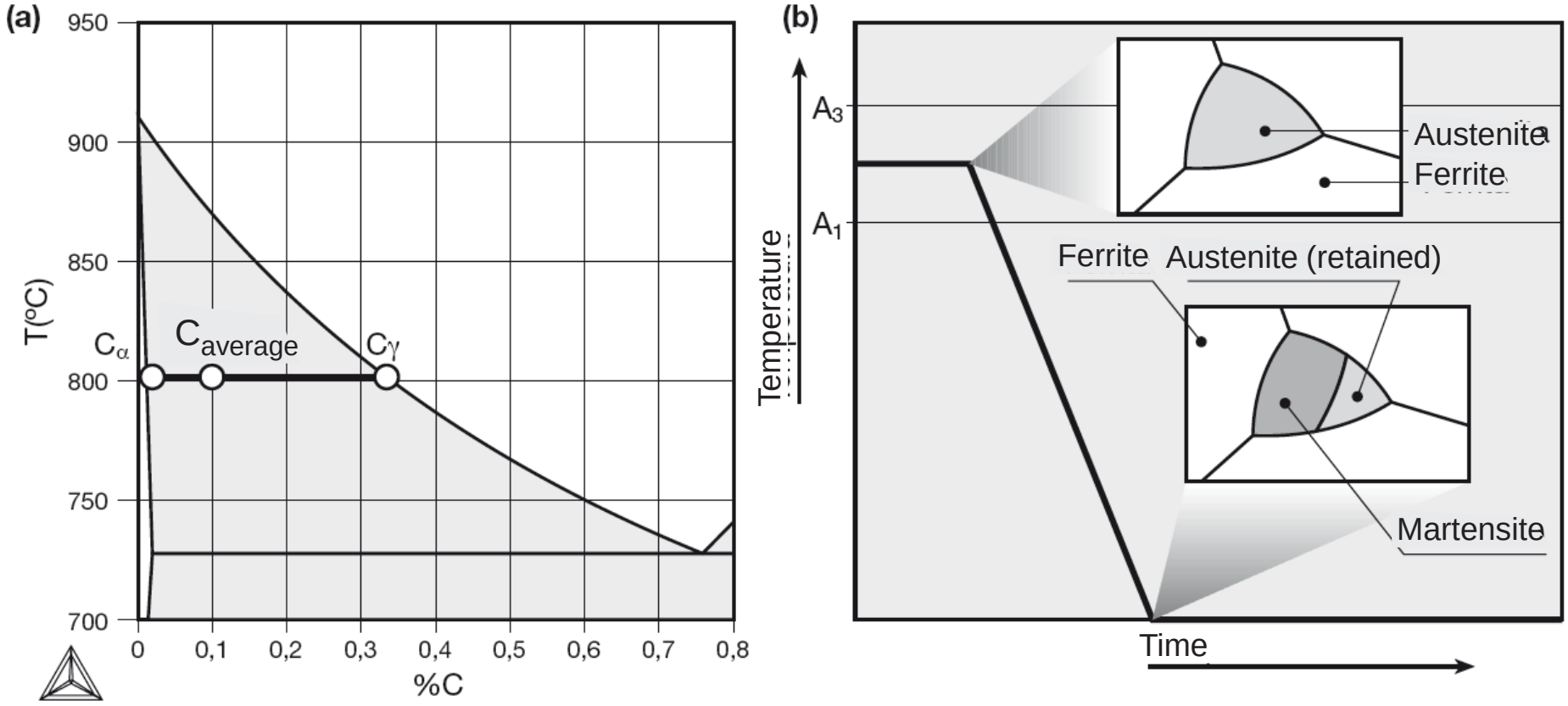
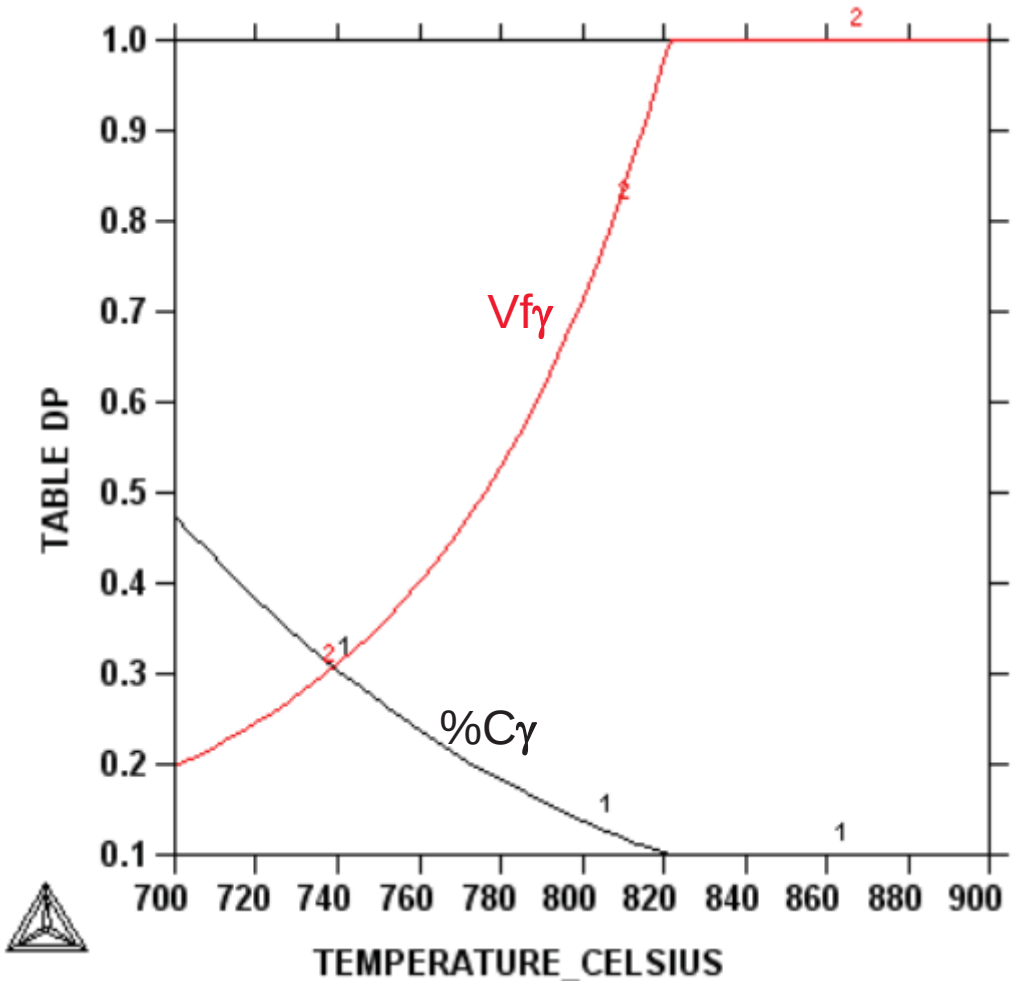


Dual Phase constitution- Effect of B addition



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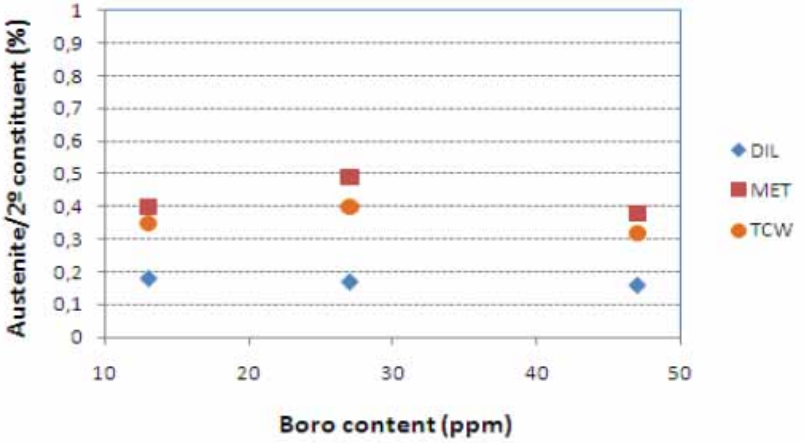
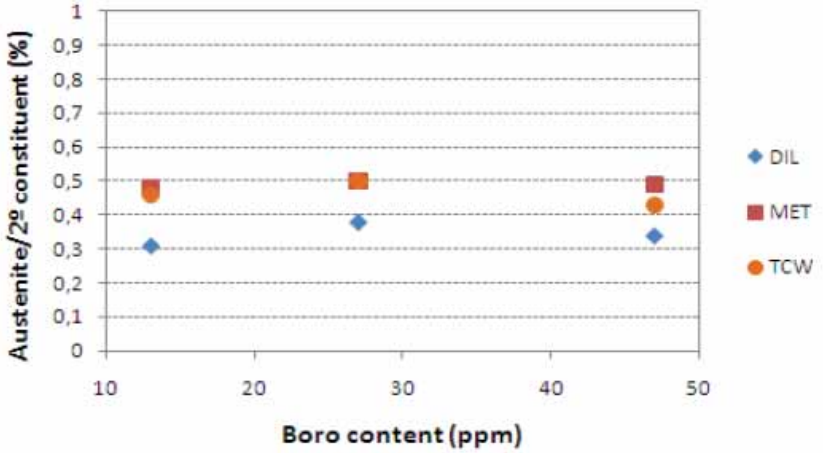
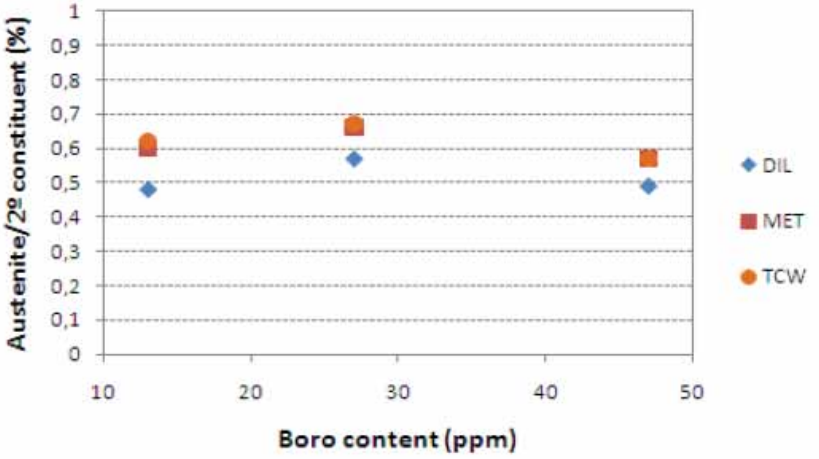
Murari, Costa e Silva, Avillez, 2015



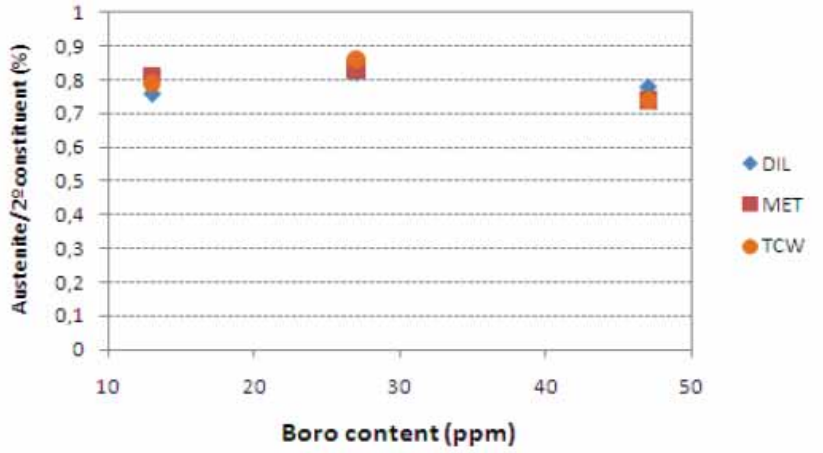
(a) 760°C



(b) 780°C



(c) 800°C



(d) 820°C

Example: Spring steels, tire cord, bearings

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1955-80

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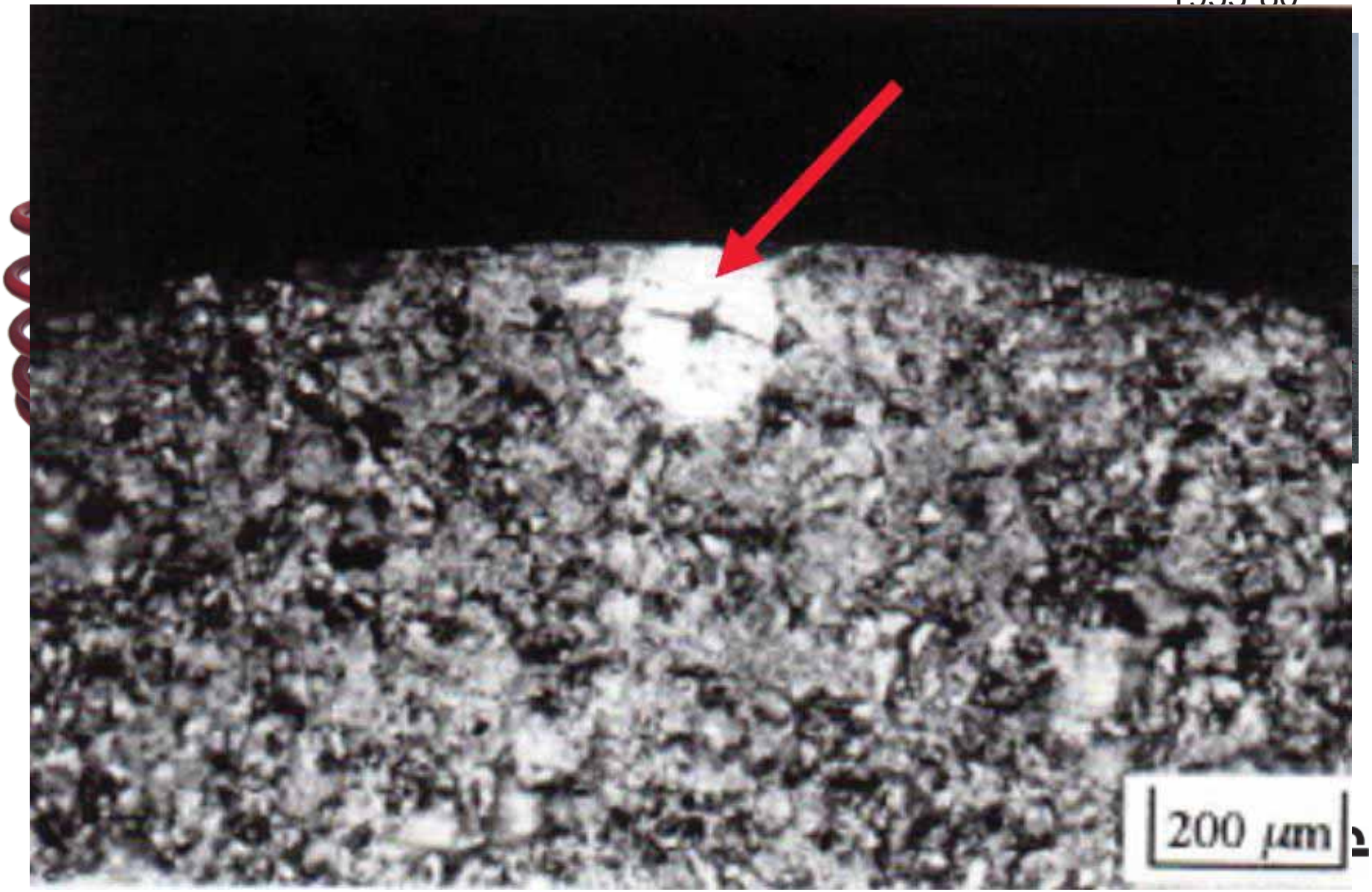
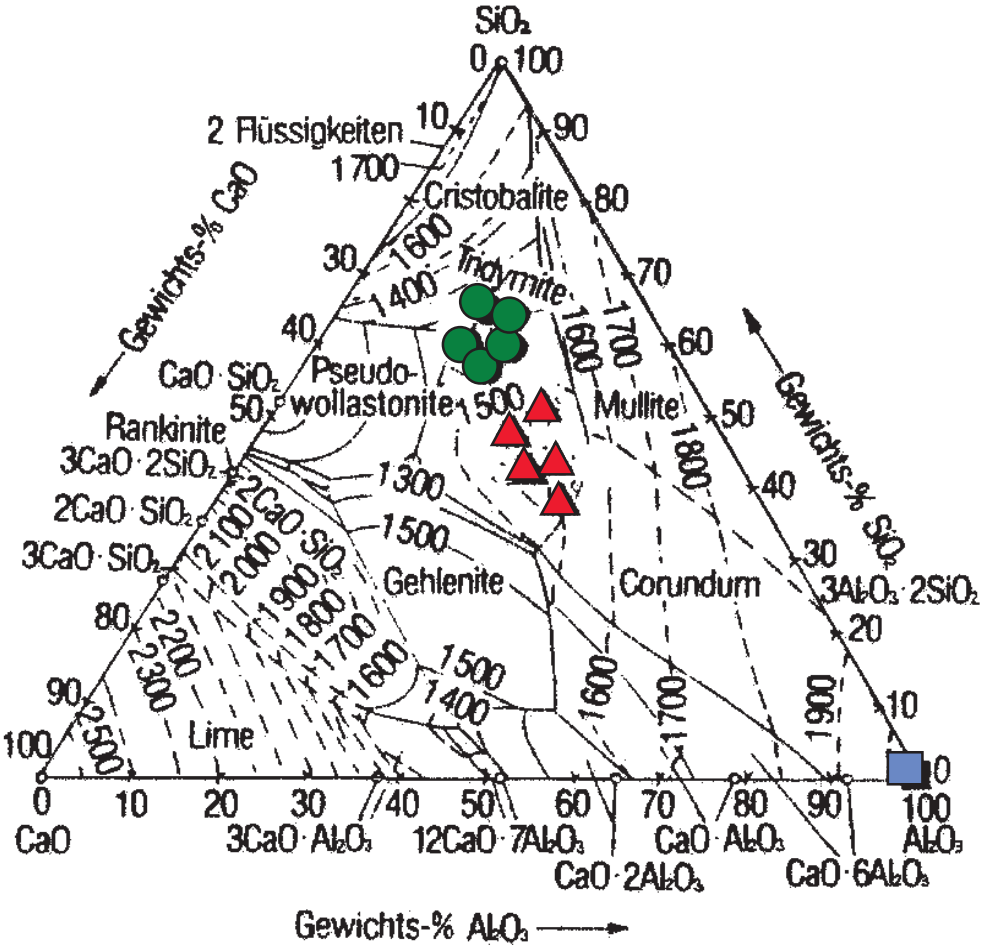
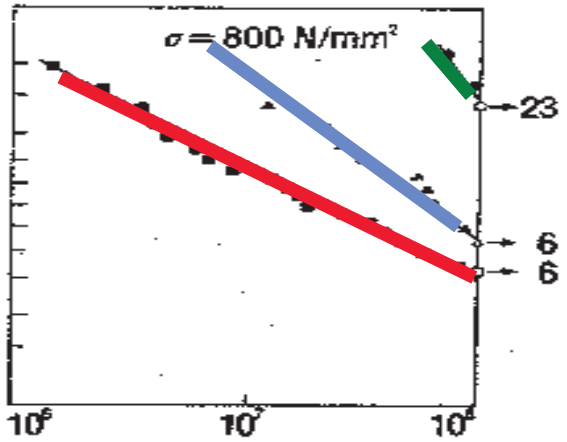


1980-20...

Inclusions vs. Fatigue

- SAE 9254 - Oshiro et al. 1989





Number of cycles

The strategy in slag-metal equilibrium processing

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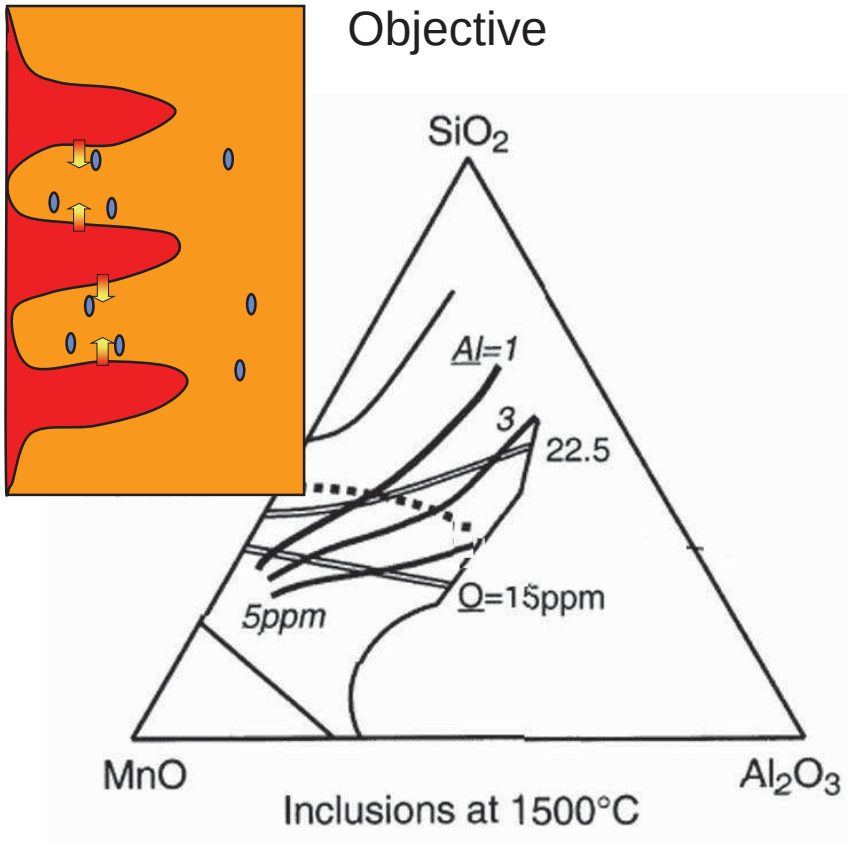

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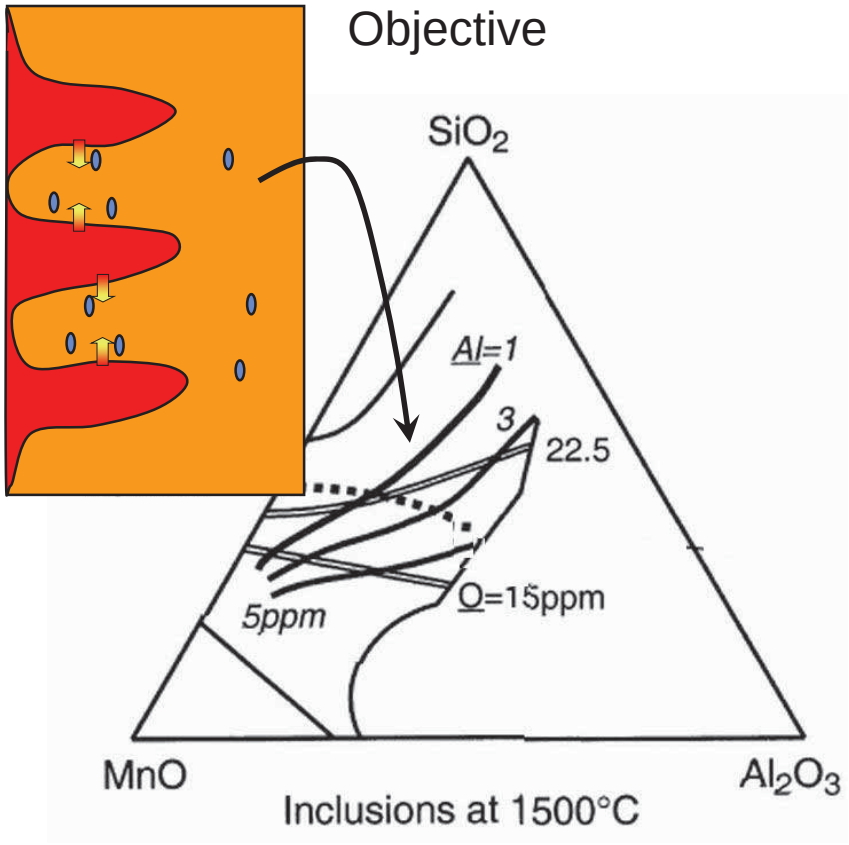

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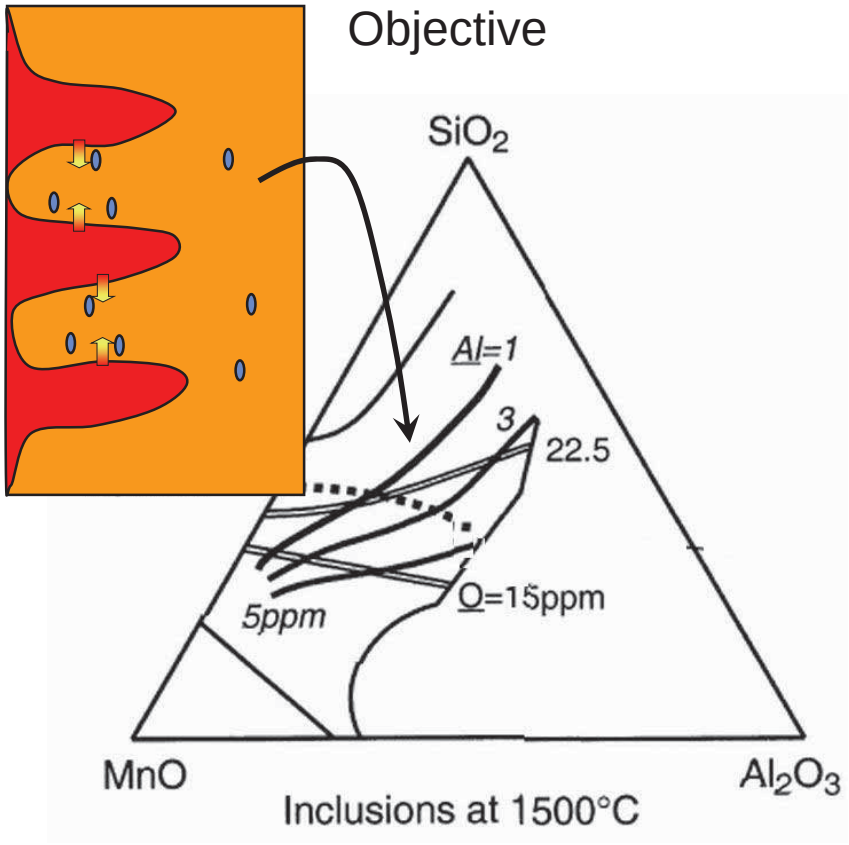
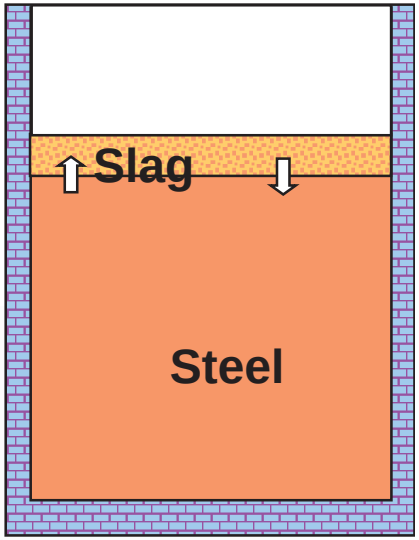
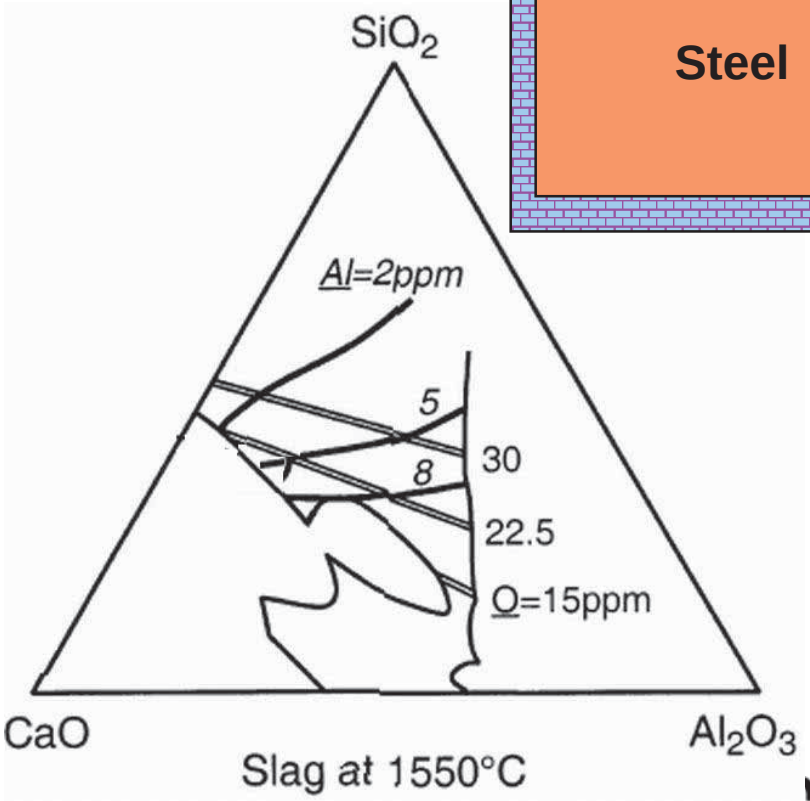


Process





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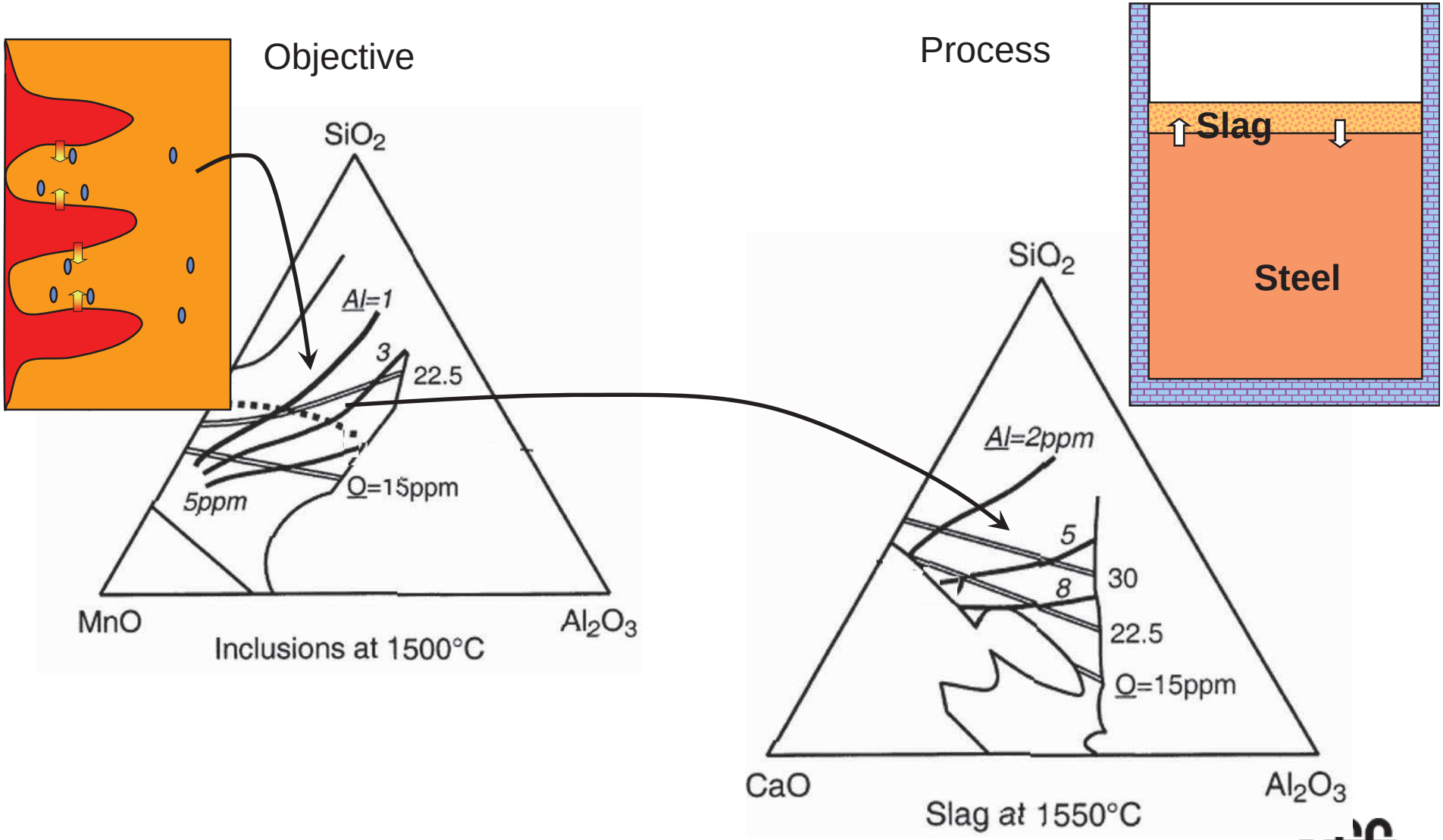

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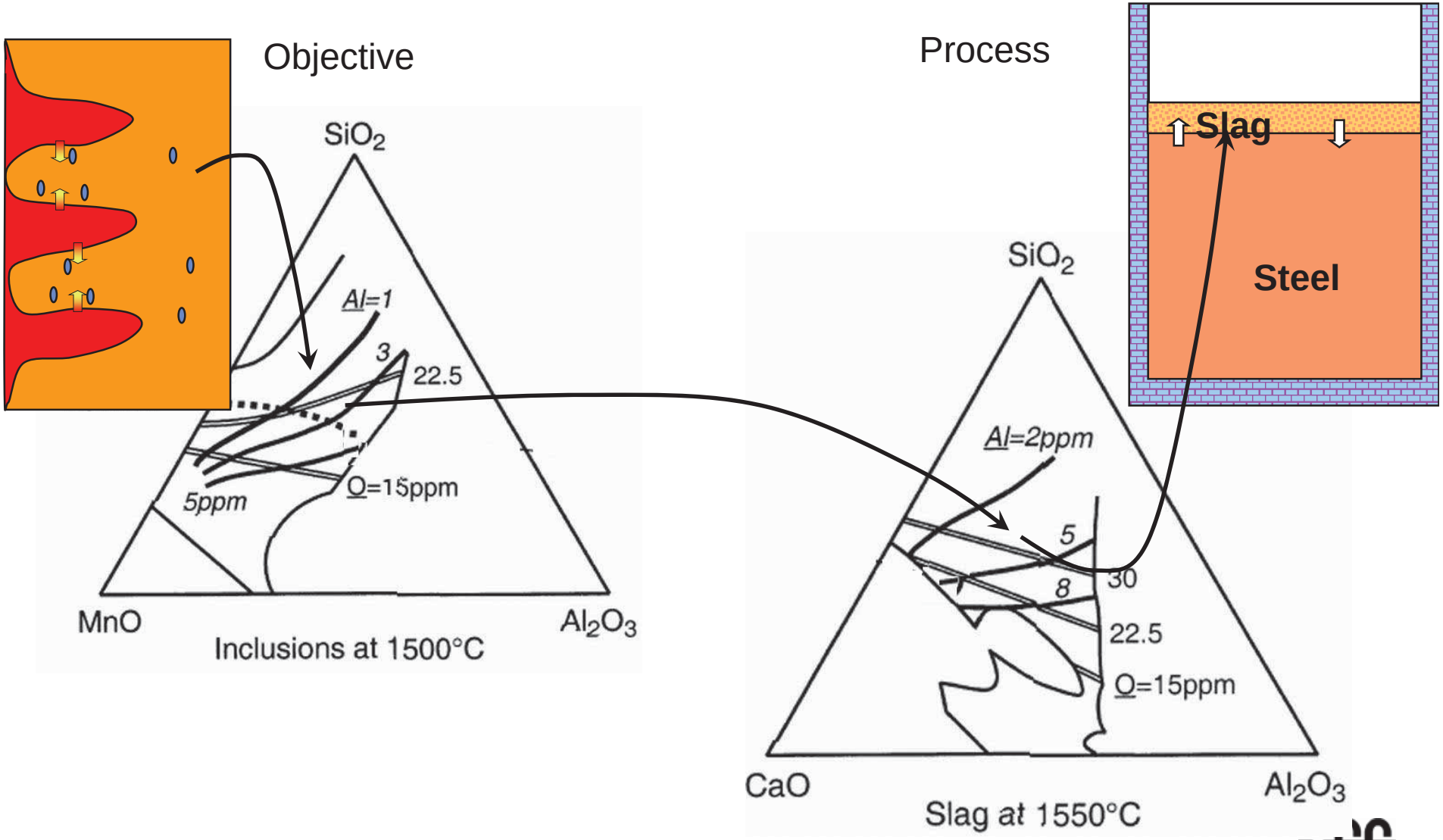

