

CT – 15:

Creating thermodynamic databases,

Examples using databases

Creating thermodynamic databases:

unary data, model compatibility, naming of phases,  
validation of databases, nano-materials.

Examples using databases:

Sigma-Phase Formation in Ni-bases Anticorrosion Superalloys,  
Intermetallic Phases in Lead-Free Soldering,  
Equilibria with Laves Phases for Aircraft Engines

# Creating thermodynamic databases

Purpose of an assessment is to provide building blocks for multicomponent thermodynamic database.

Database based on binary assessments and a limited number of ternary assessments, all centered around a „base“ element (Fe, Al, Sn,...), can give reliable extrapolations to multicomponent alloys based on that element. Such databases are valuable tool for new alloy development, because experimental investigations of multicomponent system are very expensive.

Some **ternary assessment must be included** in such databases!

There are ternary compounds that must be present in database and ternary assessment may reveal that some binary assessments require modification.

# Unary data

The data for the pure elements must be the same in all assessments in which the element appears in order to make it possible to merge them into a database.

International agreement on pure-element data (e.g. metastable modifications Cr fcc, Au bcc, etc.,) – lattice stabilities – collected by A.T.Dinsdale: CALPHAD 15 (1991) 317, and it is updated e.g. on <http://www.sgte.org>

Database dictates keeping the unary data unchanged even if it is evident, that these need to be improved. (Example: data for Laves phases as Hydrogen storage, which used value of G of fictitious end members equal to 5 kJ.mol<sup>-1</sup>)

It is desirable to develop an automatic and continuous reassessment procedure.

# Model compatibility

Phases that may form a continuous solutions from one binary system to another should be described by the same model which make it possible to combine these to give a single Gibbs energy description.

Example: Fe-Cr-C system: model  $(\text{Fe}, \text{Cr})_1(\text{C}, \text{Va})_1$  will create new fictitious end member belonging to Cr-C system. It is not enough to work with A1 and B1 structures of Fe-Cr and Fe-C systems.

Only phases with the same structure may be treated as he same.

Example: Cr-Si, Fe-Si, and Mn-Si has structure of general stoichiometry  $\text{M}_3\text{Si}$ , but  $\text{Cr}_3\text{Si}$  has another structure and it should not be combined with them.

Structurbericht notation is a great help. It is important in extrapolation to higher-order systems.

Partitioning of Gibbs energy in modeling of order-disorder transition is help in modeling in ternary systems

Example: B2 phase Al-Ni (ordered) should be combined with A2 phase Cr-Ni (A2 parts can be added, combined)

Models should be selected so, that they are compatible with the systems with which the assessment should be combined later

# Experimental database

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Assessment is working with the file containig experimental data (in Thermo-calc „\*.pop“ – file):

In this file all experimantal information should be referenced correctly and all transformations or corrections made from original publication documented. Also theoretical information should be referenced there.

(It is „temporary“ database.)

Experimental datafile should be kept for the future use (similarly as assessment logbook).

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# Naming of phases

Phases that can extend into a multicomponent system have to have a unique name.

Example: Ca-Mg-Fe-O system: CaO (lime), MgO (periclase), FeO (wustite) form continuous solution having the NaCl (B1) structure type.

In a database, the parameters for these three phases must be stored together with a single name (at present „halite“ has been selected).

Example: in iron database can be used name „ferrite“ for BCC structure and „austenite“ for FCC structure for complex alloys.

It is important to agree to use the same name for the same phase for many applications.

*Strukturbericht* notation – has no relation to the actual structure (A – pure elements, B – binary systems 1:1, C – binary systems 2:1 etc.). It is popular.

„Structure family“, e.g. ordered structures (A1, L1<sub>2</sub>, L1<sub>0</sub>) based on simple disordered lattice (FCC), (B2, D0<sub>3</sub>, L2<sub>1</sub>) based on BCC lattice, and (D0<sub>19</sub> and B<sub>19</sub>) on HCP lattice. 4 sublattice model is used for L1<sub>2</sub>, L1<sub>0</sub> ordering, but for is D0<sub>22</sub> – 8 sublattices is needed - separate phase.

Some compounds and intermetallic phases have traditional names (sigma, mju)

Liquid phase is usually treated as a single phase, aqueous solutions, polymers as separate phases (they do not mix with metallic and oxide liquids).

# Consistent database - summary

Thermodynamic database cannot be simple collection of thermodynamic assessments published by various authors for relevant binary and higher-order systems in spite of being based on sound and proper models.

