Thermo-Calc Software

Development of thermodynamic and kinetic databases for Ti/TiAl-based alloys

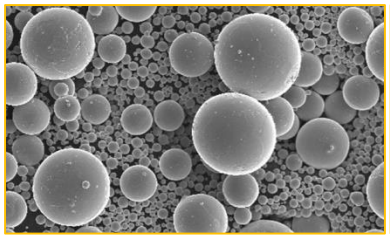
Hai-Lin Chen, Yang Yang, Ying Tang, Qing Chen, Anders Engström

Project Ti/TiAl

Thermo-Calc Software

❑ Objectives: thermodynamic & kinetic databases for

- Ti-based alloys (αTi, βTi, α+β)
- γ-TiAl-based alloys
- Alloys based on Al_3Ti, α_2-$AlTi_3$, …




❑ Challenges

- Complex equilibria: a relatively large number of phases; large solutions, difficult to make reliable extrapolations
- Extremely complex transformations, e.g. β/α'/α'', α/γ, β/ω''/ω/ordered ωs, γ/DO_{22}
- Binary & ternary systems (Ti/Zr/Hf/V/Nb/Ta/Mo/W): phase boundaries sensitive to parameters/energy; theoretical calculations do not help
- Susceptible to the impurity contamination, some systems lacking reliable experimental data

Project Ti/TiAl

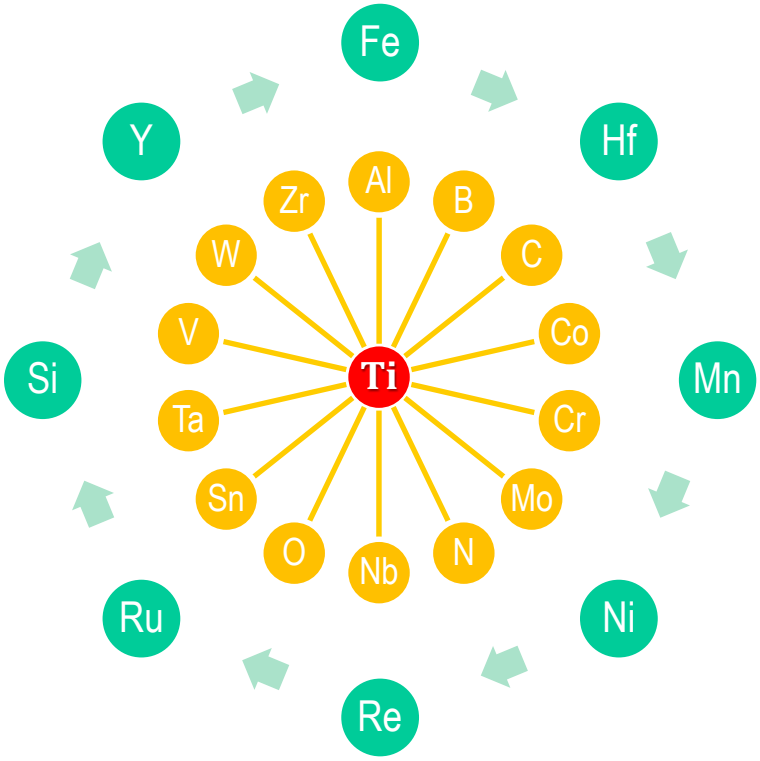
Thermo-Calc Software

❑ Strategies

- **A systematic plan and development**
  - Start with a relatively large (23 element) framework
  - Systems selected & prioritized based on a thorough consideration…
  - Model selections prior to the assessments
- **Assessments**
  - Quick review > review > modeling/extrapolation > validation
  - Aided by high-throughput DFT calculations

❑ **TCTI1: 23 elements, 236 binaries, 71 ternaries**

❑ **MOBTI2: liquid, Bcc_A2, Hcp_A3, AlTi_L10**



TCTI1 - systems

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Ti	Al	B	C	Co	Cr	Fe	Hf	Mn	Mo	N	Nb	Ni	O	Re	Ru	Si	Sn	Ta	V	W	Y	Zr
Al	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
B	3	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
C	3		2	2	2	2	2	2	2		2	2		2	2	2		2	2	2	2	2
Co	3	3	3	2	2	2	2	2	2		2	2	2	2	2	2	2	2	2	2	2	2
Cr	3	3	3		2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Fe					3	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Hf							2	2	2		2	2	2	2	2	2		2	2	2	2	2
Mn	3				3			2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Mo	3	3	3	3	3				2	2	2	2	2	2	2	2		2	2	2	2	2
N	3				3				3	2	2	2				2		2	2	2		2
Nb	3	3	3		3				3	3	2	2	2	2	2	2	2	2	2	2	2	2
Ni		3									3	2	2	2	2	2	2	2	2	2	2	2
O	3												2	2	2	2	2	2	2		2	2
Re														2	2	2		2	2	2	2	2
Ru															2	2	2	2	2	2	2	2
Si	3								3							2	2	2	2	2	2	2
Sn	3	3		3	3				3		3	3					2		2			2
Ta	3	3	3	3	3				3	3	3							2	2	2	2	2
V	3	3	3		3	3			3		3						3	3	2	2	2	2
W	3	3	3		3				3		3					3		3	3	2	2	2
Y																					2	2
Zr	3	3	3		3				3		3						3	3	3	3		2

			Elements				23
	2	2	Assessed binaries	214	+ 22	=	236
3	3	3	Assessed ternaries	35	+ 36	=	71

Highlights

Thermo-Calc Software

- ❑ Thermodynamic + kinetic databases
  - TCTI1 + MOBTI2
- ❑ for Ti alloys & TiAl-based alloys and more

In TCTI1

- ❑ Only a few ternaries taken from literature
- ❑ To include all the stable phases and important **metastable phases** in each assessed system
  - α, β, β_0, γ, α', ~~α''~~
  - O1 and O2
  - Borides, silicides, carbides
  - **ω, ~~ω''~~, ordered variants of ω**

What is the ω phase?

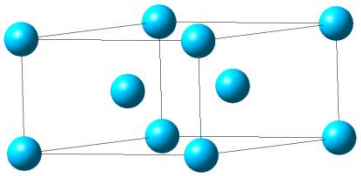
Thermo-Calc Software

- A metastable structure of Ti

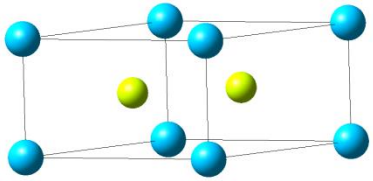
  hP3, P6/mmm

  1a (0 0 0)

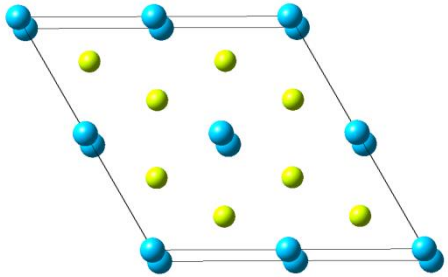
  2b (2/3 1/3 1/2) (1/3 2/3 1/2)



ωTi



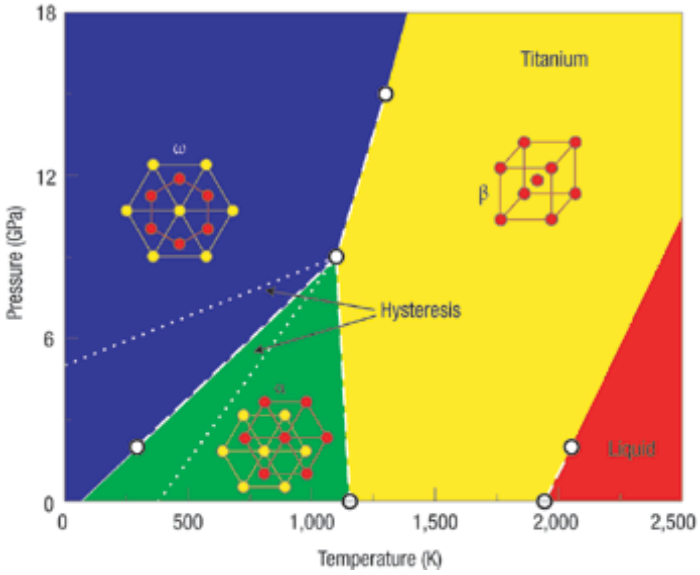
TiB_2 type (C32)



1a: a graphite-like net
2b: a hexagonal configuration

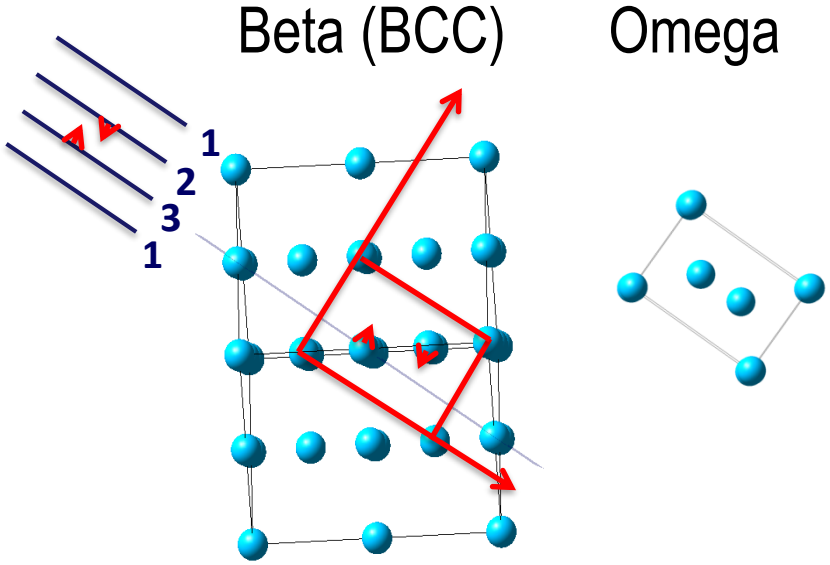
either cause brittleness or strengthen alloys

- Stable under high pressures or near 0 K



- Can be "stabilized" in binary or higher-order systems by **solutionizing or ordering**

ω collapse



[-111]β → [0001]ω

(111)β → (0001)ω

[110]β → [10-10]ω

A pure shuffle transformation
No macroscopic shape strain
Bendersky (1990)

$$c_\omega = \frac{\sqrt{3}}{2} a_\beta, a_\omega = \sqrt{2} a_\beta$$

- **Accompanying the ω collapse**
  - Shape change (c/a), e.g. 0.6082 for ωTi, vs 0.6124 (shuffled)
  - Atomic diffusion and rearrangement (ordering)
  - The parent phase may be ordered
  - Translational structures, ω', ω''
- **Lacking experimental data, while theoretical calculations are difficult**
  - Partially ordered B2
  - Partially collapsed ω''
  - Partially ordered $B8_2$

ω-related structures

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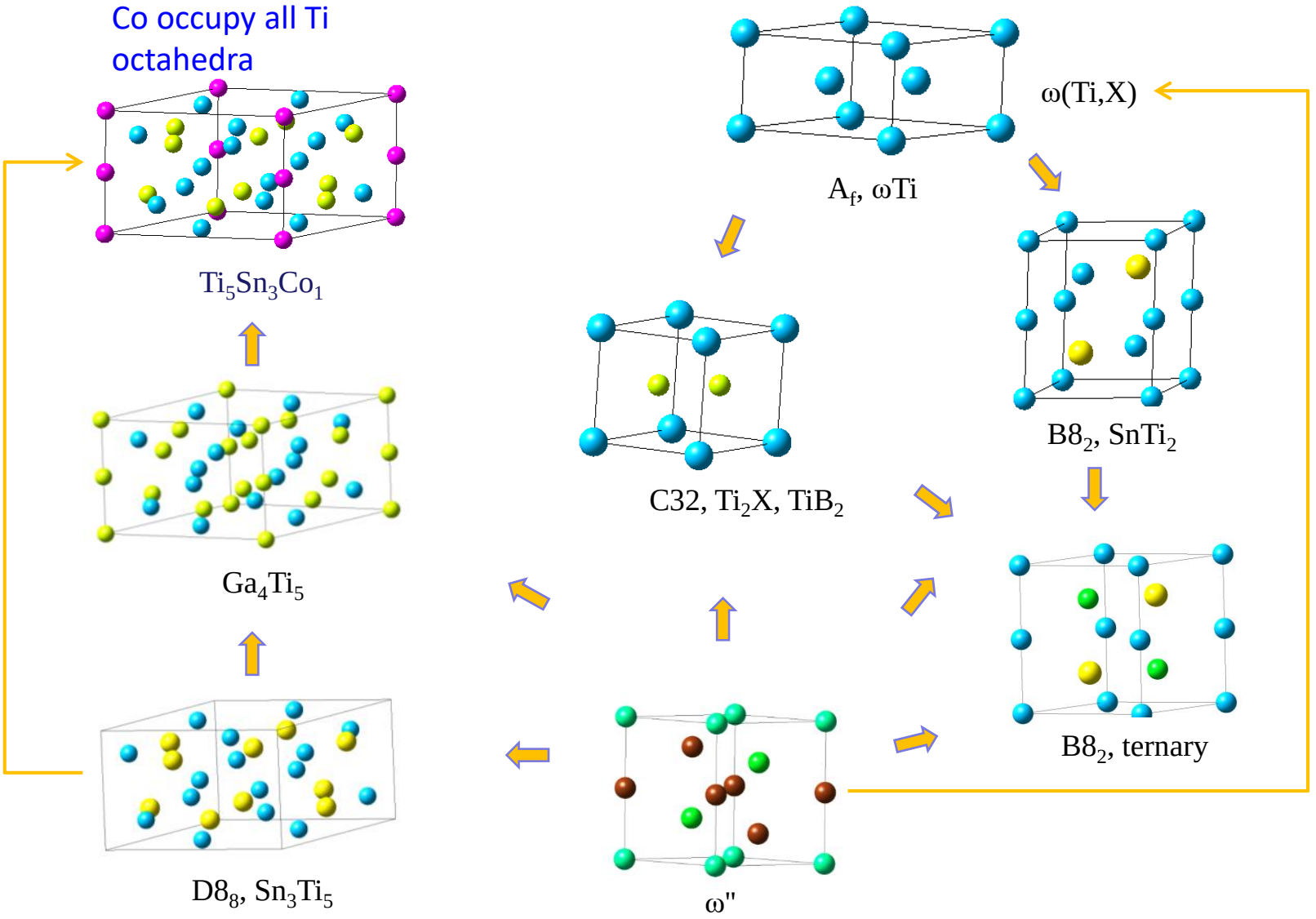
Ti_5Sn_3 >> $Ti_5Sn_3Co_1$:
Co occupy all Ti octahedra