Avoiding Al_2O_3 and tailoring non-metallic inclusions in tire cord steel

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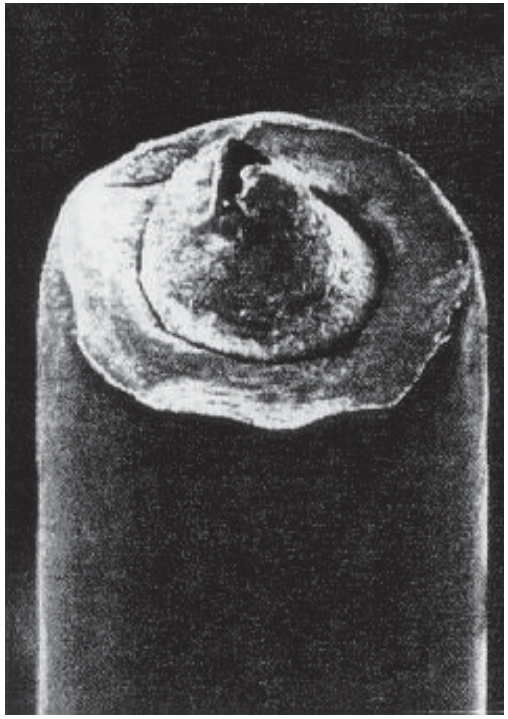

50 μm

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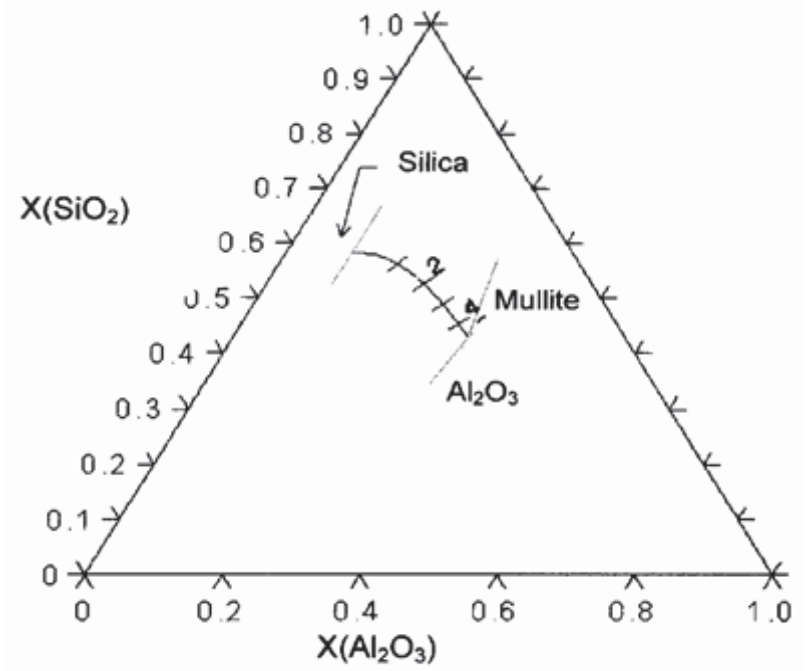

Steel C=0,8%, Mn=0.6%, Si=0,3%

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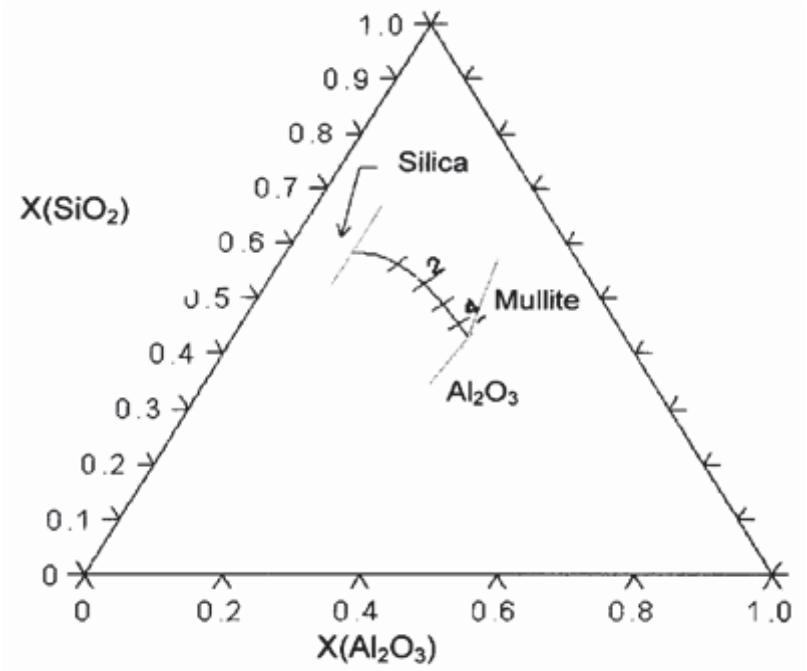

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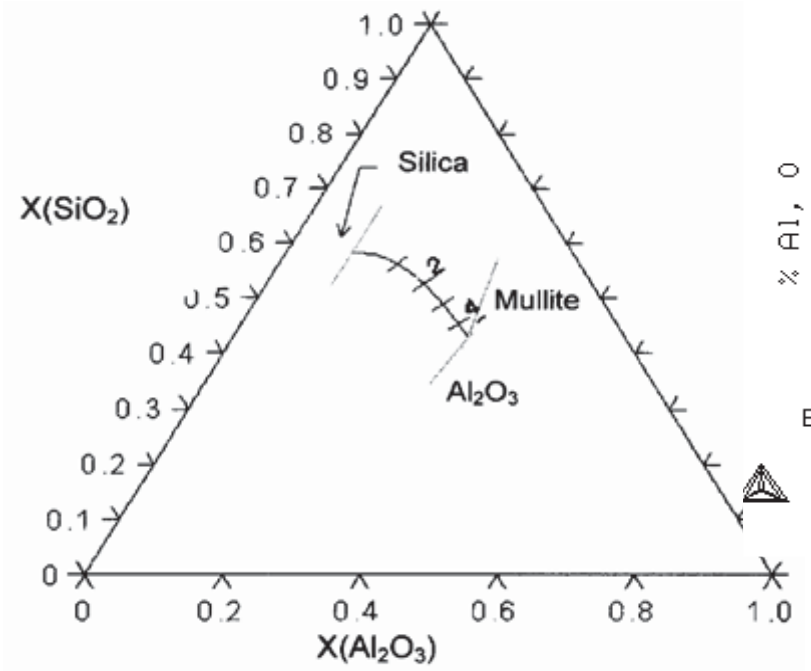

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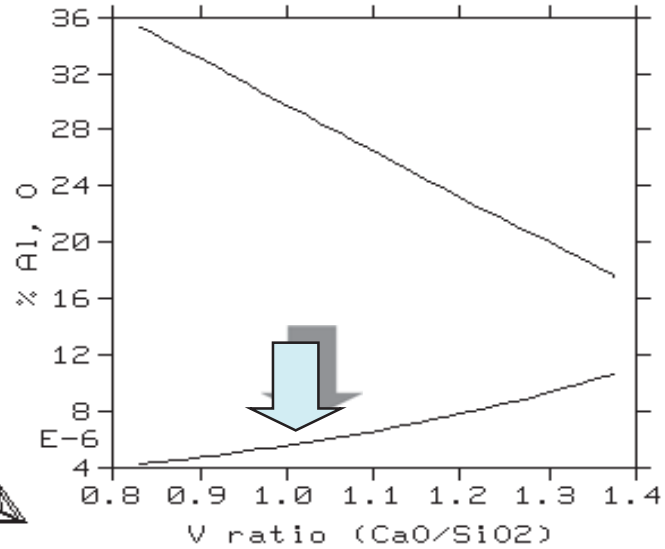
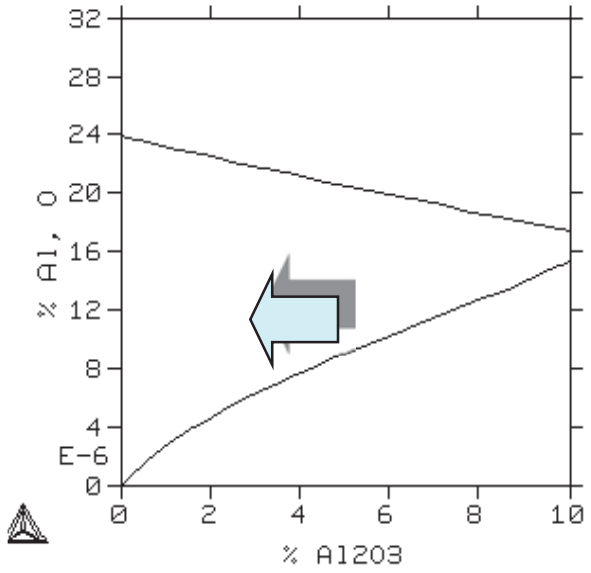
Effect of slag basicity $\%Al_2O_3$=5



Effect of slag Al_2O_3 content V=1.2



Oertel, Costa e Silva, 1999, Costa e Silva, 1999

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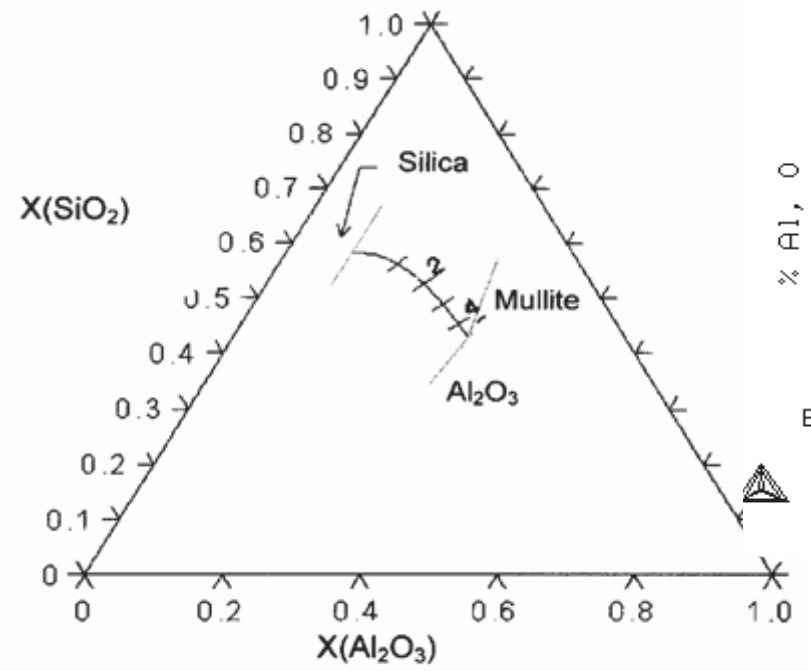

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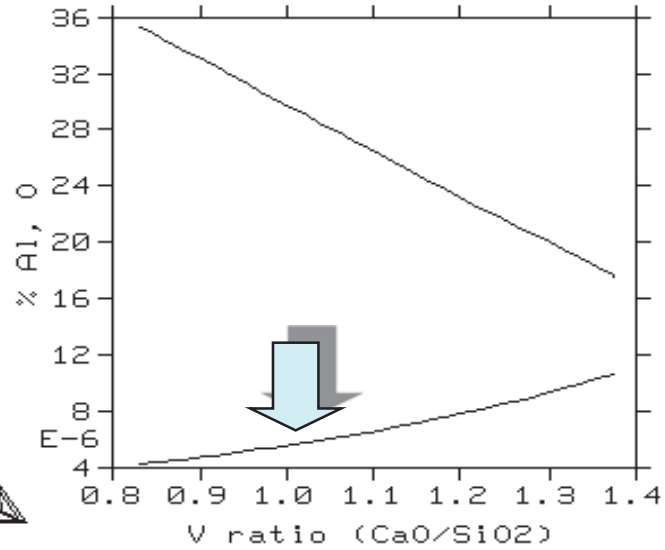

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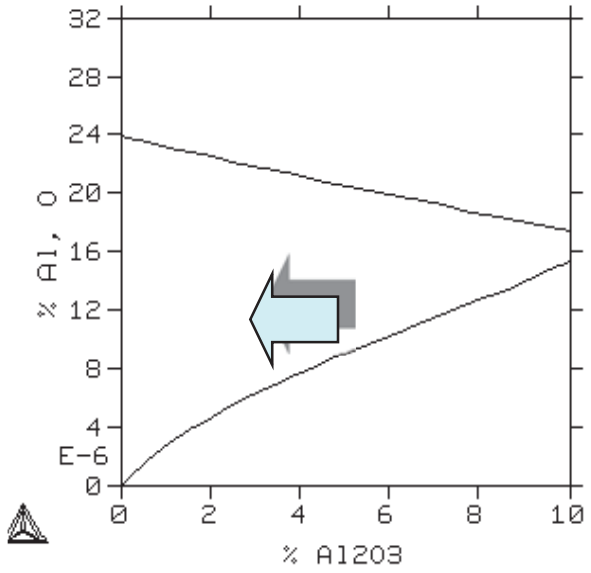

Minimizing Al and O in bearing steels (52100 or 100Cr6)

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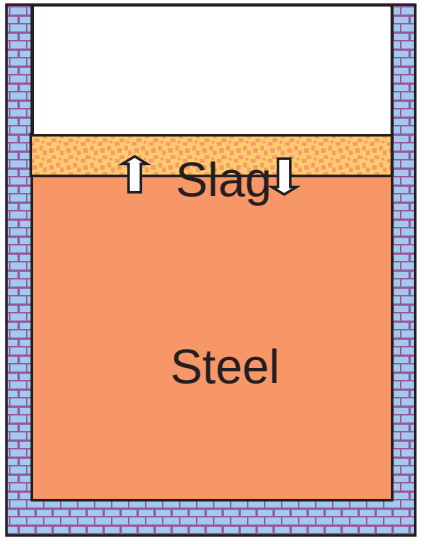

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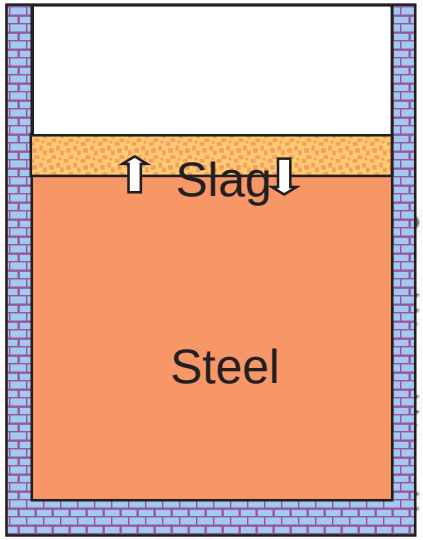

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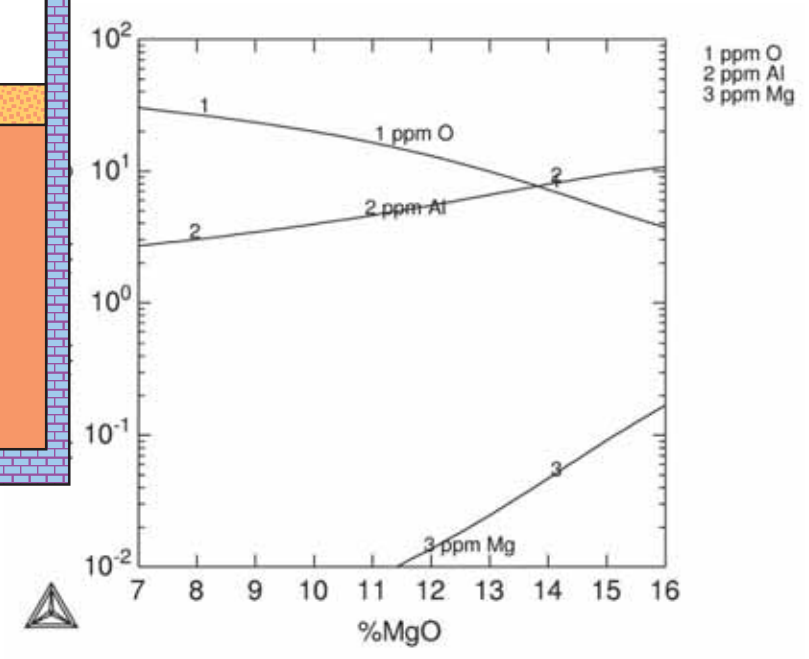

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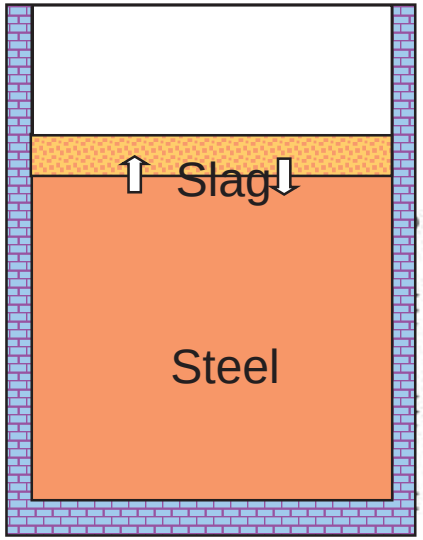

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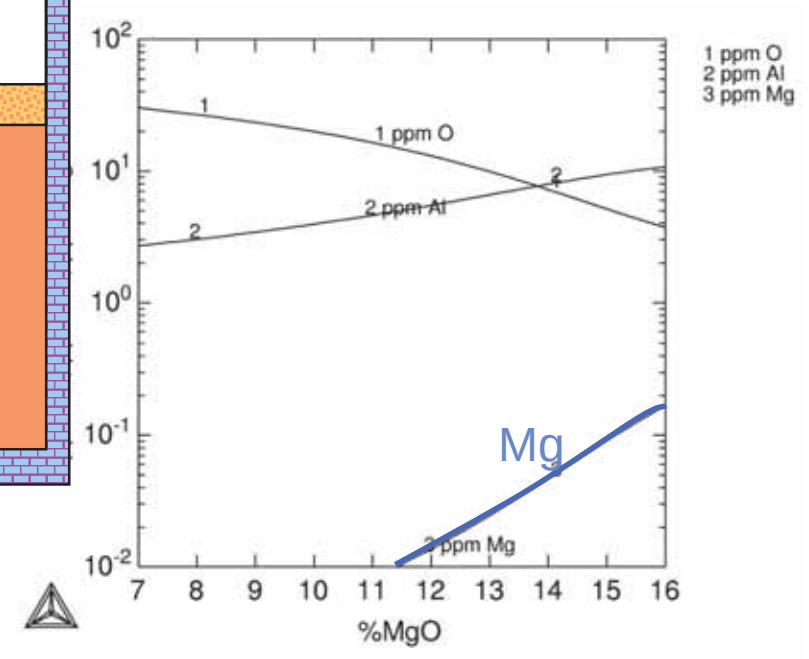

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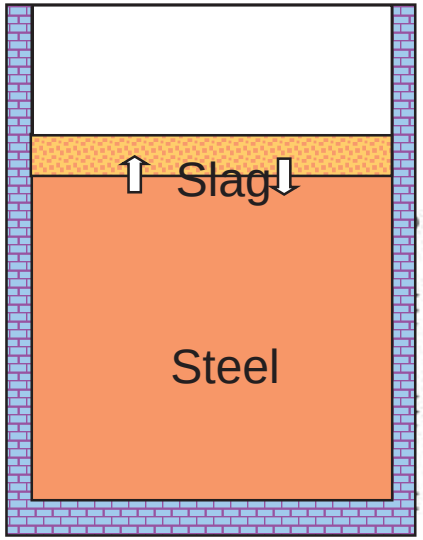

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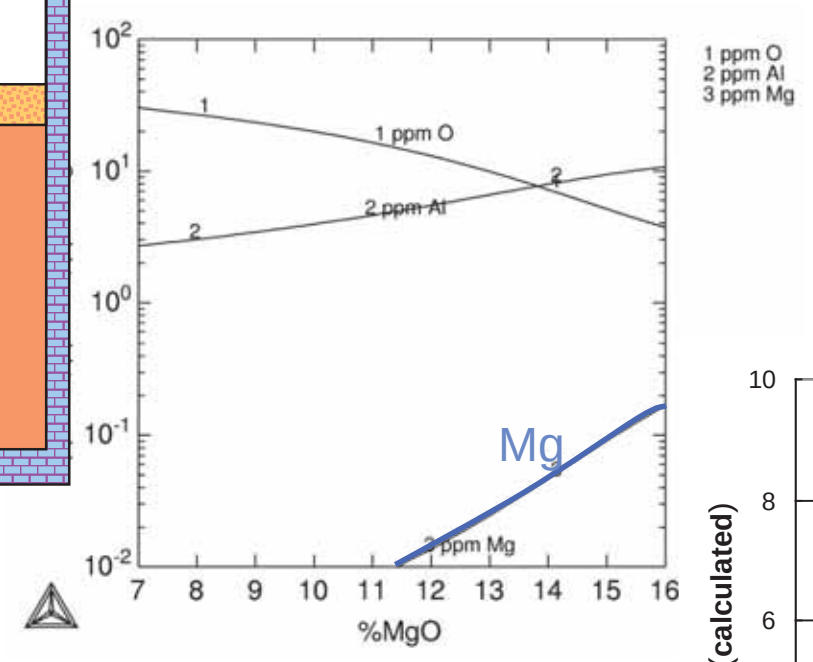
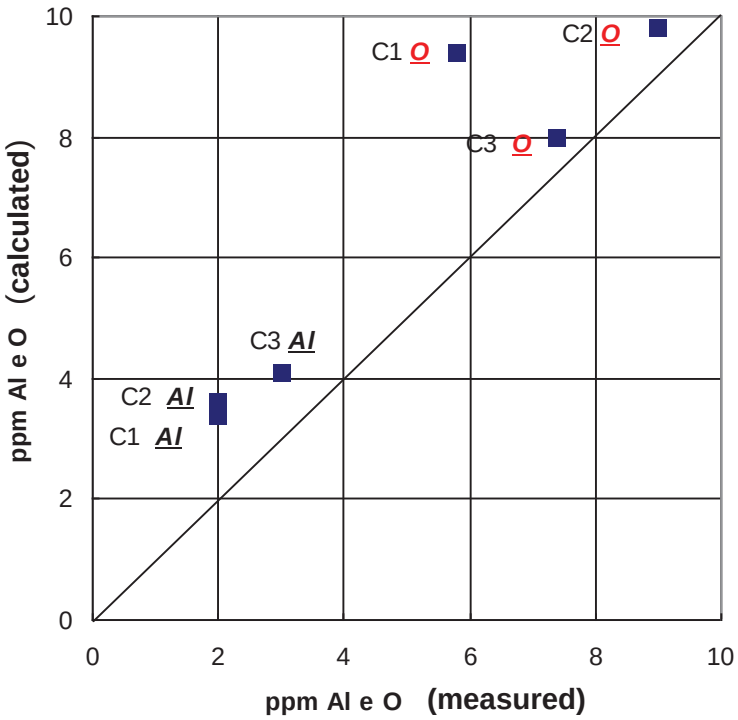
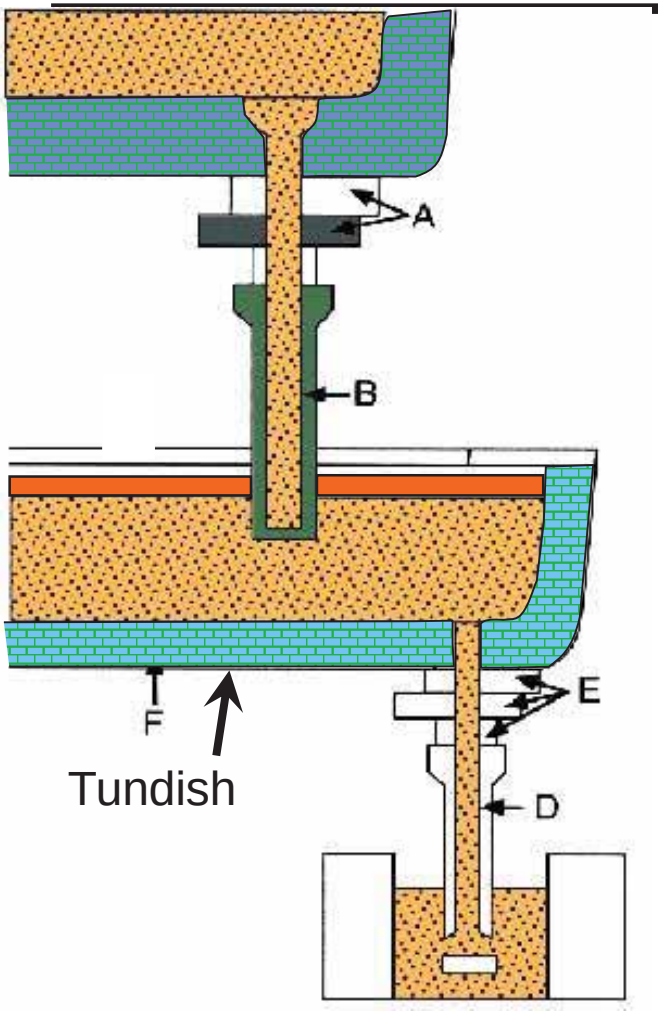


Costa e Silva, 2006, Costa e Silva, 2013



Nozzle clogging



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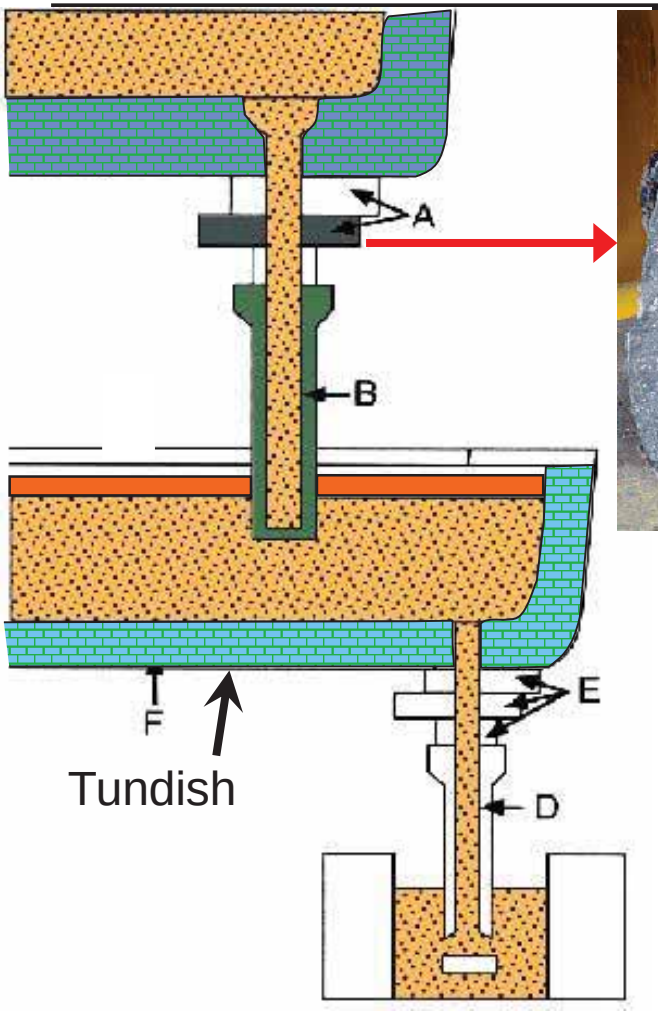

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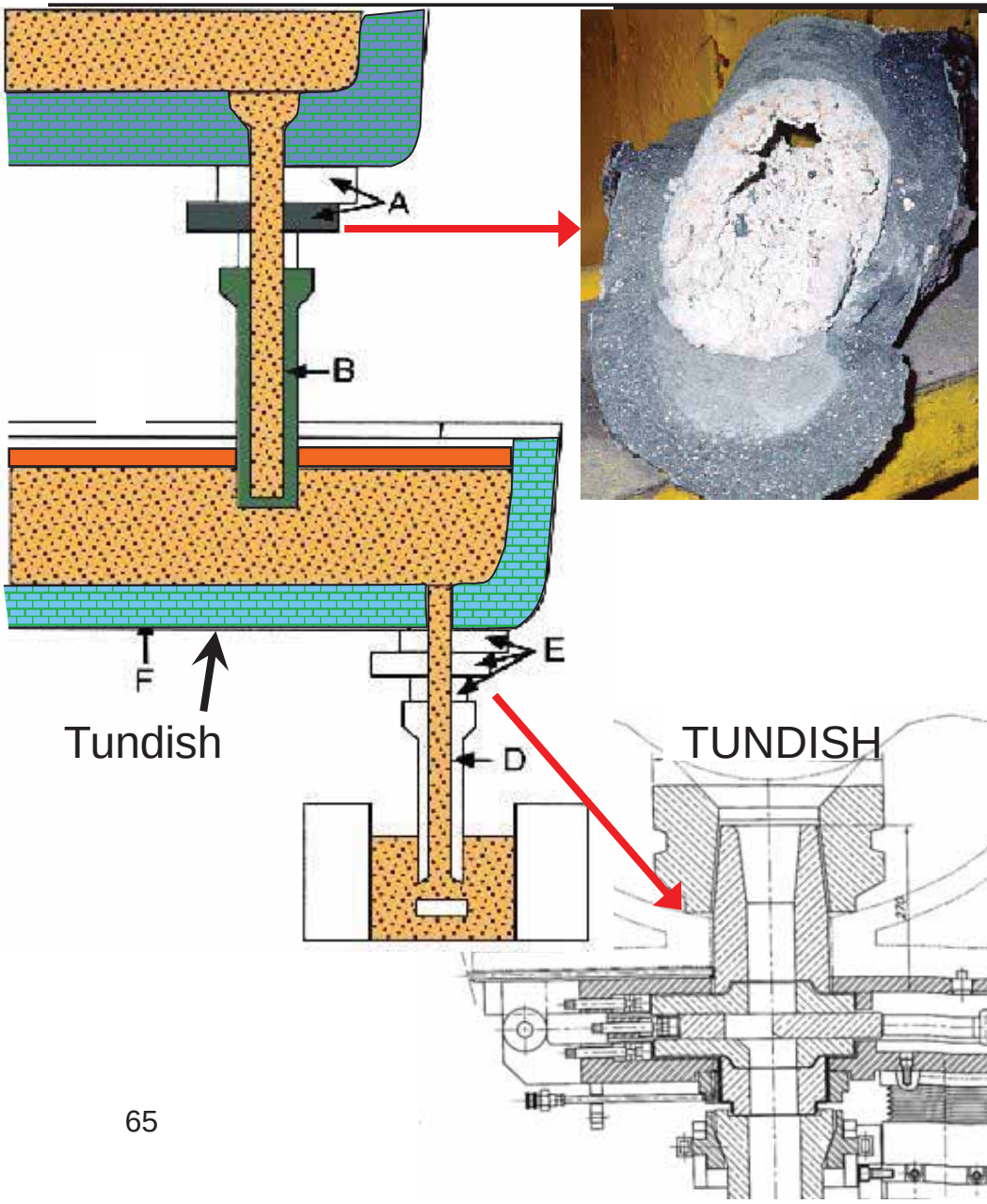

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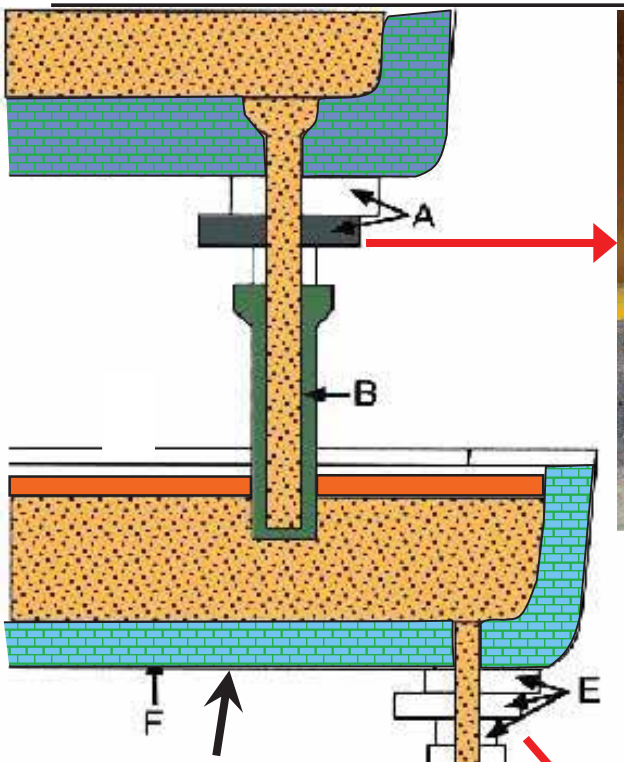