## Condition of consistency of database:

- The **models used** have to represent Gibbs energy of a phase (unary and interactions). Violating this may lead to that e.g. order (sequence) of elements in parameter in various assessments ( $L_{A:B}$  vs.  $L_{B:A}$ ) may require the change of sign in odd RK parameters – therefore, alphabetical order of element is recommended. Other (different) polynomials used, (e.g. Thermodynamically Adapted Polynomial – TAP), may create problems.
- The models and **names used** for description of the same phase existing in different systems have to be the same (sublattice model used in CEF must be the same, e.g. the number of sublattices, site occupancies etc.)
- The thermodynamic data for Gibbs energies of the same element in related systems (**Lattice Stability**) have to be the same - difference in unary data between SGTE1 and SGTE4 in fictitious structures (continuous revision). It is an opportunity to involve the *ab initio* modeling in applied research.

# From assessment to database

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A database is (not only) a merged set of thermodynamic assessments of binary, ternary and higher-order systems.

Individual assessments is advantageous to keep in separate files for check (of unary data, models used, parameter values) – first task is to reproduce the original publication!

Further, phase names should be unified (software exists for it).

Transformation softwares for transformation of format of databases exist (e.g MTDATA to Thermocalc and vice versa).

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# Unassessed parameters

The **specific format** of databases – there are programs for their conversion

Example: Laves phases  $(A,B)_2(A,B)_1$  and  $(A,C)_2(A,C)_1$  are in database and ternary Laves phase exists, modeled by  $(A,B,C)_2(A,B,C)_1$ .

Parameters  ${}^\circ G_{B:C}$  and  ${}^\circ G_{C:B}$  are „unassessed“ and in most softwares are treated as zero. It might not be a good assumption!

All unassessed parameters can be listed by program usually (e.g. in GES module of Thermocalc) and estimated value can be set to them.

Clear reference must be given for each estimated parameter

# Missing parameters

- Example: Cu-Fe system has no stable HCP\_A3 phase. Adding Zn to database in systems Cu-Zn and Fe-Zn, the ternary HCP phase (in Cu-Fe-Zn) can be modeled successfully taking Cu-Fe HCP phase as ideal (interaction equal zero).
- In the Figure, it is evident that missing parameter must be assessed.

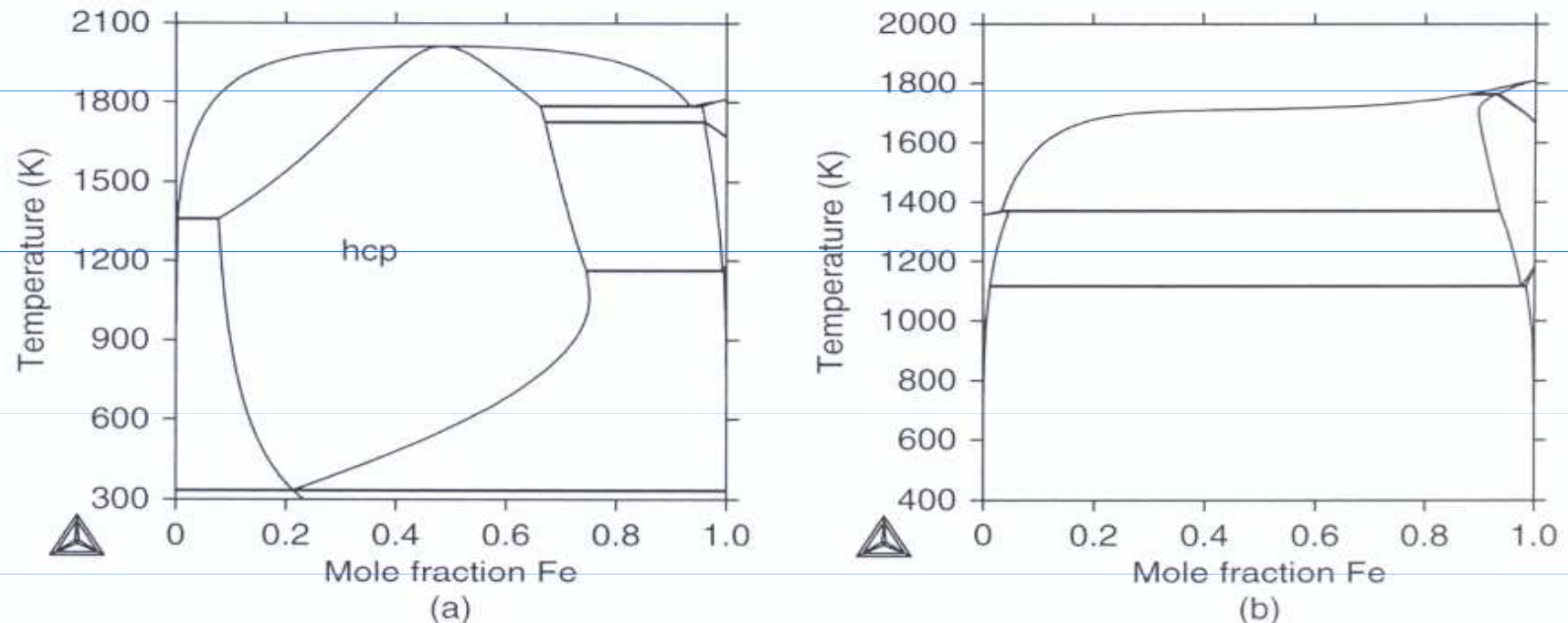


Figure 8.1 What may happen when a binary is added to a database. (a) The Cu-Fe system with an ideal modeling for the hcp phase. (b) The Cu-Fe system with the interaction for the hcp phase as for the fcc phase.