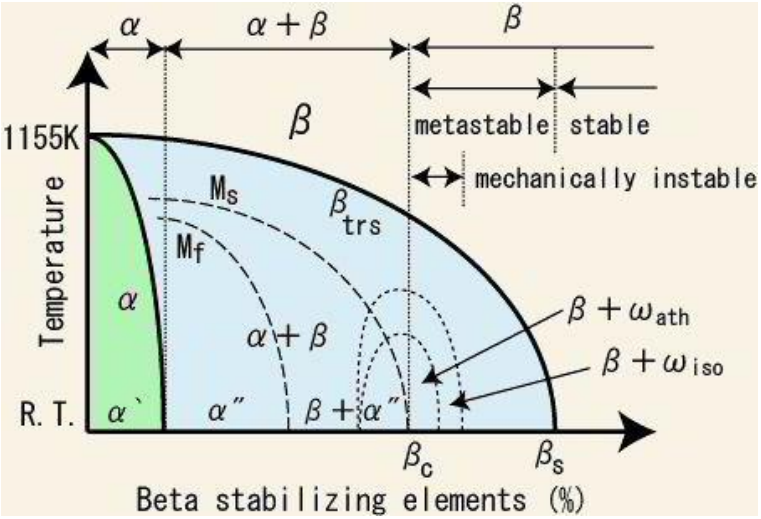


ω-related structures

- **"Athermal ω"**
  - transformed from the parent phase via a displacive mechanism
  - deformation-induced
  - during quenching
  - Long-distance diffusion suppressed
  - Ordering possible?

- **"Isothermal ω"**
  - Forming during aging
  - More or less ordered
  - C32, $B8_2$ or more complex structures.

- **"ω_0"**
  - $B8_2$, not necessarily.



ω solution and C32

P6/mmm, hP3

Separately modelled

ω solution

A_f *

2b	Ti
1a	Ti

$(Ti, X...)_1$

- Ti-Mo
- Ti-Nb
- Ti-Ta
- Ti-V
- Ti-Sn-V
- …

Ti_2X

C32

2b	Ti
1a	X

$(Ti)_2(X, ...)_1$

- Rarely reported in Ti alloys

TiB_2

C32

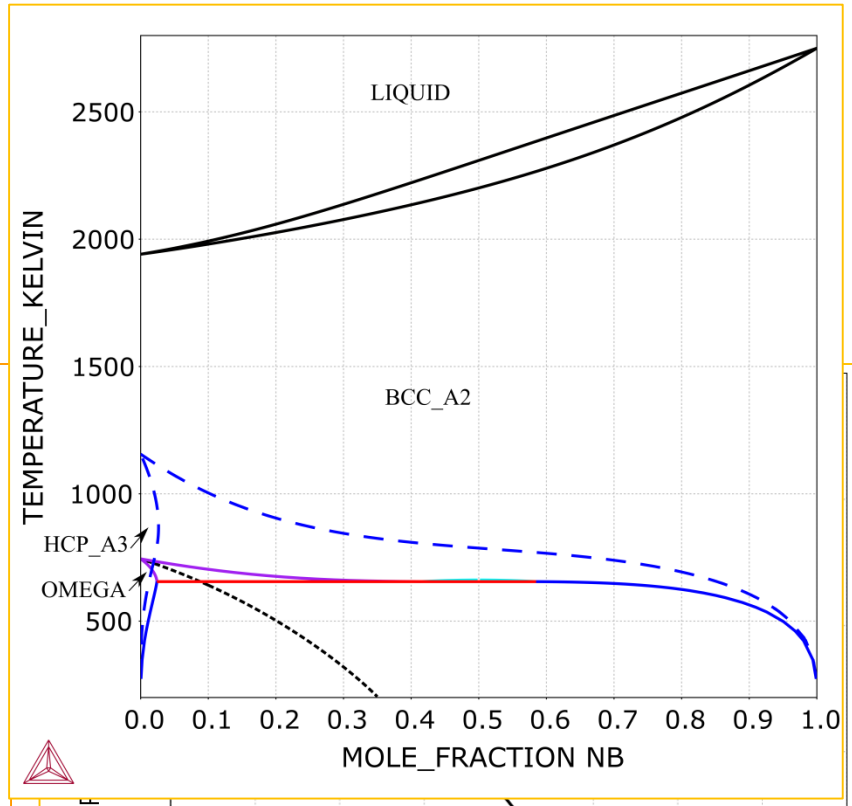
2b	B
1a	Ti

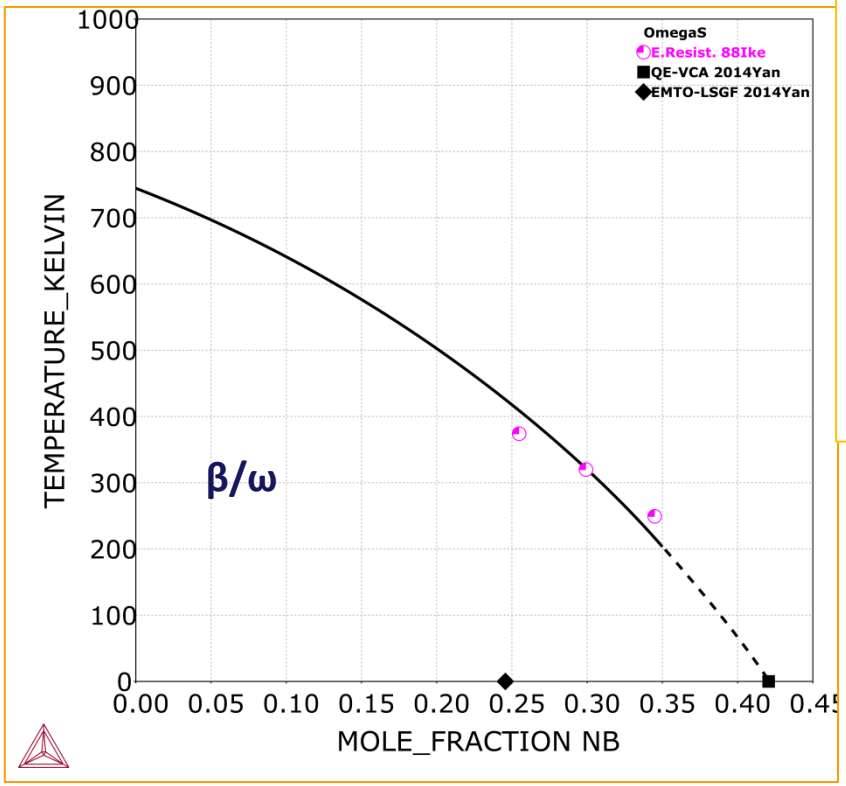
$(B, …)_2(Ti, ...)_1$

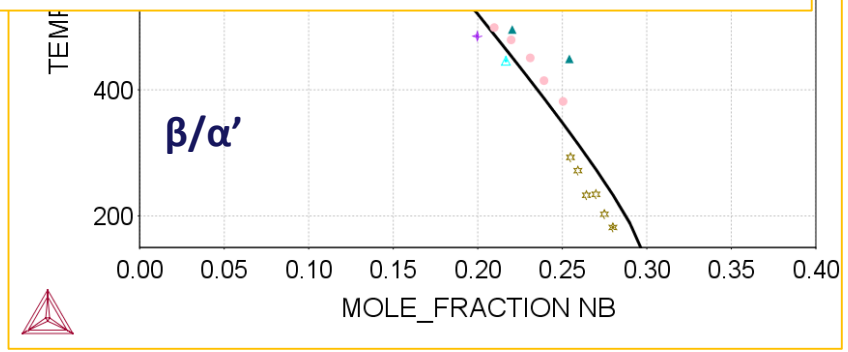
- AlB_2
- CrB_2
- MnB_2
- MoB_2
- NbB_2
- TaB_2
- TiB_2
- VB_2
- YB_2
- ZrB_2

ω solution: Ti-Nb

- Martensitic transformation
- T0-line
- Ti-Al/Zr: (As + Af)/2 or (Ms + Mf)/2
- Ti-Fe/Mo/Nb/V: very narrow window







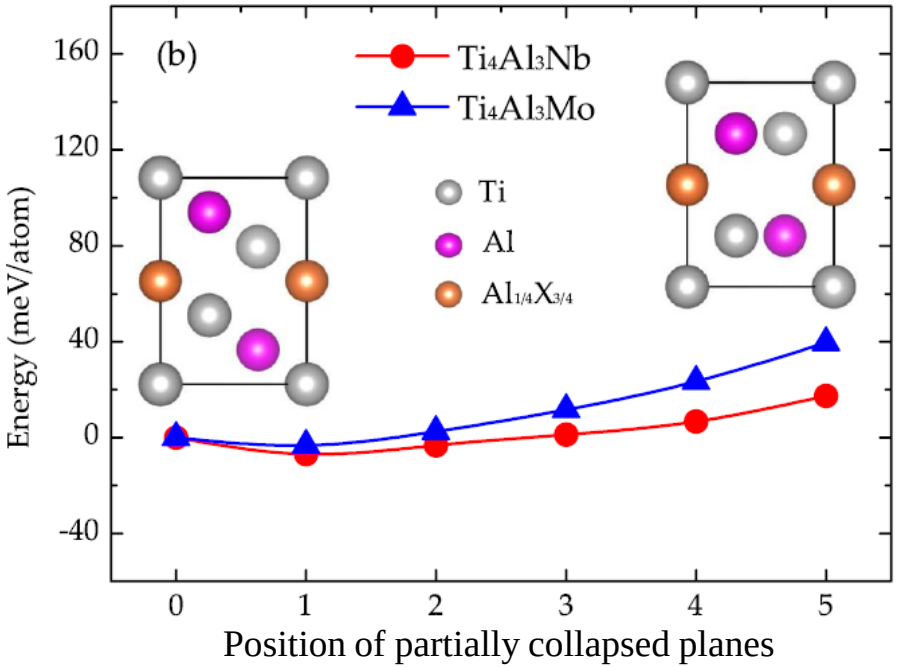
Jiayi Yan et al., PhD thesis, 2014

ω''

- **4SL model**
  - $(M)_1(M)_1(M)_2(M)_2$
- **Few experimental data**
- **Difficulties in theoretical calculations**
  - Cell relaxation
  - Position of partially collapsed planes
  - Atomic arrangements
  - Mixed occupancies

$P\bar{3}m1$

1a(1): Ti
1b(4): $\frac{1}{4}$Al$\frac{3}{4}$Nb
2d$_1$(2,6): Al
2d$_2$(3,5): Ti



Hu et al., Phys. Rev. B 90 (2014) 054109

However, site occupancies and c/a ratio must be changed as well, in order to find the minimal.