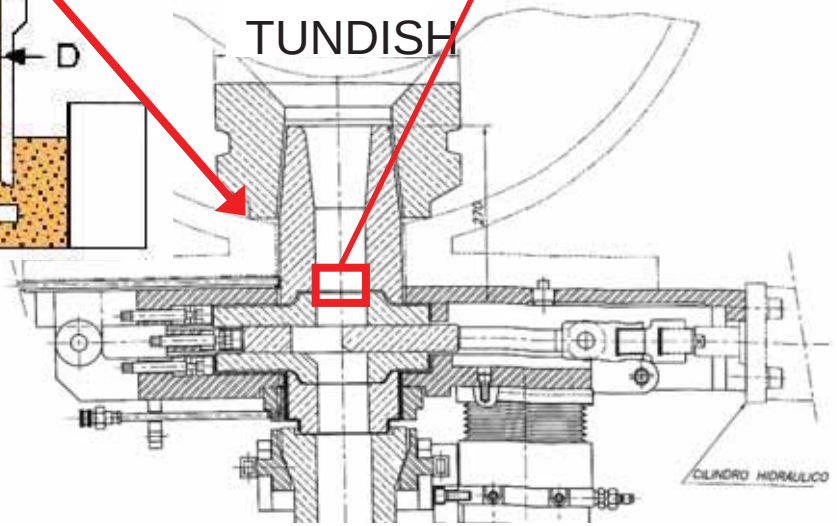

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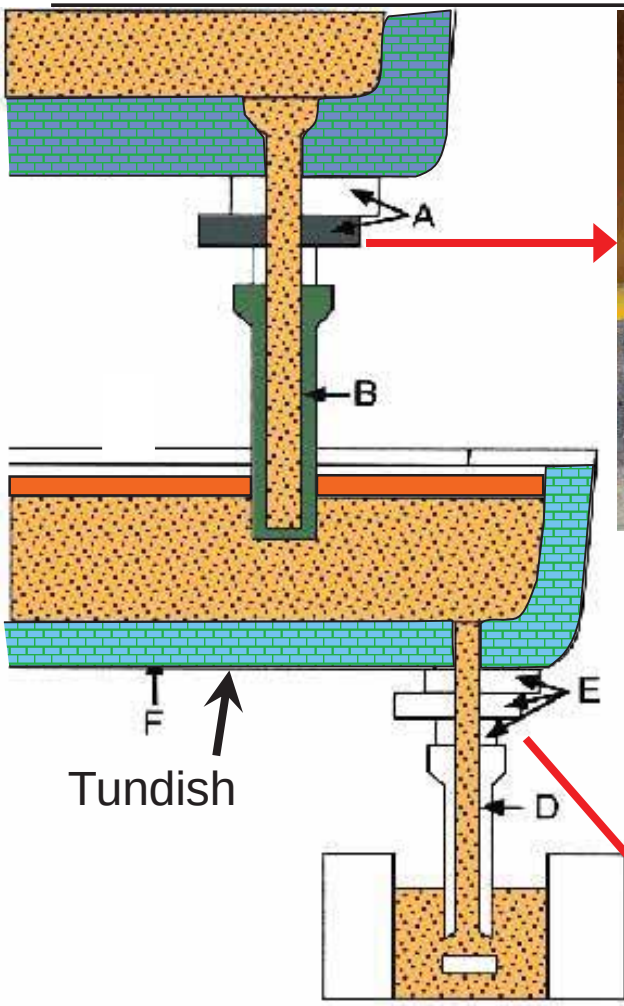
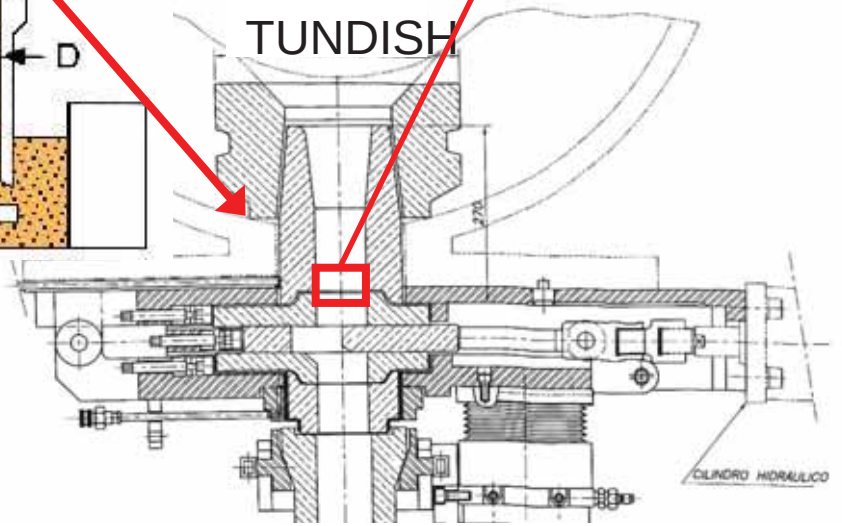
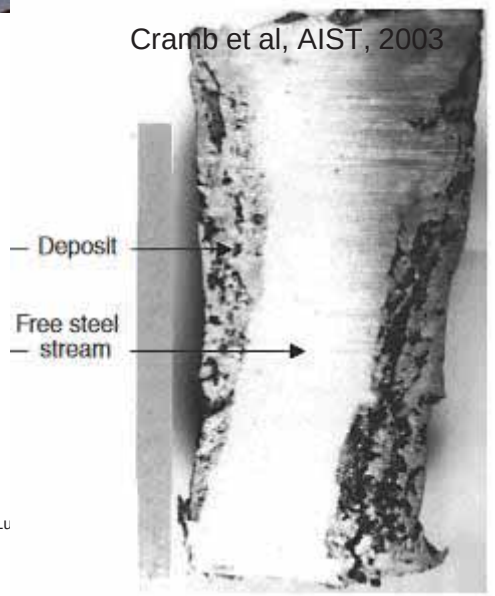
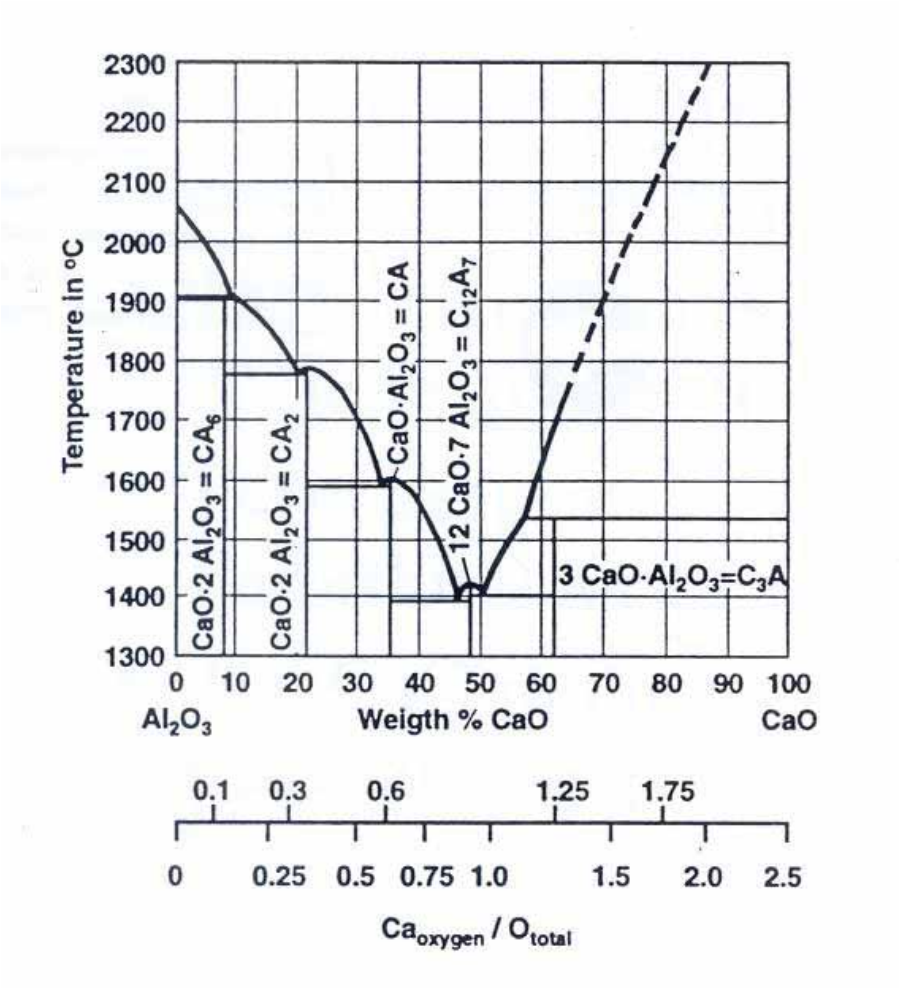




Cramb et al, AIST, 2003



“Classical Al2O3 clogging”
Semi-empirical- Increasing Ca additions



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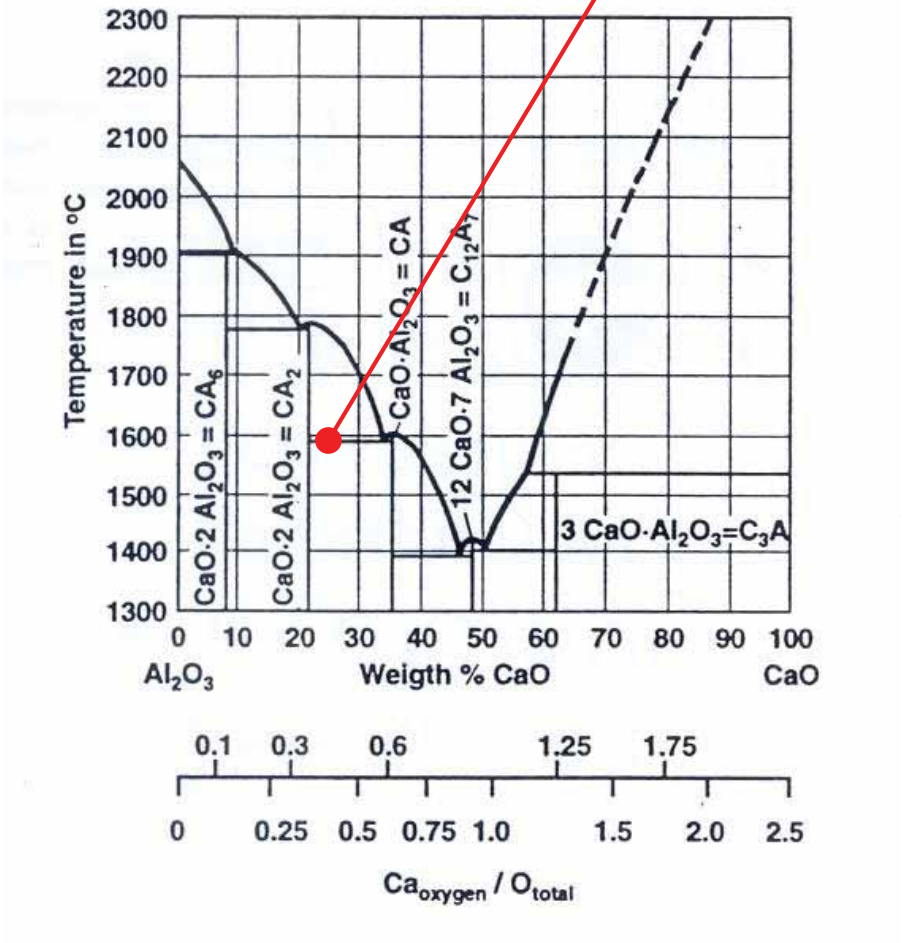

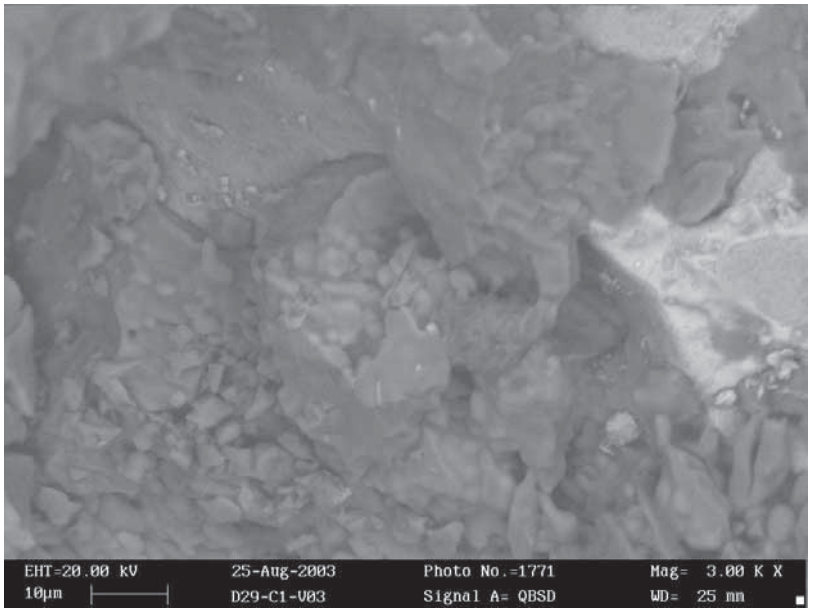

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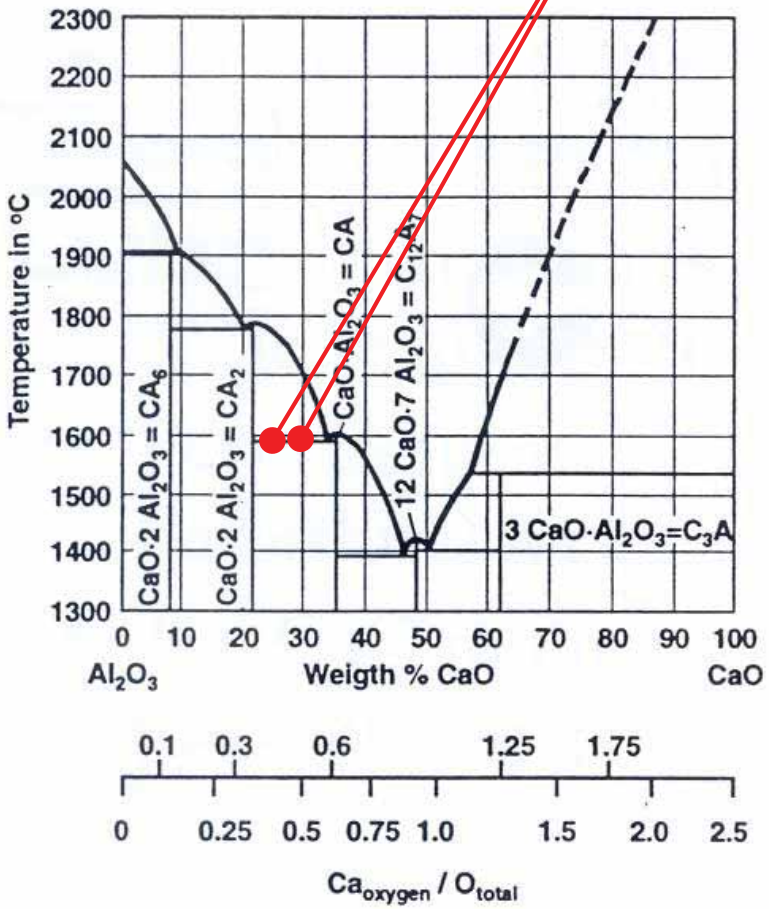

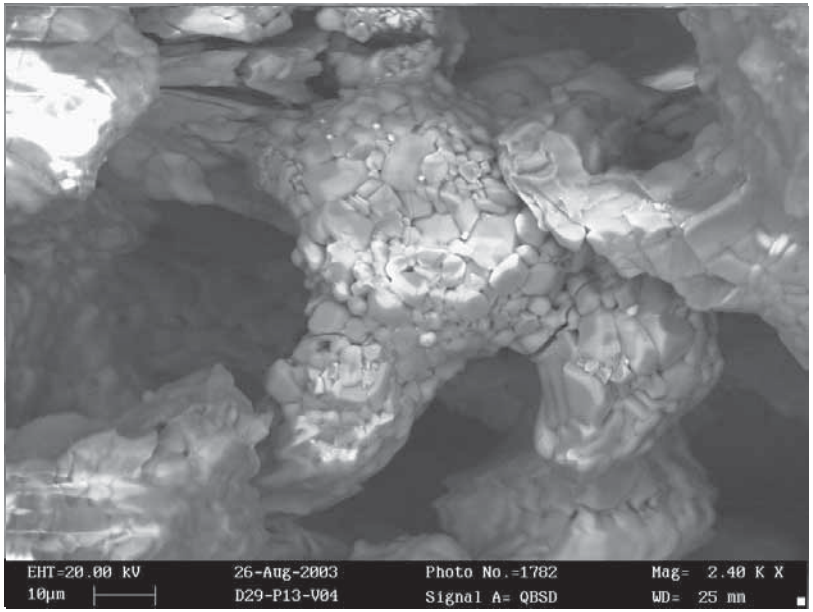

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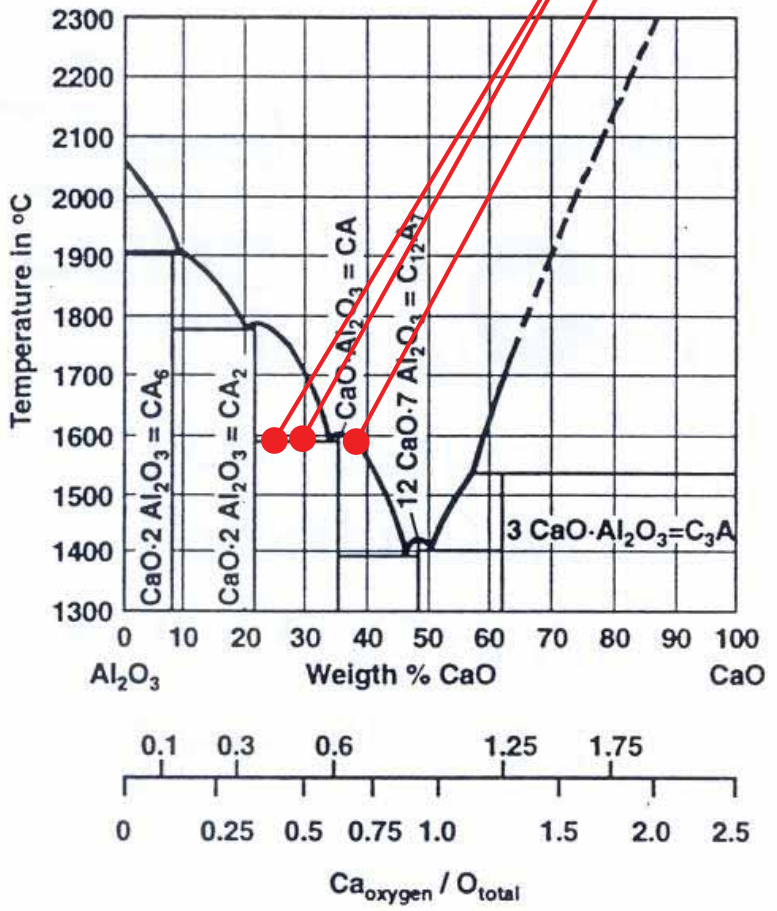

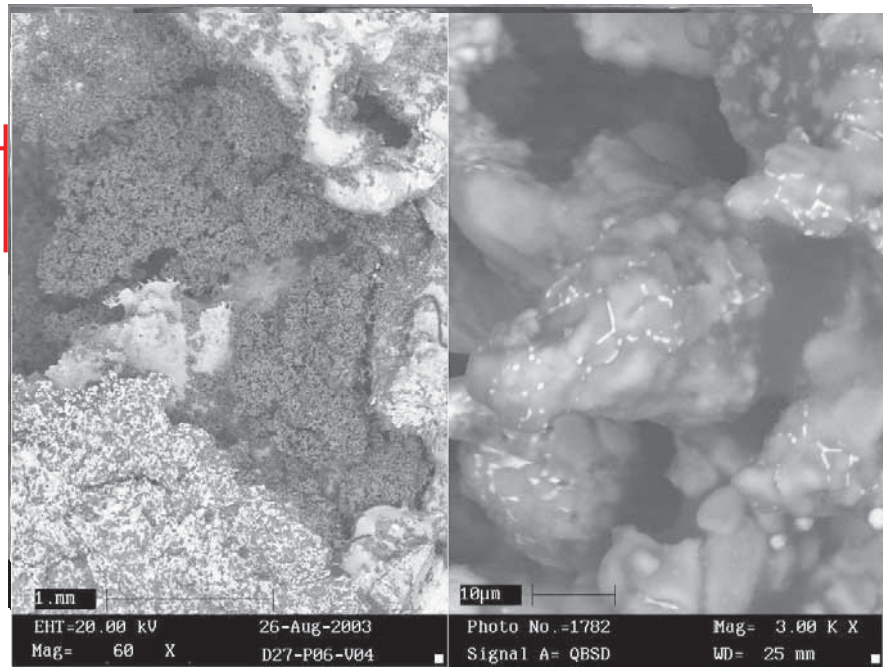

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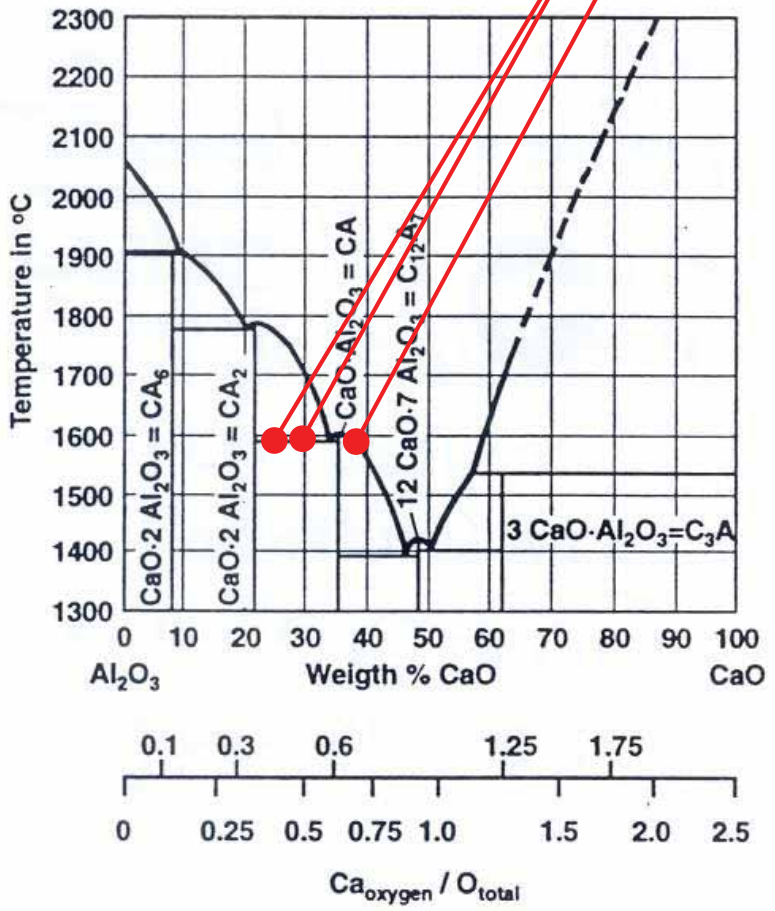
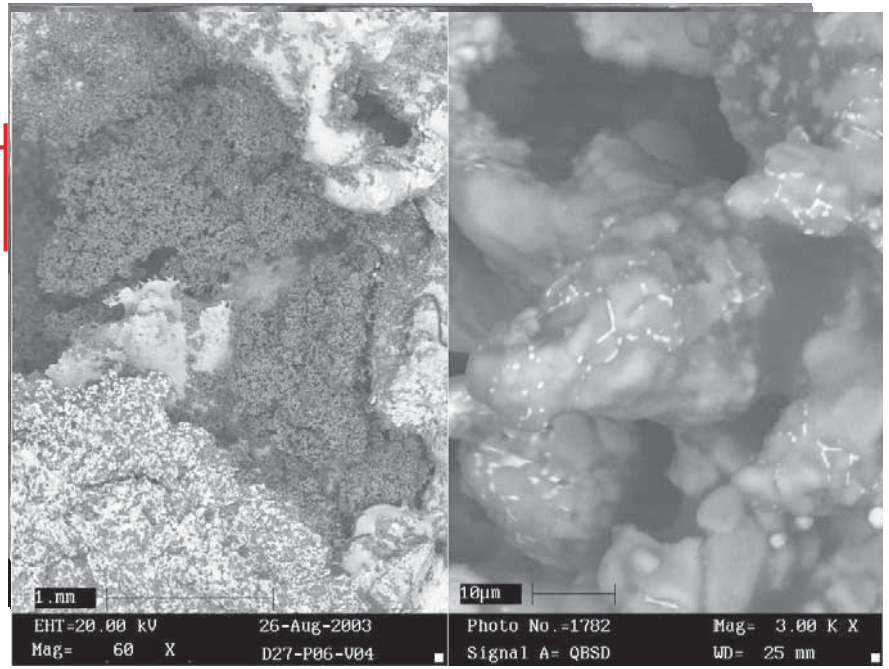


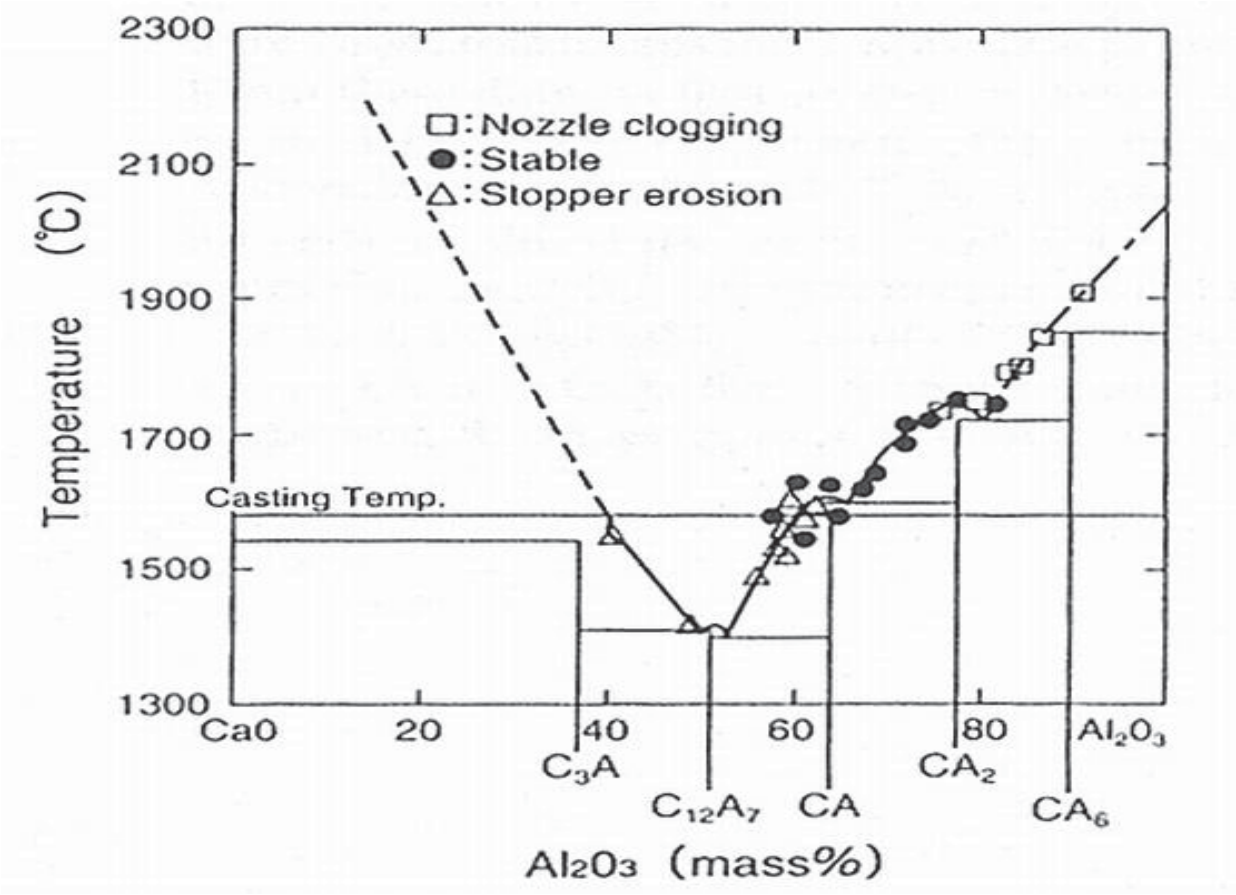


Courtesy AM Tubarão, 2006

Total O, S and T must be constant

Tailoring the Steel composition for Liquid Inclusions ("castability window")

$CaO-Al_2O_3$ pseudo-binary



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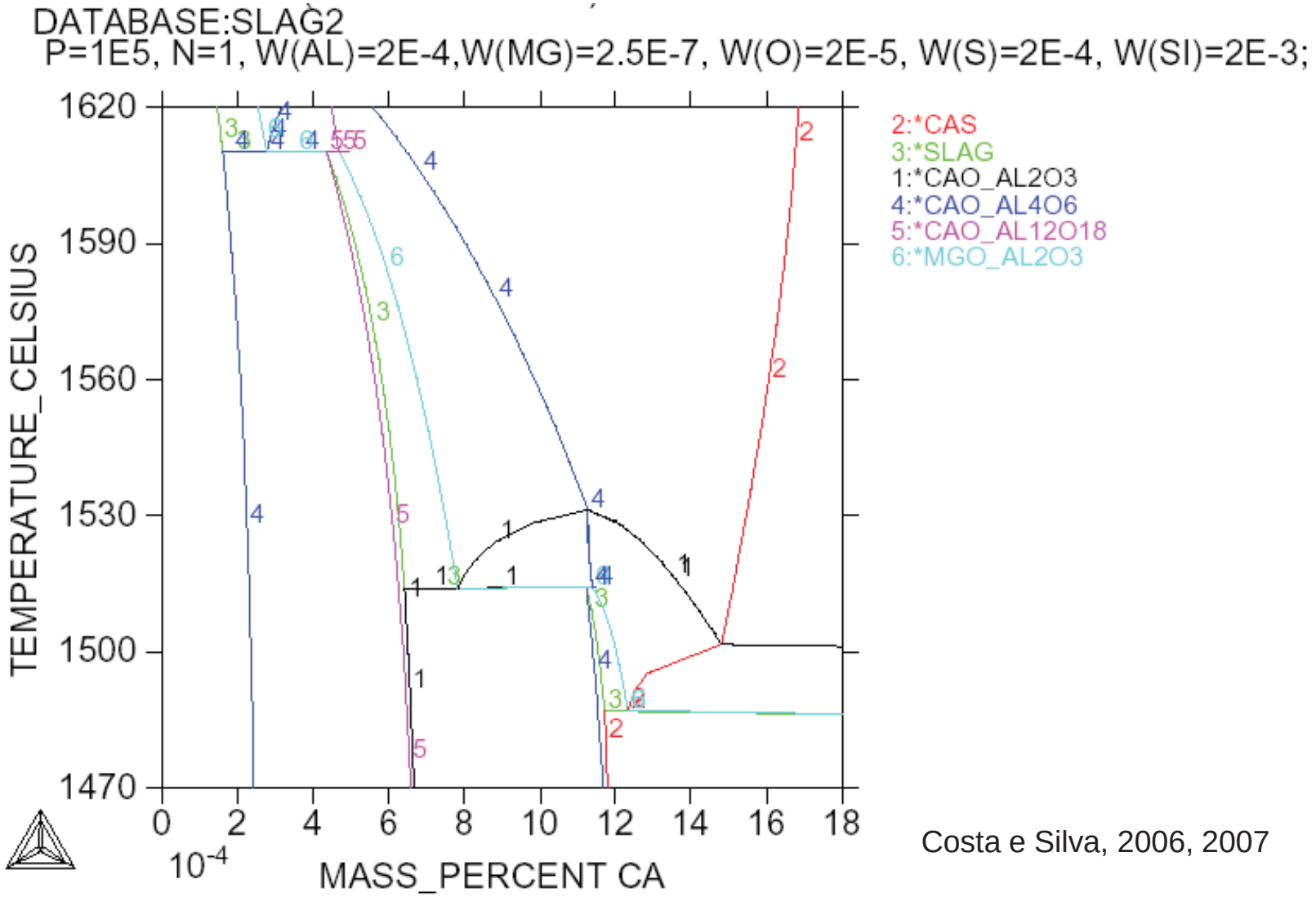

Costa e Silva, 2006, 2007

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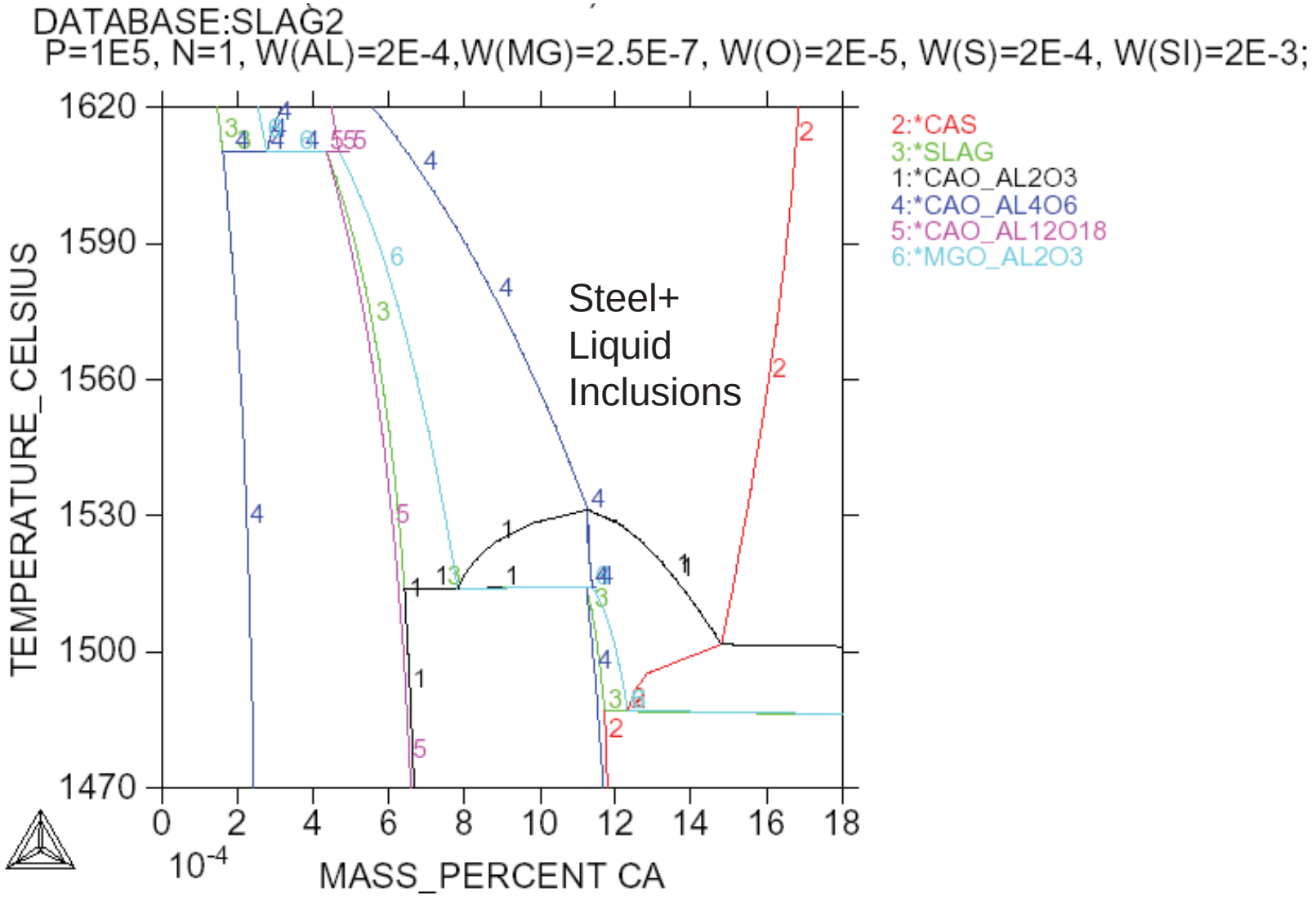

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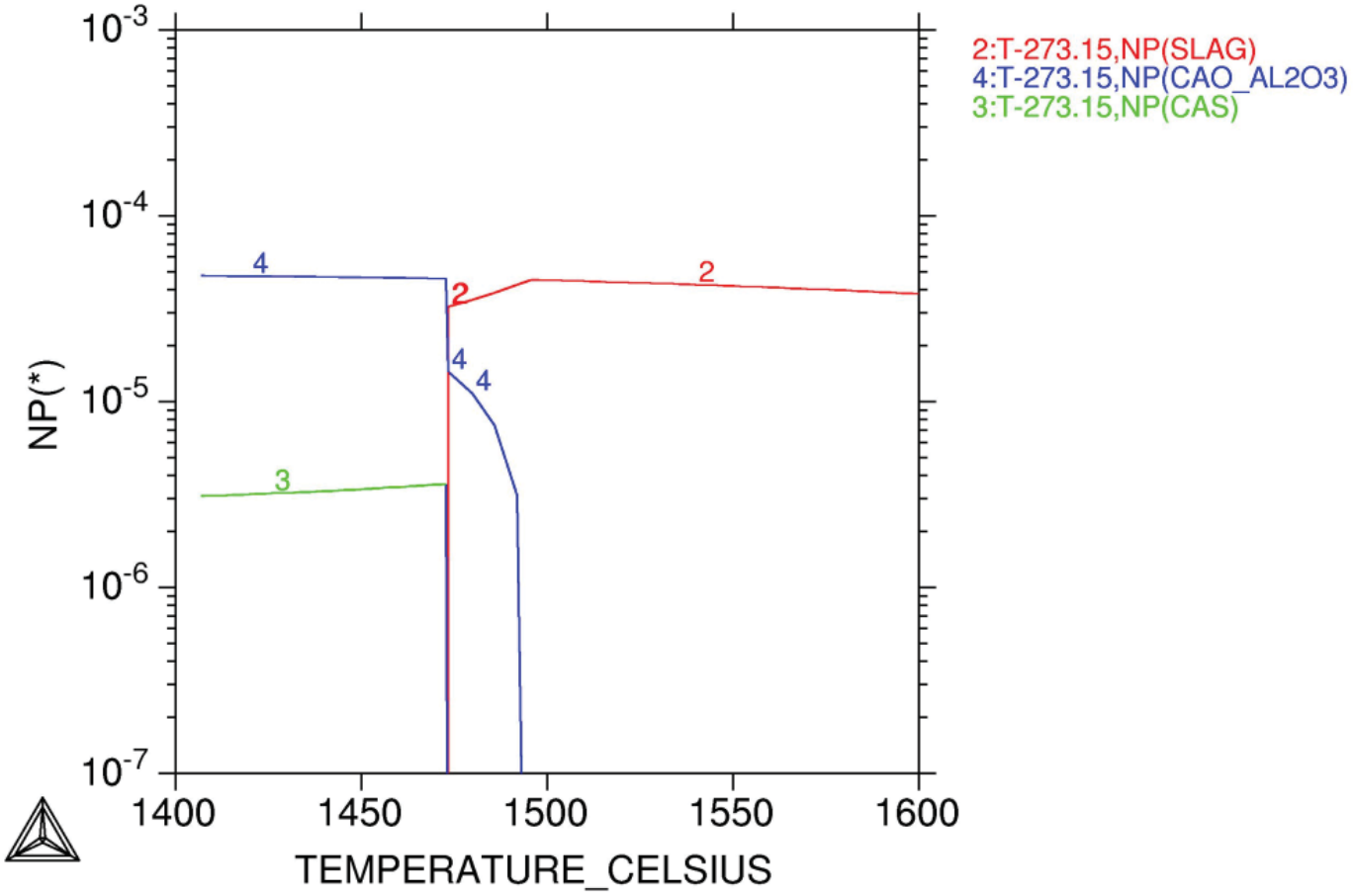

