Metastable phase thermodynamics

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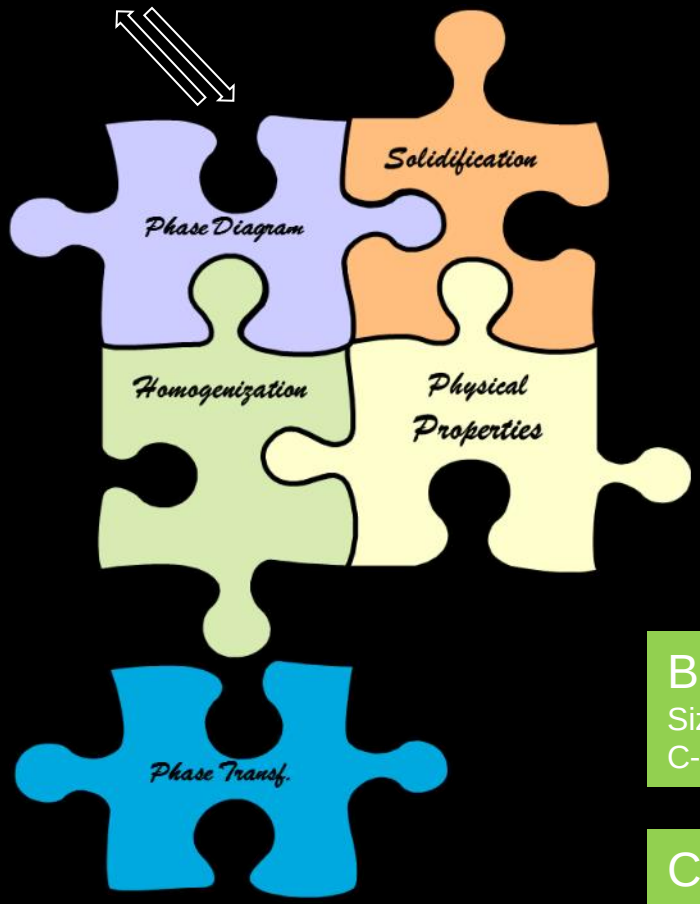
Constellium

Constellium has a strong metallurgical simulation platform to accelerate alloys development