Al-Nb-Ti $B8_2$

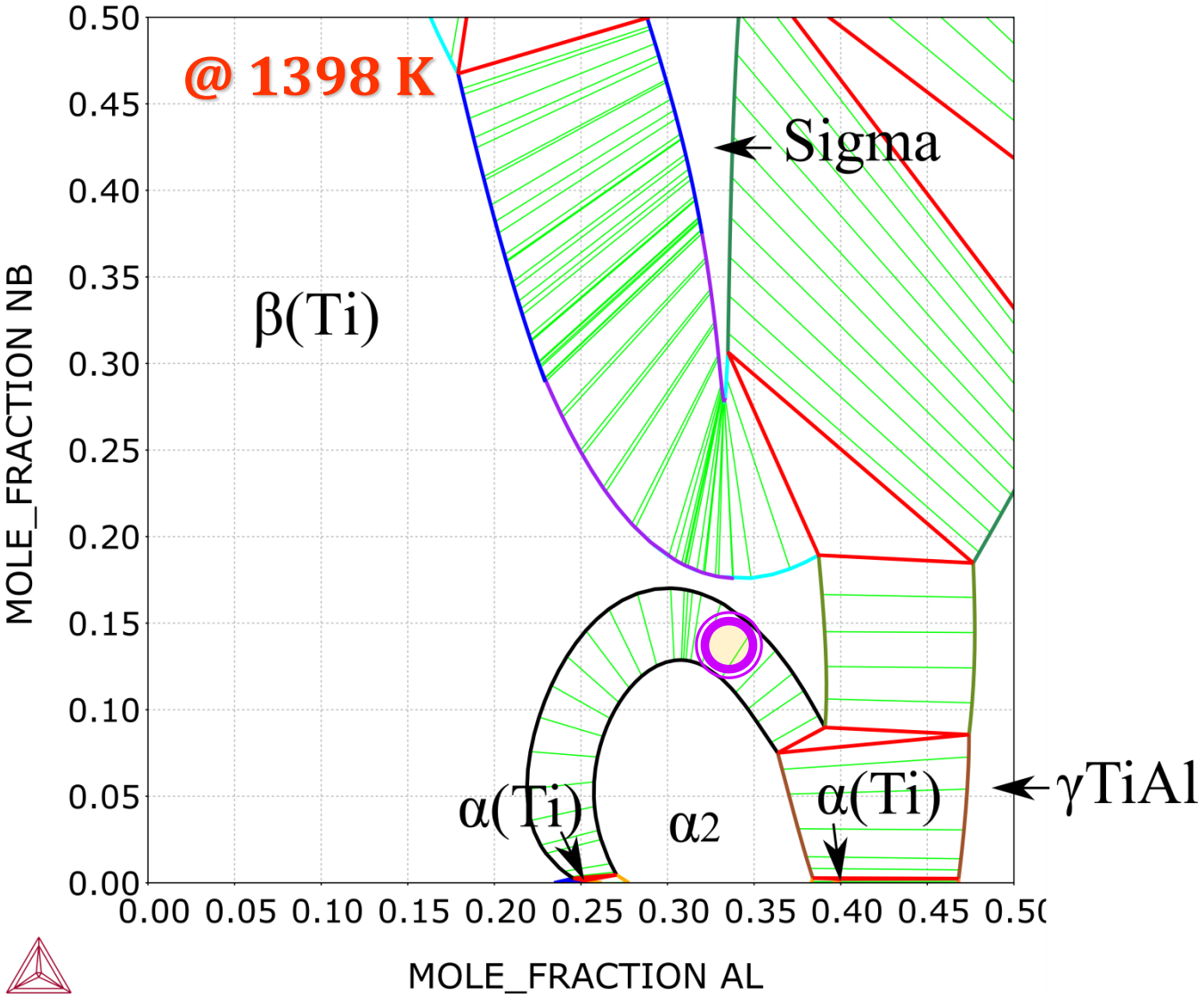
$(Al, Sn, ...)_1$
$(Nb, Ti, ...)_1$
$(Ti, ...)_1$

$B8_2$, $P6_3/mmc$, $hP6$

2d Ti

2c Al

2a Ti+Nb(+Al)



Al-Ta-Ti $B8_2$

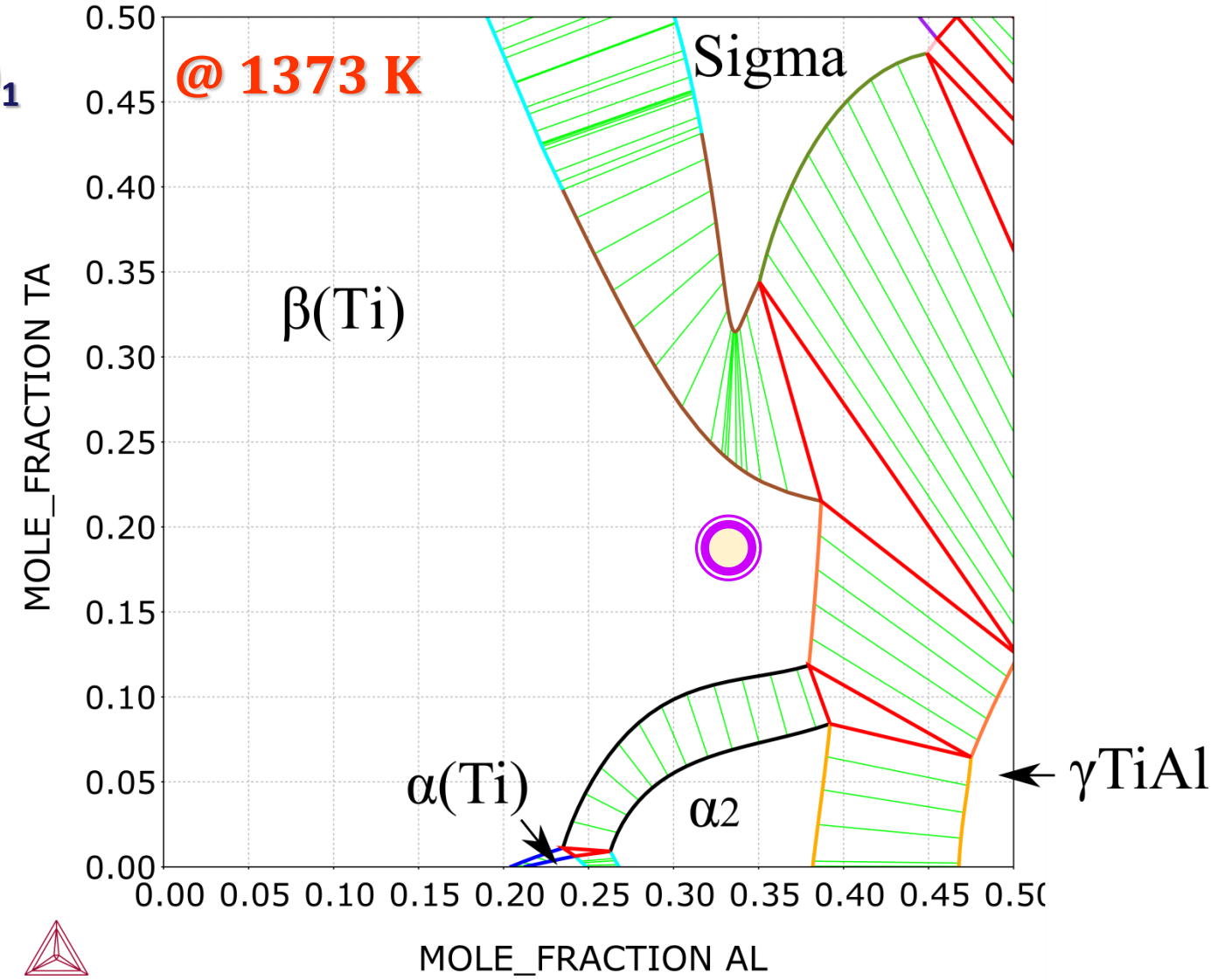
$(Al, Sn, ...)_1$
$(Nb, Ta, Ti, ...)_1$
$(Ti, ...)_1$

$B8_2$, $P6_3/mmc$, $hP6$

2d Ti

2c Al

2a Ti+Ta(+Al)

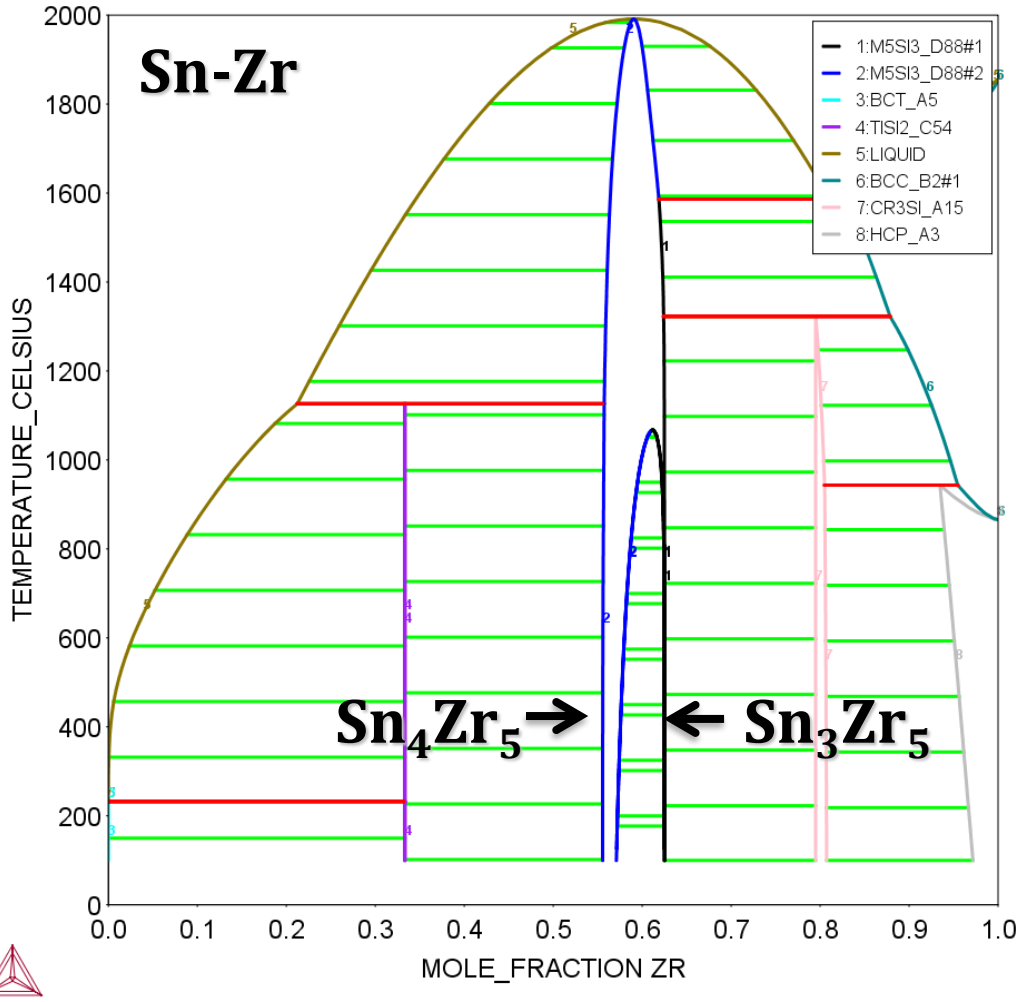


$D8_8$ & Ga_4Ti_5-type

$(Cr, Fe, Hf, Ti, \mathbf{Zr})_2$
$(Al, \mathbf{Sn}, Si)_3$
$(Cr, Fe, Hf, Ti, \mathbf{Zr})_3$
$(Co, \mathbf{Sn}, \mathbf{Va})_1$

$D8_8$, $P6_3/mcm$, $hP16$

6g	Zr
6g	Sn
4d	Zr
2b	Va → Sn



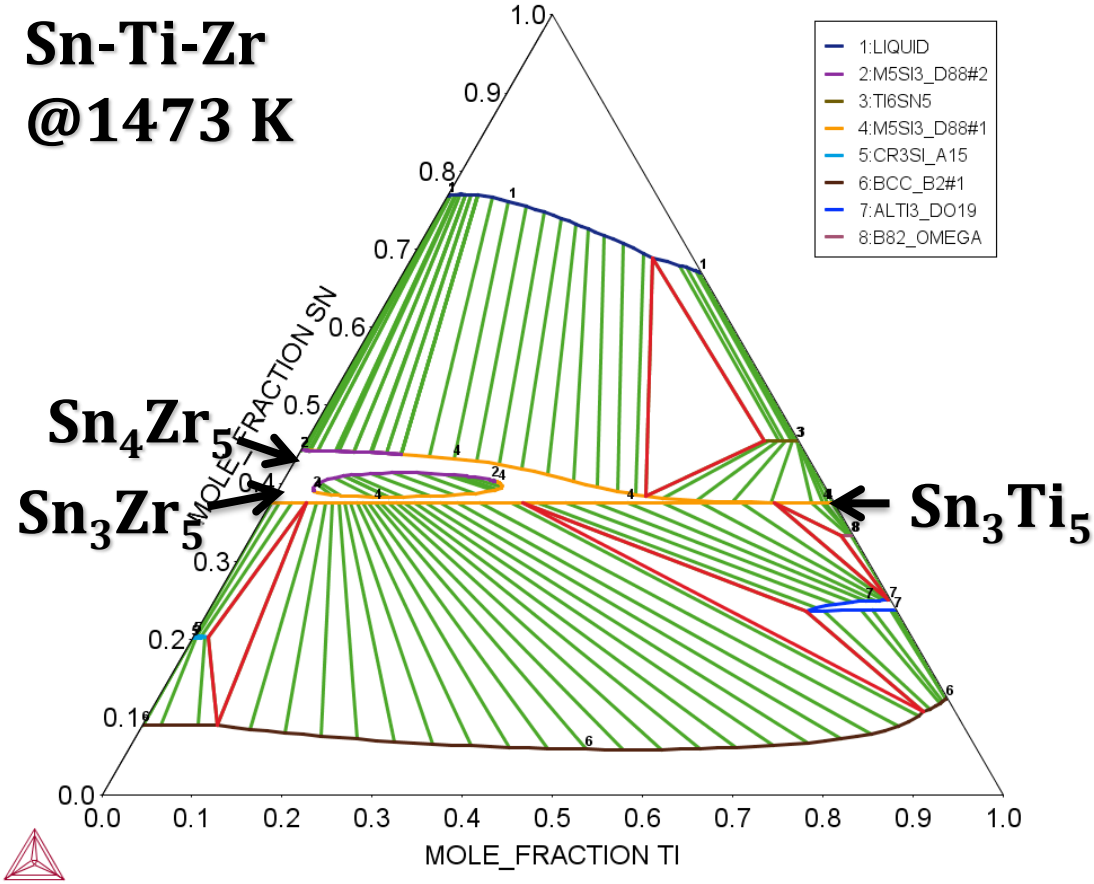
R. Jerlerud Pérez, C. Toffolon-Masclet, J. M. Joubert, B. Sundman, Calphad 32(3) (2008) 593.