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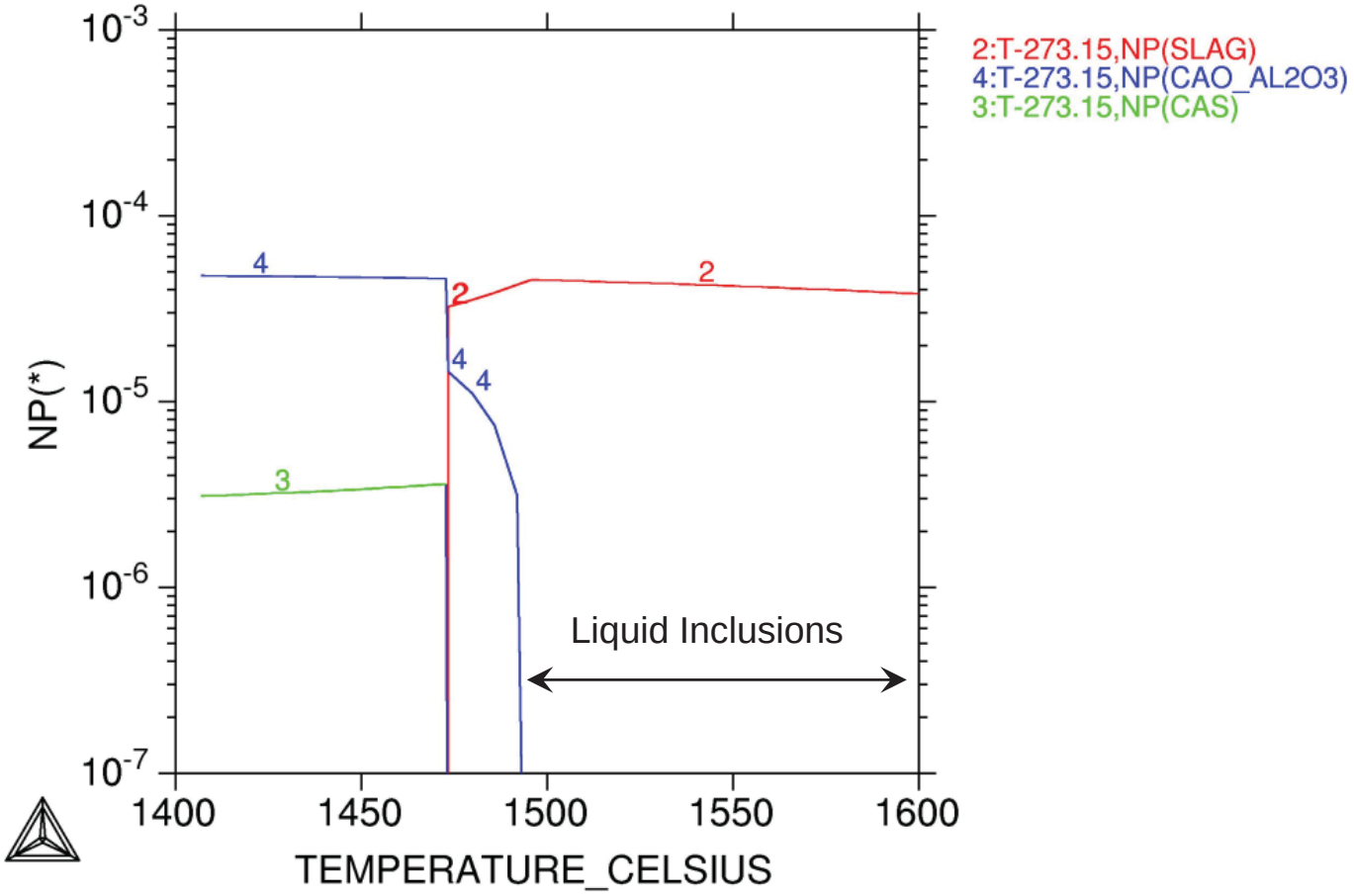

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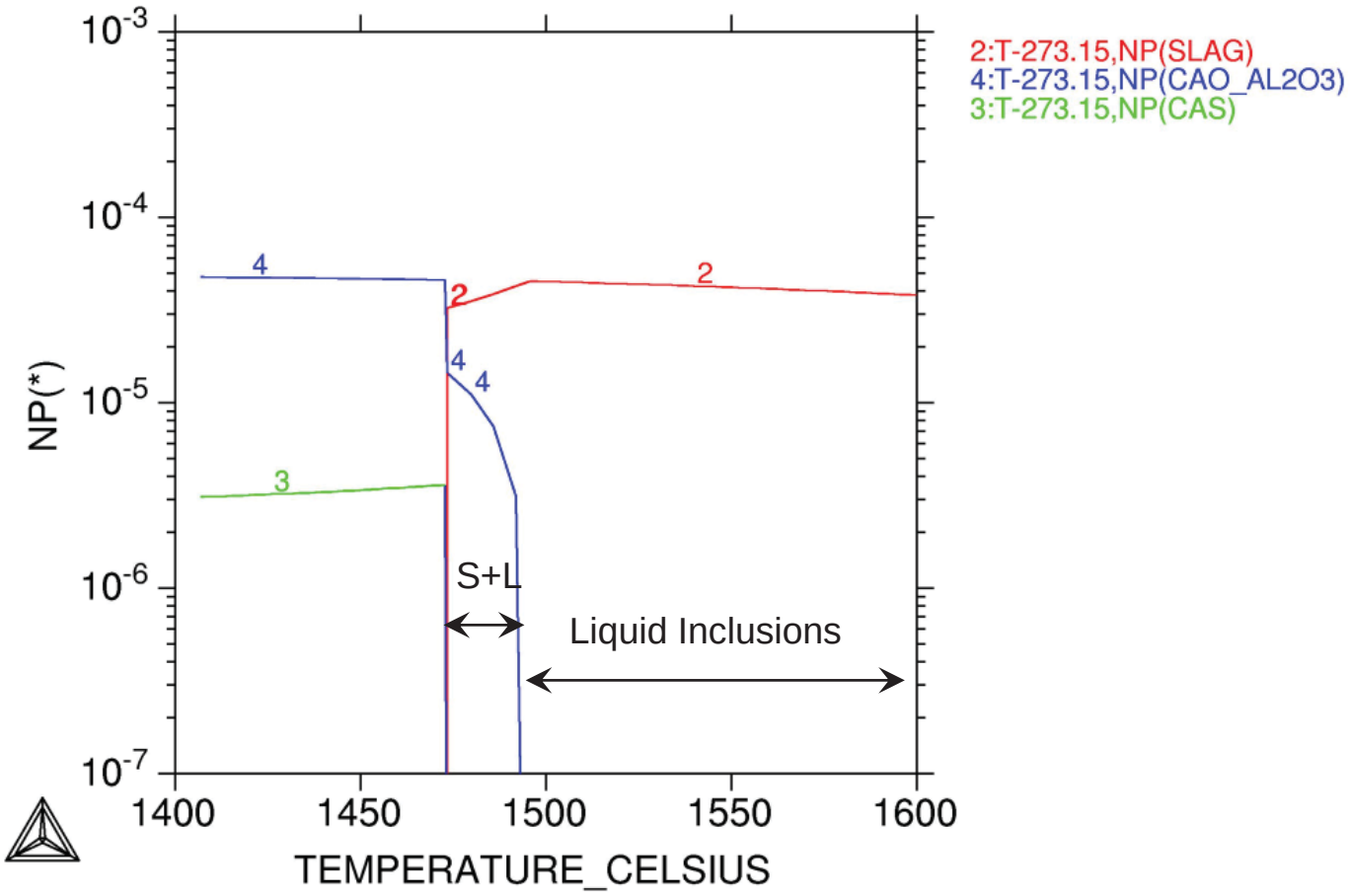

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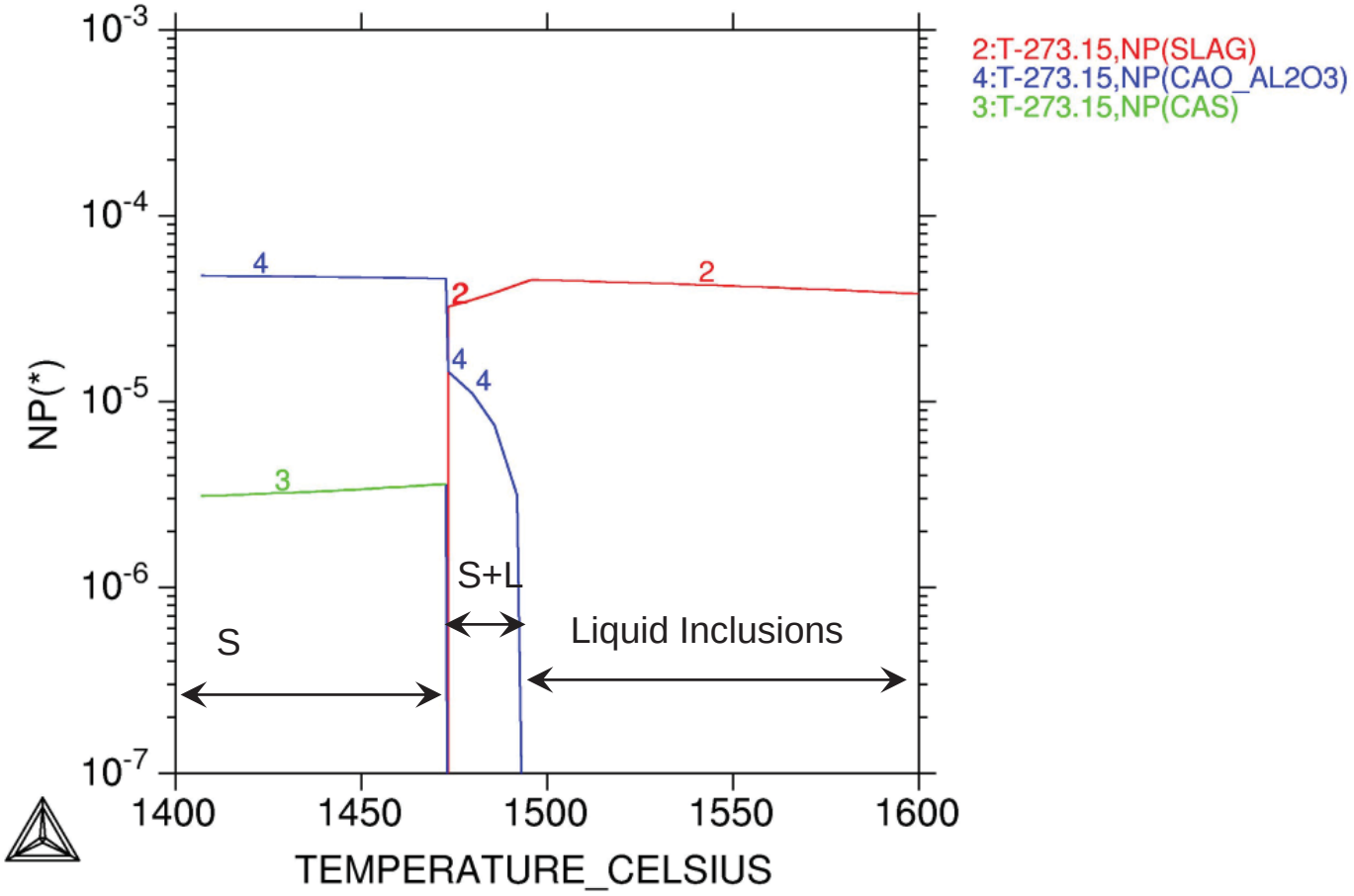
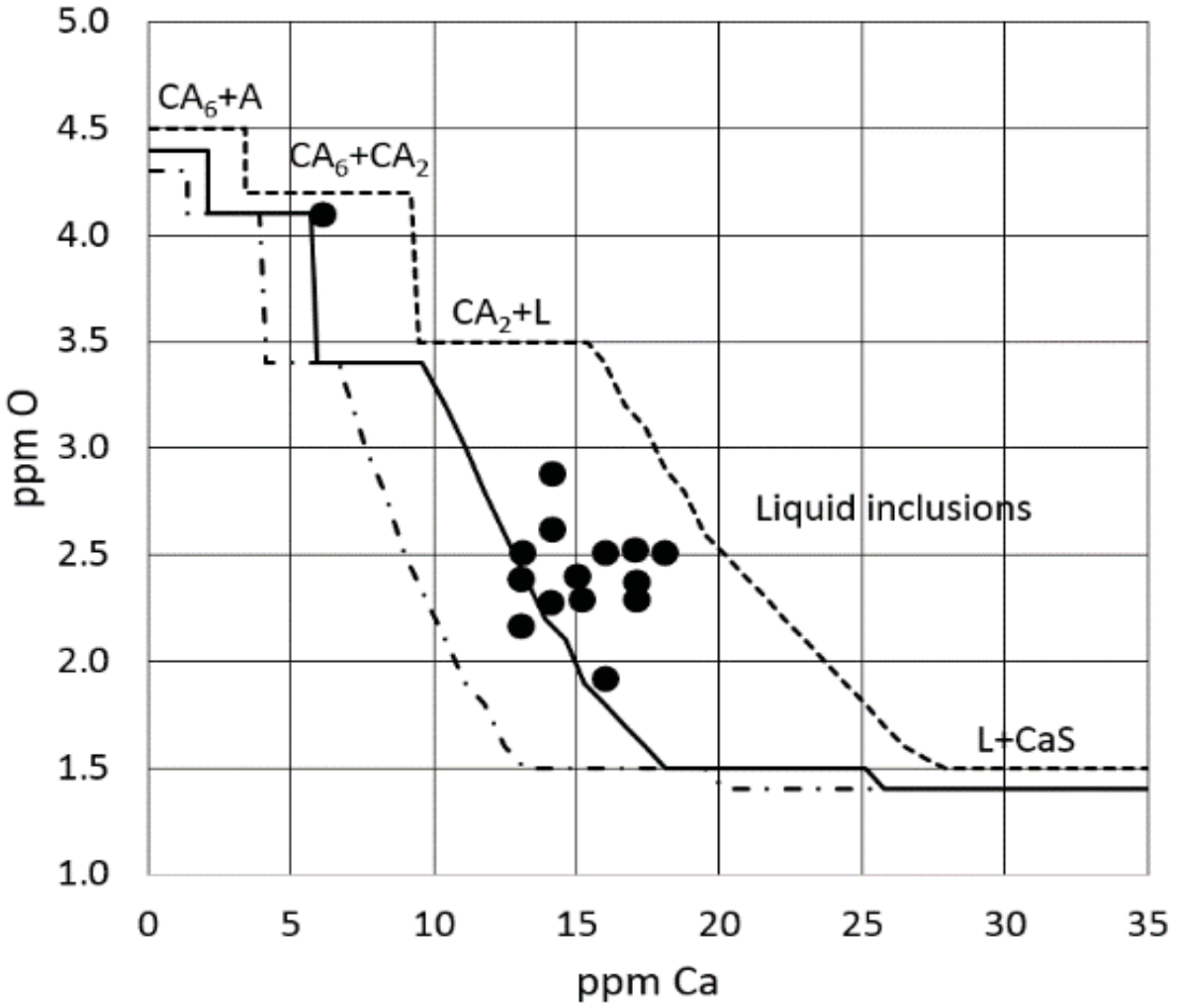


Monitoring Ca injection via soluble oxygen (CELOX®)



Mercier, 2014, Kattner et al, to be published, 2016

Spinel clogging in Si-Mn long products - Ladle metallurgy

)

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1. Low S- **High B_2**
   Good de-ox (low
   $\boldsymbol{\mu\ O\ steel}$) $\boldsymbol{O\ steel\ eel\ O\ steel\ O\ steel}$
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1. Protect refractory- **MgO**

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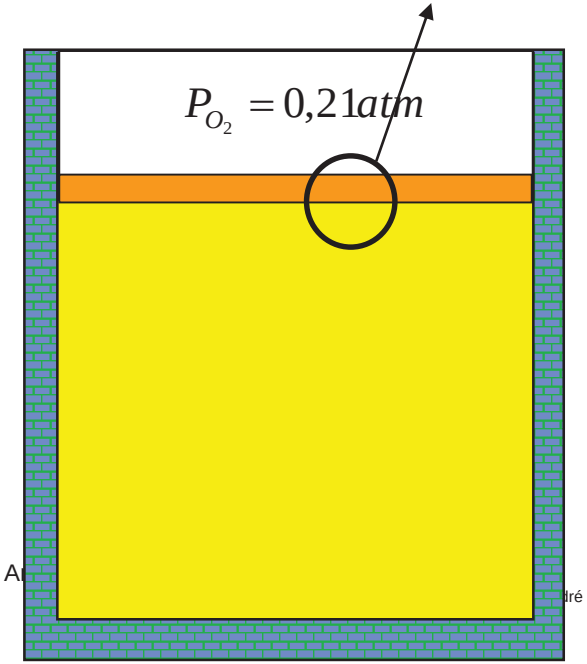

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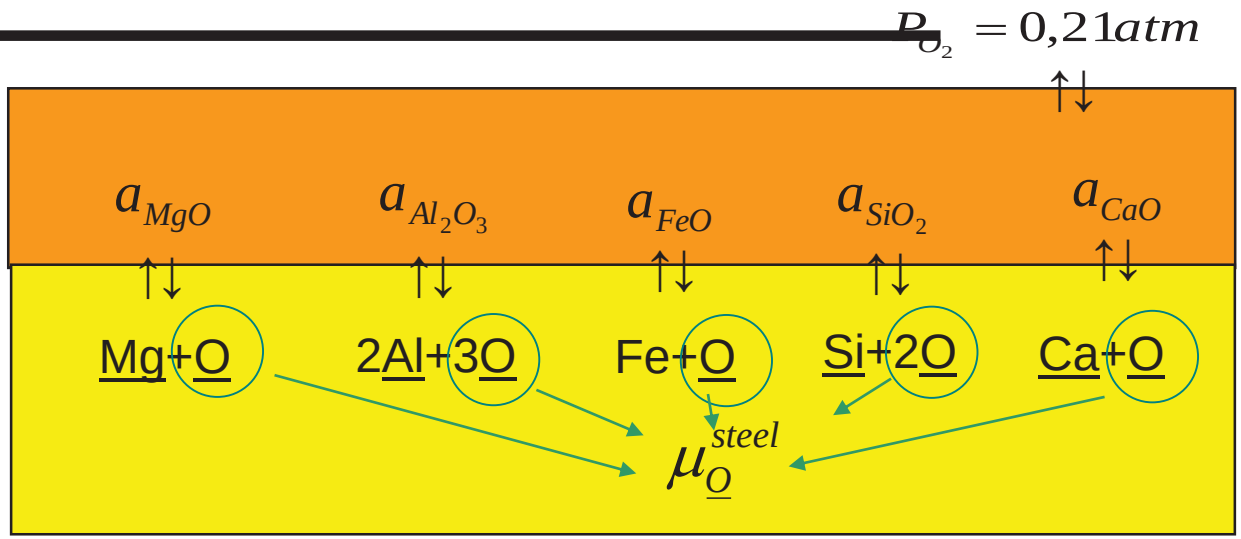
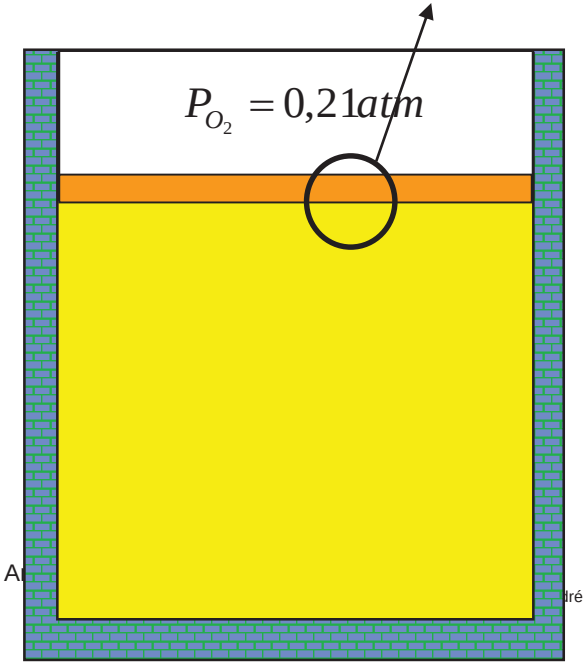


Botelho et al 2016



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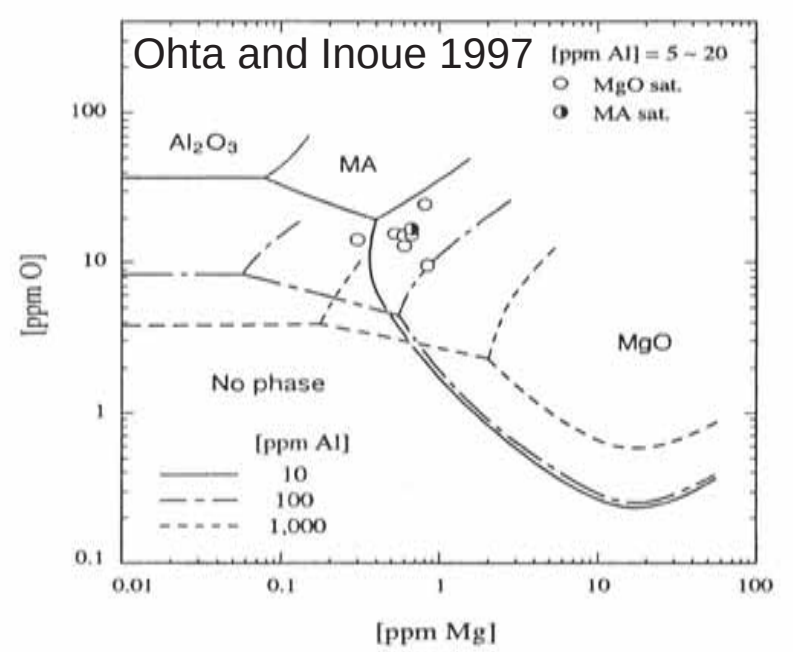

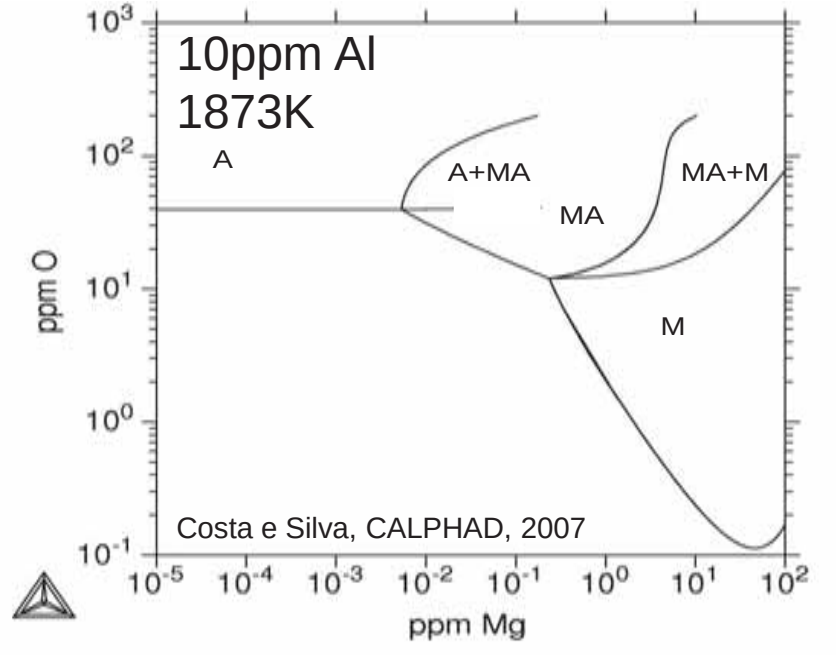

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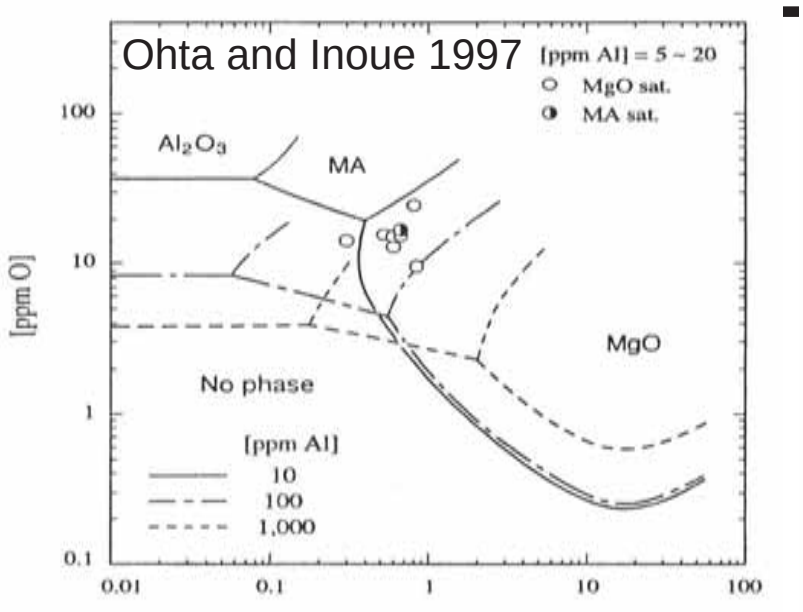

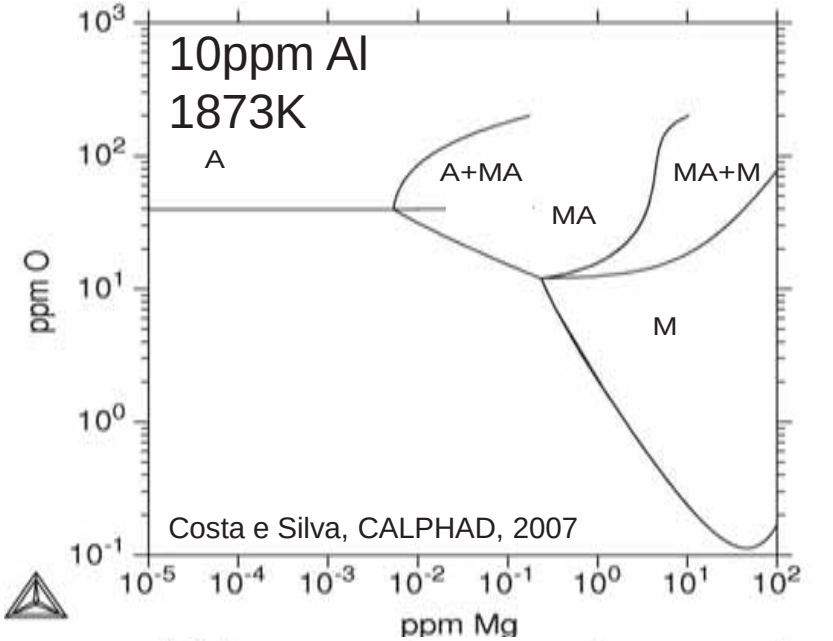

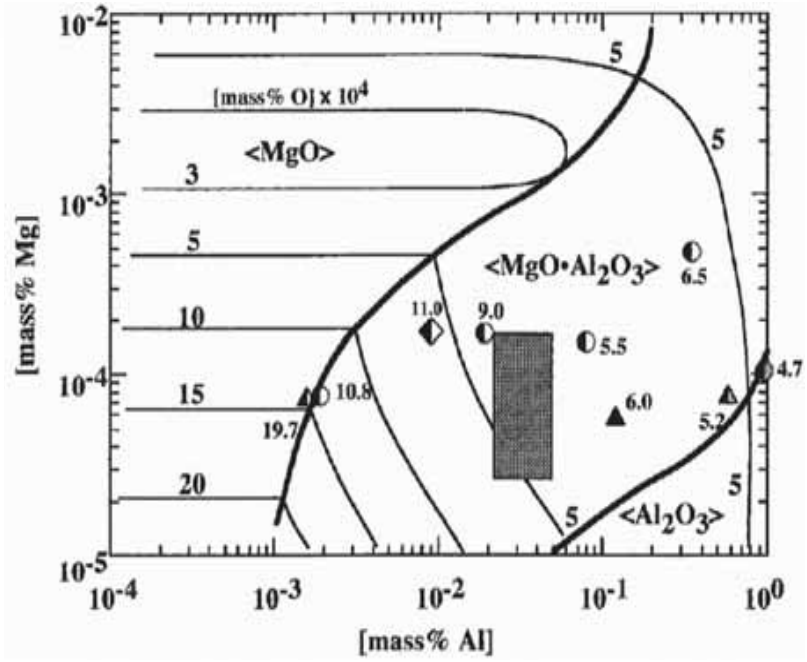

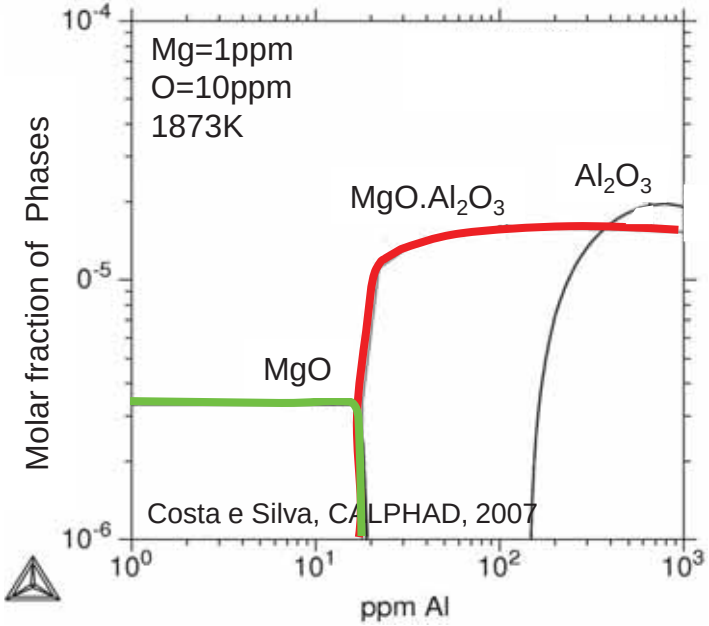

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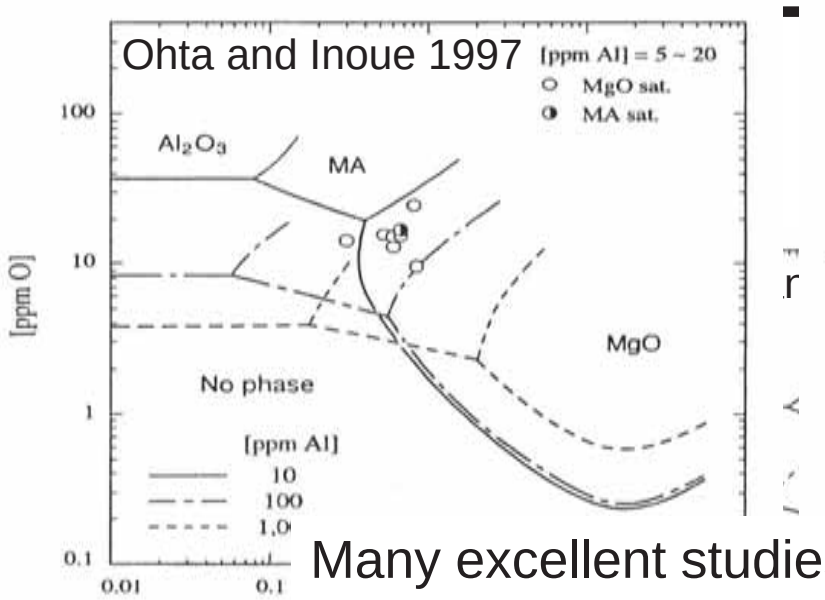
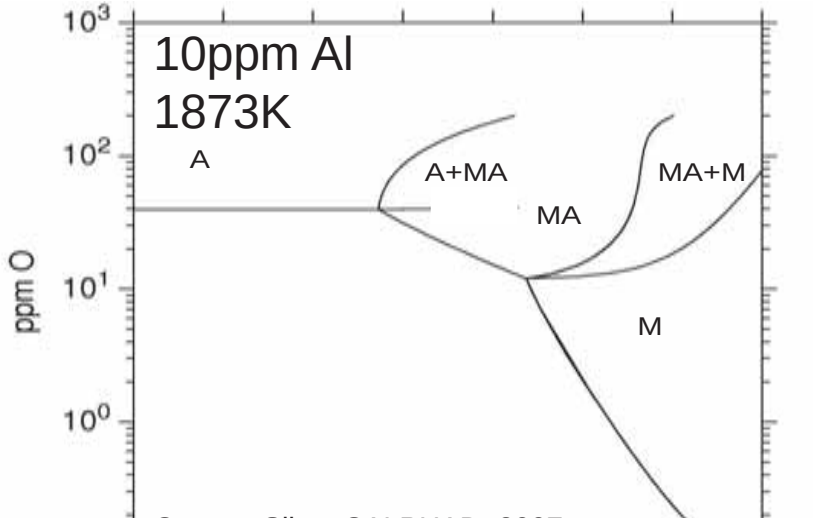
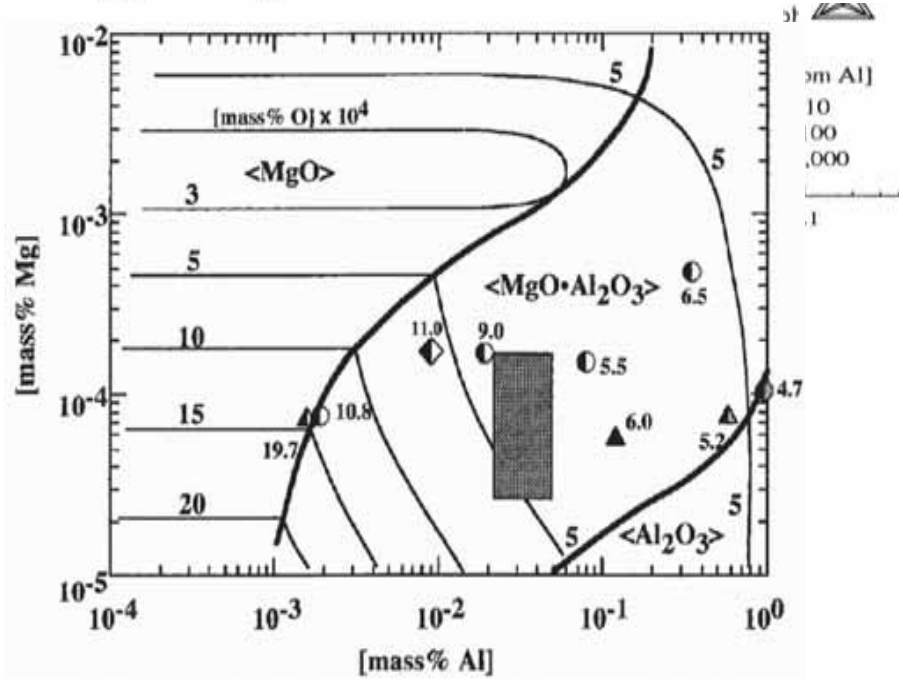
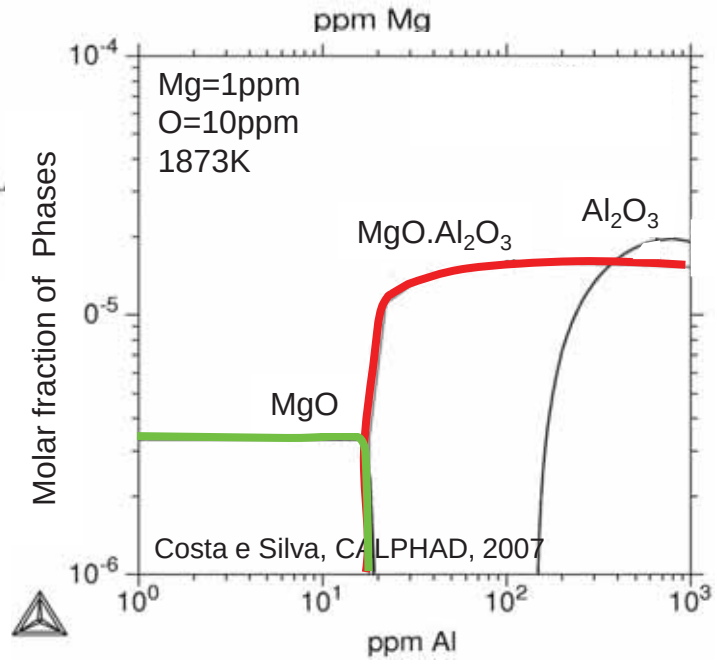




Many excellent studies in high alloy and in high value steels!