OpenCalphad

QUANTUMESPRESSO

Metastable Phases



Prophase:
120 users in Constellium
Half C-TEC
Half factories

Monte Carlo

Bal:Precipitation
Size distribution precipitation model
C-TEC use

Cluster Dynamic Method

Some High quality Open Source software are used in this platform

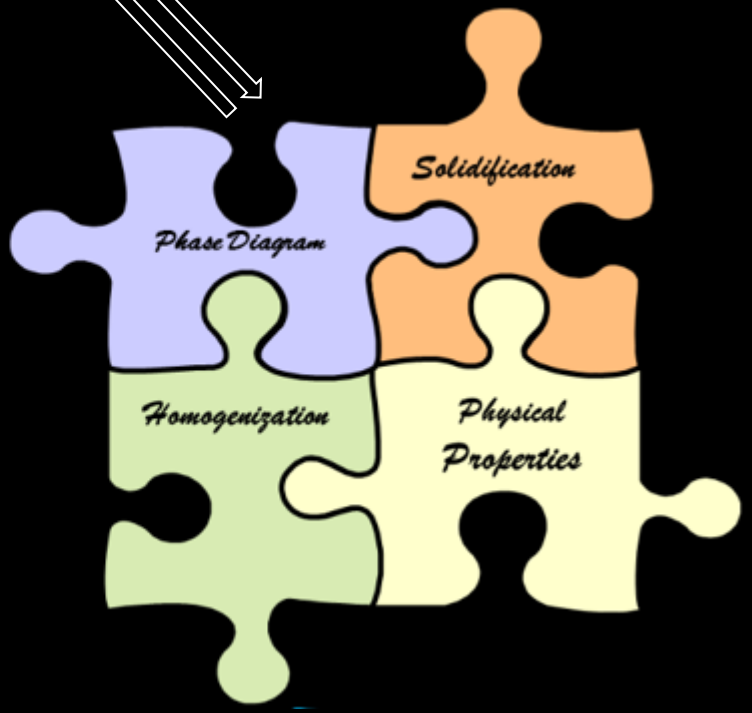
OpenCalphad

Part 1

QUANTUMESPRESSO

Metastable Phases

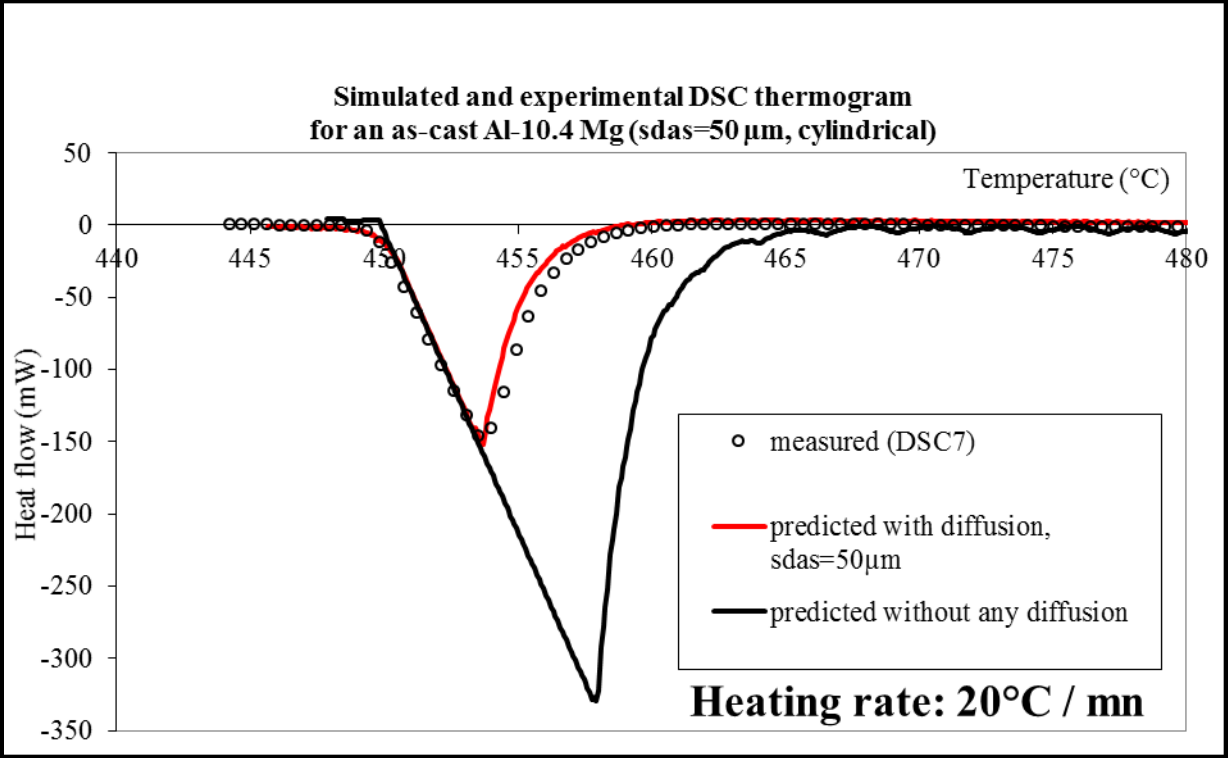
Part 2



Diffusion in FCC (Al) is key for solidification simulations

Casting

- Scheil Model (local equilibrium at interface, no diffusion in Fcc, infinit diffusion in liquid)
- Scheil + Long Range Diffusion within solid solution (Ficks law, Finite Difference,)

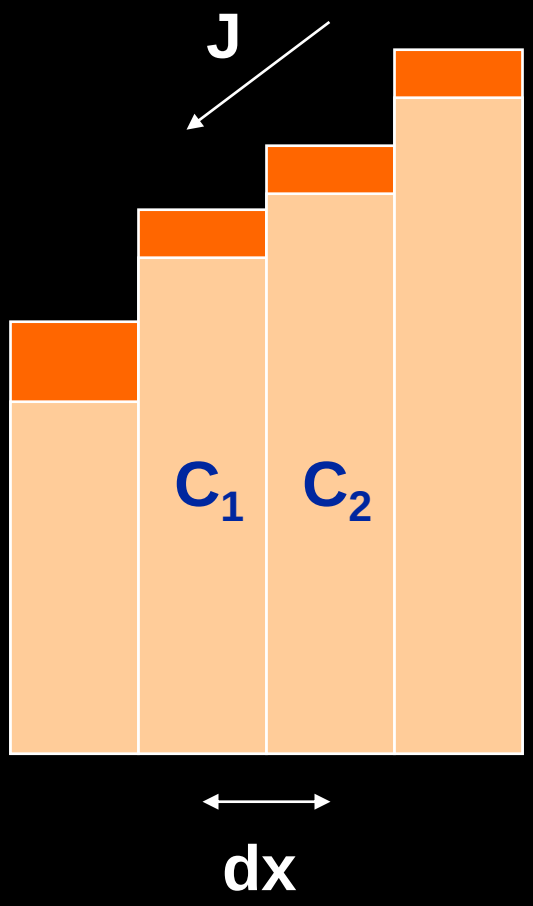


Diffusion is simulated using explicit finite difference

$$J = -D \times \frac{\partial C}{\partial x}$$

or

$$J = -\frac{Dc}{RT} \times \frac{\partial \mu}{\partial x}$$



! In each volume element, an equilibrium calculation is performed.