$D8_8$ & Ga_4Ti_5-type

$(Cr, Fe, Hf, Ti, Zr)_2$
$(Al, Sn, Si)_3$
$(Cr, Fe, Hf, Ti, Zr)_3$
$(Co, Sn, Va)_1$

$D8_8$, $P6_3/mcm$, $hP16$

6g	Ti, Zr
6g	Sn
4d	Ti, Zr
2b	Va → Sn



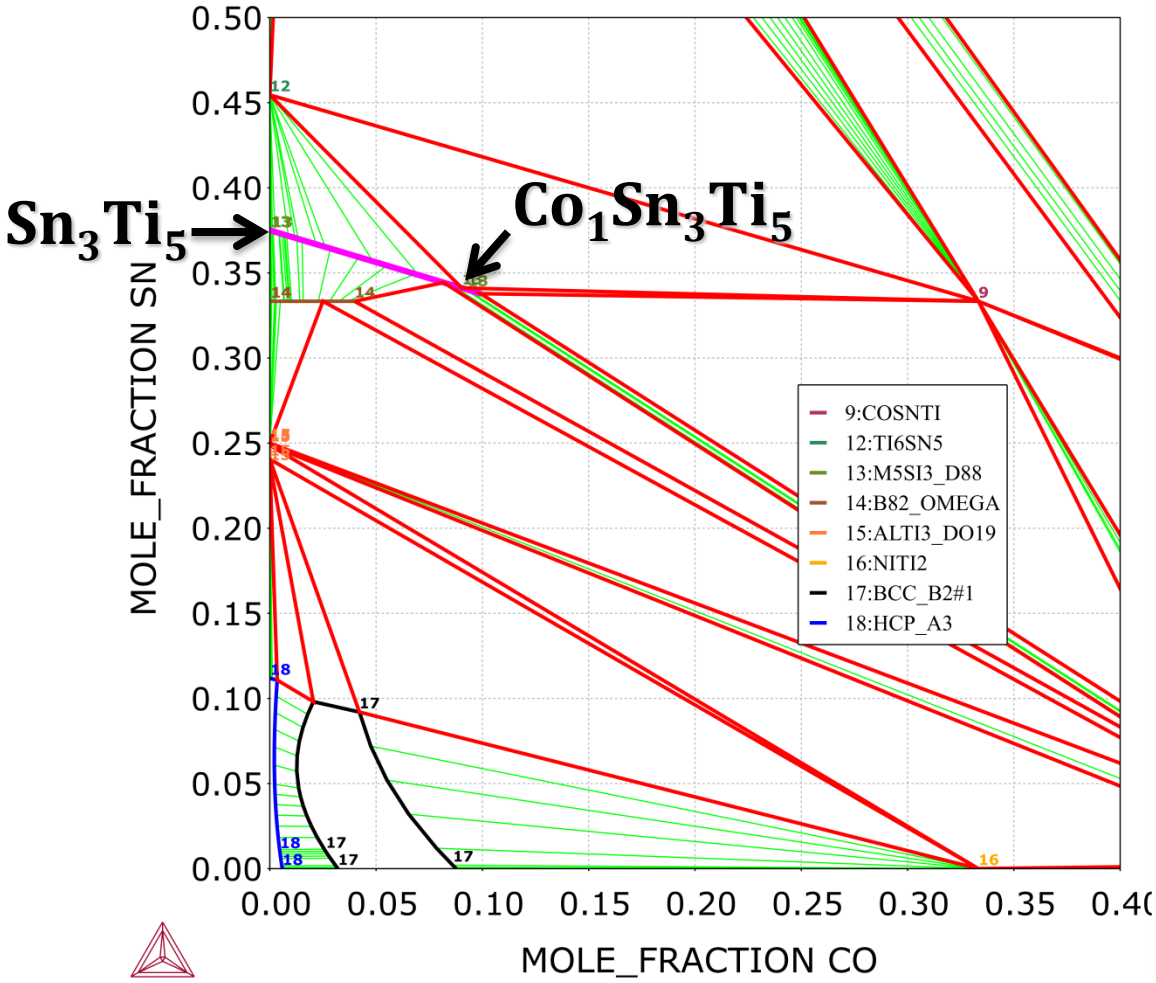
Extrapolated Sn-Ti-Zr isothermal section at 1473 K

$D8_8$ & Ga_4Ti_5-type

(Cr, Fe, Hf, **Ti**, Zr)2
(Al, **Sn**, Si)$_3$
(Cr, Fe, Hf, **Ti**, Zr)3
(**Co**, Sn, **Va**)$_1$

$D8_8$, $P6_3/mcm$, $hP16$

6g	Ti
6g	Sn
4d	Ti
2b	Va → Co



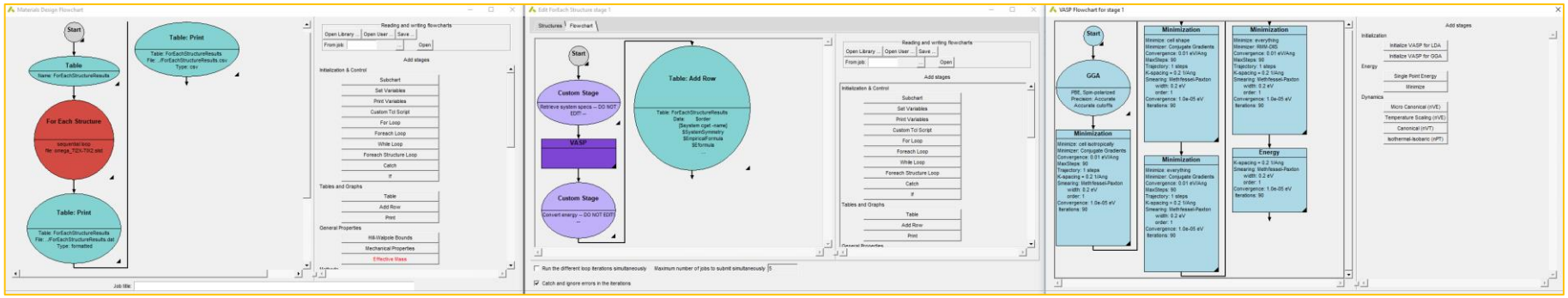
Co-Sn-Ti @ 1073 K

- $Ti_5Sn_3Co_x$ (x=0-1) at 870 and 1070 K

Yu. Stadnyk, L. Romaka, A. Horyn, A. Tkachuk, Yu. Gorelenko, P. Rogl, J. Alloys Compd. 387 (2005) 251.

HT DFT calculations

VASP + MedeA flowcharts



- **Stoichiometric compounds**
- **(Partly) disordered compounds**
  - Calculation of end-members
  - Calculation with supercells
- **Binary solid solutions**
  - SQSs (Special quasirandom structures)
  - CPA (Coherent potential approximation)
- **Ternary solid solutions**
  - SSOSs **(a small set of ordered structures)**

High throughput DFT calculations

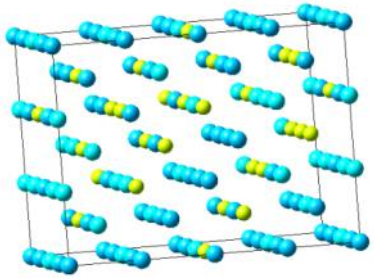
Thermo-Calc Software

Accuracy & Efficiency

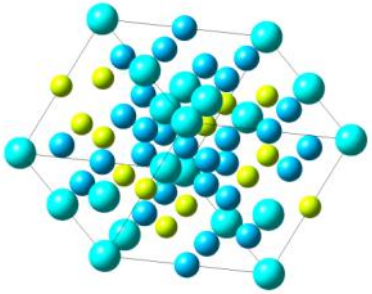
- **SQSs** (Special quasirandom structures)
- **SSOSs** (a small set of ordered structures) Jiang & Uberuaga (2016)

Supercells → SQSs → SSOSs

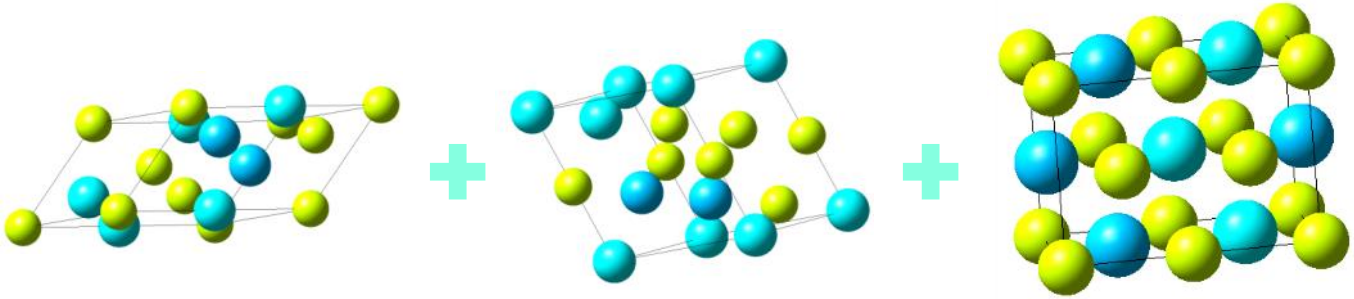
- higher efficiency
- comparable accuracy



96 atom Supercell
Several different supercells are needed.



32 atom SQS



SSOSs Ti_2AlV

Jiang (2016): **SSOSs for ternary Fcc_A1, Bcc_A2, Hcp_A3**, e.g. ⇗

HT DFT calculations

Thermo-Calc Software

ω, pure elements

- Al, B, C, Co, Cr, Cu, Fe, Hf, Mn, Mo, Nb, Ni, Pd, Pt, Re, Ru, Si, Ta, Ti, V, W, Y, Zr

ω , ordered structures

- C32 and $B8_2$
- $Ti_2X + TiX_2$

ω Ti-X

- SQS Ti36X12
- Supercell $Ti_{96}X_{12}$, $Ti_{81}X_{27}$, $Ti_{54}X_{54}$ for X ≠ Z
- Supercell $Ti_{96}X_{12}$, $Ti_{81}X_{27}$, for Z=Cr, Mo, Nb, Ta, V, W

A2 Ti-X

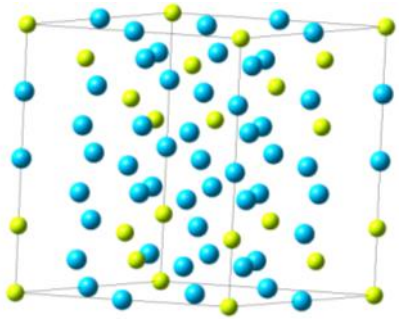
- SQS @ 25, 50, 75 at.% X
- Supercell @ 25, 50 at.% X

A3 Ti-X

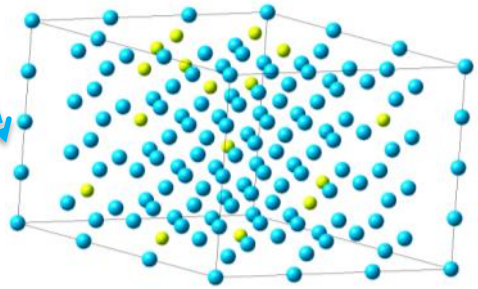
- SQS @ 25 at.% X
- Supercell @ 25, 50, 75 at.% X

Other structures (only for systems calculations are necessary)