Evaluation of slag-metal equilibrium for Si-Mn deoxidized long products (1585ºC, in Ladle Furnace (LF))

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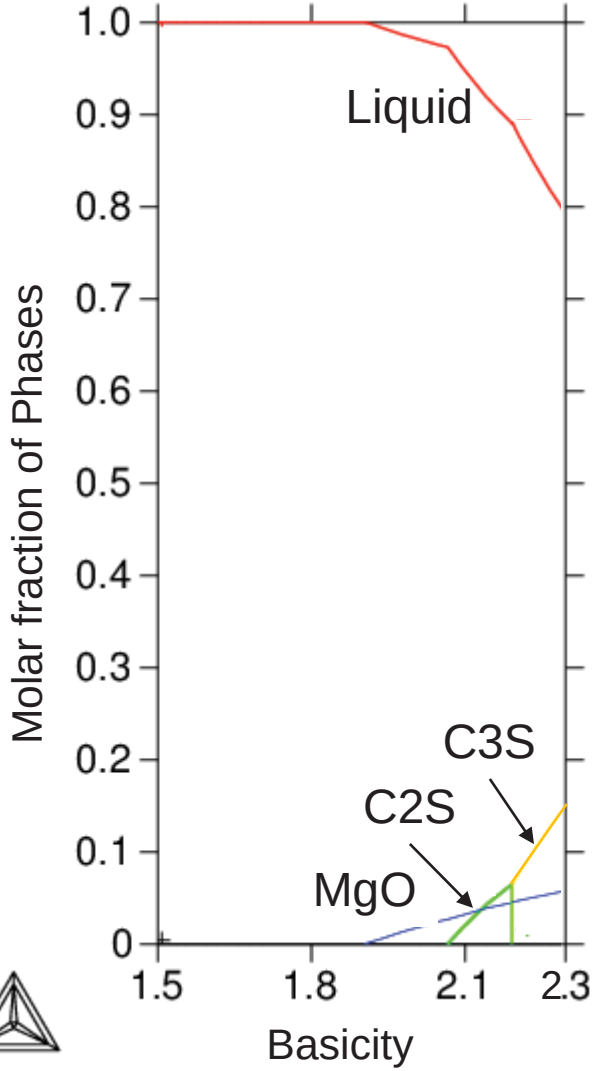

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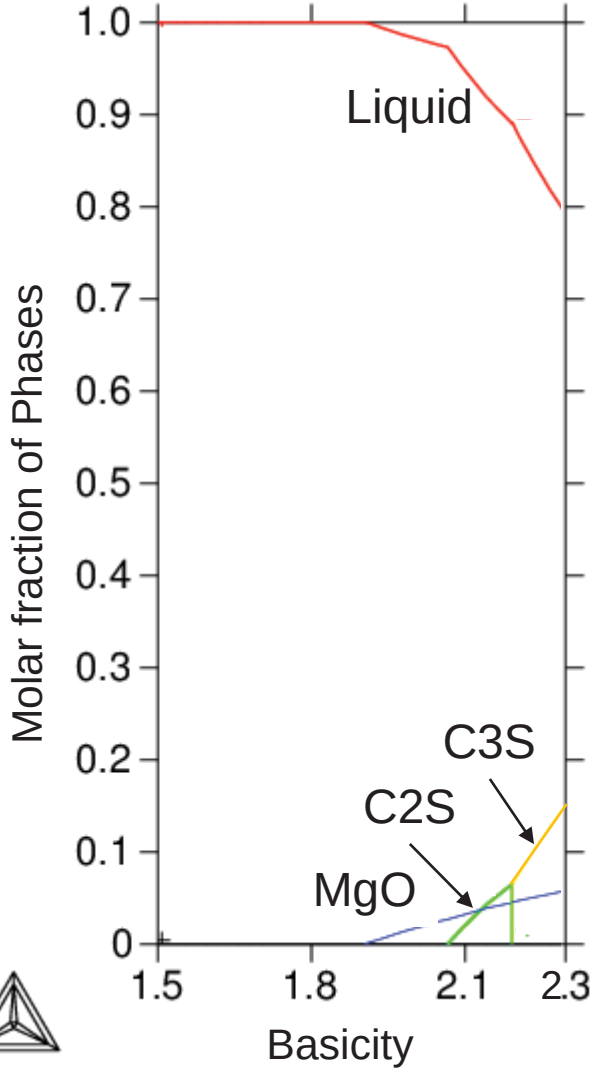
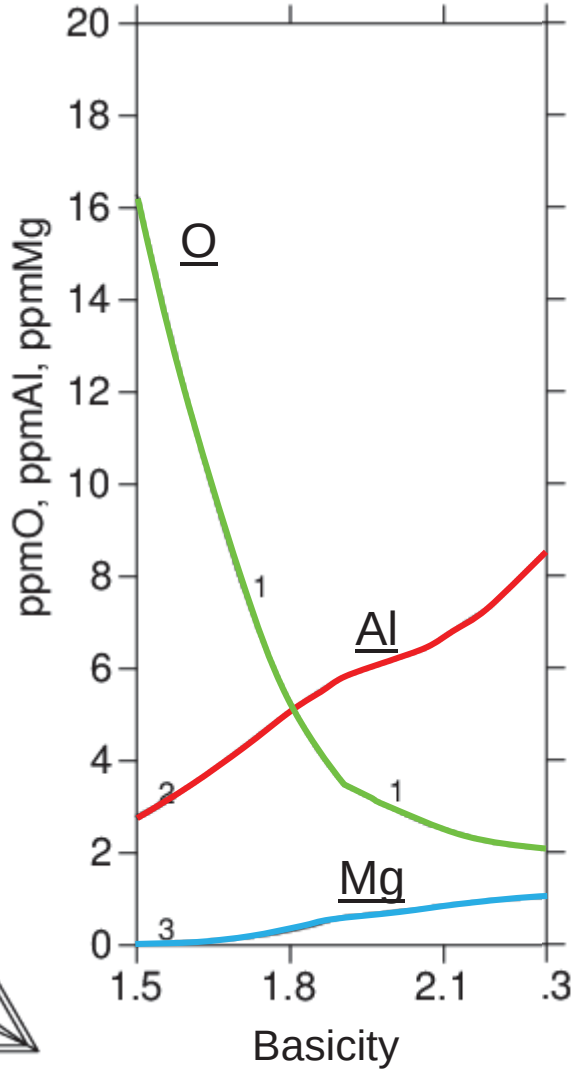
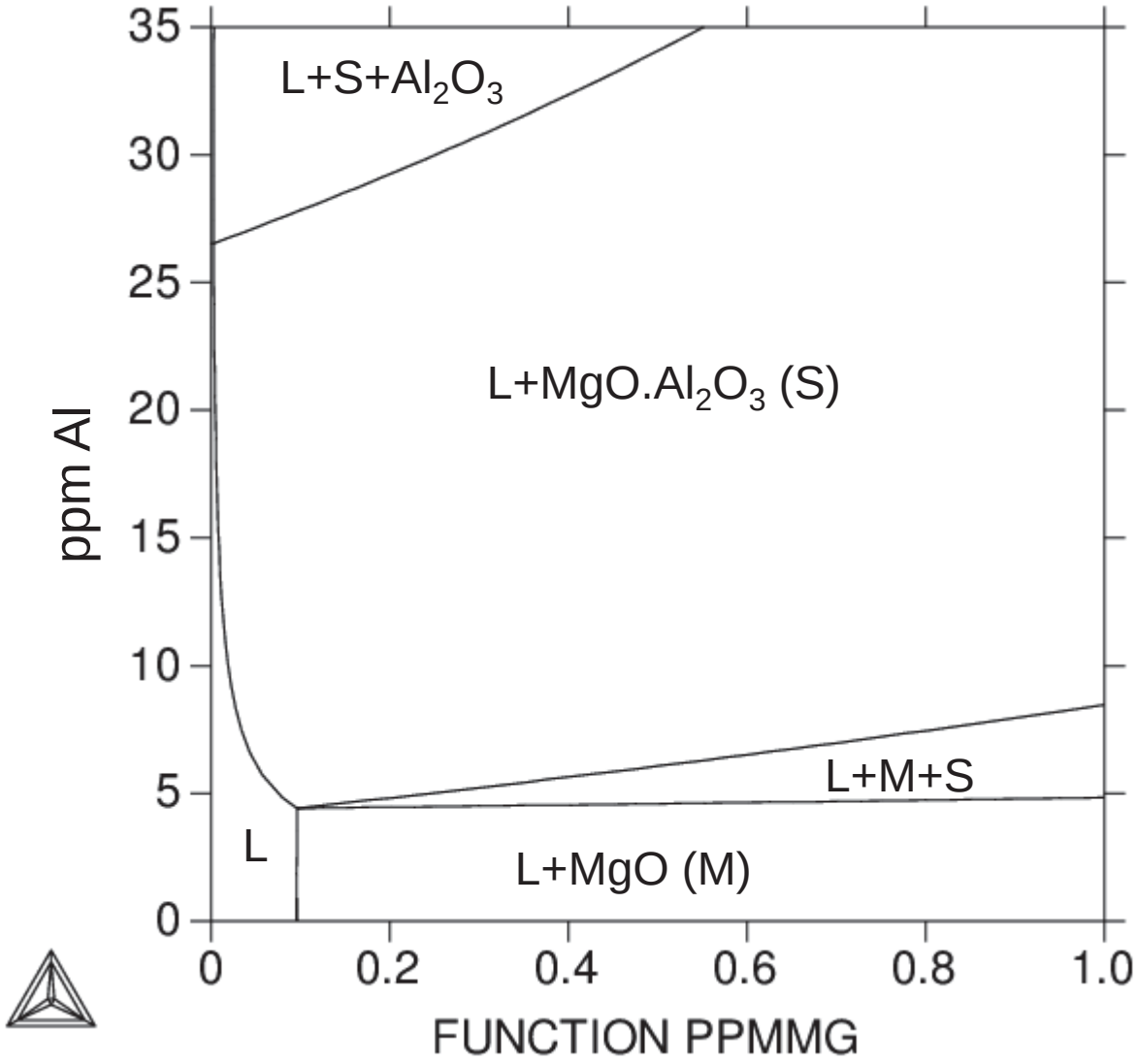
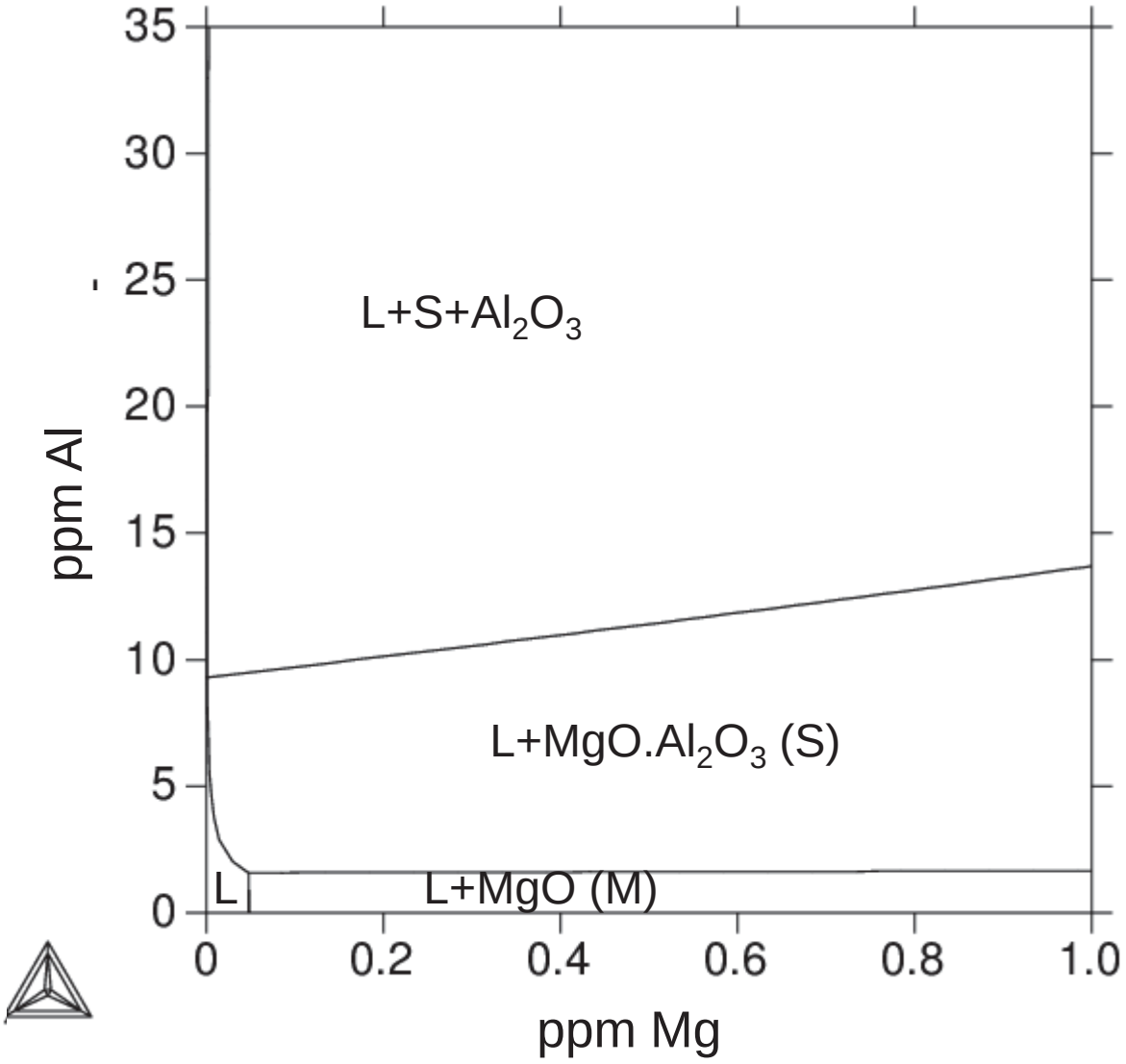




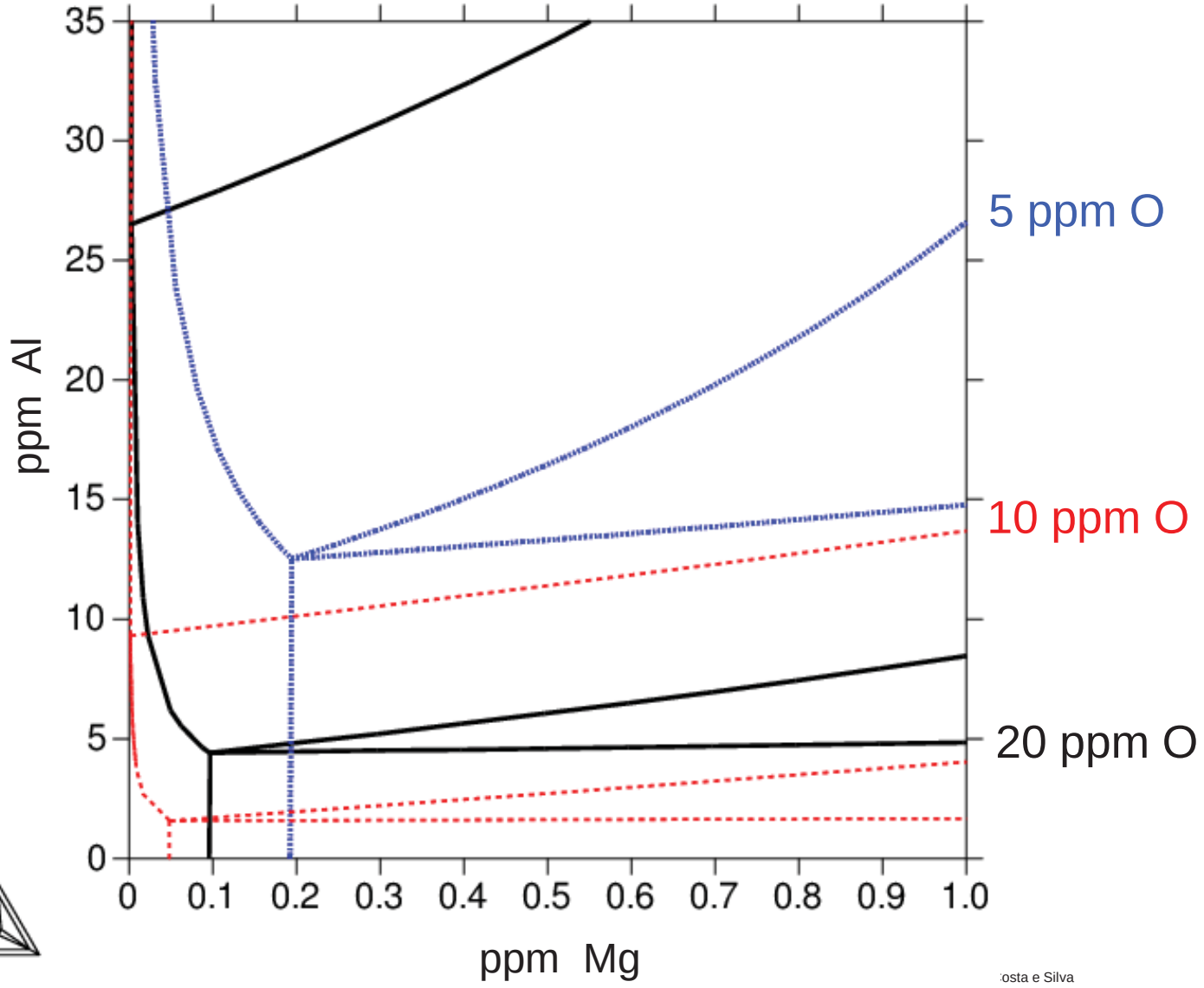
What happens during casting: 1550ºC, 1( ) ppm O



What happens during casting: 1550ºC , 20 ppm O

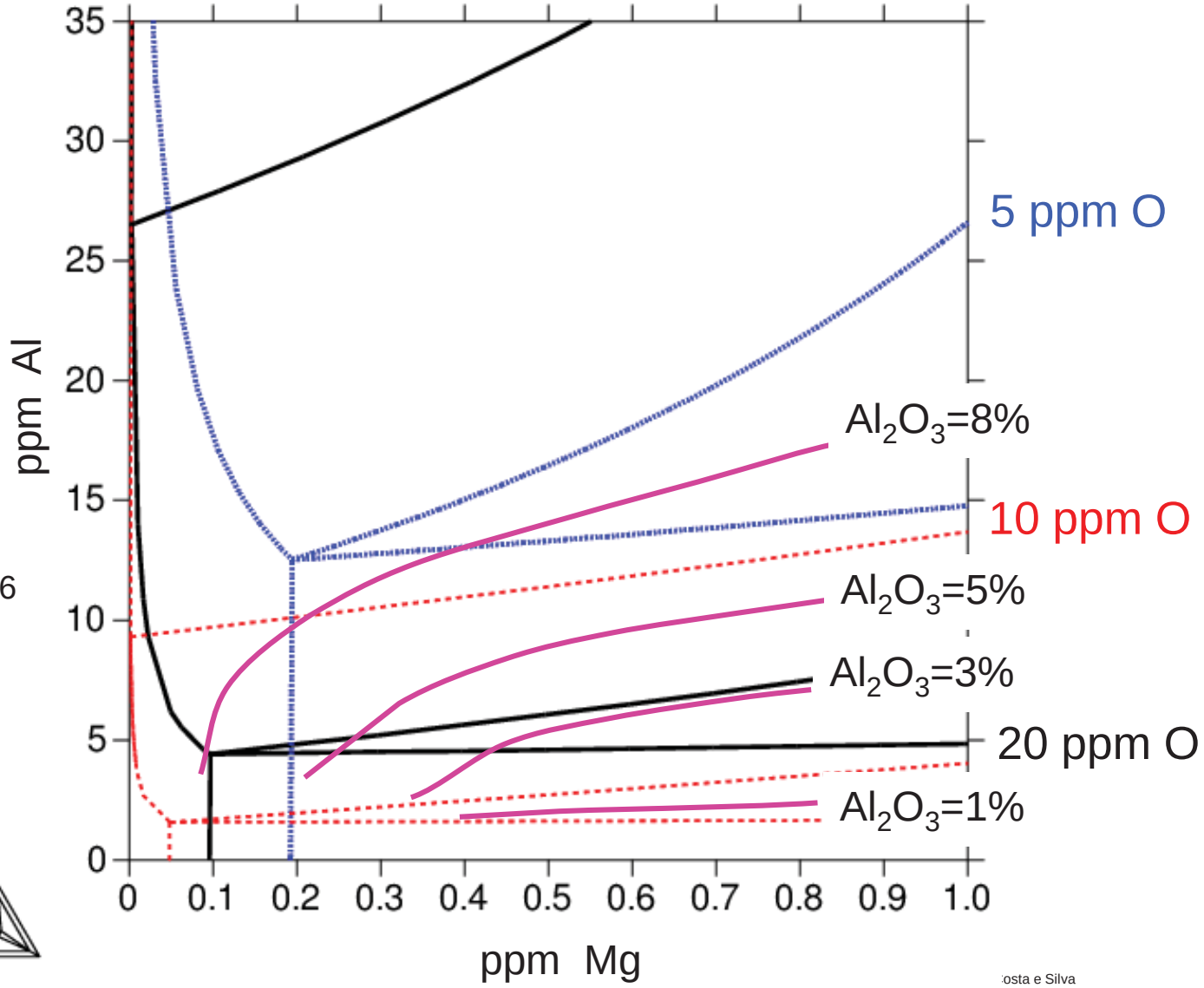


Explore processing conditions: Different slags in LF and possible reoxidation conditions

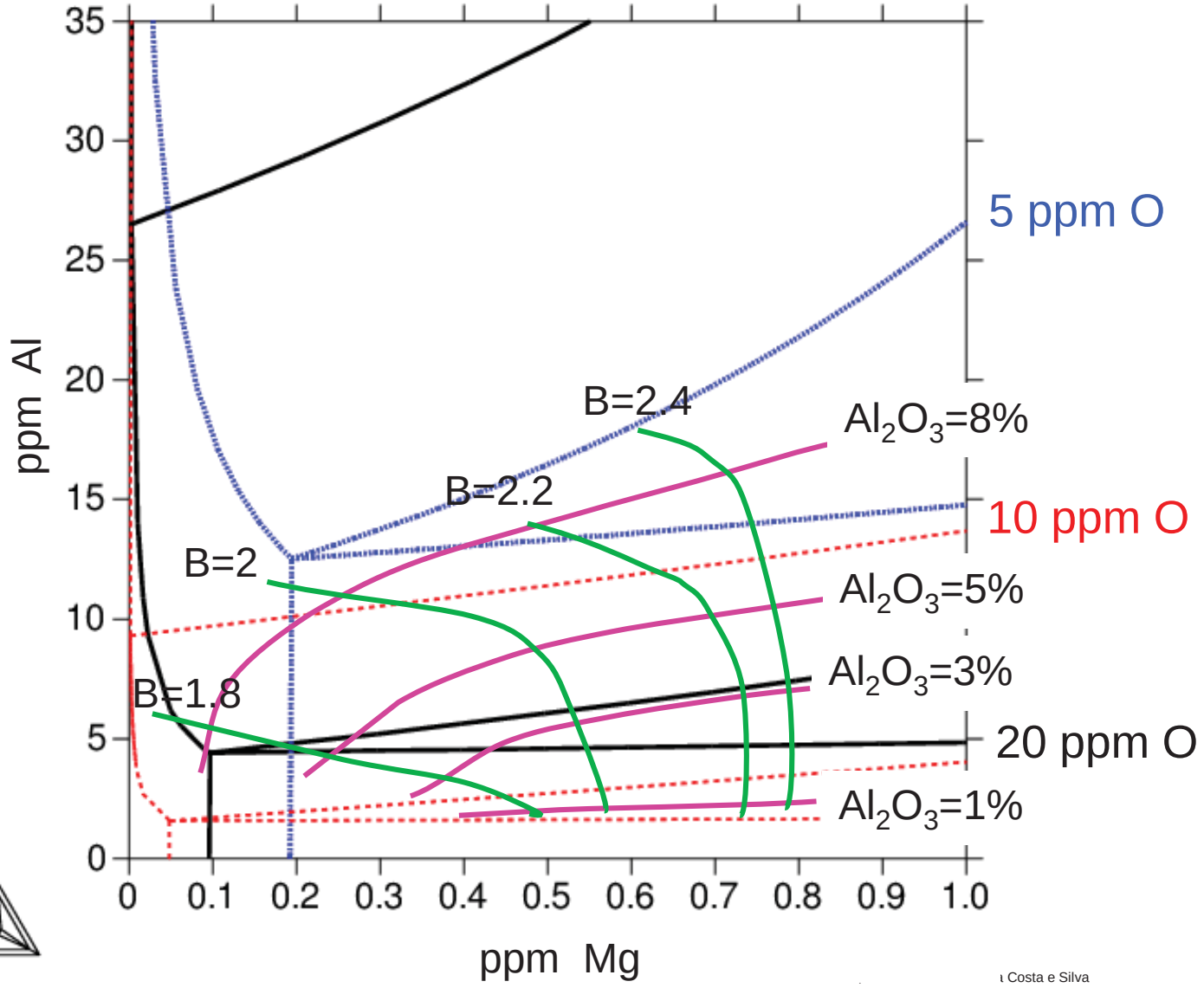


Explore processing conditions: Different slags in LF and possible reoxidation conditions

Botelho et al 2016



Explore processing conditions: Different slags in LF and possible reoxidation conditions



Sub-sea manifolds – Extensive use of duplex SS

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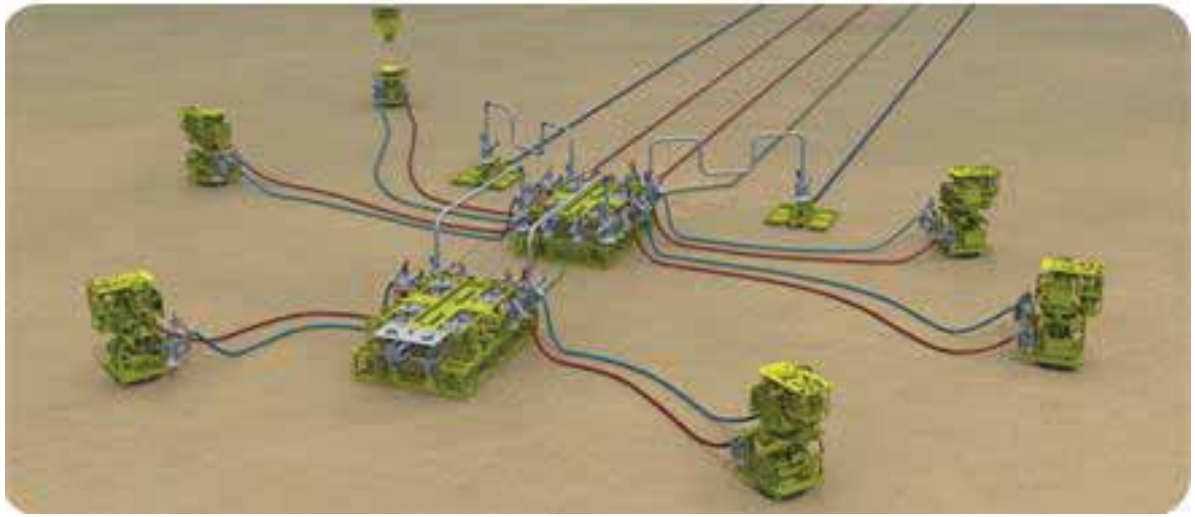

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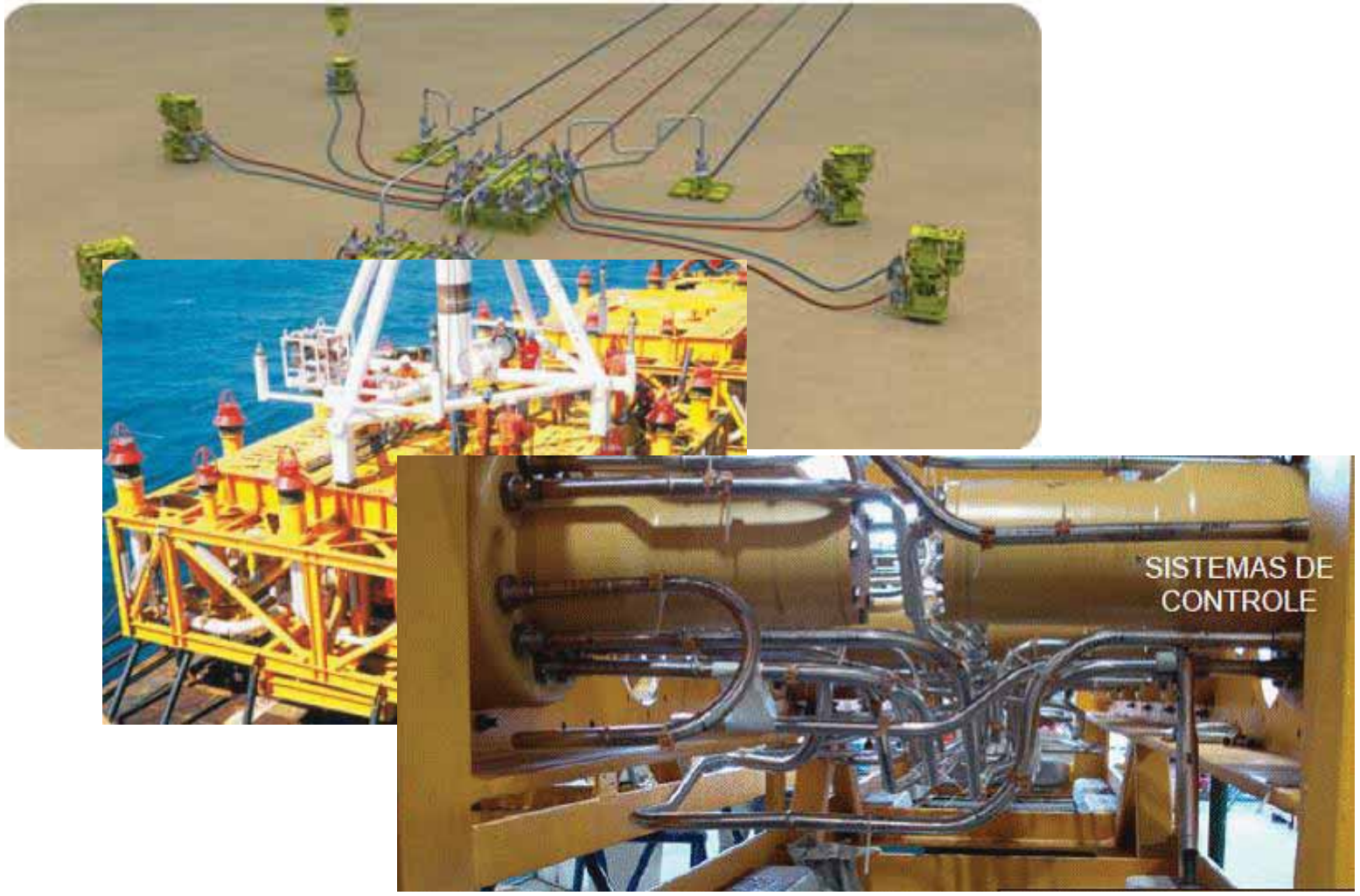


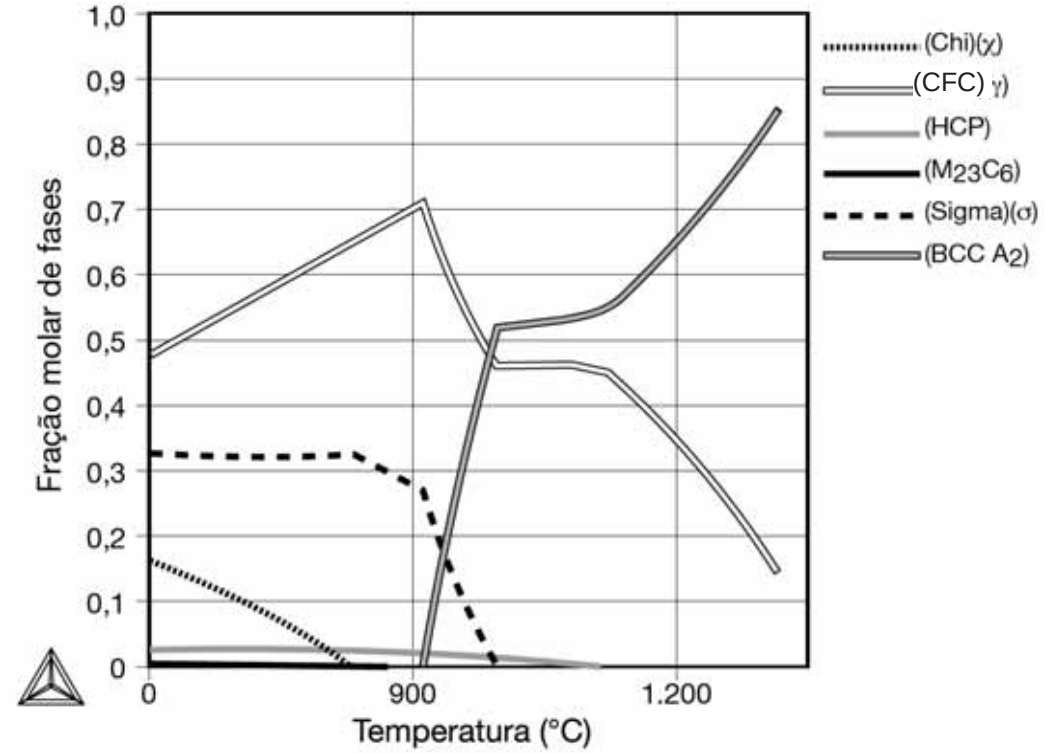
Sigma phase cracking – large Duplex Stainless steel casting

M Martins, 2008

Sigma in ASTM A890 Gr 6A

Costa e Silva, Avillez, 2009

N=1, P=1.01325E5, W(C)=2E-4, W(CR)=0.2584, W(NI)=5.94E-2, W(MN)=8.8E-3, W(SI)=9.2E-3, W(MO)=3.79E-2, W(N)=2.5E-3, W(CU)=1.5E-2;



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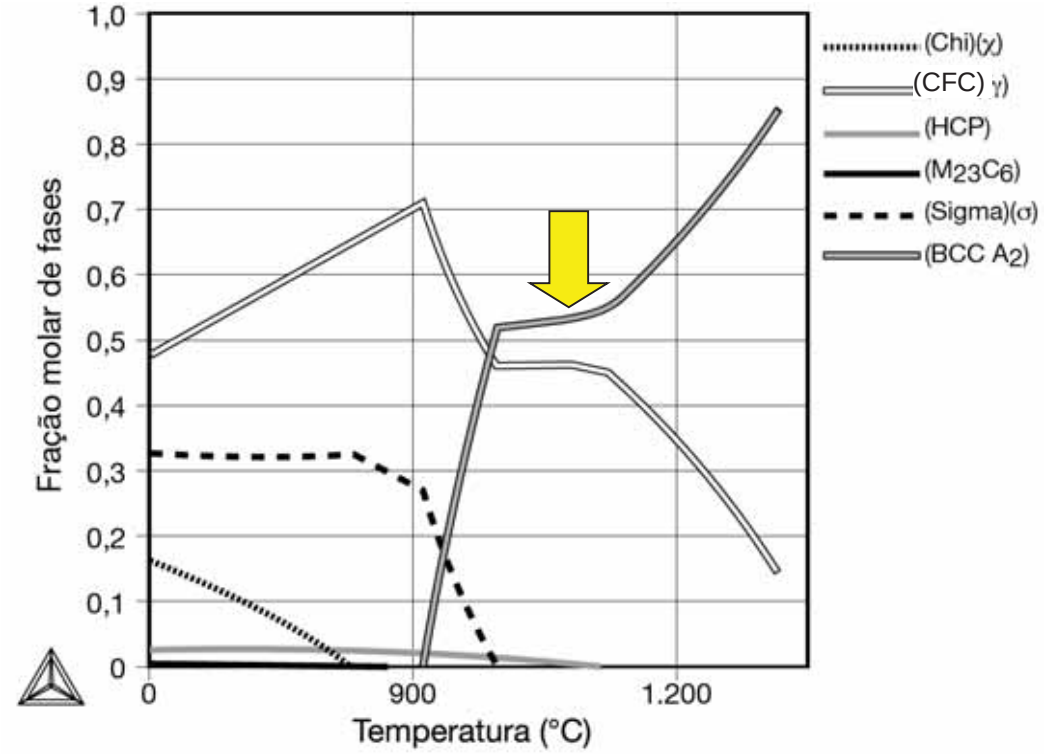