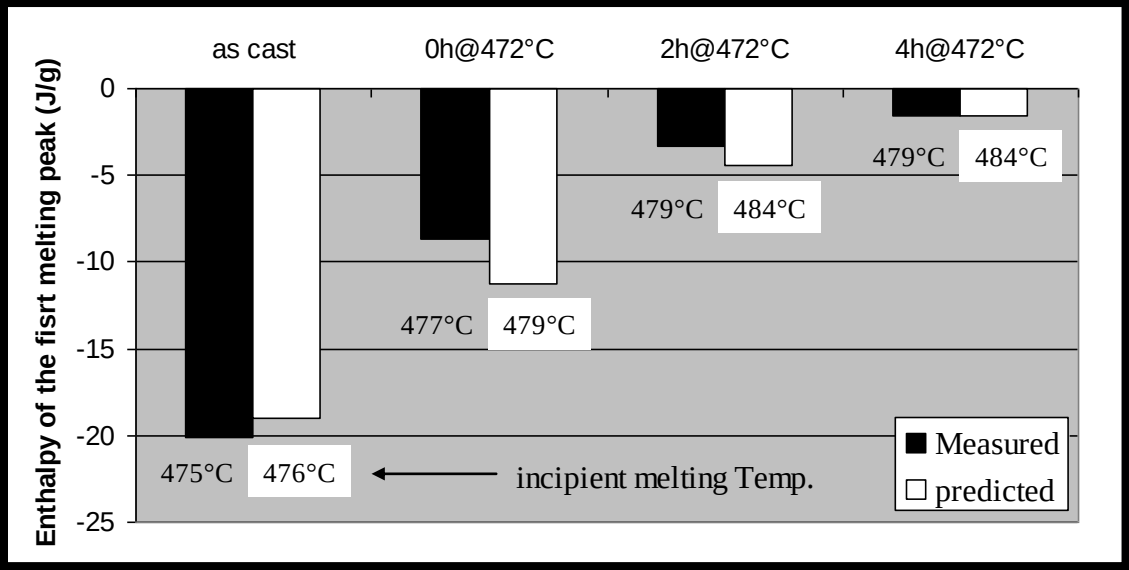
These calculations are independent and can be parallelized

The coupling with parallel Open Calphad is very efficient.

Collaborartion with Bosse Sundman (CEA, INSTN)
Development of a C++ Parallel interface

OpenCalphad

Simulated and predicted incipient melting temperatures and enthalpies of the first melting peak during DSC (20°C/mn) (Aerospace alloy 7449 , as cast & homogenized, small lab casts)



Atomistics DFT predictions are very valuable when measurements are difficult / not feasible.

Examples of valuable predictions:

- Free energies of metastable phases,
- Binding energy between different solutes in the aluminum solid solution,
- Binding energies between solutes and vacancies in the aluminum sol. sol,
- Free energy of clusters.

DFT: Density Functional Theory of electrons

In the Al-Zr system DFT predictions describes very well the phase stability difference