# Missing parameters – cont.

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HCP phase will appear in Cu-Fe system even when HCP\_A3 phase is explicitly suspended.

Some hints in the cases of no parameters:

- HCP can have the same parameter as FCC
  - HCP and FCC parameters can be set equal to the values for Liquid or BCC
  - BCC parameter can be set equal to parameter for Liquid (for unstable BCC)
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# Validation of the database

- Checking that the assessed system can be recalculated from the database
- Checking that the extrapolations from assessed systems are reasonable (valid composition range for each component in database)

Example: Cr, Ni, Mo steel: all binaries and ternaries assessed

Problem: austenite/ferrite equilibria at 1150 °C were not reproduced (duplex stainless steel)

Solution: introducing the same positive interaction in the FCC\_A1 phase in the Cr-Mo system as for the BCC\_A2 phase and reassessing the Fe-Cr-Mo system

Example: Nicrofer and Avesta superaustenitic steel: equilibrium state after long-term annealing used for validation of database

# Database management and updating

Constant updating of database is necessary.

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**Updating:** adding new assessments

replacing existing assessments

- Individual assessments used to create the database must be kept in separate files all the time.
- Estimated parameters which was added to database should be also kept in special file.
- Extrapolation to higher-order systems must be checked after each updating

Adding a binary data that was missing from the original database may not improve the database. (Addition of estimations of missing parameters may disturb).

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# Documentation of a database

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Documentation is necessary for the management of database (change of the manager).

Documentation: systems included, test points used for extrapolation, list of references of all assessed systems in database, each parameter should be referenced to paper or other source (in „TDB format“ at the end of statement)

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# Existing thermodynamic databases

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Several databases are available – classified in terms of their main component (e.g. Al database, Ni database etc.) or physical property (semiconductor database) or special application (solder database).  
More: CALPHAD 26 (2002) 141-312.

(Our databases available: Steel-ex.tdb, solder.tdb)

Reference in publication: database name, supplier, year and version

It is important as an instrument for measurement! Website should be added.

New commercial databases are coded (not readable)!!!

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# Complementing database – Mobility database

Computational thermodynamics is most important for simulating phase transformations.

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Thermodynamic description of the phase – source of chemical potentials of the components and the thermodynamic factor of diffusion.

In addition, mobility of the elements in the various phases have to be available. Source of that data: self-diffusion (or tracer diffusion) experiments. Mobility is often closely related to bulk modulus, which can be easily calculated using *ab initio* technique. It is possibility to estimate mobilities.

There is special version of PARROT module of Thermocalc program for assessment of mobilities using diffusion data or concentration profiles.

Thermodynamic description is the base for it (calculating thermodynamic factor and chemical potential)

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A few commercial mobility databases exist (e.g. Thermocalc).



# Nano-materials

Polycrystalline materials (grain size  $> 100$  nm) have isotropic mechanical properties (monocrystals are used for a few applications only – e.g. turbine blades).

„Bulk“ polycrystalline material: surface properties several order less important than bulk properties.

Interface region between two different crystalline grains (grain boundaries) have larger density of defects than inner regions of the grains and the atoms on the interface can have different coordination number from those in bulk.

Therefore, interface properties are different from those of the „perfect“ crystal by a factor up to 30%.

Reducing the size of the grains to nanometers make the number of atoms in the grain comparable to the number of atoms at the interface – „nanomaterials“ – metastable equilibrium state.

# Nano-materials - example

Nanoparticles **have different melting temperature** than bulk material.

$$G^{Ph} = \sum_i y_i^0 G_i^{Ph} + G^{id} + G^E + G^{mag} + G^{surf} \dots$$

$$G^{surf} = S.n.\sigma = (3M_r \sigma / \rho) (1/r) \quad (\text{spherical particles, } n = (r_M/r)^3)$$