Sigma in ASTM A890 Gr 6A

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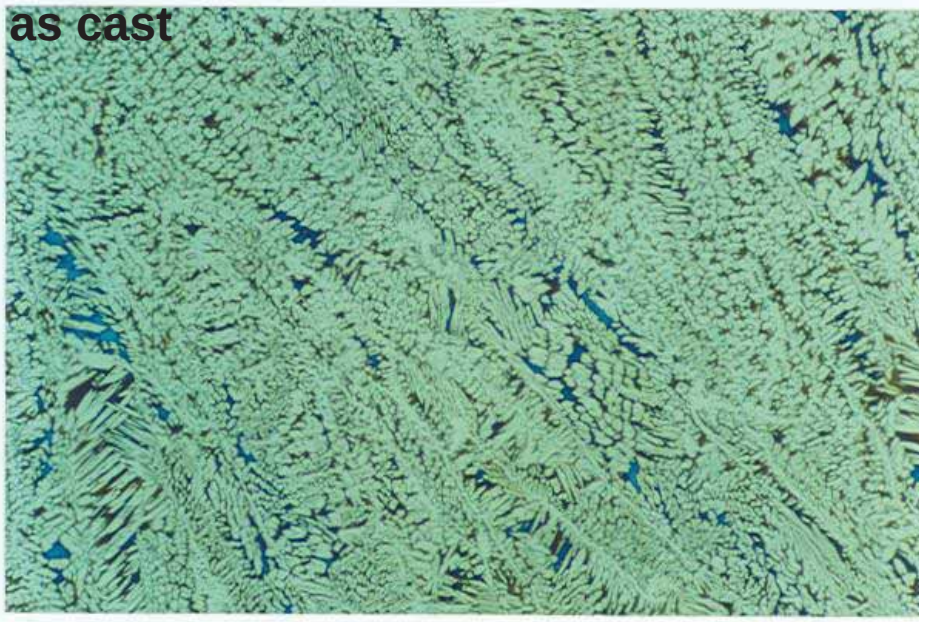

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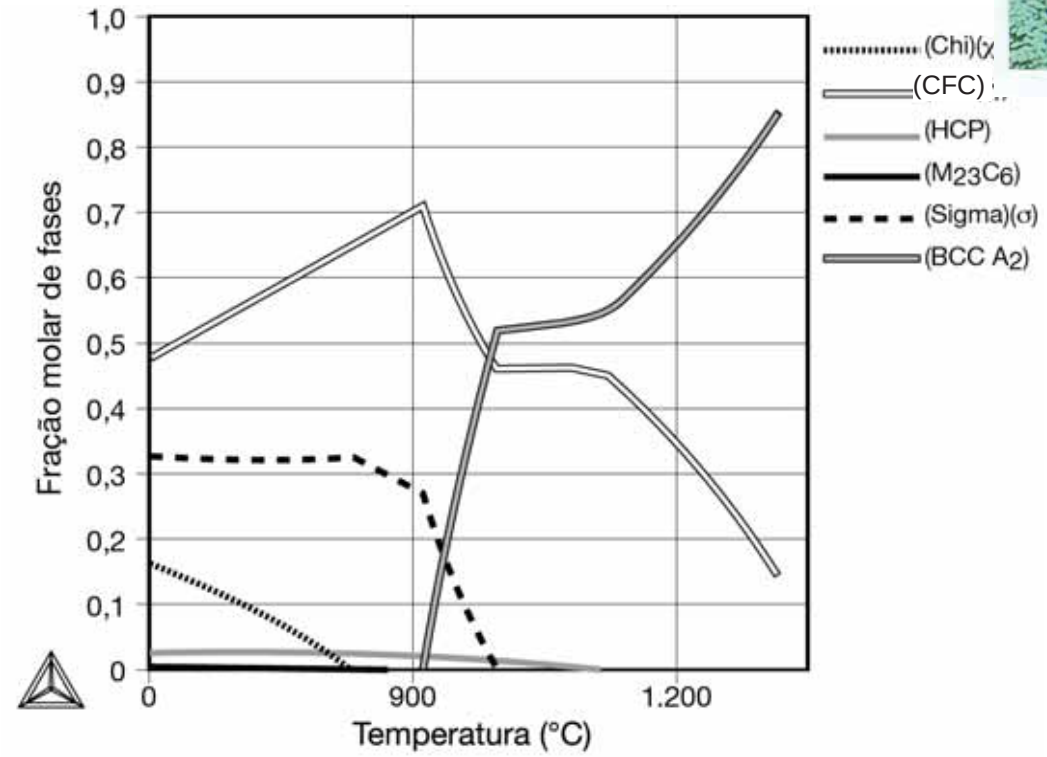
W(SI)=9.2E-3, W(MO)=3.79E-2, W(N)=2.5E-3, W(CU)=1.5



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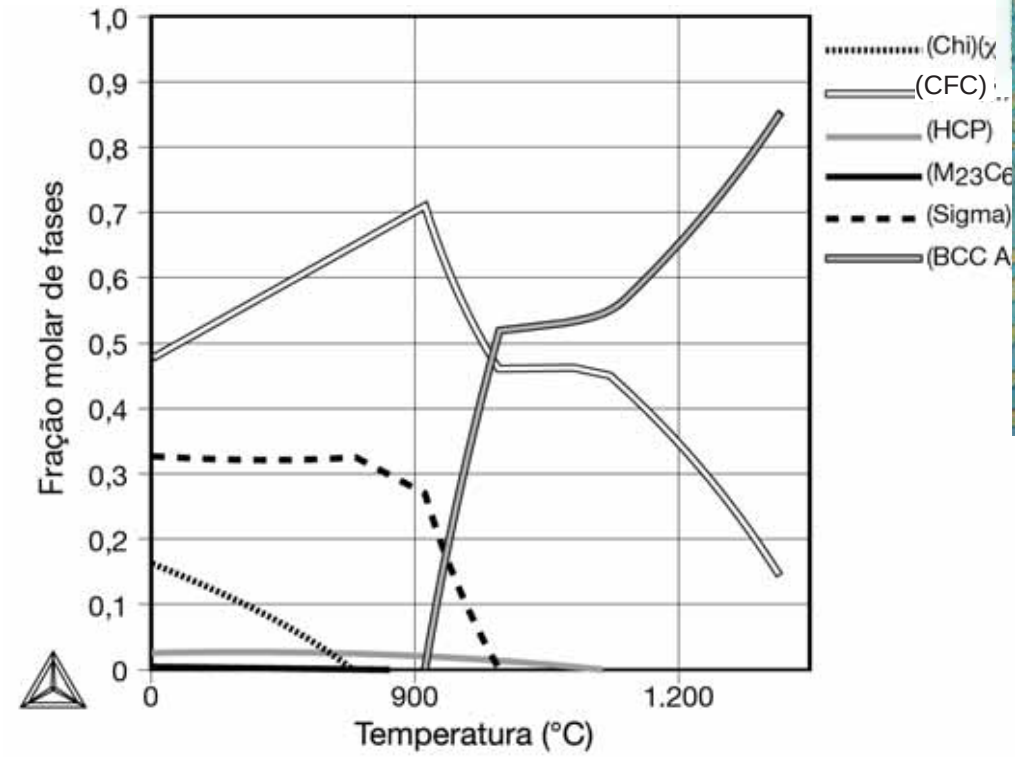

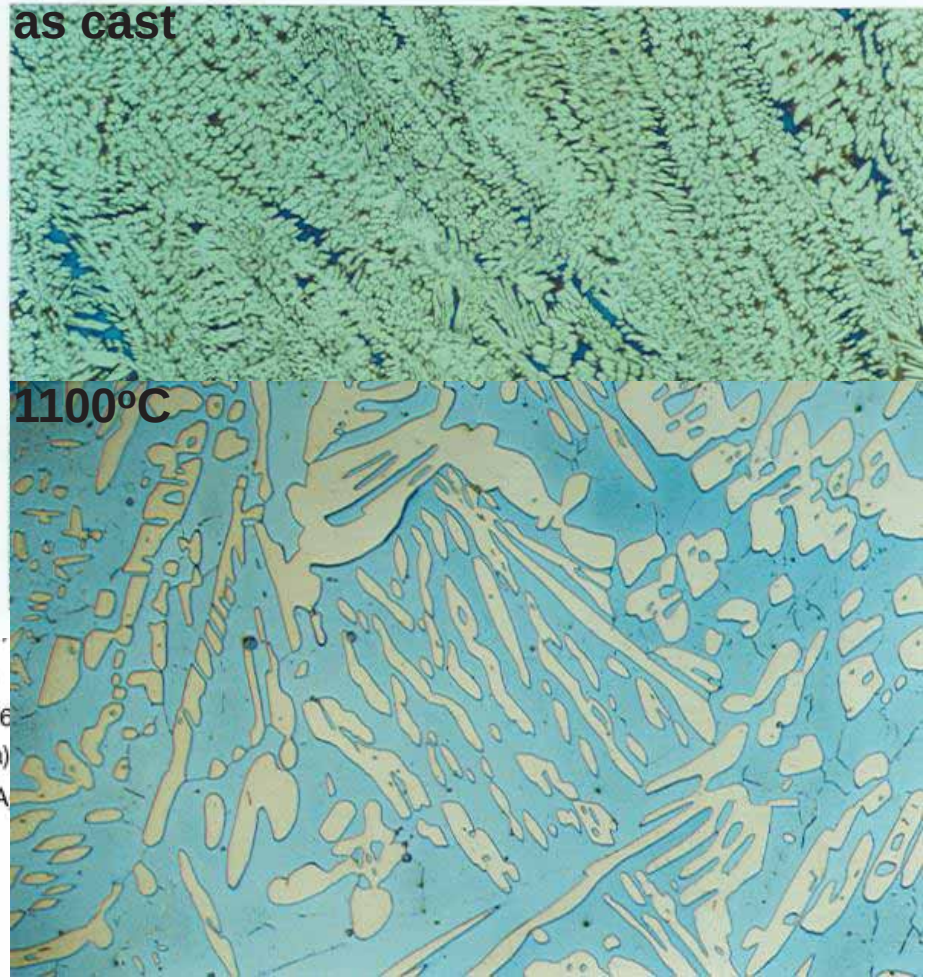

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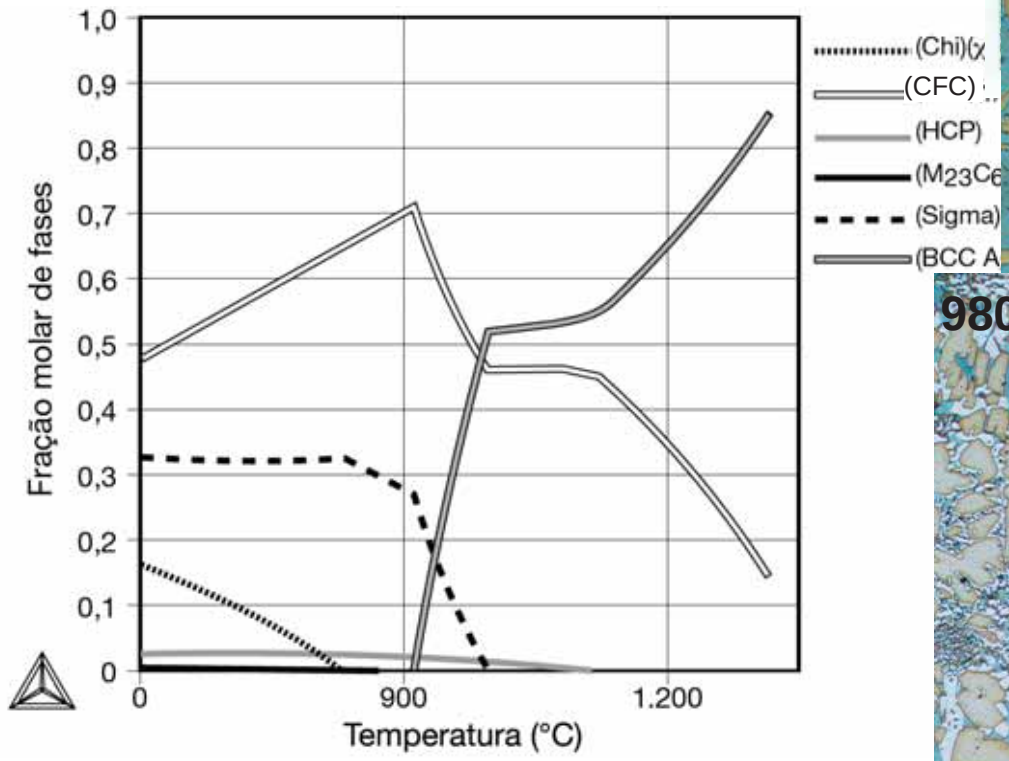
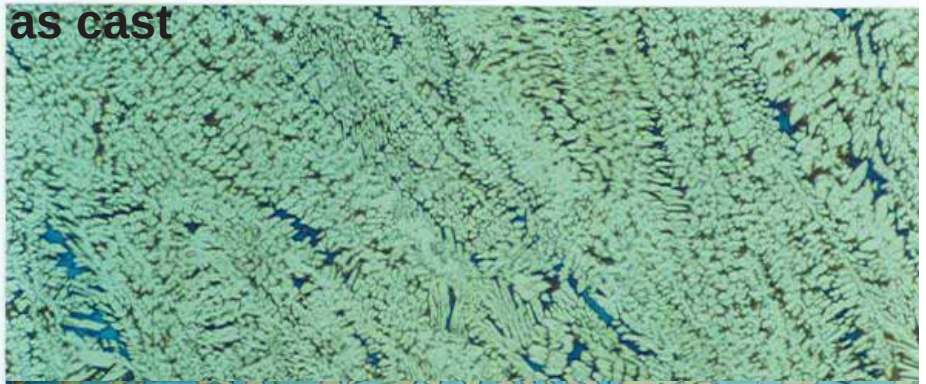
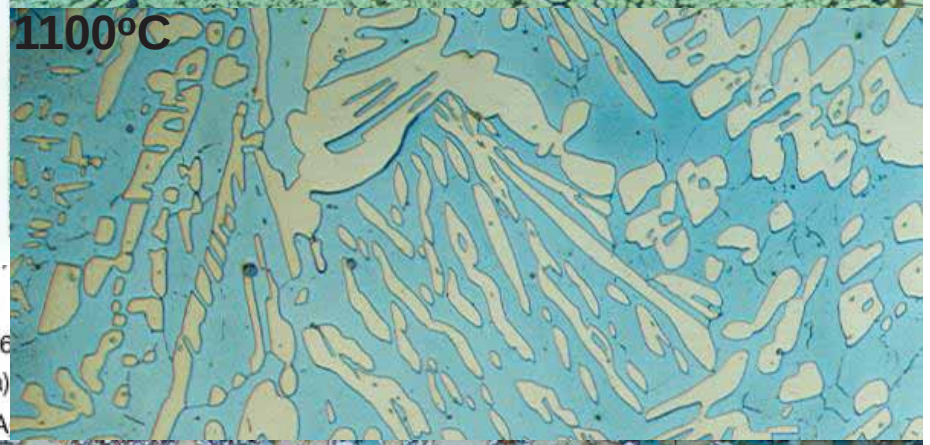
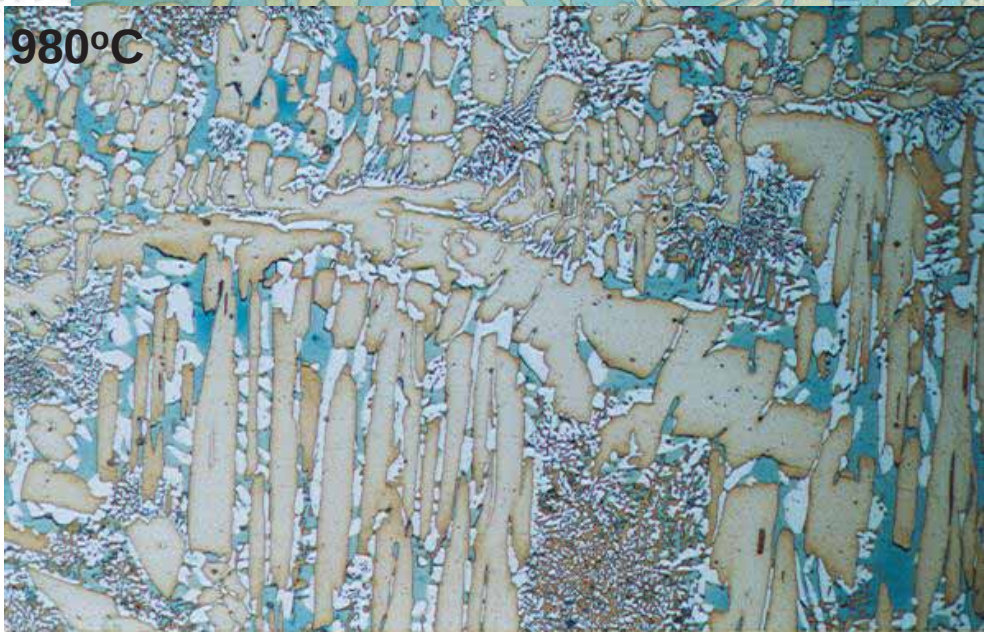
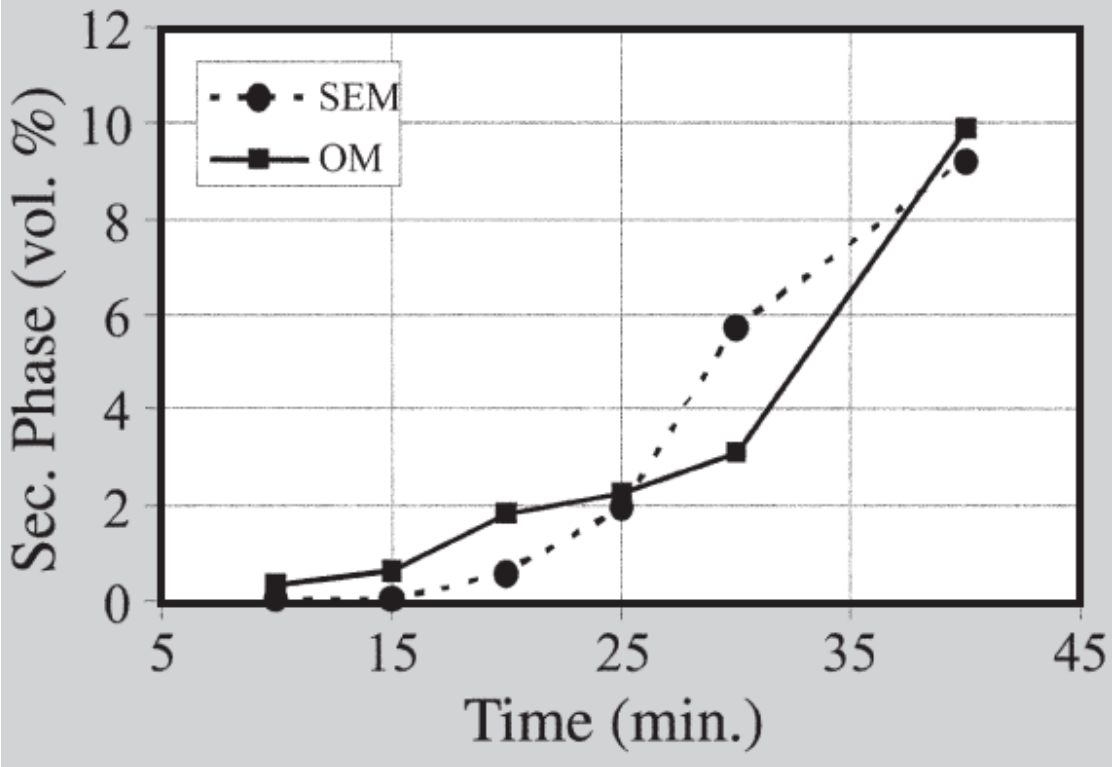




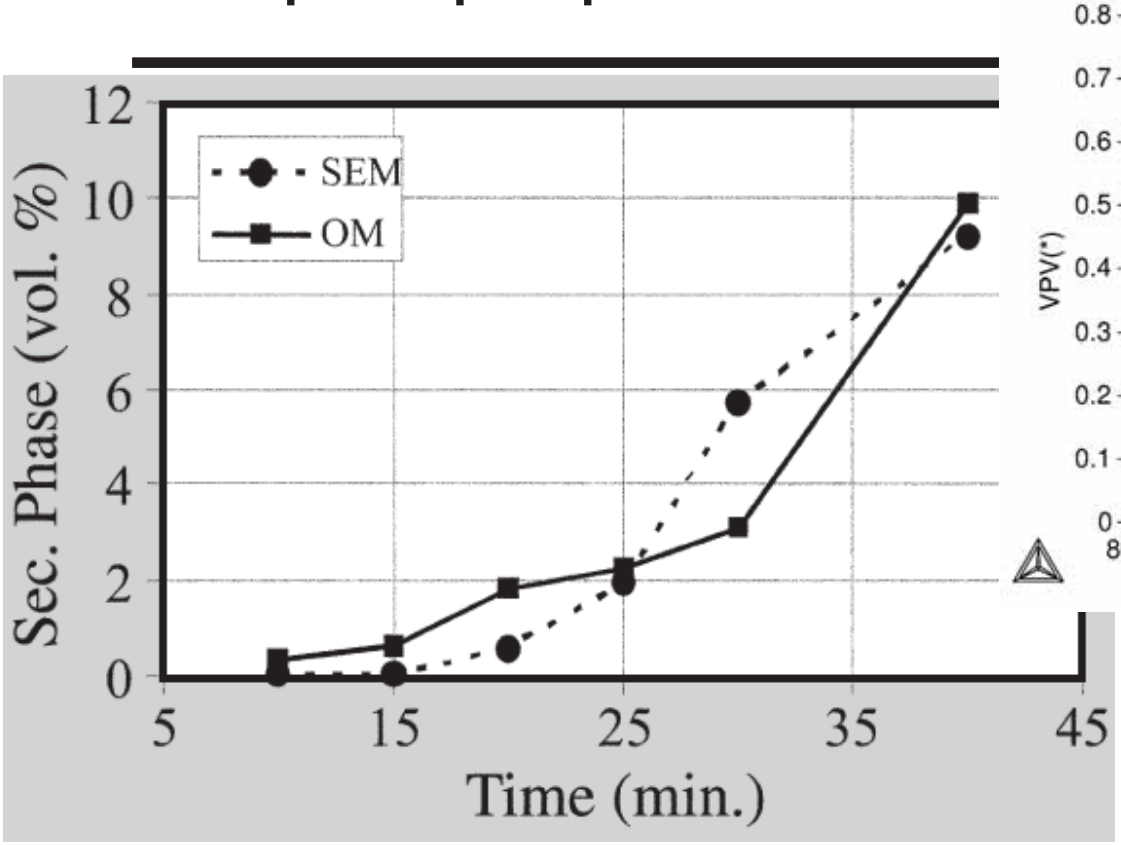


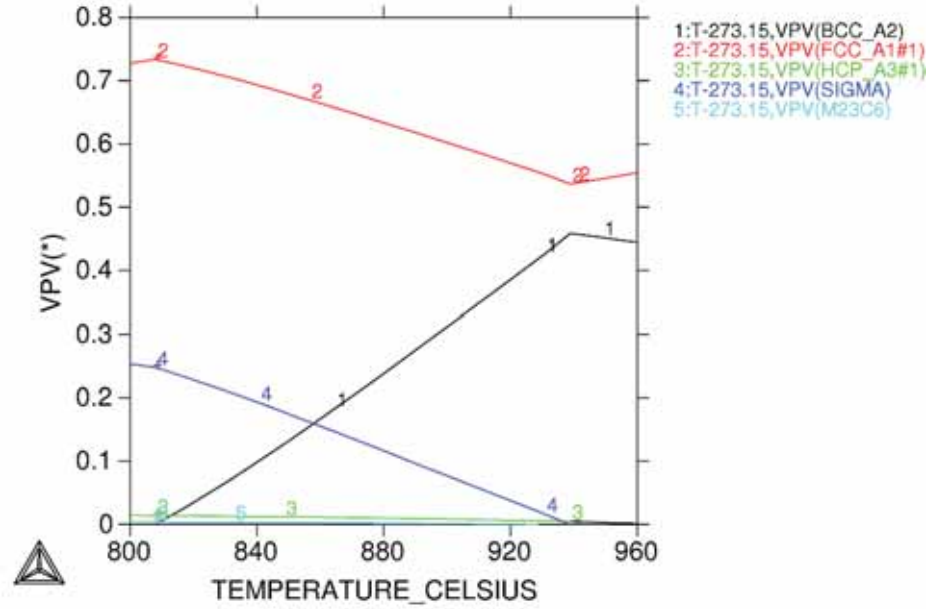


Second phase precipitation in 2205 at 900ºC, I. Calliari, JOM 2009

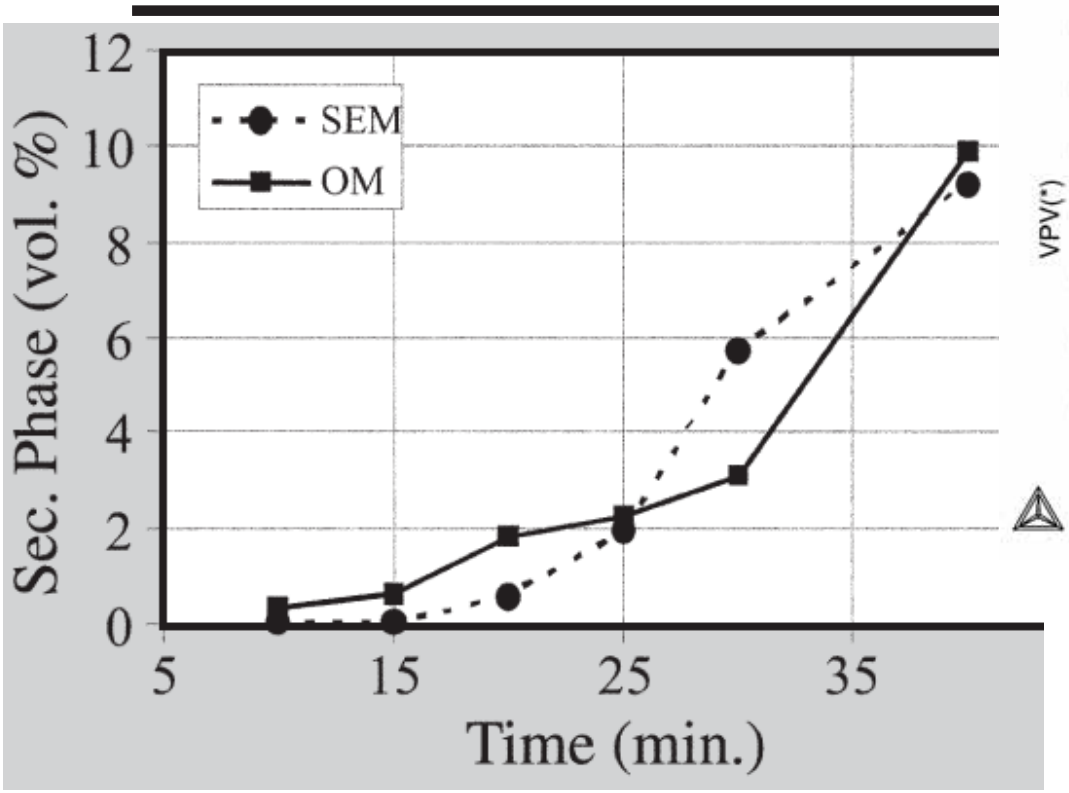


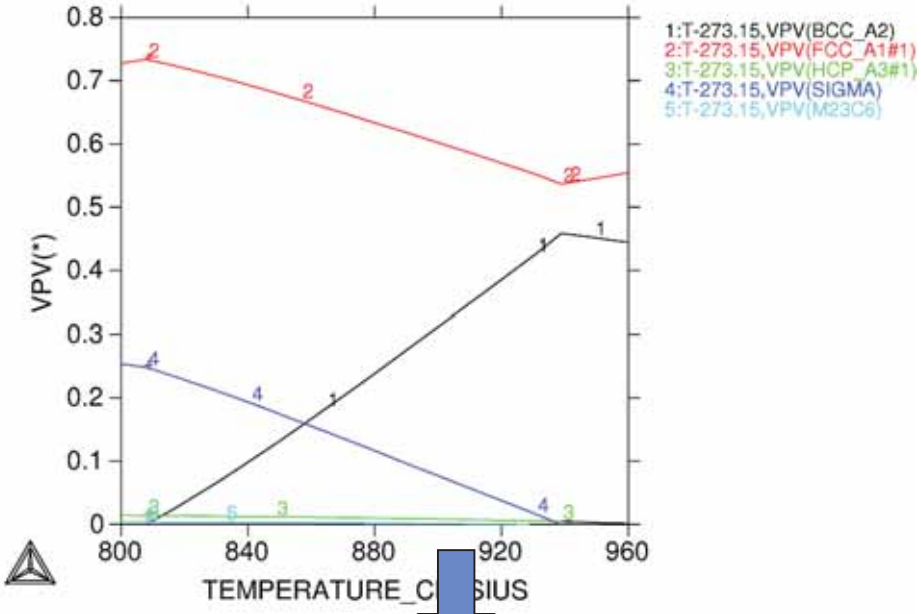
Second phase precipitation in 2205 at 900ºC. I. Calliari. JOM 2009

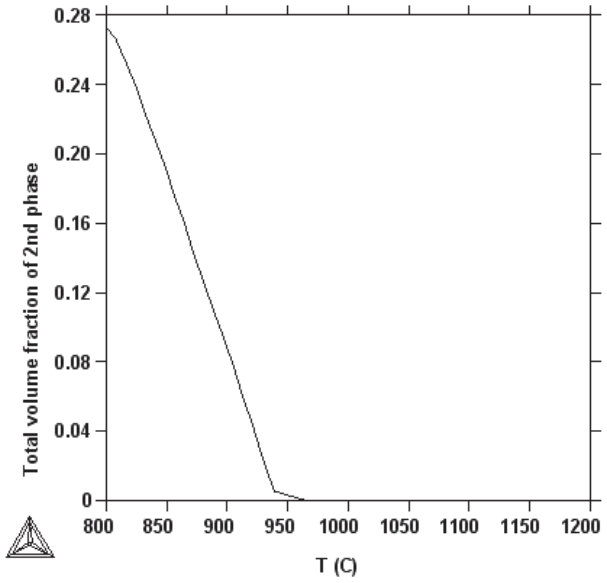




Second phase precipitation in 2205 at 900ºC. I. Calliari. JOM 2009







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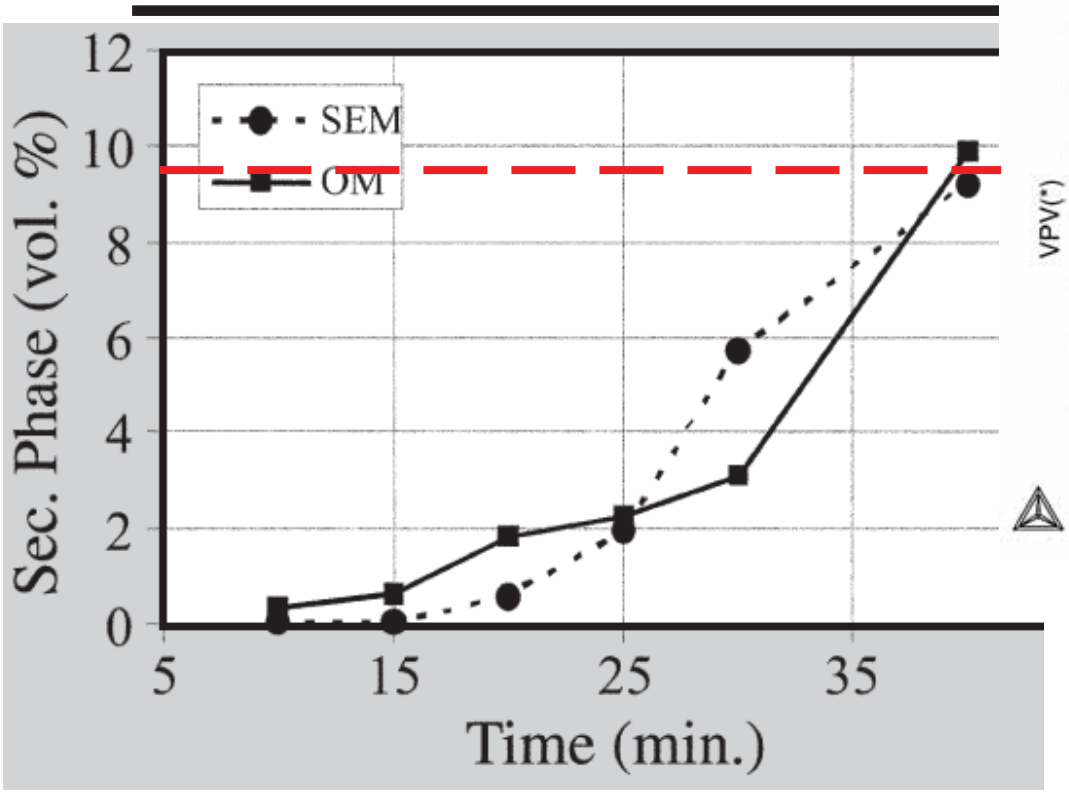
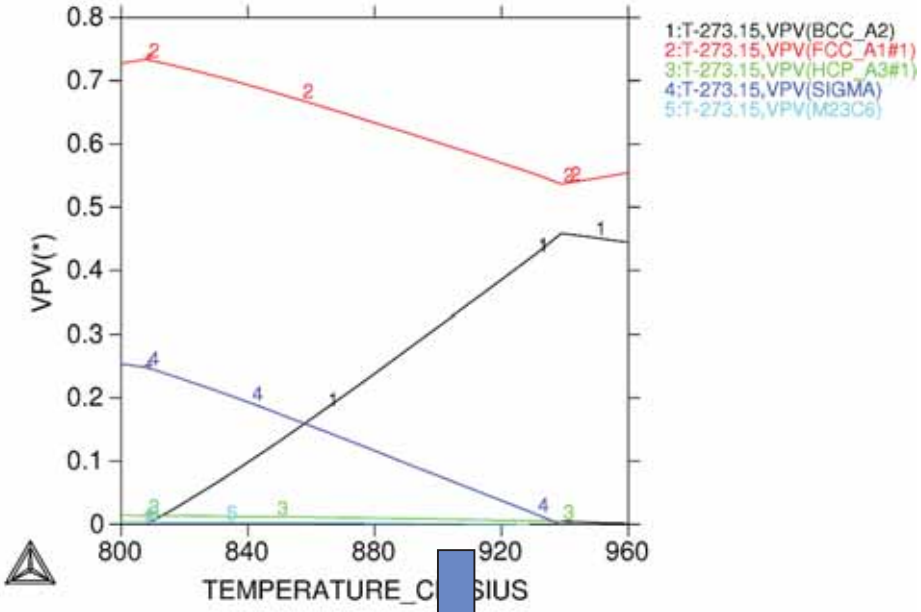
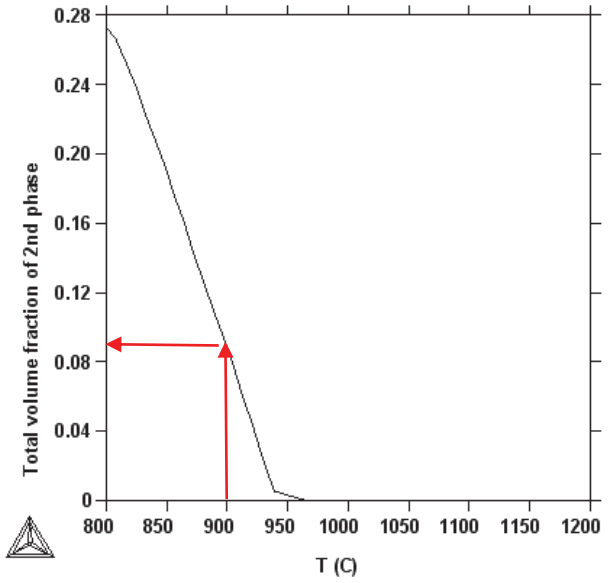
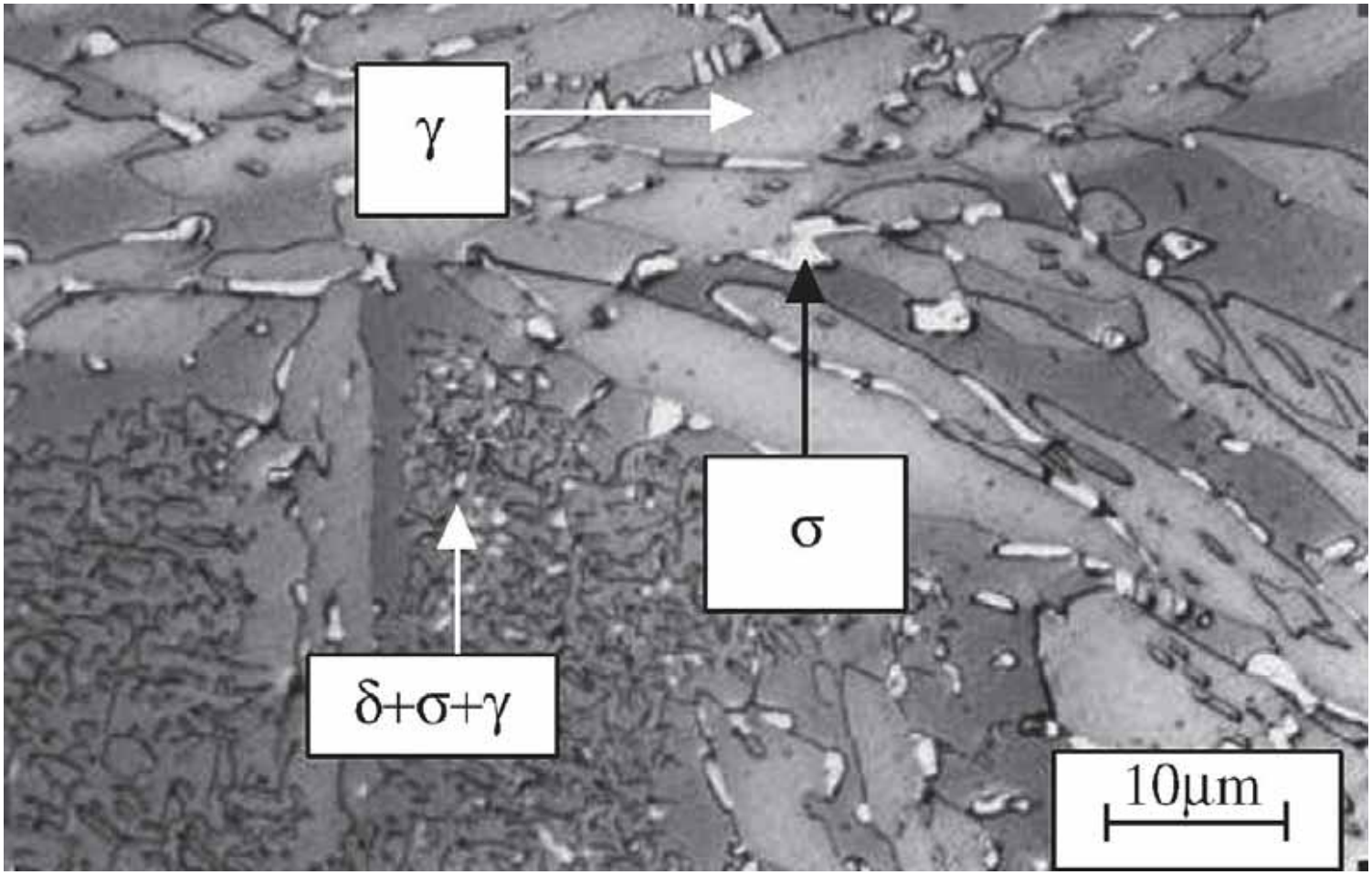