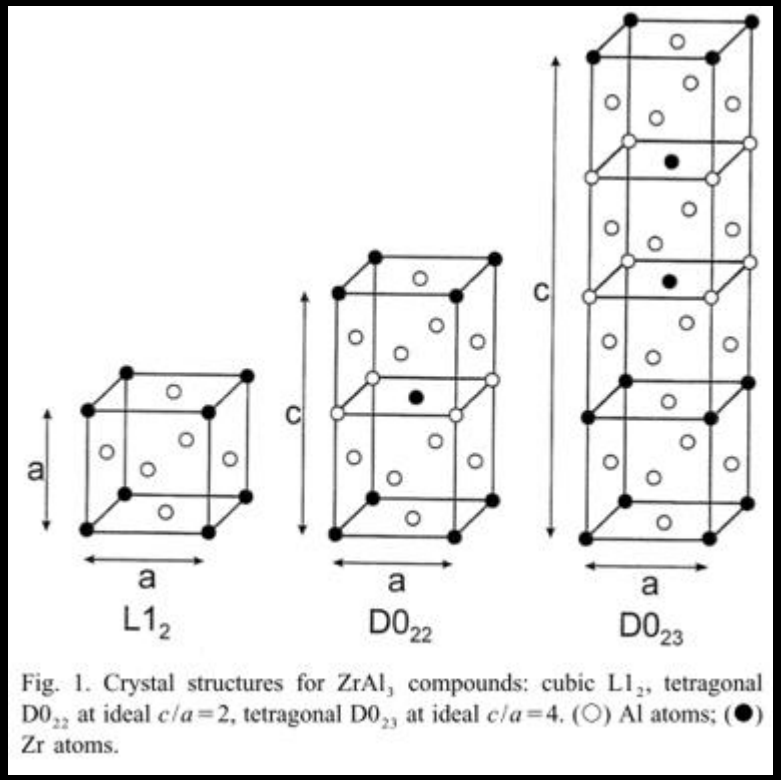


Fig. 1. Crystal structures for $ZrAl_3$ compounds: cubic $L1_2$, tetragonal $D0_{22}$ at ideal $c/a=2$, tetragonal $D0_{23}$ at ideal $c/a=4$. (○) Al atoms; (●) Zr atoms.

Often observed

Stable

DFT -48.6 Kj/mole

Enthalpy for DO23

experimental	uncertainty
-48.4	1.3
-49.0	4.0
-44.0	2.0

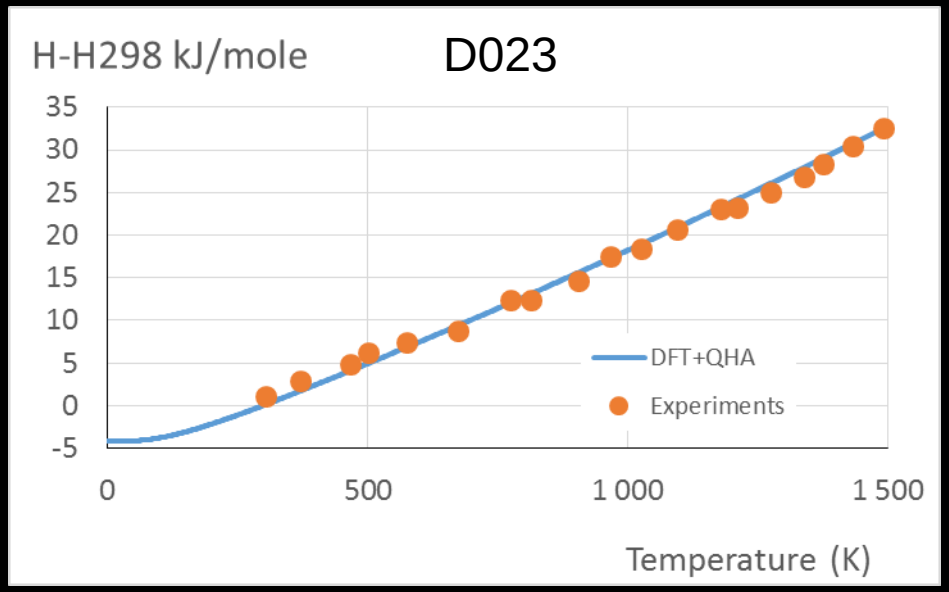
H(L12)-H(D023)

Exp :2.22 kJ/mole

DFT :2.27 kJ/mole

Desch, P., R. Schwarz, and P. Nash, *Formation of metastable L12 phases in Al3Zr and Al-12.5% X-25% Zr (X≡ Li, Cr, Fe, Ni, Cu)*. Journal of the Less Common Metals, 1991. **168**(1): p. 69-80.

Vibrational contributions are also well described (QHA). They do need HPC capabilities for large unit cells.