- Complex intermetallics
- Partly ordered compounds
- Ternary solid solutions



SQS $Ti_{36}X_{12}$

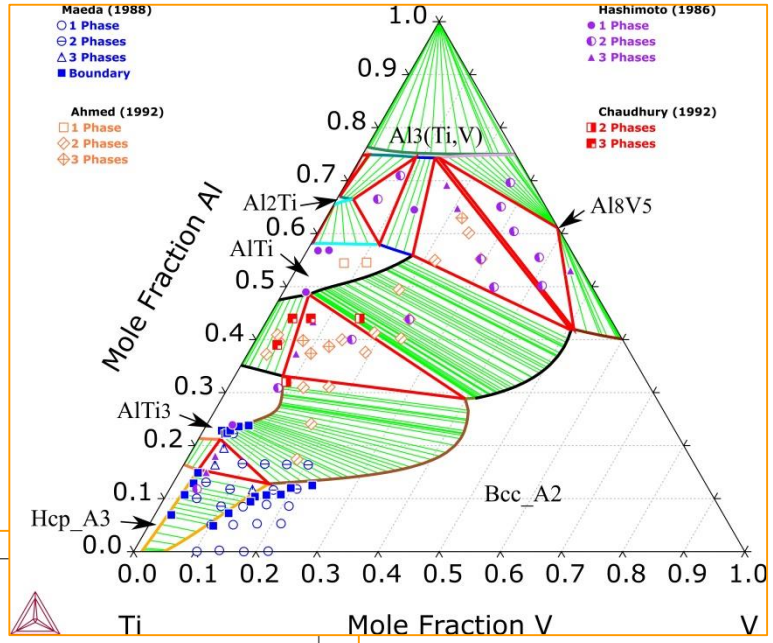


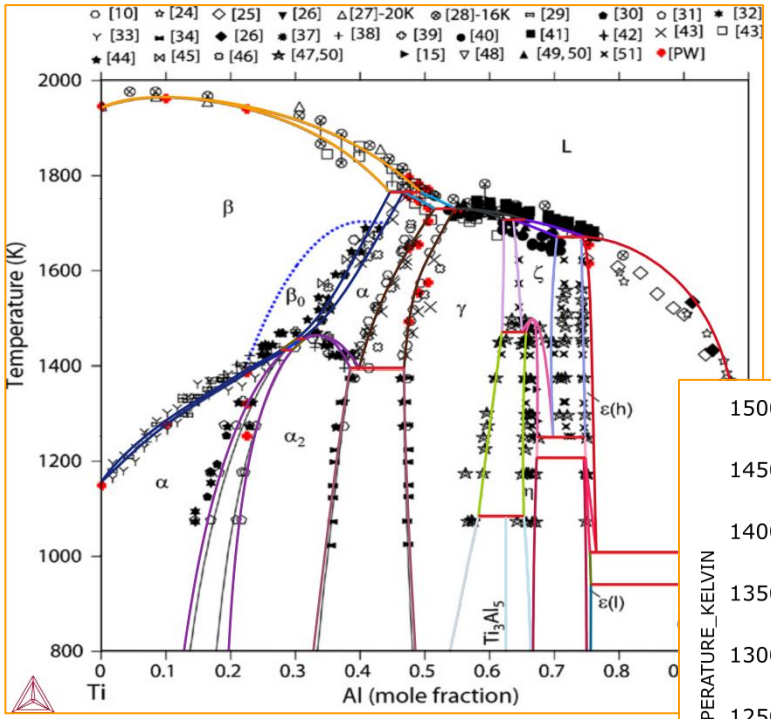
Supercell $Ti_{96}X_{12}$
108 (3 × 3 × 4)

Calculations

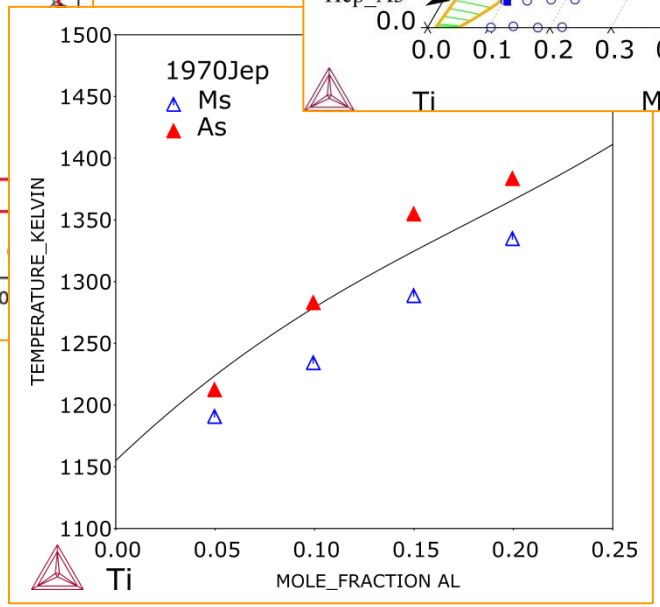
- **Ti-Al-V: the most important titanium alloy system**
- **Ti-Al: subsystem of Ti-Al-V & basis of all TiAl-X alloys**

Al-Ti-V isothermal section at 1073 K ⇩





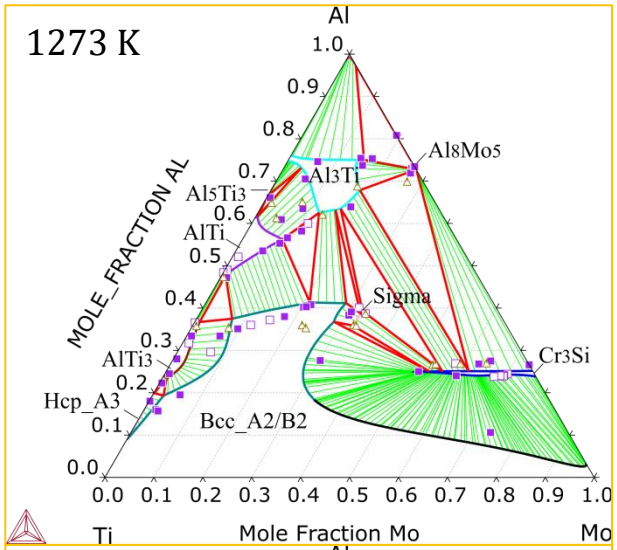
Modified Al-Ti phase diagram ⇧
Based on Witusiewicz, J Alloys Compd (2008)

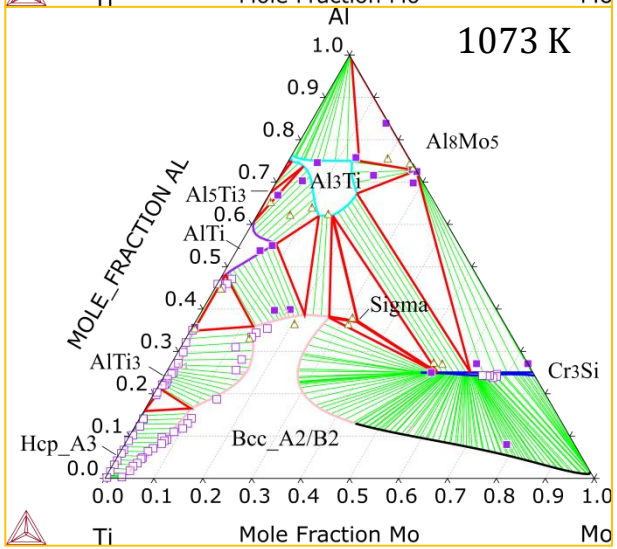


Calculated β/α
T_0-line in Al-Ti ⇨

Calculations

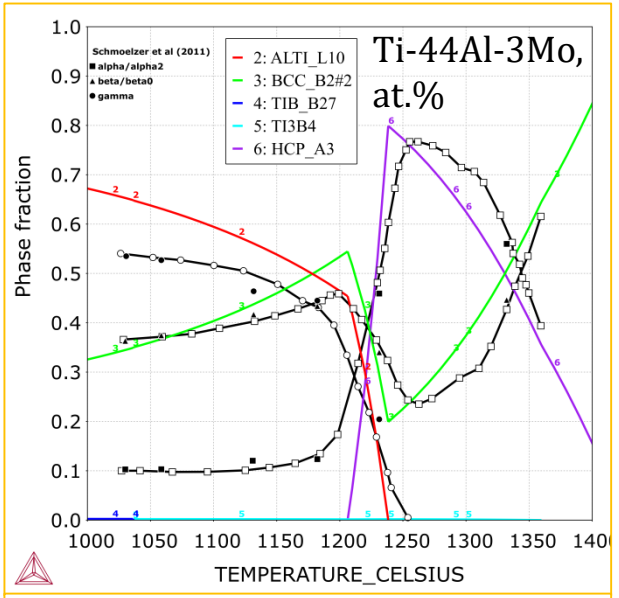
- **Ti-Al-Mo: important Ti-Al system**

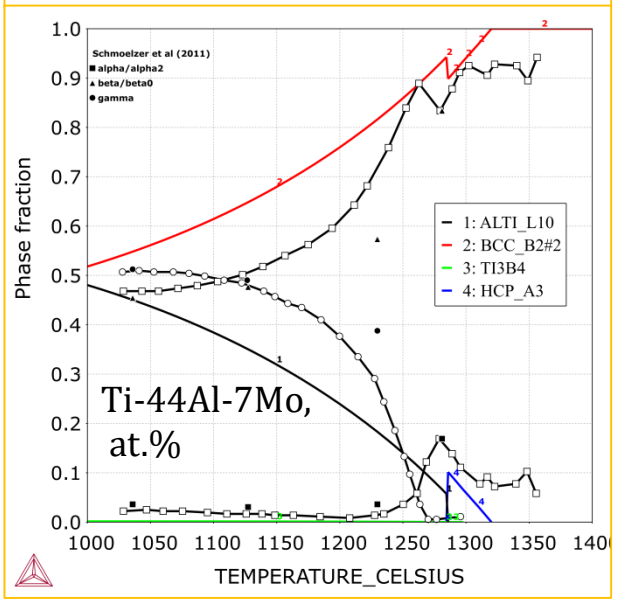




⇦ ⇙ Mainly based on phase equilibria @ 1073, 1173, 1273, 1373, 1473 K from Huang (2017)

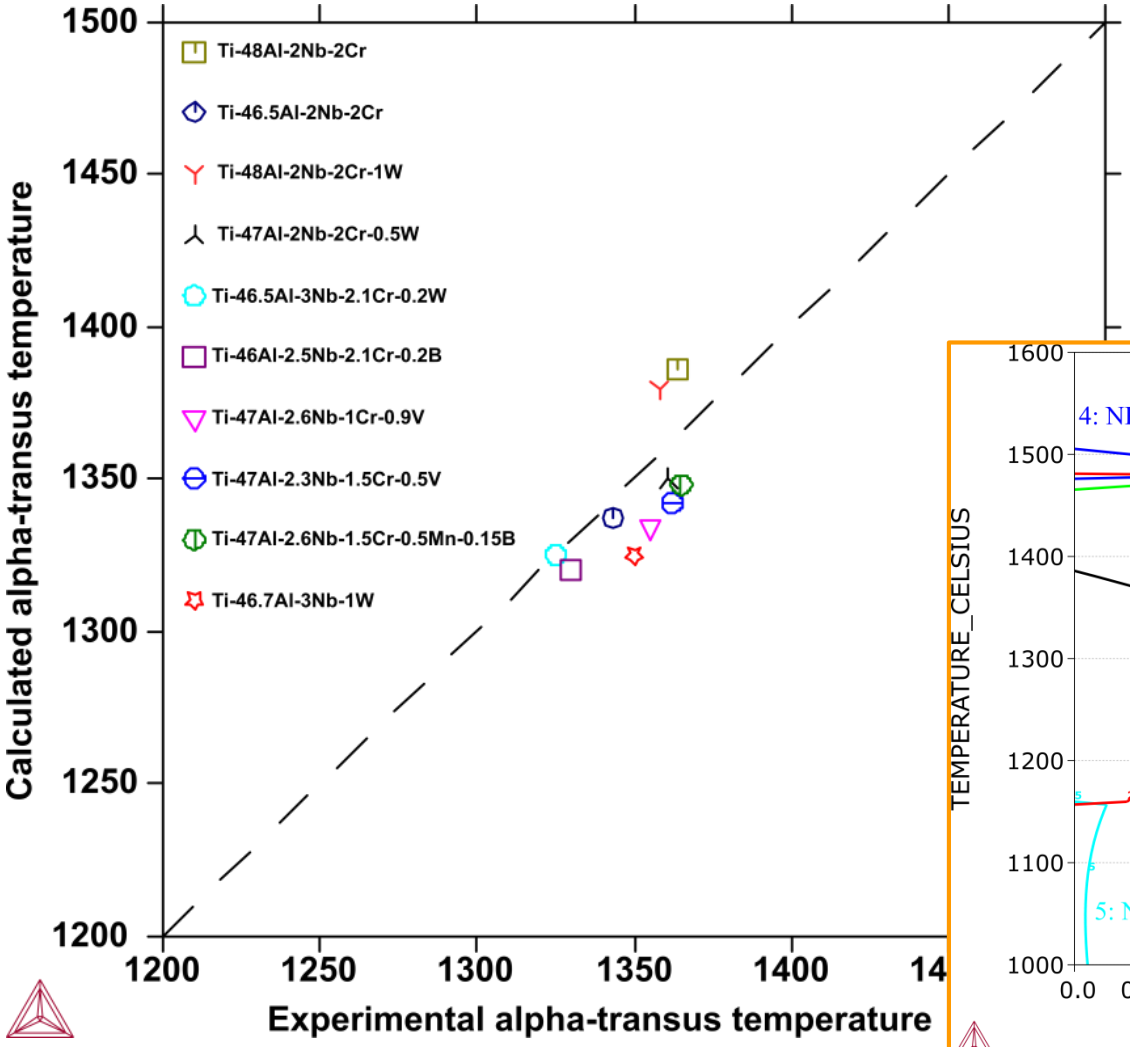
Non-equilibrium data from synchrotron by Schmölzer (2011) for comparison only ⇨⇗





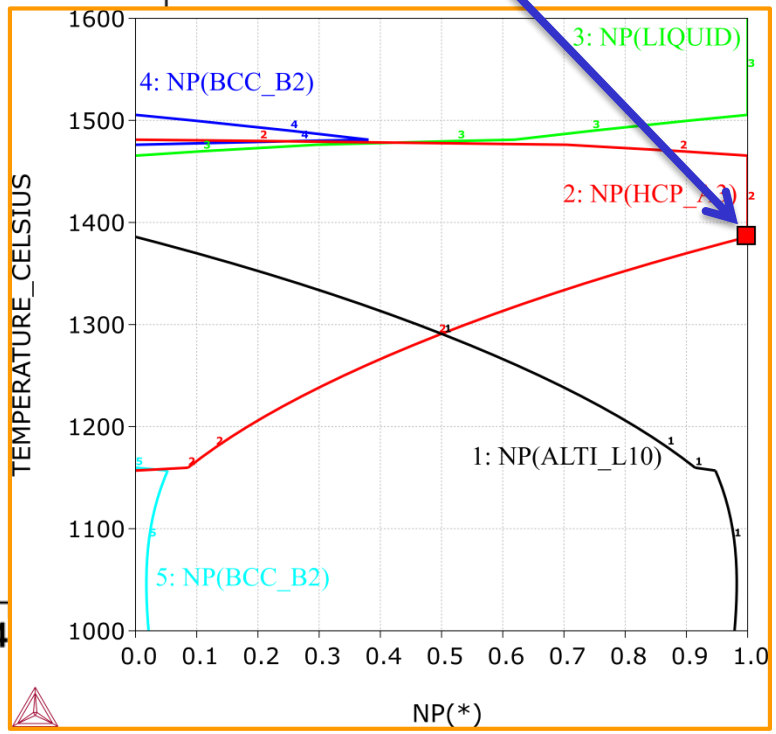
Validations

- **Typical Multicomponent Ti-Al alloys**



α transus temperature:

the lowest temperature where 100% α (Hcp_A3) exits, or where α → γ starts in TiAl-based alloys.