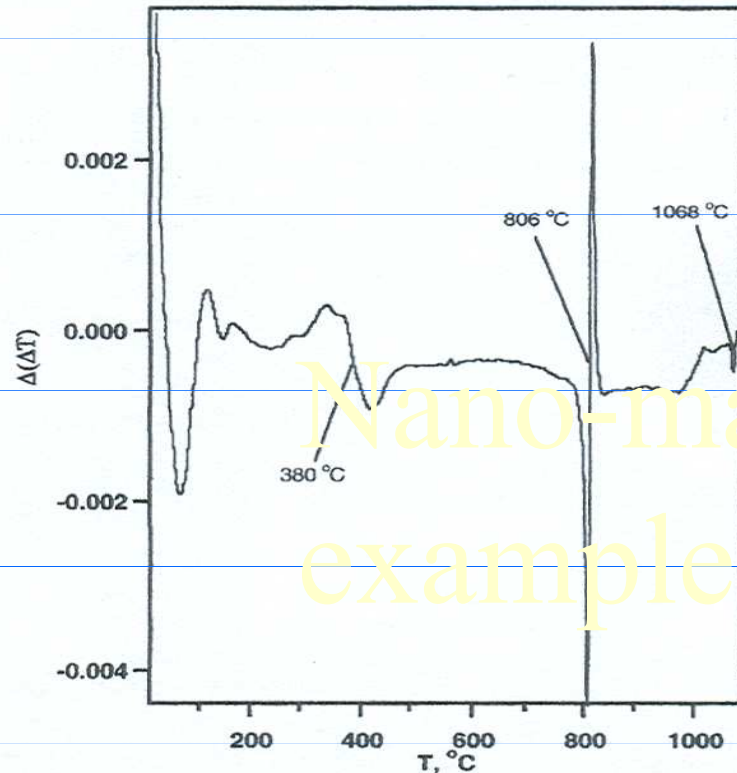
at  $T_m$ :  $G_{liq} = G_{sol}$  and melting temperature  $T$  is given by:

$$T = T_m - 3M_r (T_m / \Delta H_m) (-1/r_{solid}) [(\sigma / \rho)_{liquid} - (\sigma / \rho)_{solid}]$$

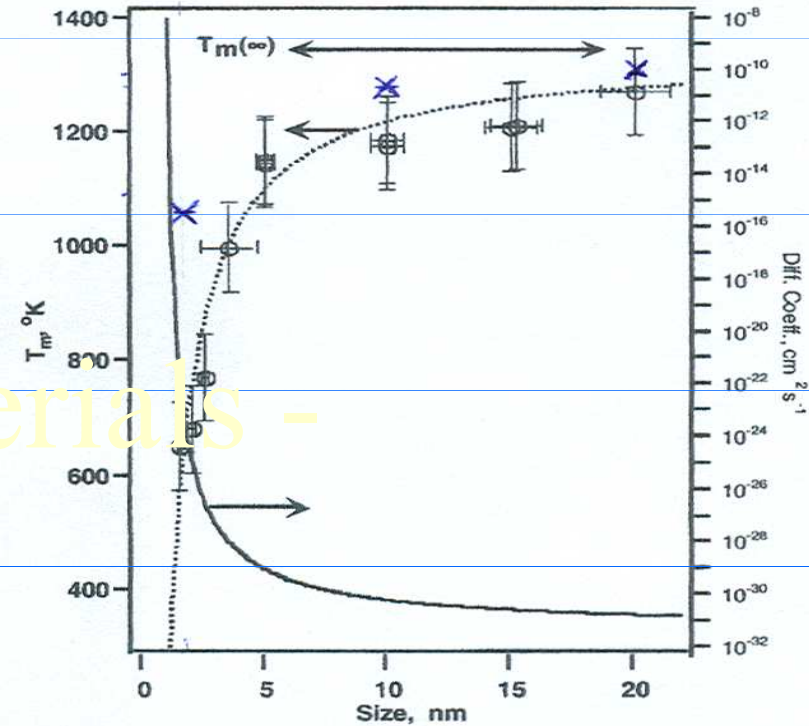
# Nano-materials - example

ARTICLES

Dick et al.



**Figure 3.** First derivative DTA profile of 1.5 nm silica-encapsulated gold particles. The large endotherm at ~800 °C is melting of NaCl, the broad one at 380 °C is melting of the particles, and the band at 1068 °C is melting of bulk gold.



**Figure 4.** Size dependence of the melting point and diffusion coefficient of silica-encapsulated gold particles. The dotted curve is calculated using eq 2 and the parameters given in the text for “naked” gold. The bulk melting temperature of Au is indicated by the double arrow as  $T_m(\infty)$ . The solid curve (right-hand side axis) is the calculated Au self-diffusion coefficient.