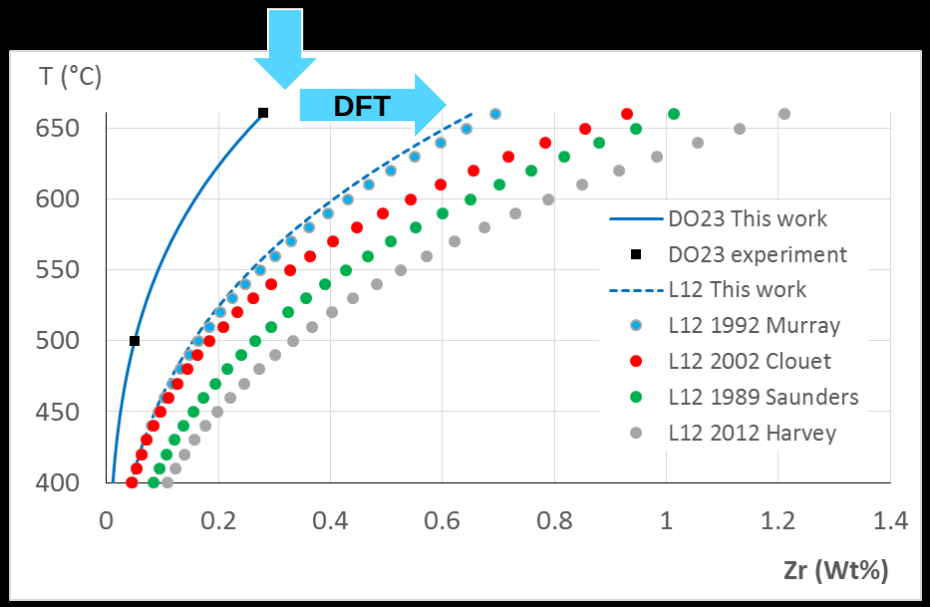


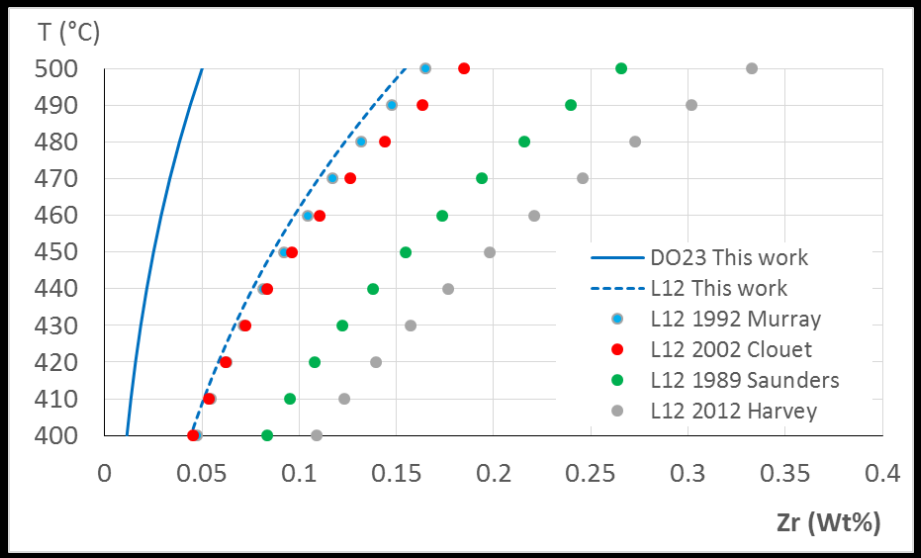
Esin, Y.O., et al., Temperature dependence of enthalpy and heat capacity of zirconium aluminides in solid and liquid states. Izvestiya Vysshikh Uchebnykh Zavedenij. Chernaya Metallurgiya, 1985. 19(16): p. 1-3.

QHA: Quasi-Harmonic Approximation

A metastable solubility related to AL3Zr-L12 can be predicted: good agreement with J. Murray assessment

DFT + calphad tuning (one parameter)





Saunders, N., *Calculated Stable and Metastable Phase Equilibria in Al-Li-Zr Alloys.* Z. Metallkd., 1989. **80**: p. 894.

Murray, J., A. Peruzzi, and J.P. Abriata, *The Al-Zr (Aluminum-Zirconium) System.* Journal of Phase Equilibria, 1992. **13**(3): p. 277.

Clouet E., C. Sigli and J. M. Sanchez (2002). "First Principle Study of the Solubility of Zr in Al." Phys. Rev. B **65**(9).

Harvey, J.-P., *PhD thesis,* 2012, UNIVERSITÉ DE MONTRÉAL.

Conclusions

- Open Calphad package is an efficient (fast) tool to perform several equilibria in parallel. It has been used here to simulate diffusion in the fcc solid solution.

- DFT calculations have demonstrated a good accuracy for Al-Zr system and allow the calculation of a metastable phase diagram. Large unit cells require HPC capabilities.

Perspectives: Ageing of Aluminum Alloys

- DFT is a very attractive tool to unravel some of the physics behind ageing of aluminum alloys (6xxx alloys for example):
  - solute-solute or solute-vacancies interactions,
  - most stable clusters prediction,
  - energy barriers for diffusion,
  - simulation of kinetics through Kinetic Monte Carlo,
  - cluster strengthening.

- Must go beyond the usual Bragg-Williams CALPHAD approach to describe Short Range Order (CVM, Monte-Carlo, Cluster Dynamics)