Overview

Thermo-Calc Software

❑ MOBTI2

Atomic mobility database for Ti/TiAl based alloys

Ti	Al	B	C	Co	Cr	Hf	Fe	Mn	Mo	N	Nb
Ni	O	Sn	Si	Ta	Re	Ru	V	W	Y	Zr	

- ❑ 23 elements
- ❑ 4 phases: LIQUID, BCC_A2, HCP_A3, ALTI_L10
- ❑ 20 binary systems (5 for LIQUID, 14 for BCC_A2, 1 for ALTI_L10)
- ❑ 7 ternary systems (3 for BCC_A2, 4 for ALTI_L10)

Note: ***MOBTI2*** is compatible and recommended for use in combination with the ***TCTI1***

Thermo-Calc Software

❑ Modeling Strategy for Liquid Phase

- Difficult to measure due to convection and microgravity
- Limited experimental data

Case 1: With experimental data --- *Critical assessment*

Case 2: No experimental data --- *Estimate by modified Sutherland equation*

Modified Sutherland equation

Self- and impurity diffusion coefficients in liquid phase

$$D = \frac{k_B T}{6\pi\mu r}\left(\frac{1+\frac{2\mu}{\beta r}}{1+\frac{3\mu}{\beta r}}\right)^{-1}$$

k_B, Boltzmanns constant

$$\mu_i = C_1 \frac{M_i^{1/2}}{V_i^{2/3}} T^{1/2} \exp\left(C_2 \frac{T_i^m}{T}\right)$$

Kaptay's viscosity formula

$$r_i(T) = 0.644\times10^{-8}\left(\frac{M_i}{\rho_i^m}\right)^{1/3}\left(1-0.112\sqrt{\frac{T}{T_i^m}}\right)$$

Proptopapas's effective radius equation

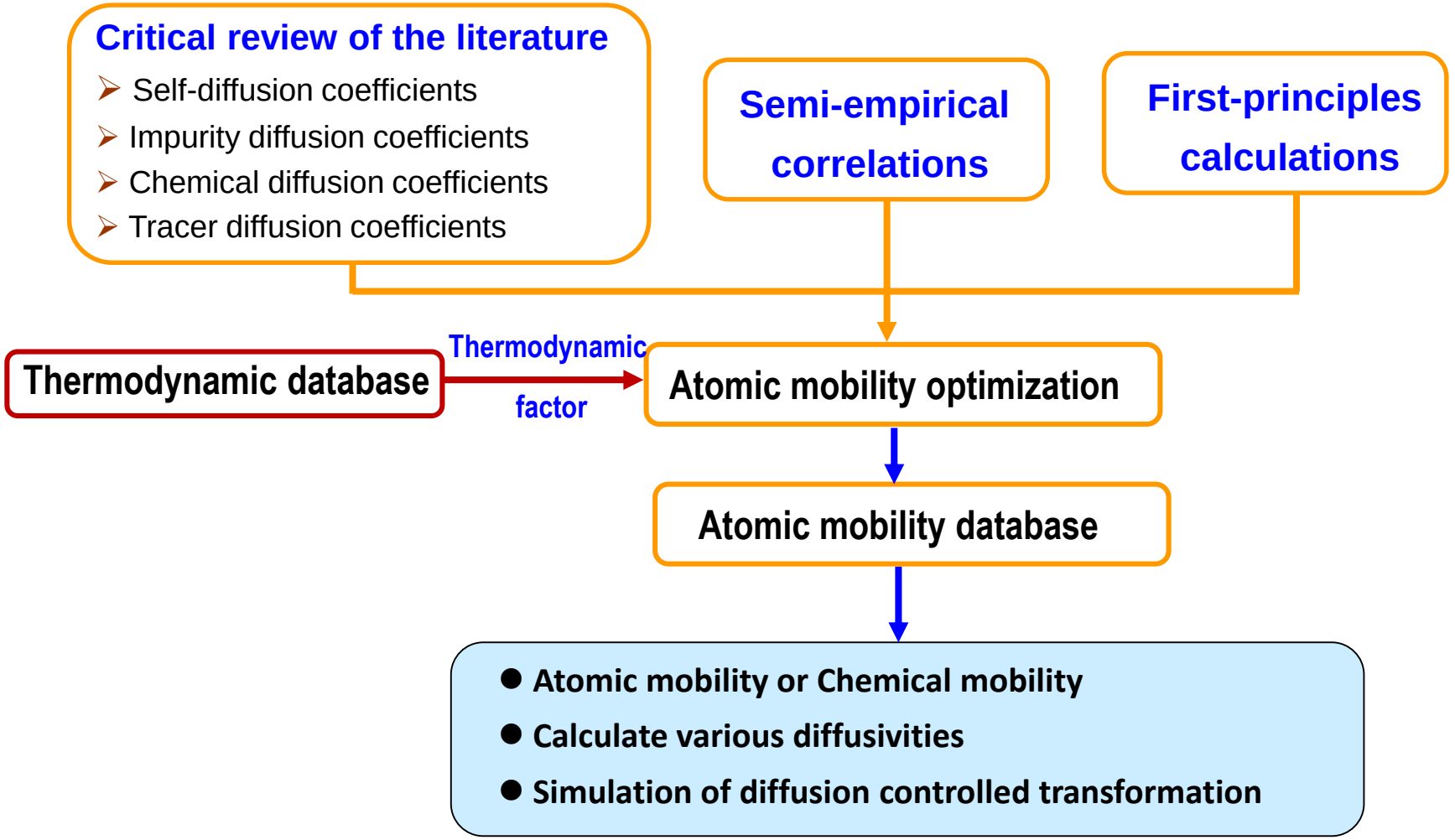
$$\beta = \begin{cases} 0 (r_A \le r_B) \\ \infty (r_A > r_B) \end{cases}$$

Sliding friction coefficient

W.M. Chen, L.J. Zhang, Y. Du et al., Philosophical Magazine 94 (2014) 1552-1577

Thermo-Calc Software

❑ Modeling Strategy for Solid Phase -- *BCC, HCP & ALTI_L10*



Results

Thermo-Calc Software

❑ Liquid Phase

- **Self-diffusivities**

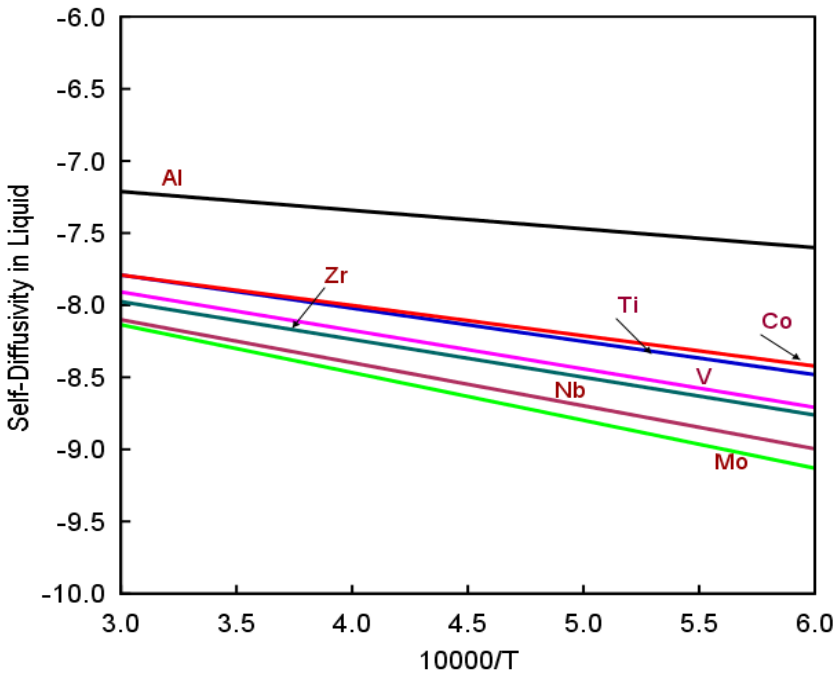


Fig. 1 Summary presently calculated self-diffusivities in liquid phase.

- **Impurity diffusivities**

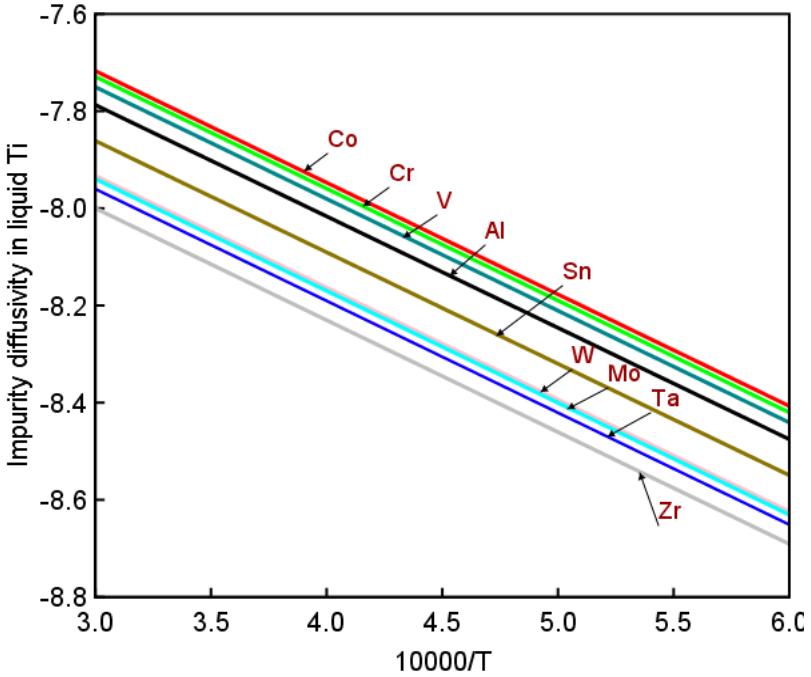


Fig. 2 Summary presently calculated impurity diffusivities in liquid Ti.

Results

Thermo-Calc Software

❑ BCC_A2 Phase

- **Al-Ti binary system**

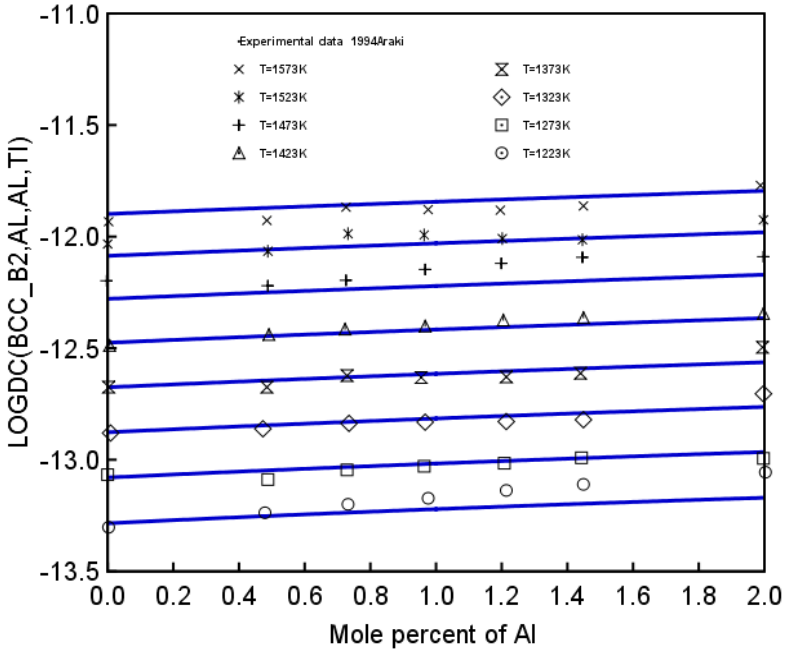


Fig. 5 Calculated interdiffusivities in BCC Al-Ti alloys.