Dick K. et al., JACS 124 (10), 2312-2317 (2002), Au

■ Crosses: Calculation with estimation for Au (Buffat, Borel):

■  $(\sigma / \rho)_{\text{liquid}} = 0,74/17300 = 4,28 \cdot 10^{-5}$

■  $(\sigma / \rho)_{\text{solid}} = 0,90/19000 = 4,74 \cdot 10^{-5}$

# Nano-materials - example

Influence of substrate on the melting temperature of nanoparticles

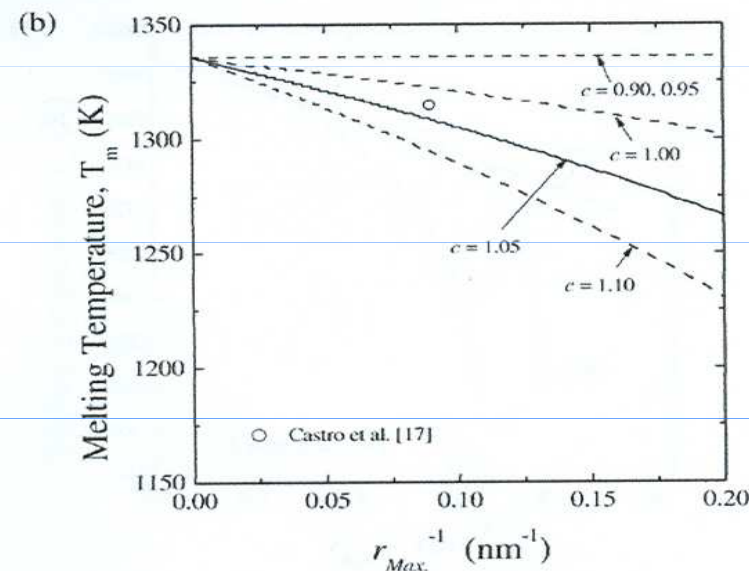
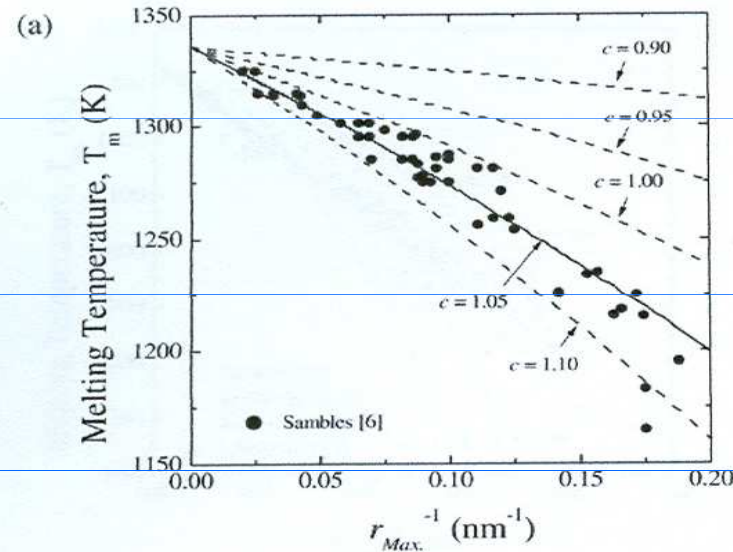
Melting temperature of gold nanoparticles ( $r > 5\text{nm}$ )

a) Graphite substrate

b) Tungsten substrate

Role of substrate only when it shows good wettability

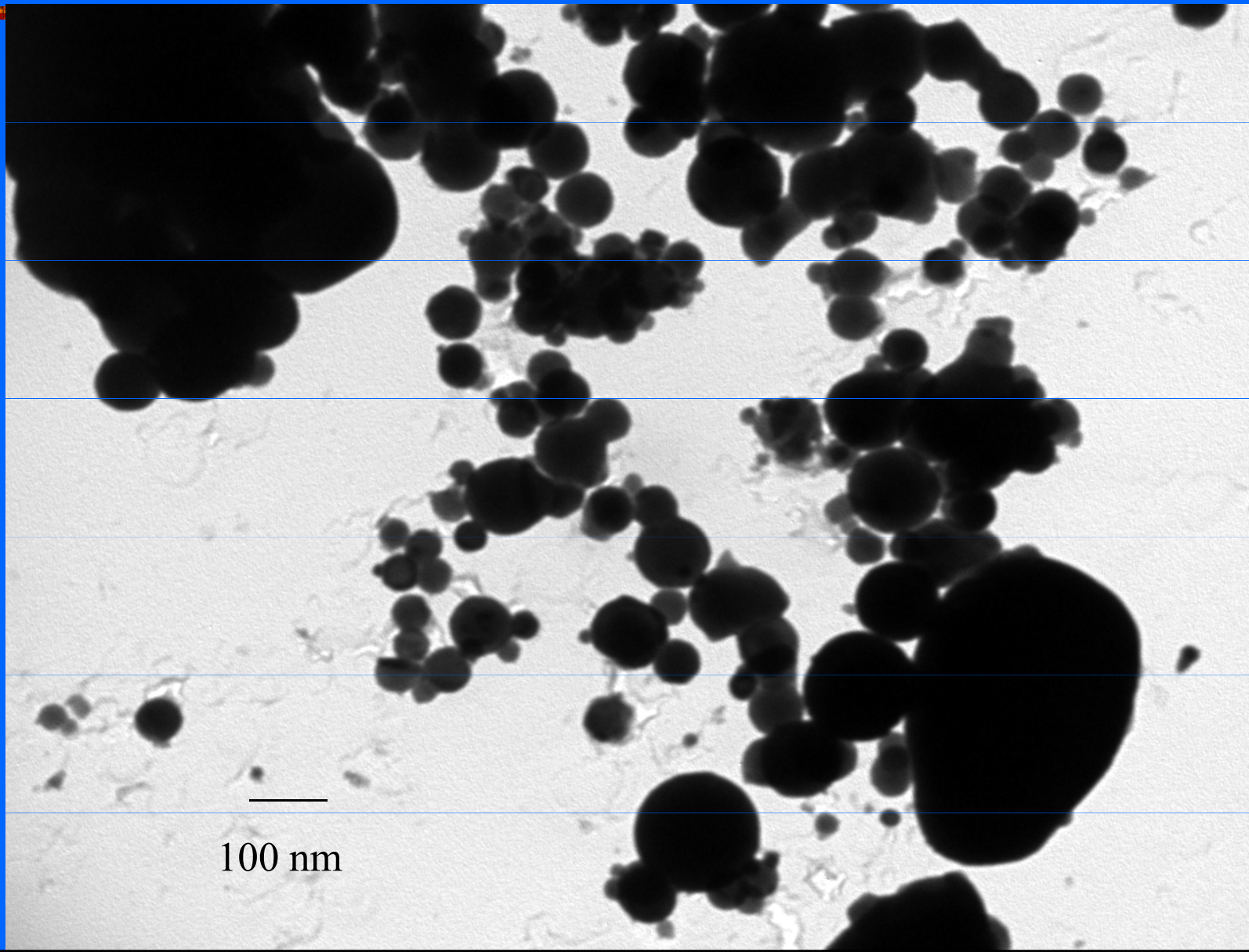
*J. Lee et al. / Computer Coupling of Phase Diagrams 31 (2007) 106 - 111*