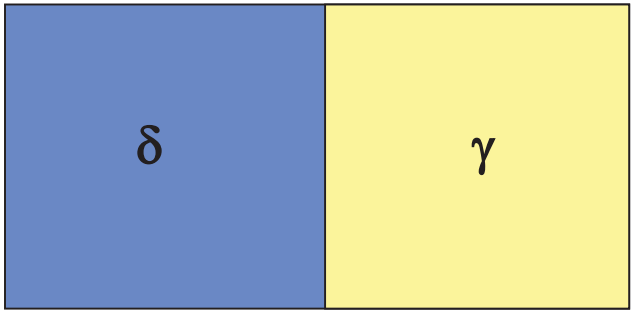
ASTM A890 Gr 6A
Isothermal 1040 ºC σ location



Martins 2005

DICTRA Modeling (CALPHAD 2009)

Modeling the formation of sigma at γ–δ interface



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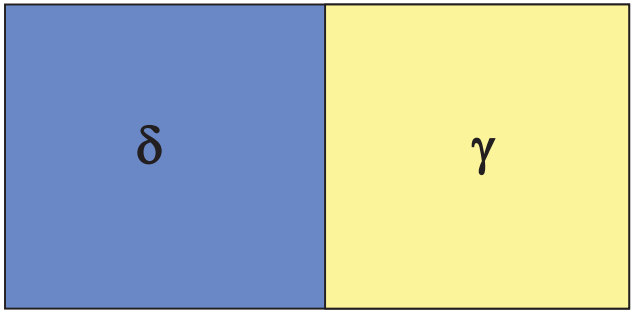

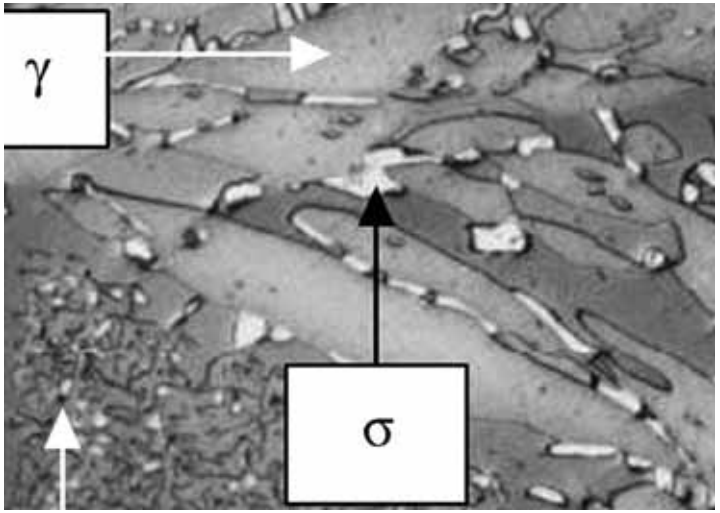

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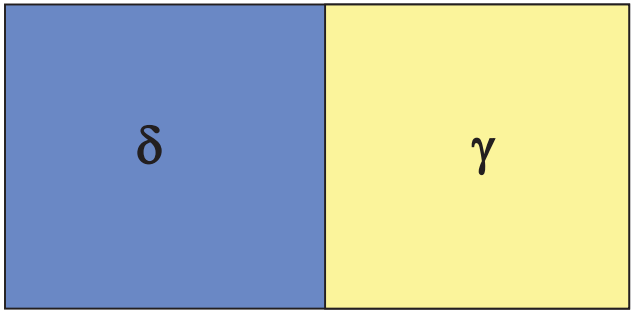

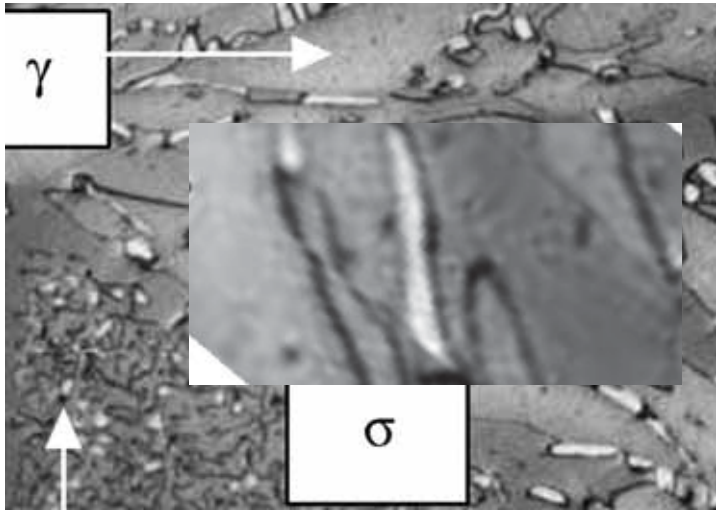

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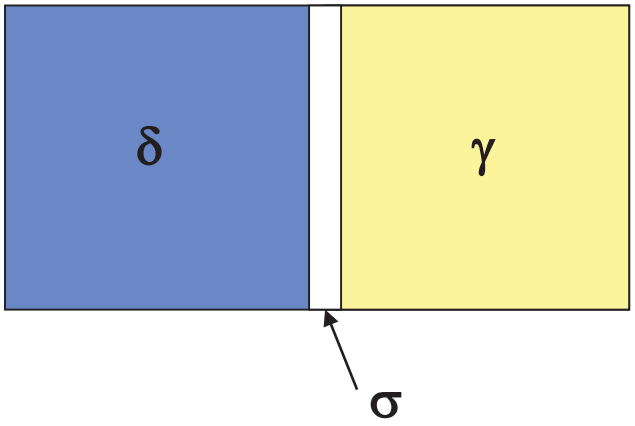

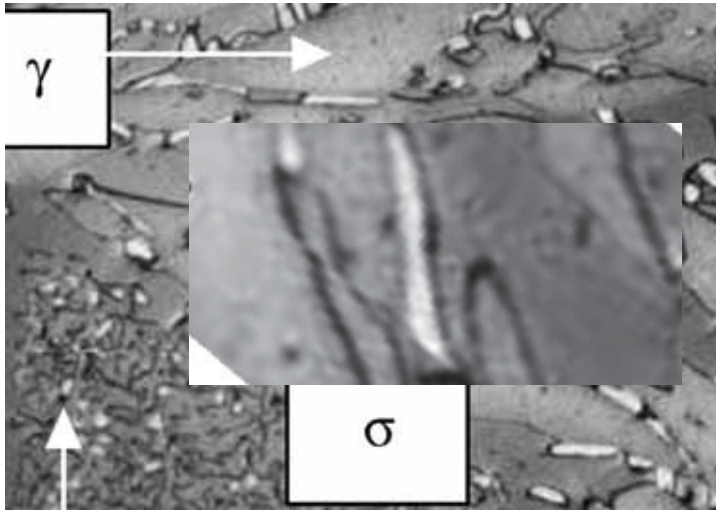

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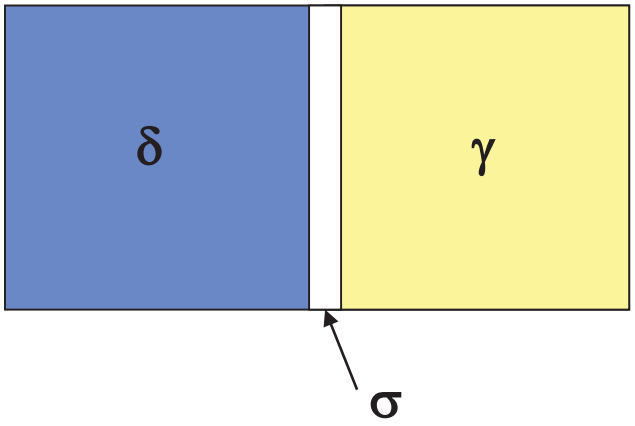
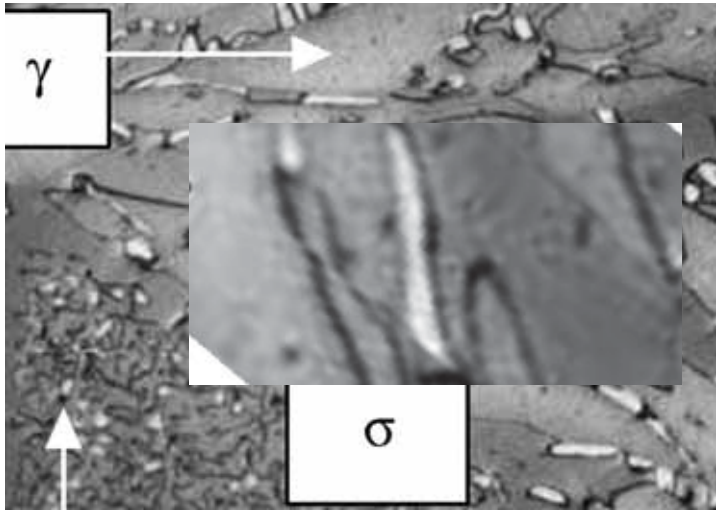
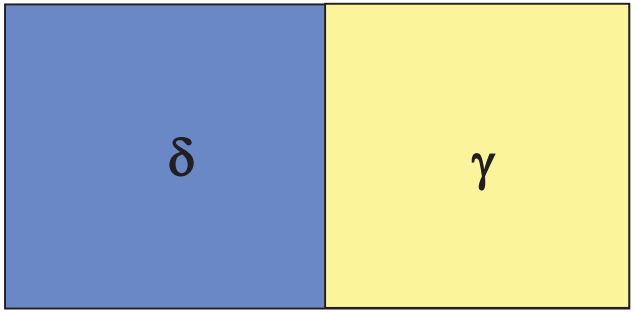




Cooperative growth - Modeling the growth



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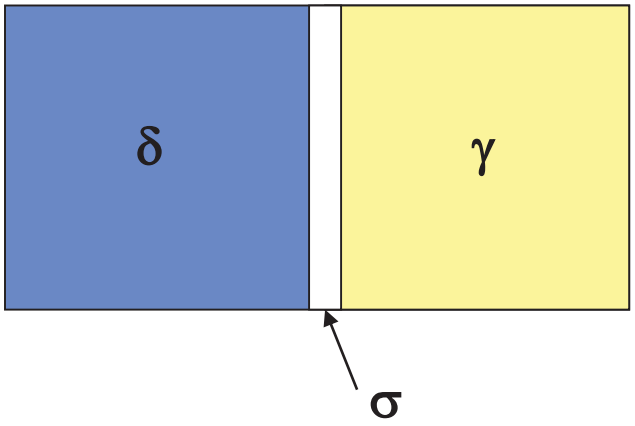

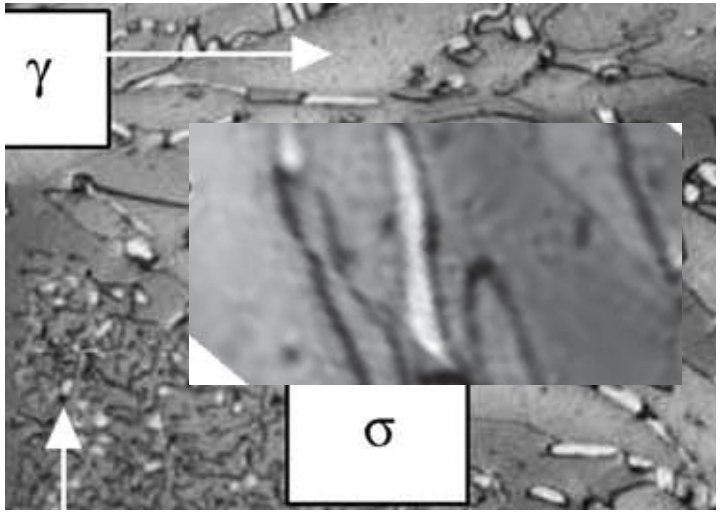

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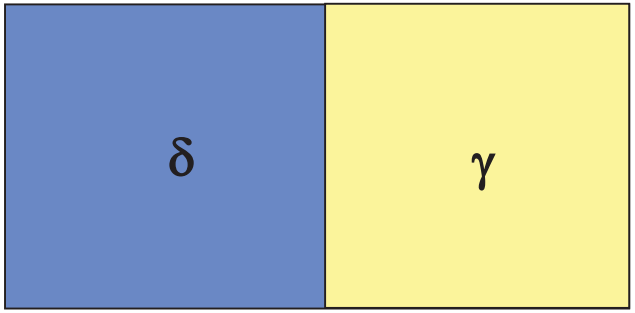

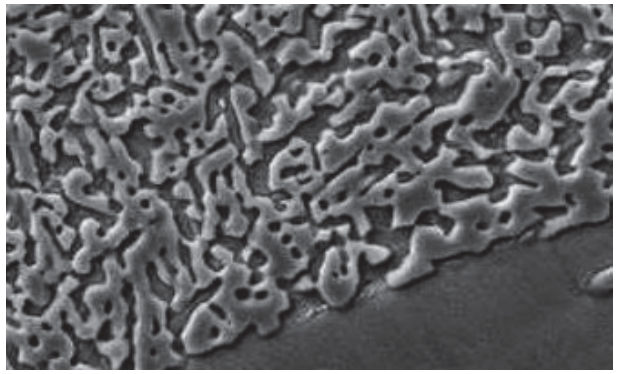

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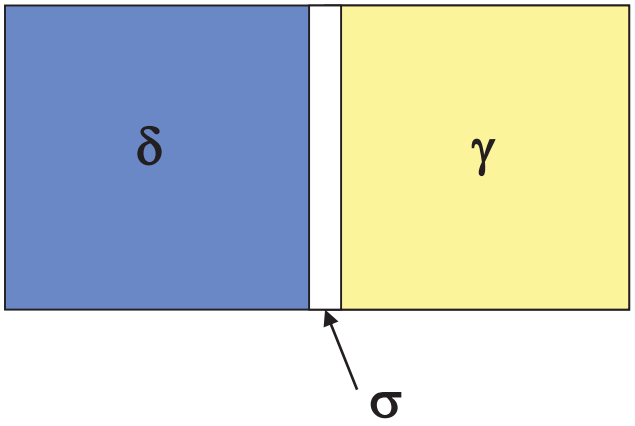
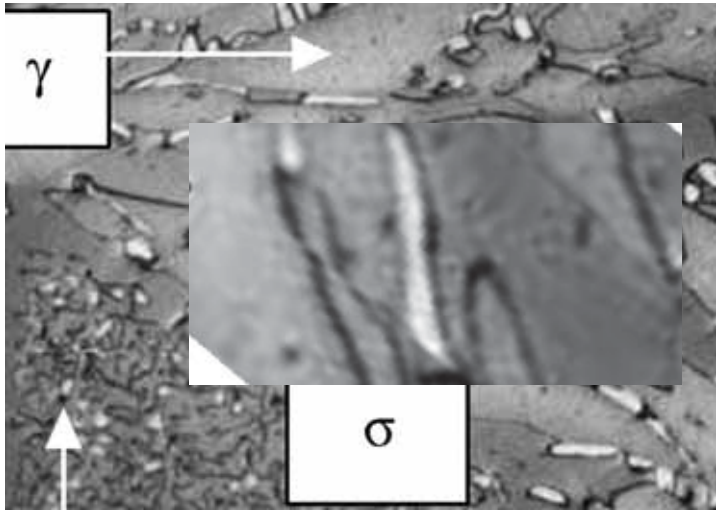
Modeling the formation of sigma at γ–δ interface





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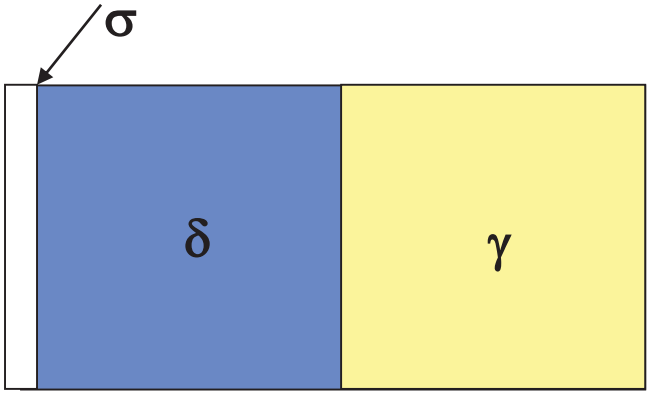
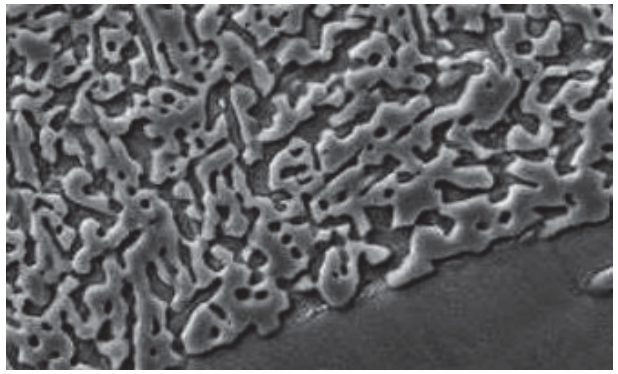
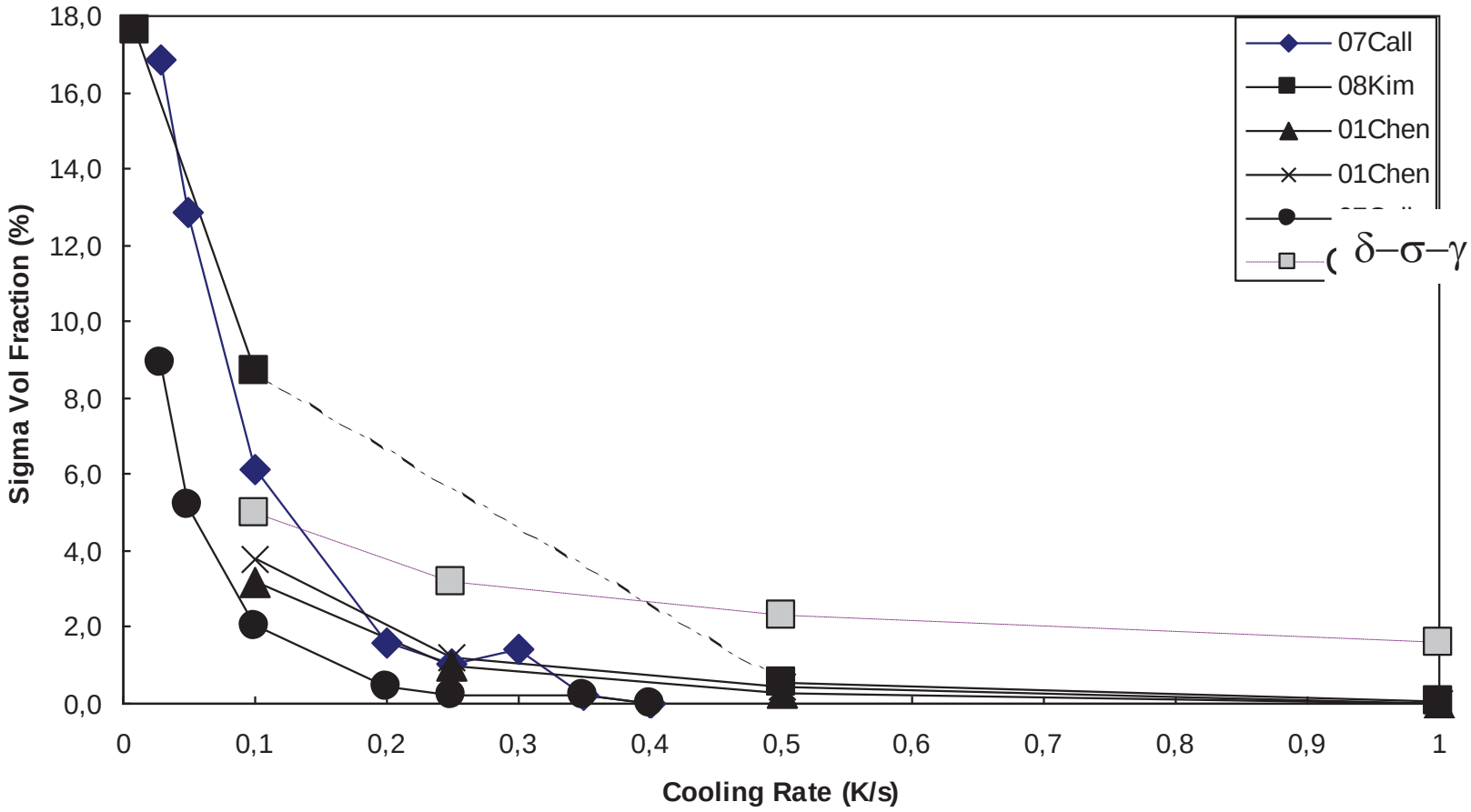




DICTRA results of σ and γ growth into δ



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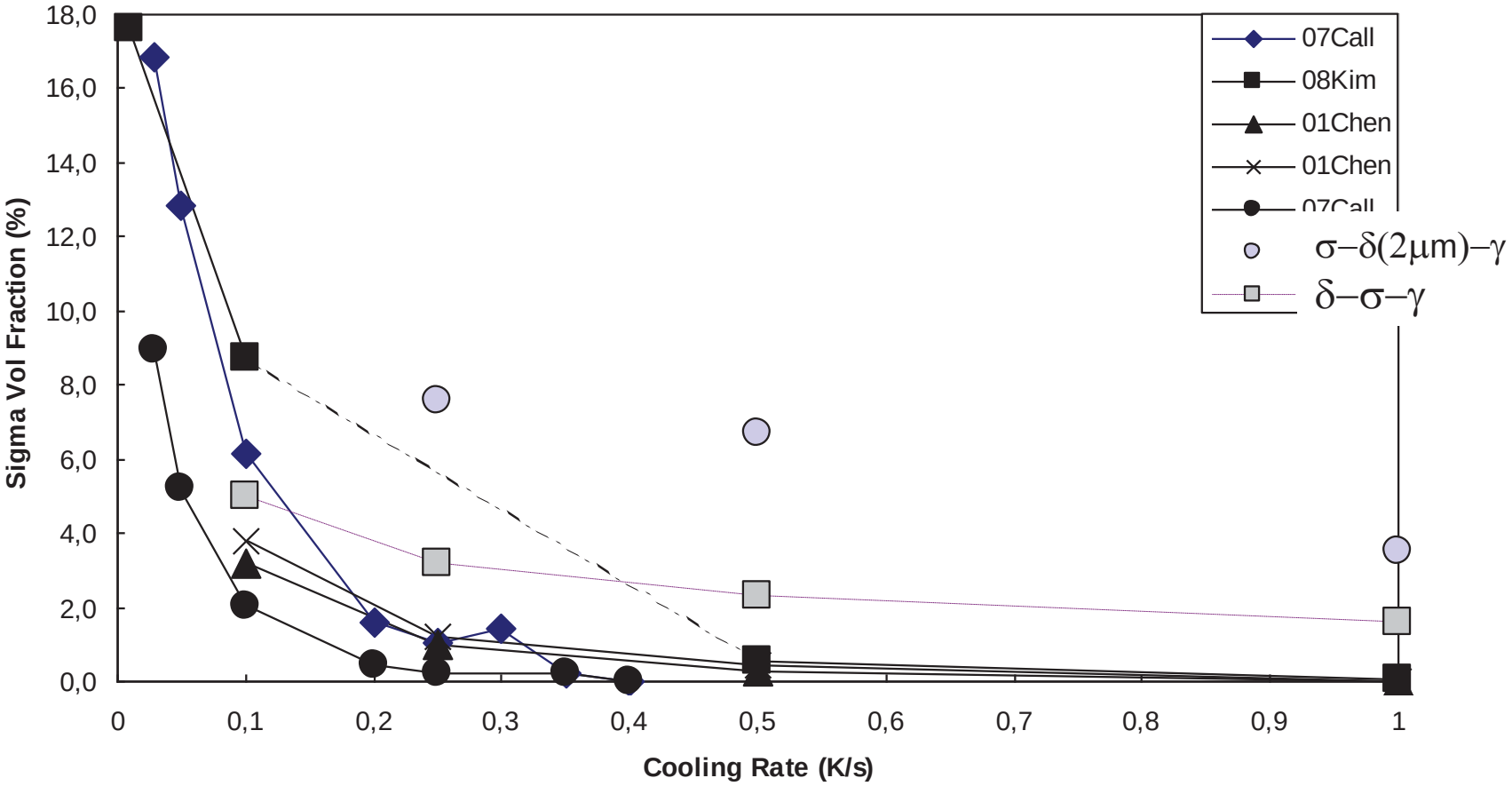
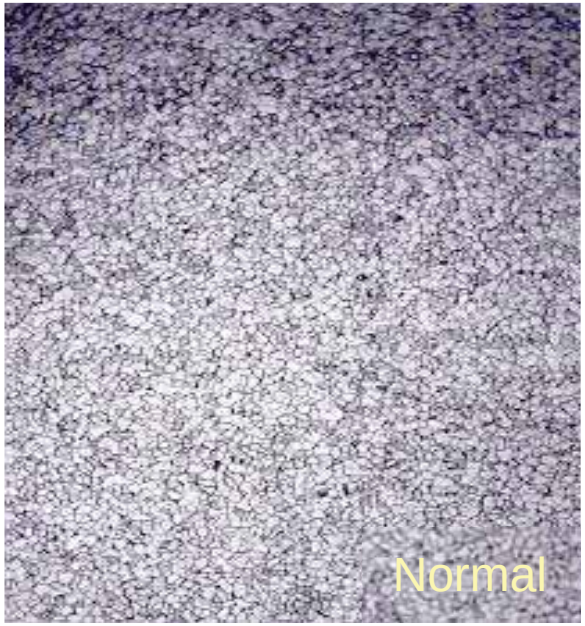


Int. Oxidation

N control in steel for cold forming



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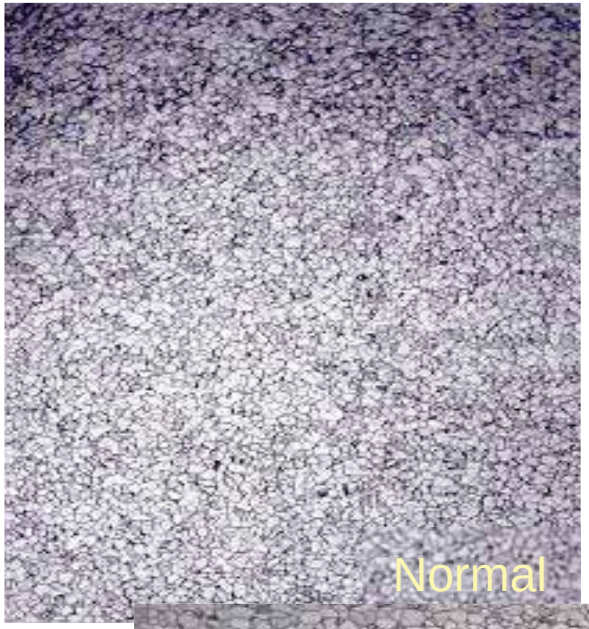
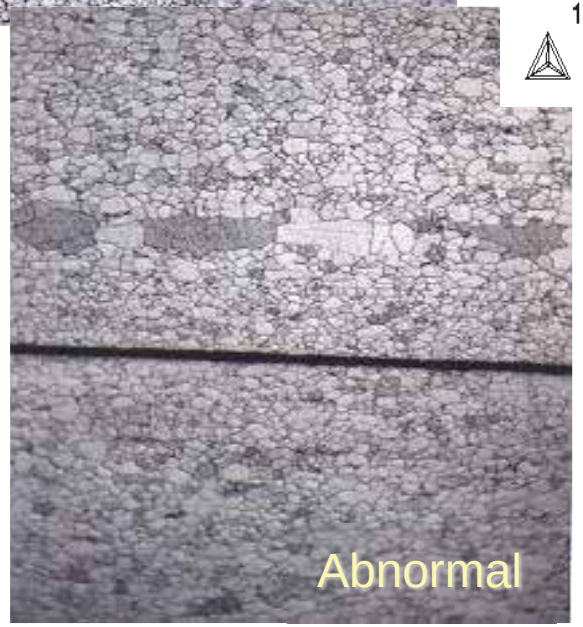
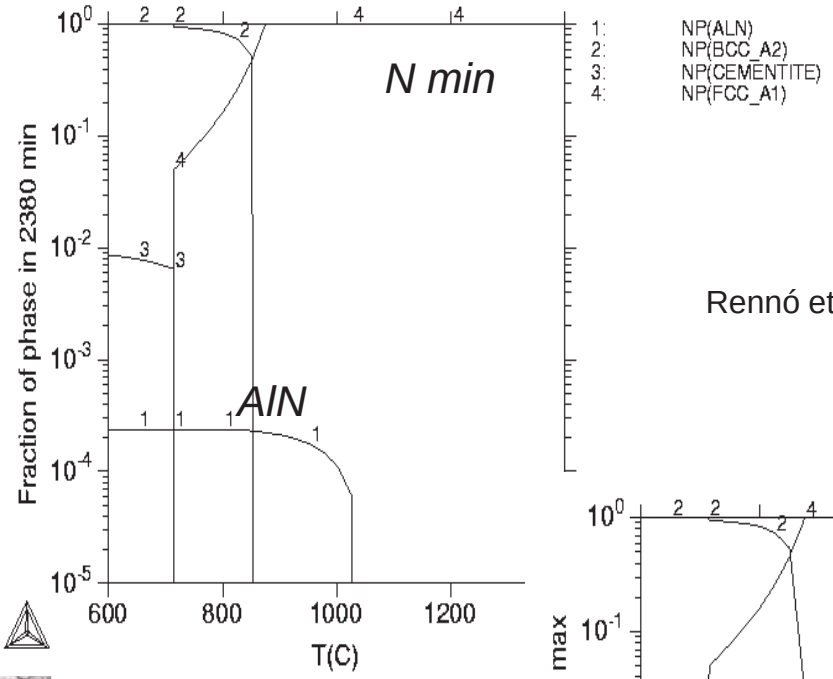
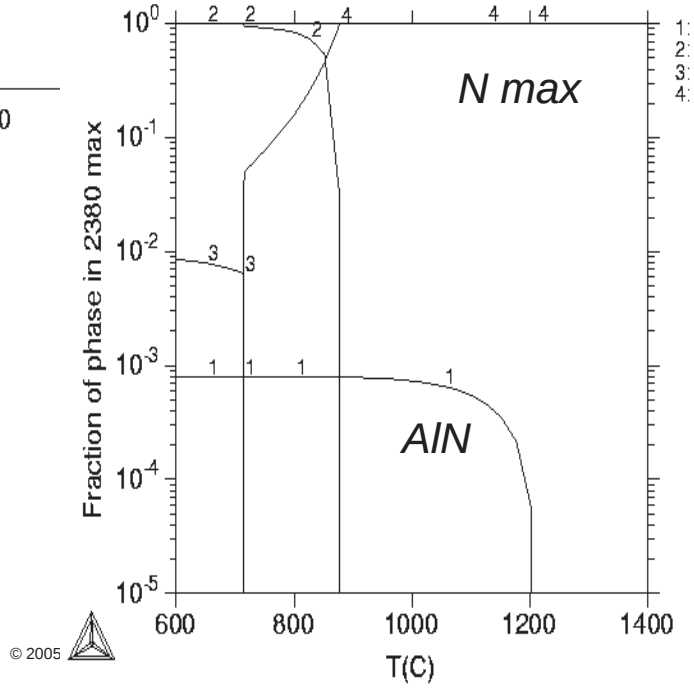






Rennó et al 1997



Kinetics of Precipitation of AlN with CALPHAD data (PRISMA)

2012 Costa e Silva, Nakamura, Rizzo

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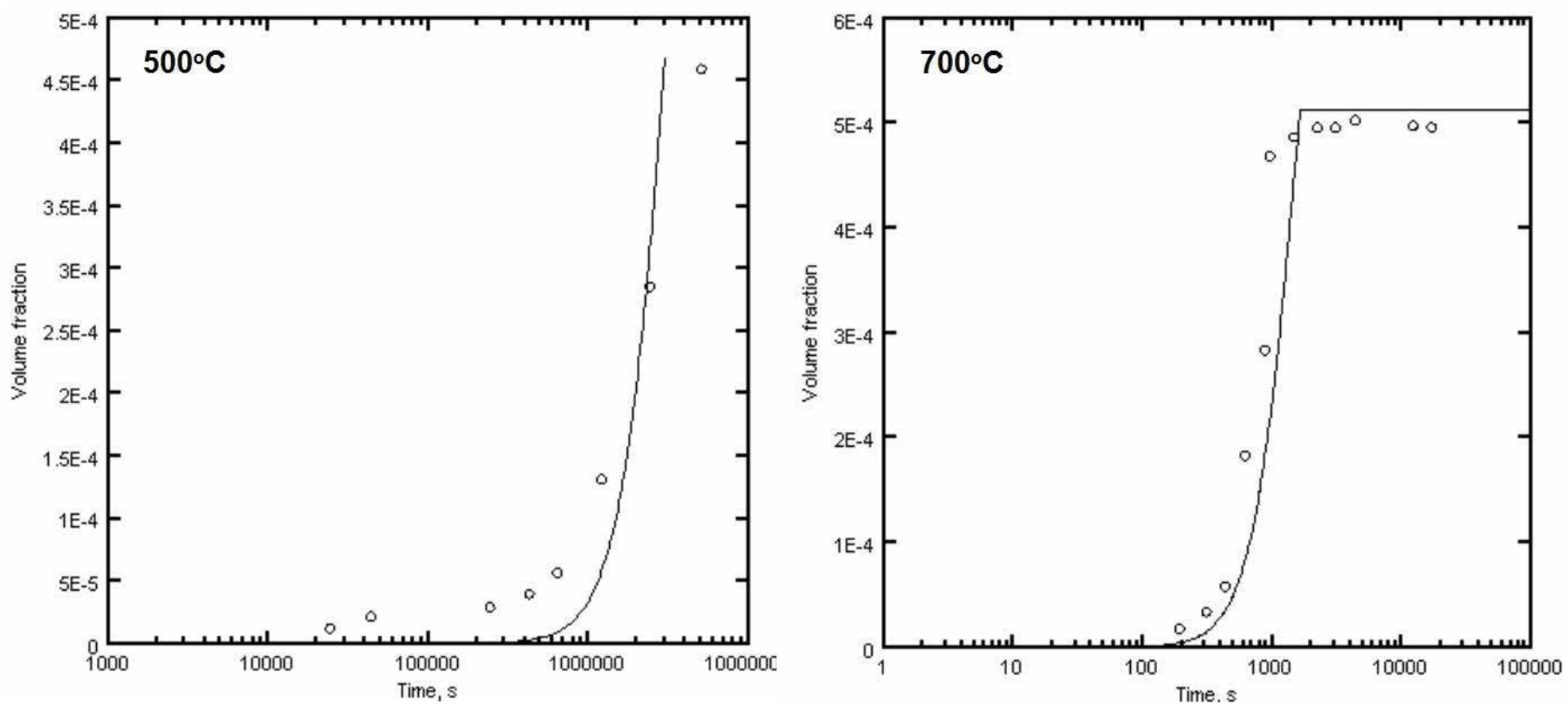

2012 Costa e Silva, Nakamura, Rizzo

Final deposit (Yucca?) precipitation in Alloy 22 (NiCrMoW) (10.000 yrs)
L. Kaufman, P. Turchi, DICTRA calculations

Final deposit (Yucca?) precipitation in Alloy 22 (NiCrMoW) (10.000 yrs) L. Kaufman, P. Turchi, DICTRA calculations

For the “first”10,000 years, the EPA would retain the dose limit of 15 millirem per year.