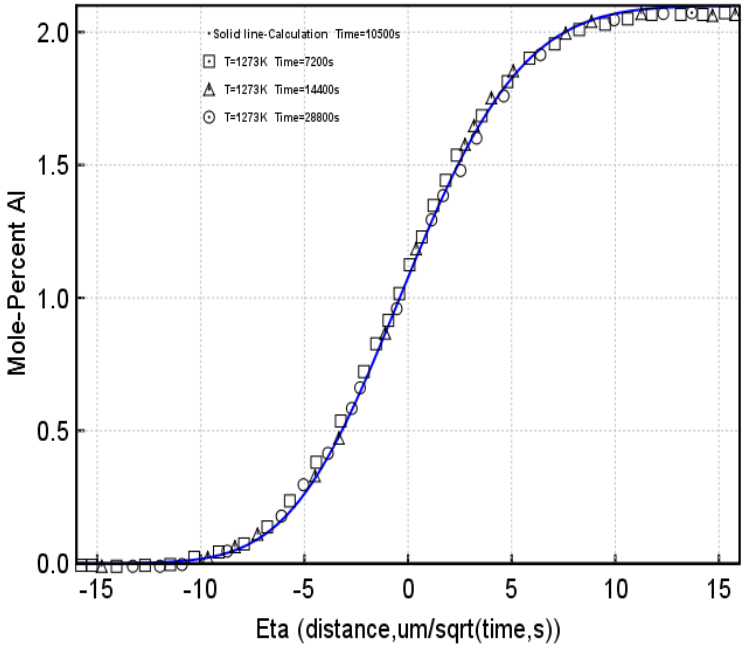


Fig. 6 Simulated concentration profile of Al in BCC Ti/Ti-0.021Al diffusion couple.

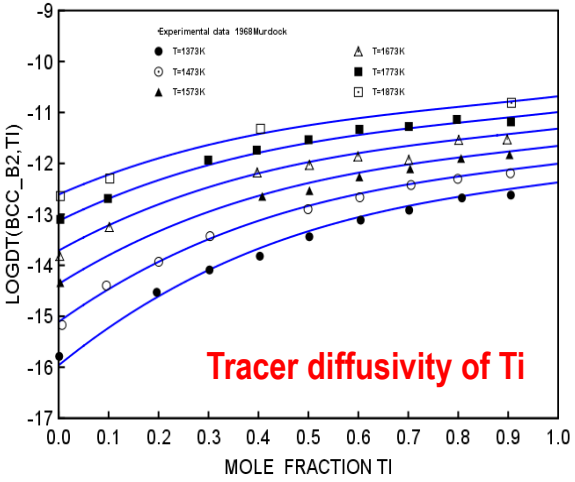
Experiments from: H. Araki, et al., Metall. Mater. Trans. A. 25A (1994) 874-876.

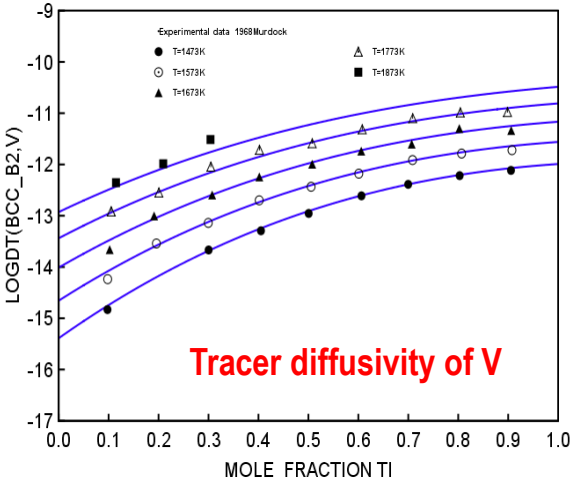
D. Goold, Inst. Met., 88 (1959) 444-448.

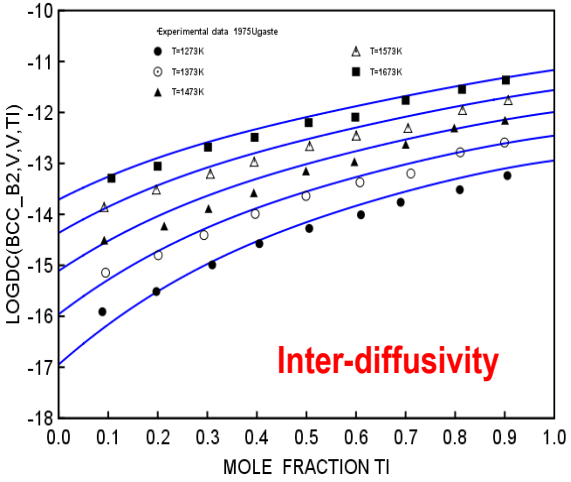
Results

❑ BCC_A2 Phase

- **Ti-V binary system**







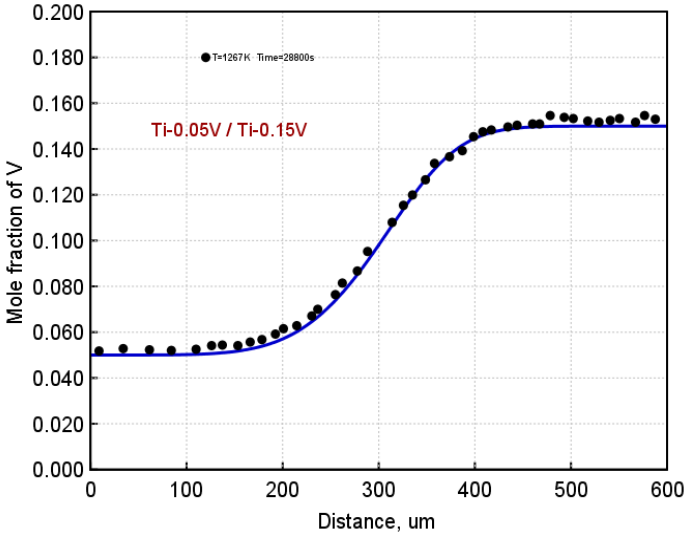


Fig. 7 Simulated concentration profile of V in BCC Ti-0.05V//Ti-0.15V diffusion couple.

Experiments from:

J. Murdock et al., Acta Metall. 16 (1968) 493–500.

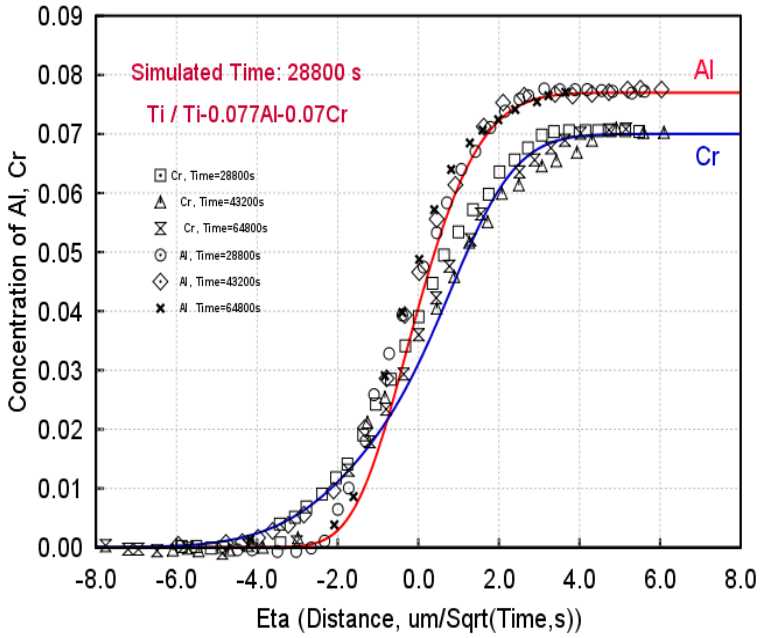
Y. Ugaste,et al., Fiz. Metal. Metalloved 40 (1975) 567–575.

W. Sprengel, et al., Def. Diff. Forum 143–147 (1997) 431–436.

Results

❑ BCC_A2 Phase

- **Ti-Al-Cr ternary system**



- **Ti-Al-Fe ternary system**

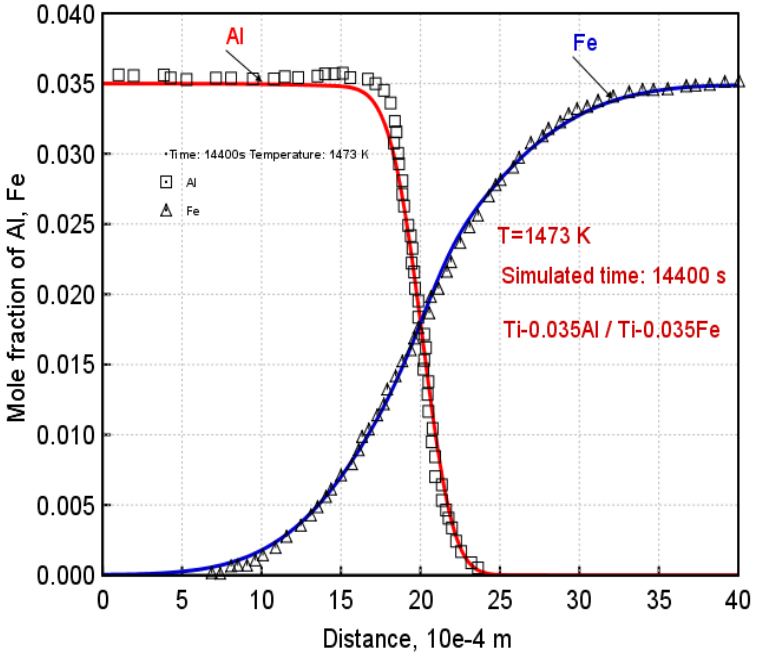


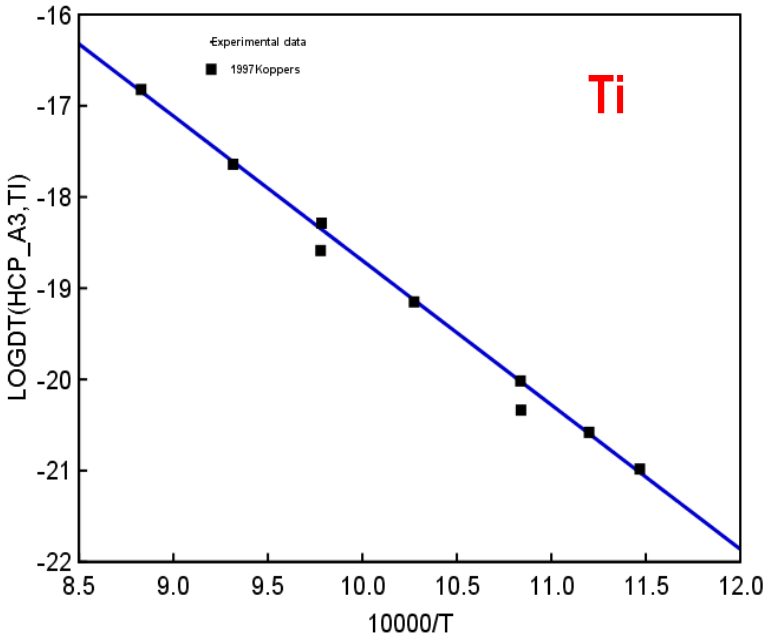
Fig. 8 Simulated concentration profile compared with experimental data **(a)** Ti//Ti-0.077Al-0.07Cr diffusion couple, **(b)** Ti-0.035Al//Ti-0.035Fe diffusion couple in BCC phase.

Experiments from: T. Takahashi, et al., J. Japan Inst. Light Met. 54 (2004) 280.
T. Takahashi, et al., J. Jpn. Inst. Met. 60 (2010) 444–450.