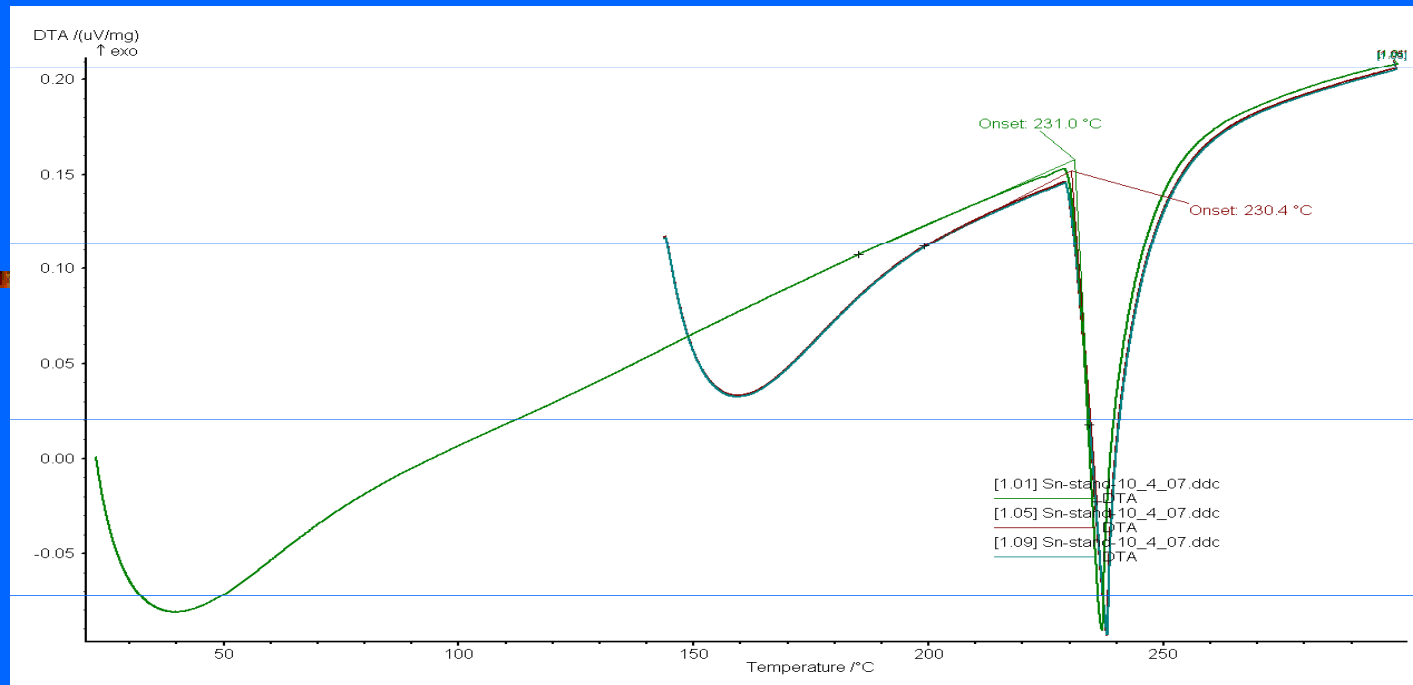
# Nano-materials - example

- Nanoparticles of tin before heating

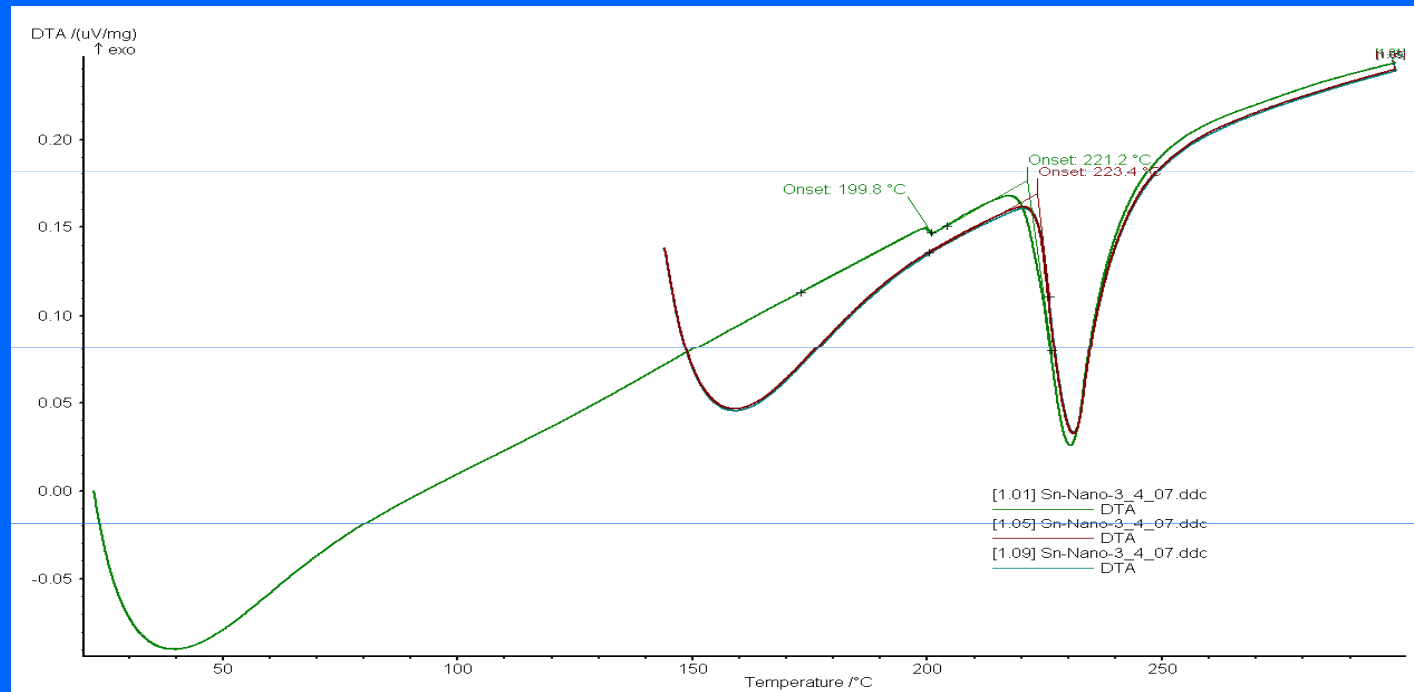
J.Vrestal: WG1 COST MP0602 meeting, Genova 2007,