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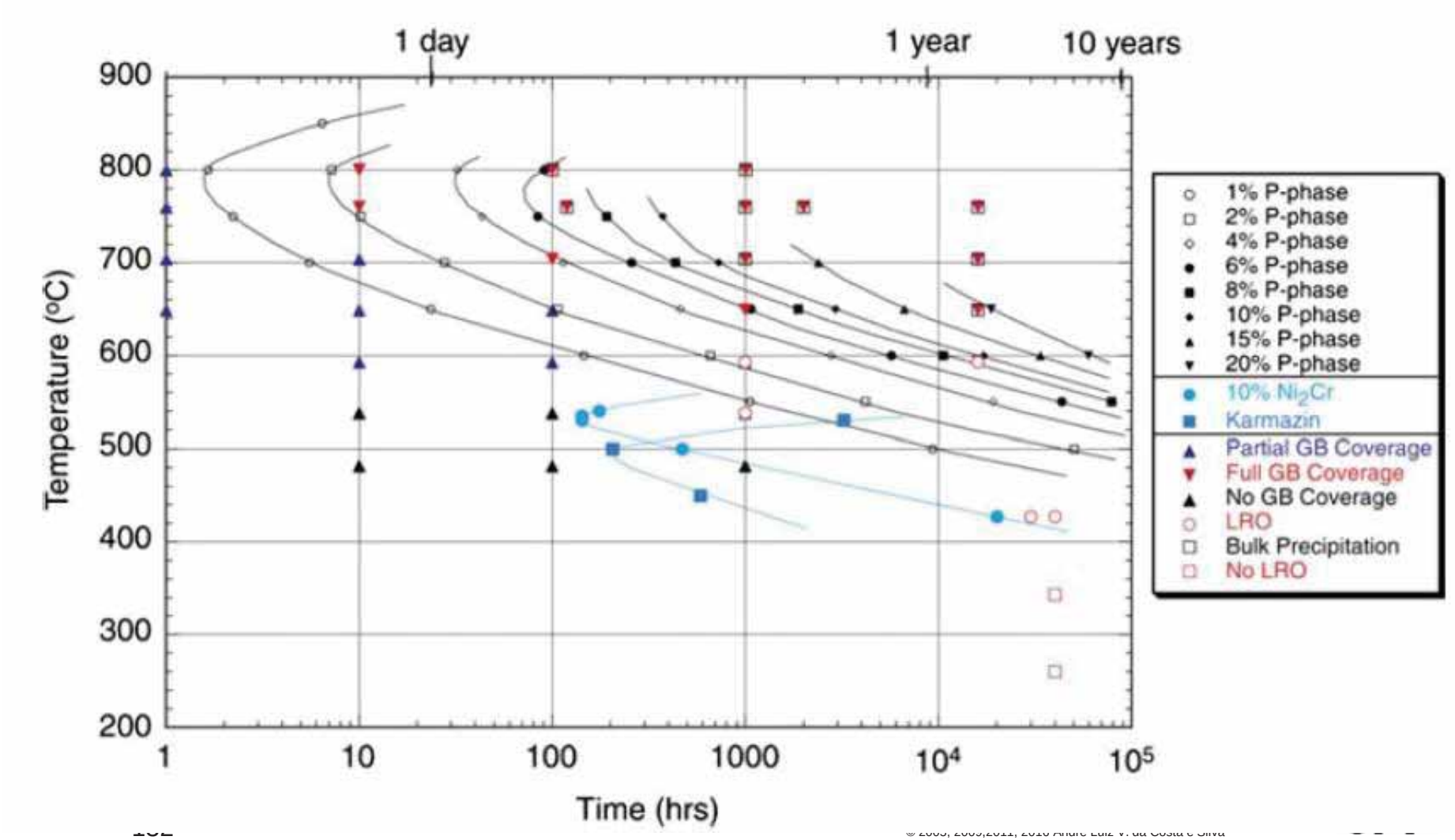

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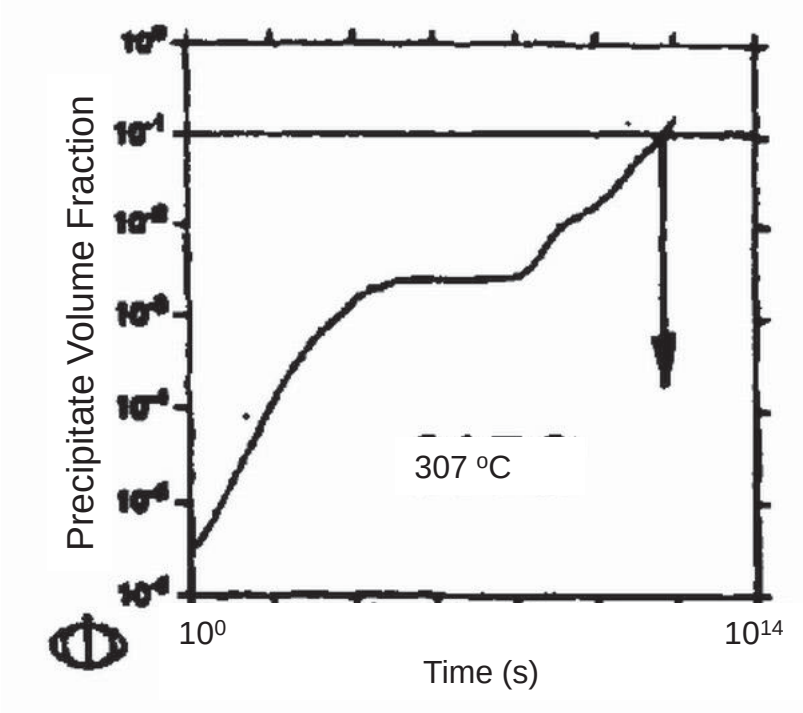

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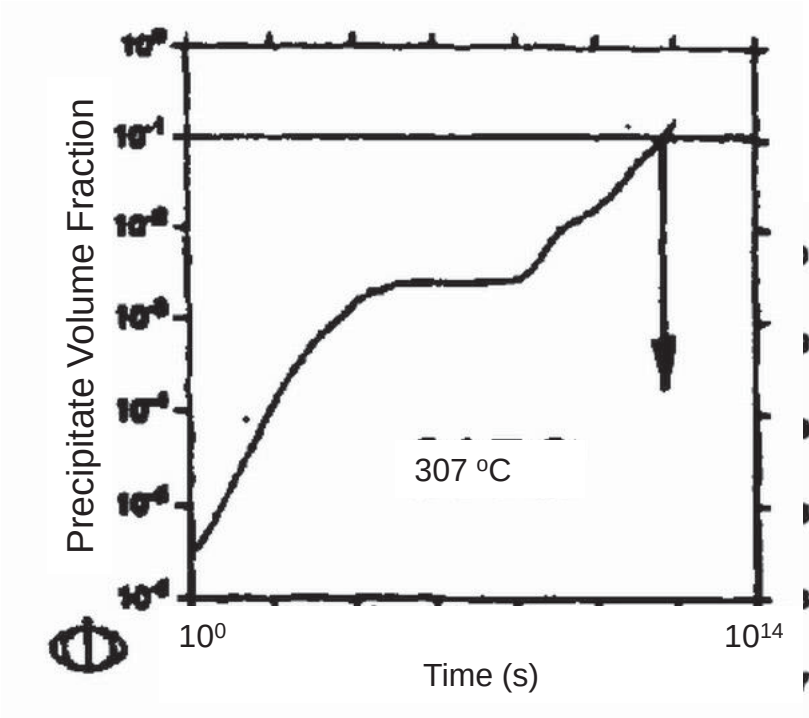
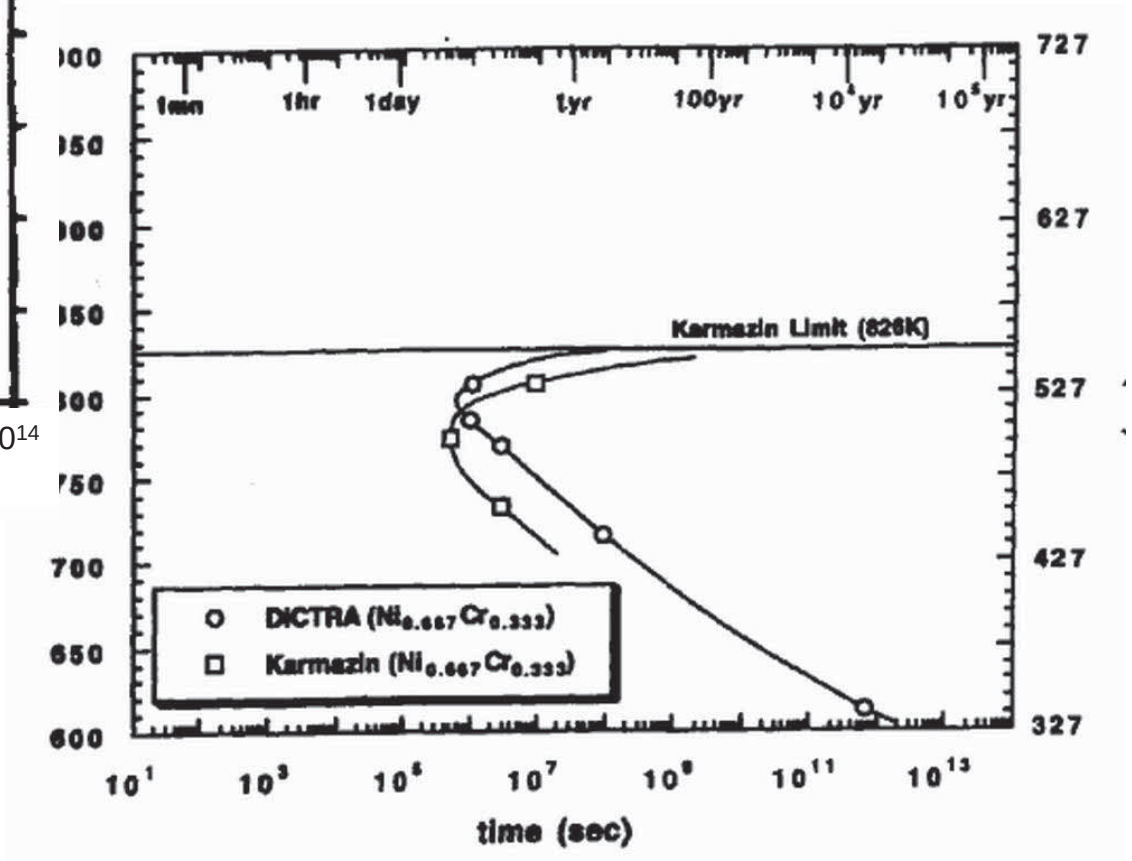
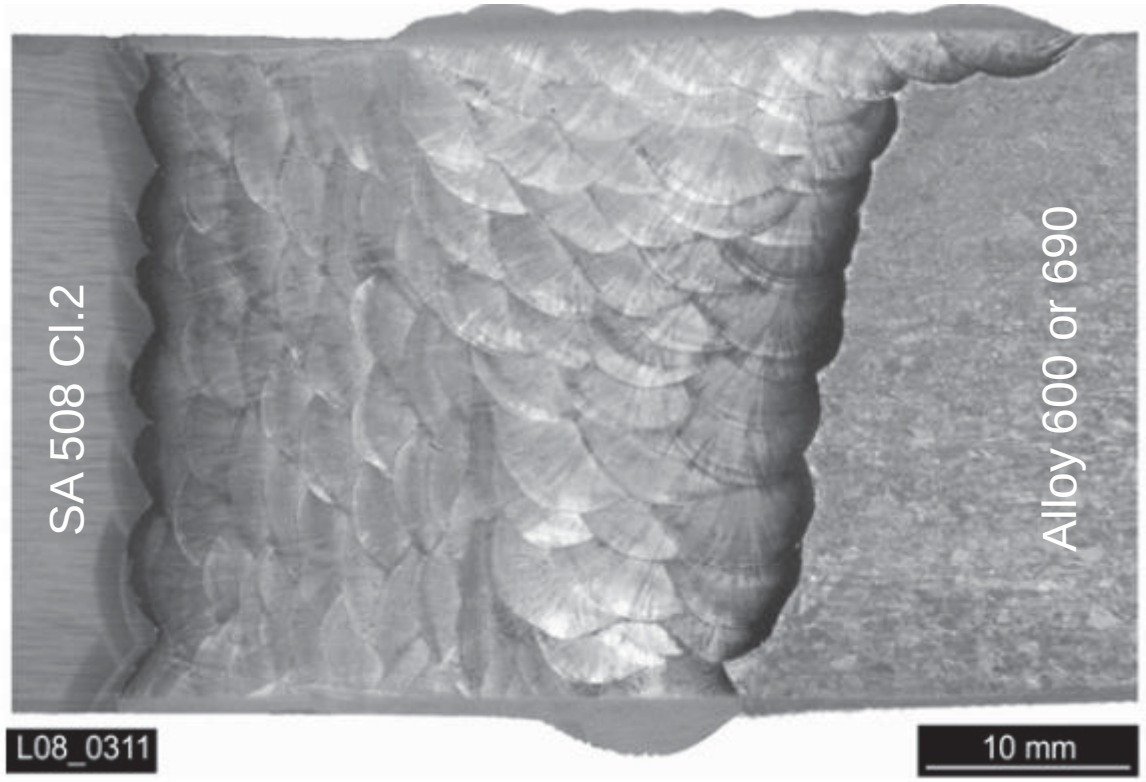
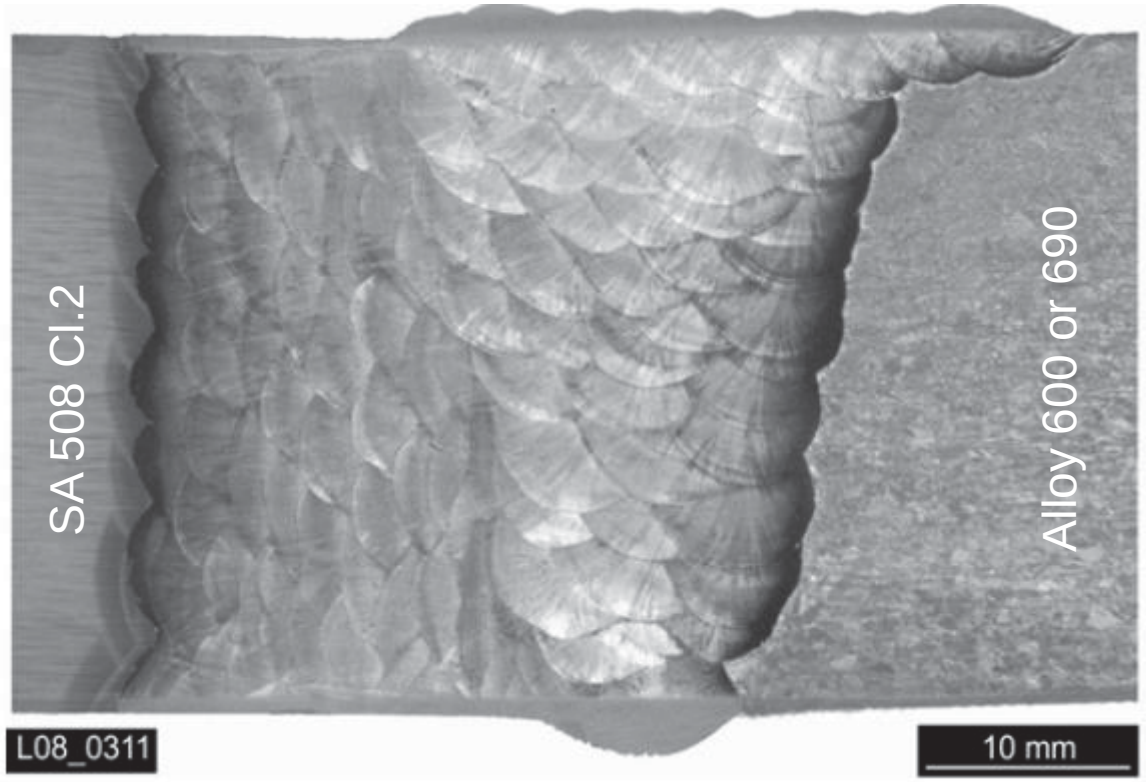




Ageing of “safe ends” in PWR’s



Ageing of “safe ends” in PWR’s 40, 60, 100 yrs?



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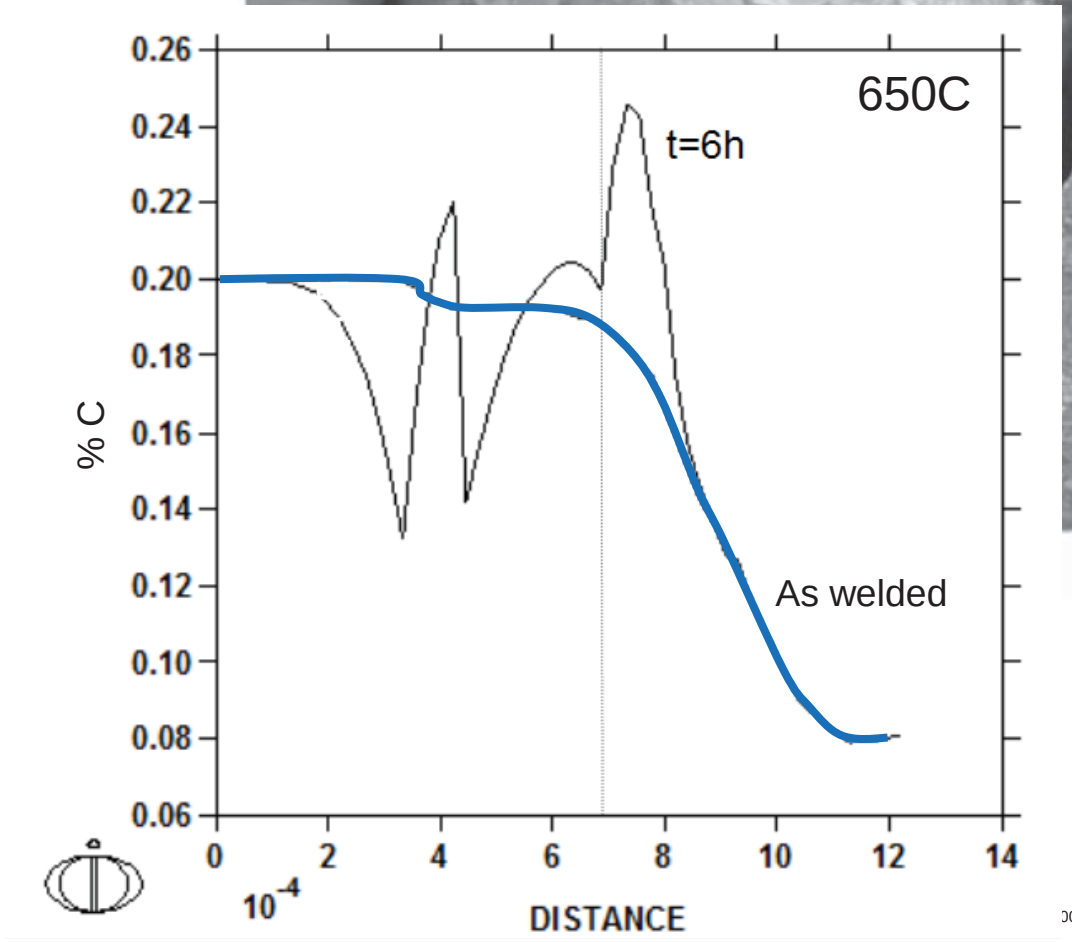

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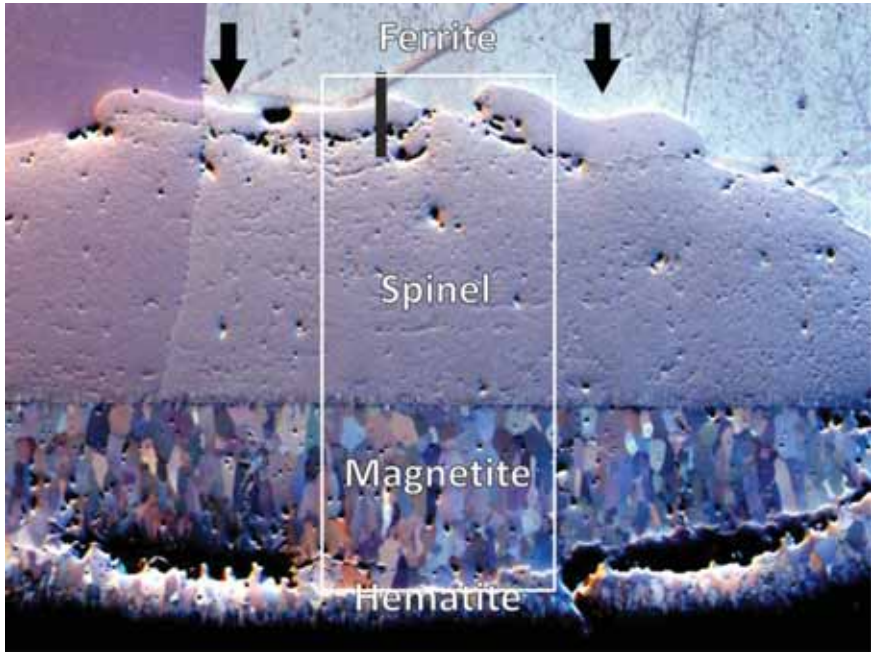
Understanding internal oxidation for alloy design

Fe-12 Cr



High T water vapor

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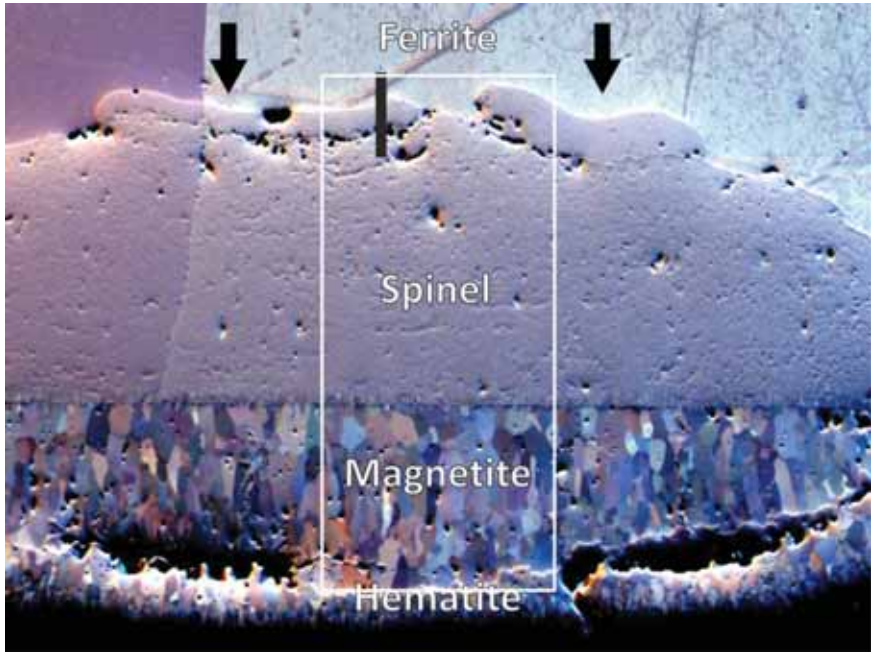

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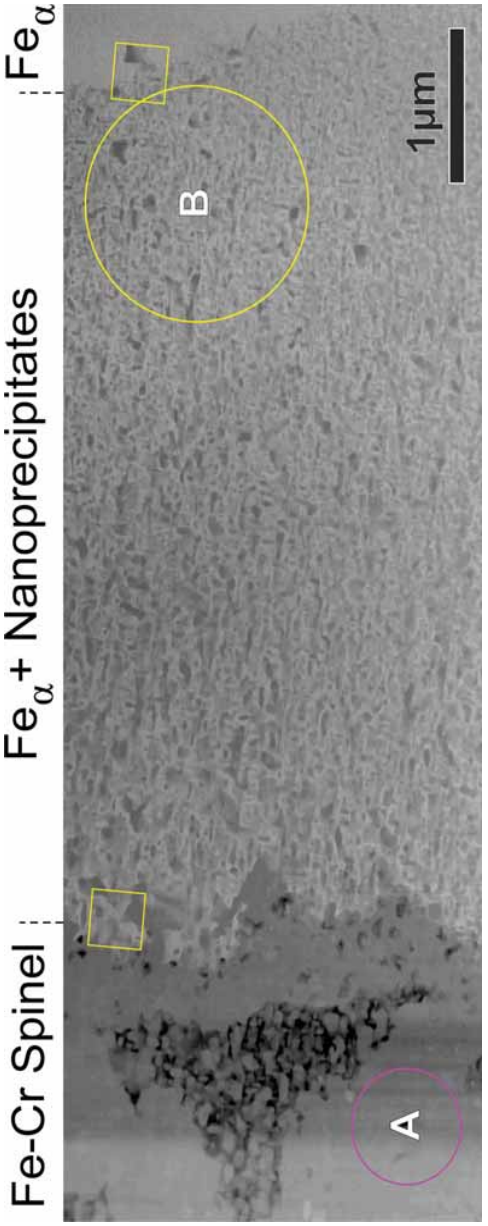
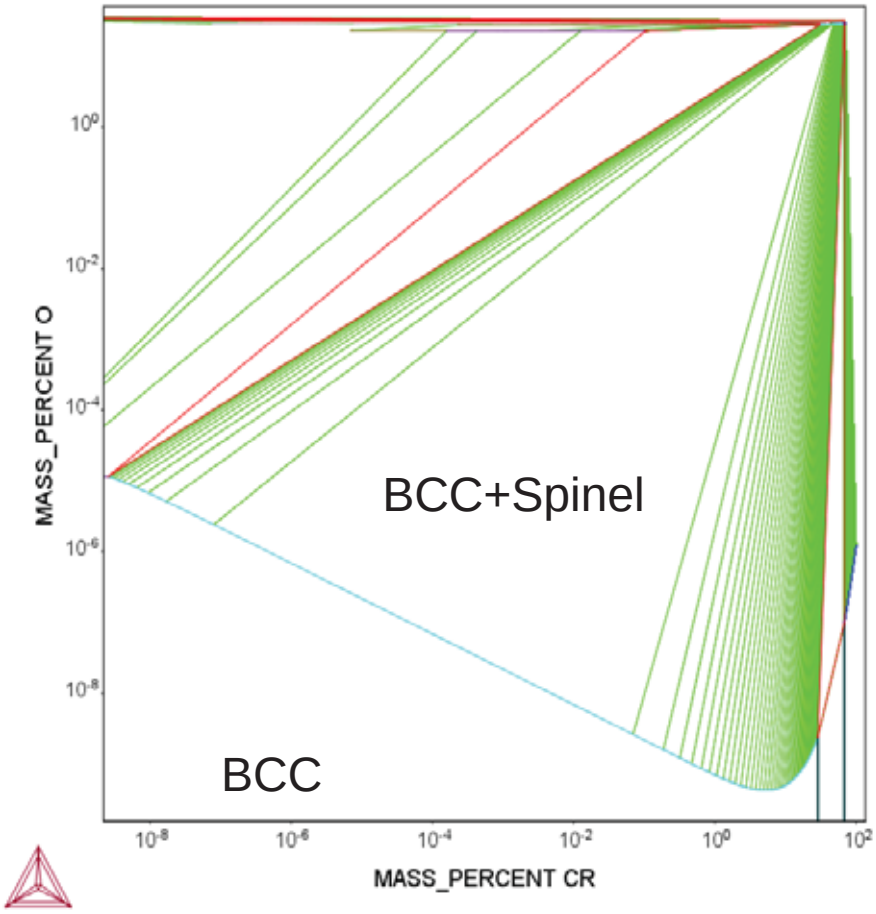


Diffusion path considering metastable oxidation



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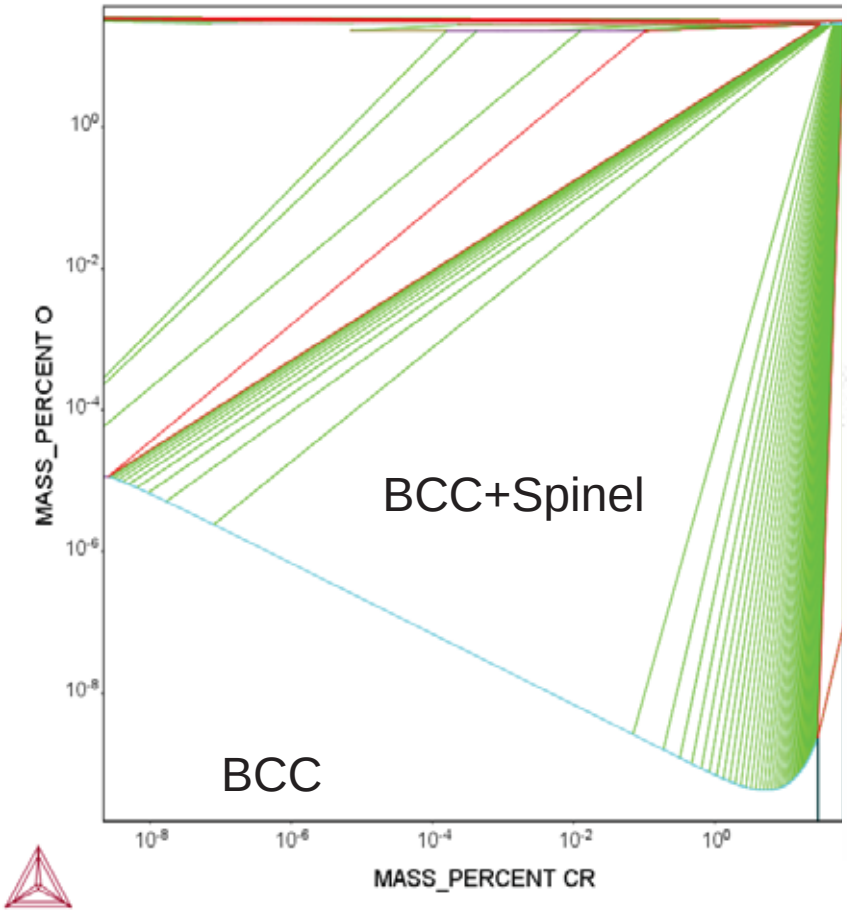

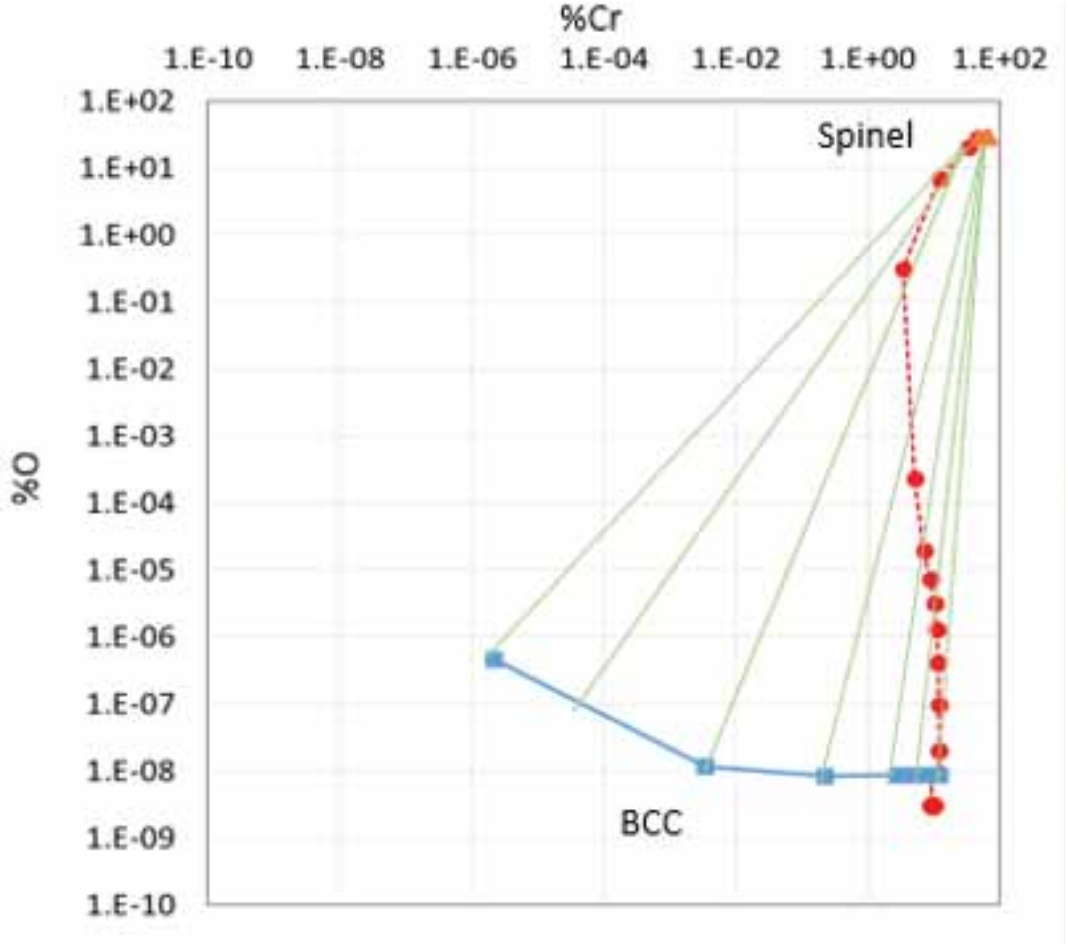

Rizzo et al 2016

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- **Computational thermodynamics can “perform” some “impossible” experiments that are relevant in alloy design.**

Thank you!