Results

❑ HCP_A3 Phase

- **Self-diffusivities**



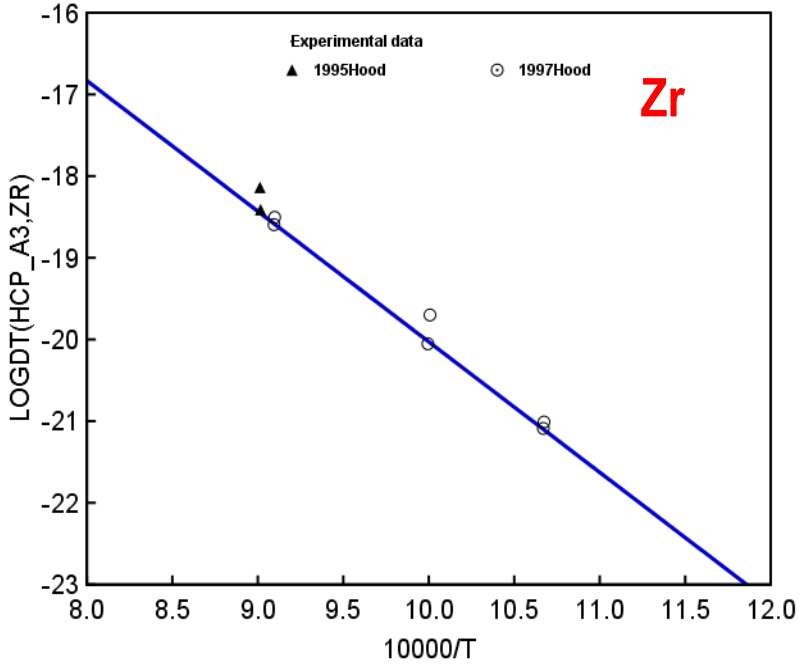


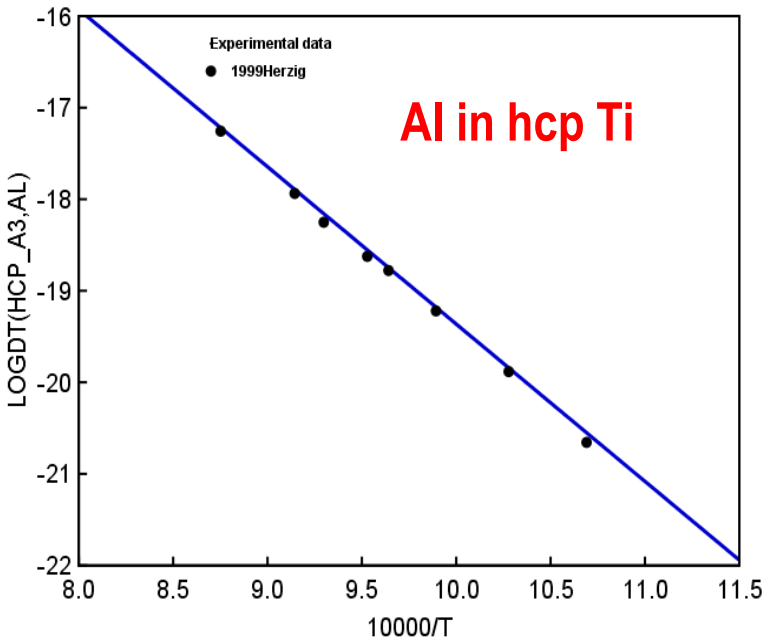
Fig. 9 Calculated self-diffusivities of **(a)** Ti, **(b)** Zr in HCP_A3 phase.

Experiments from: M. Koppers, et al., Acta Mater. 45 (1997) 4181.
G.M. Hood, et al., J. Nucl. Mater. 223 (1995) 122.
G.M. Hood, et al., Defect and Diffusion Forum 143–147 (1997) 49.

Results

❑ HCP_A3 Phase

- **Impurity diffusivities**



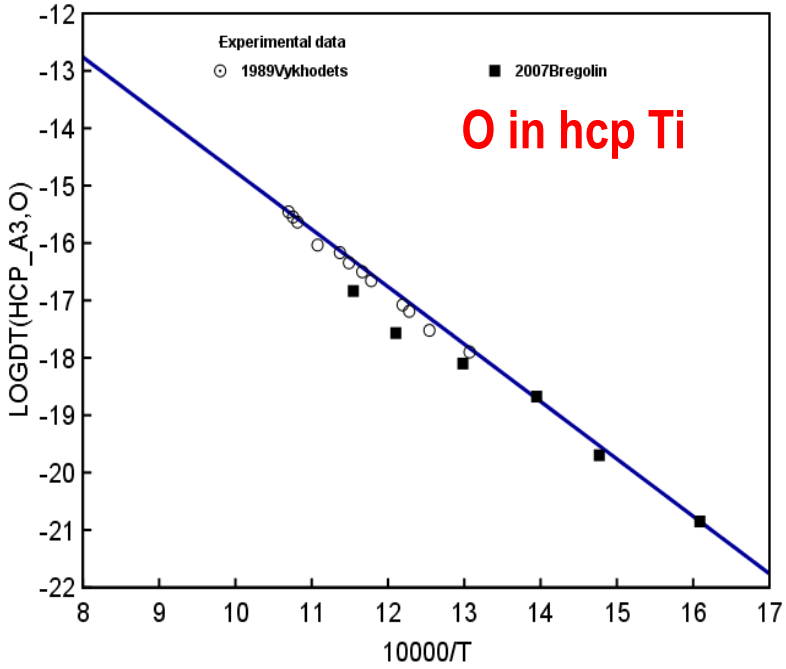


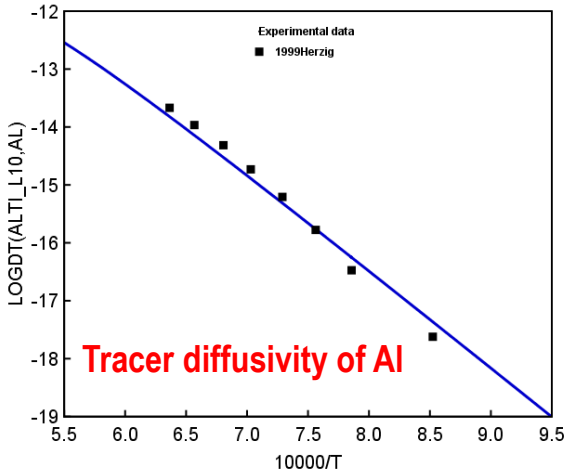
Fig. 10 Calculated impurity diffusivities of **(a)** Al, **(b)** O in HCP Ti phase, compared with experimental data.

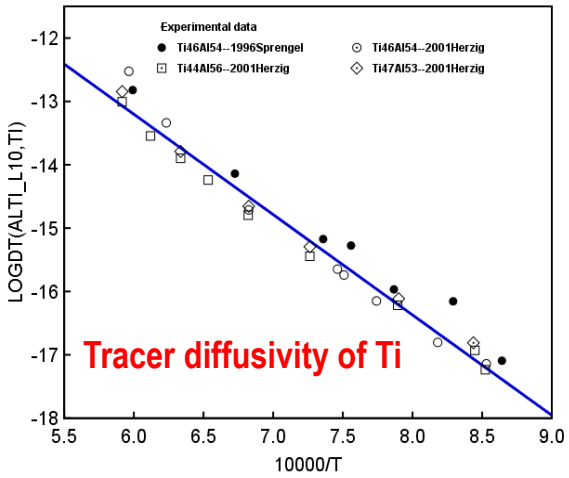
Experiments from: M. Koppers, et al., Acta Mater. 45 (1997) 4181.
V. B. Vykhodets, et al., Phys. Met. Metallogr. 68, (1989) 94.
F. L. Bregolin, et al. , Appl. Phys. A 86 (2007) 481.

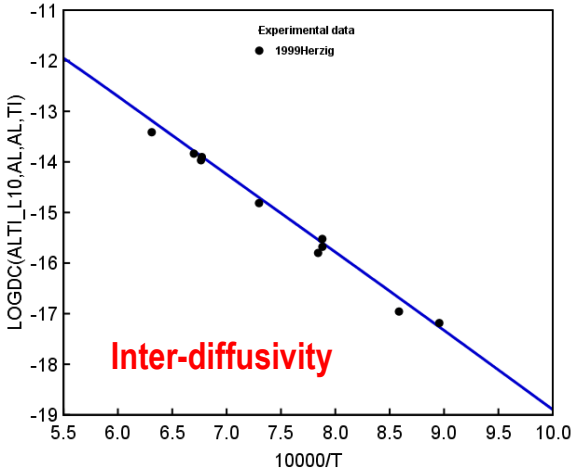
Results

❑ ALTI_L10 Phase

- **Ti-Al binary system**







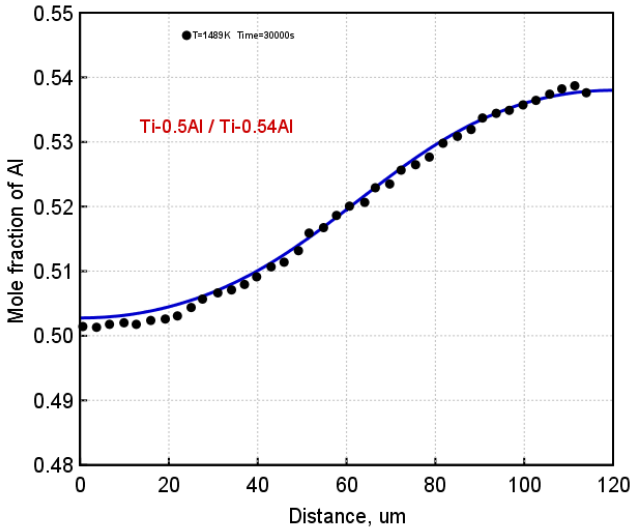


Fig. 11 Simulated concentration profile Ti-0.5Al//Ti-0.54Al diffusion couple in AlTi_L10 phase.

Experiments from :

C. Herzig, et al. Intermetallics, 7(1998) 389.

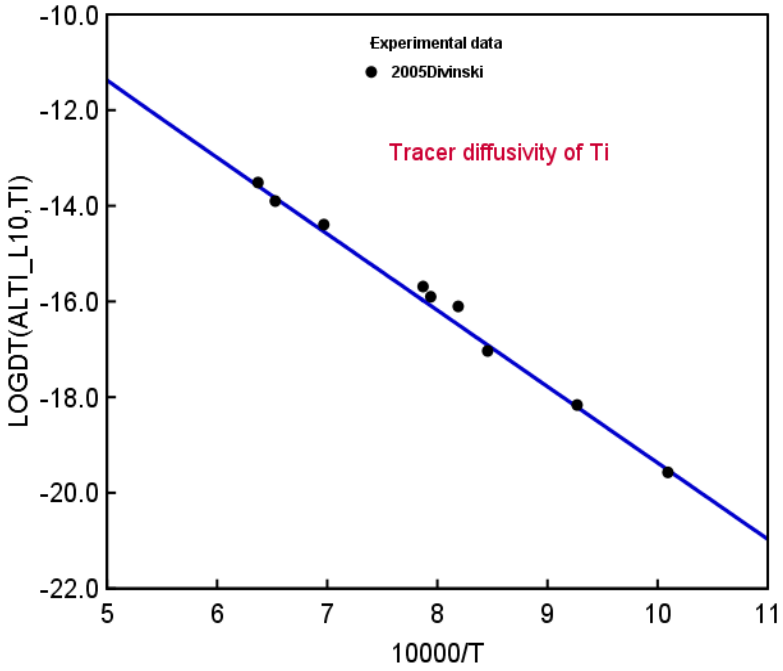
W. Sprengel, et al., Intermetdlics 4 (1996) 185-189.

C. Herziga, et al., Intermetallics 9 (2001) 461–472.

Results

❑ ALTI_L10 Phase

- **Ti-Al-Nb ternary system**



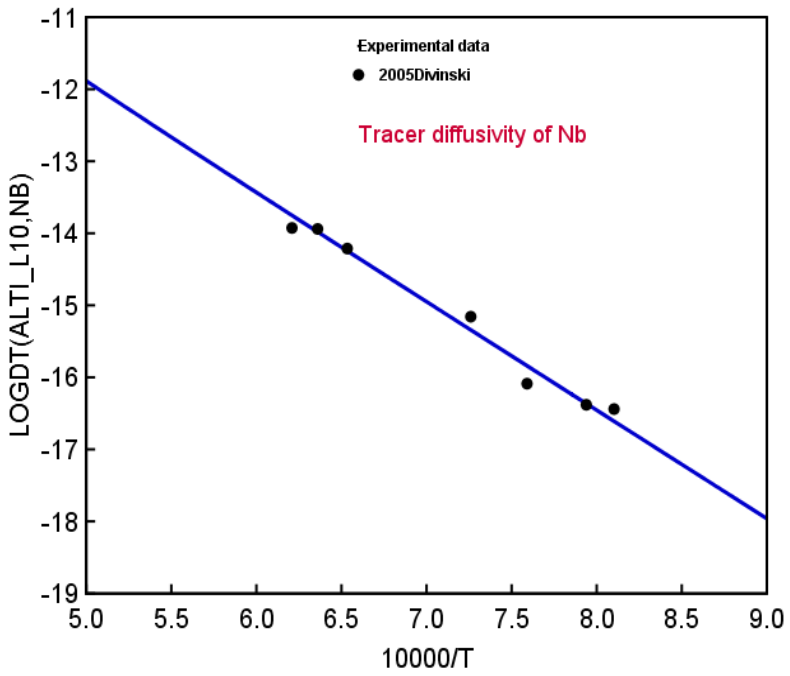


Fig. 12 Calculated tracer diffusivities of **(a)** Ti, **(b)** Nb in Ti-0.54Al-0.1Nb ternary alloy (ALTI_L10 phase)

Experiments from: S. Divinski, C. Klinkenberg, C. Herzig, JPEDAV 26(2005) 452-457.

Summary

- The first database for both Ti alloys & TiAl materials
  - 23 elements, 236 binaries, 70 ternaries in TCTI1
  - Compatible mobility parameters in MOBTI2
- Descriptions of both stable and metastable phases, such as ω
- High throughput DFT calculations in assessing thermodynamic model parameters related to metastable regions and metastable phases
- Capable to predict both equilibrium and non-equilibrium phase transformations, e.g. martensite start temperature.