# DSC - bulk Sn, atmosphere Ar, 5N

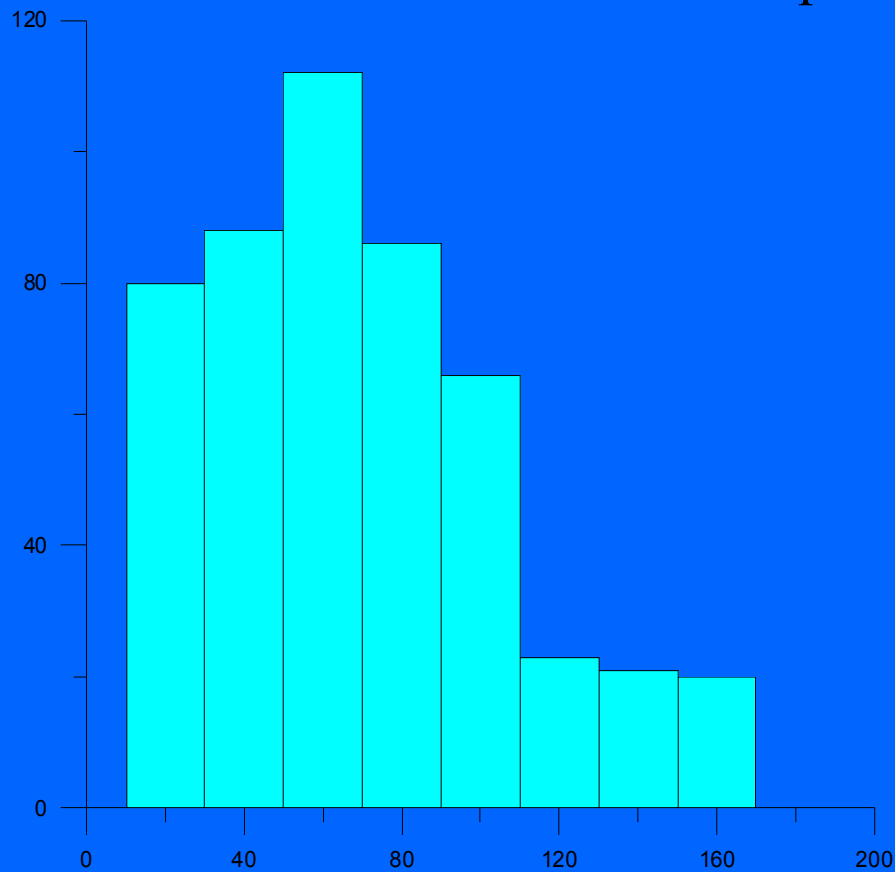


# DSC - nano Sn, atmosphere Ar, 5N



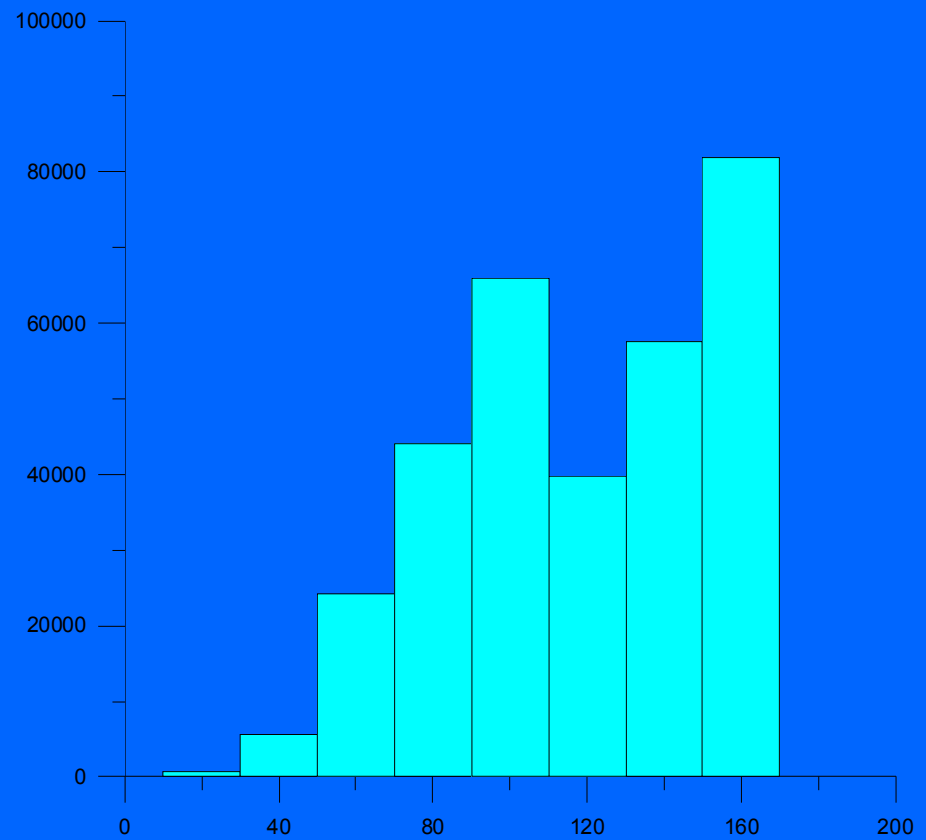
# Distribution of particle size before heating

N particles



Diameter of particles / nm

V particles /  $\cdot 10^{-3} \text{ nm}^3$



Diameter of particles / nm

# Surface in materials

Grain boundary can move and at increasing temperature grains can grow, minimizing its surface energy.

Mechanical properties are usually better for materials with small grains  
Effort to stabilizing grains against changing temperature was devoted –  
e.g. pinning the grain boundaries by placement of particles.

Relative stability of different phases at the phase interface is the most important factor for determining the interface movement.

Crystal lattice and the composition change across a phase interface and thus bulk diffusions are also needed for the interface to move.

„Local equilibrium“ assumption at the phase interface: compositions at the interface are given by an equilibrium tie-line in the phase diagram.

For very different mobilities of elements (e.g. C in Fe) – „para-equilibrium“ assumption is valid.

All of these models for phase transformations needs good description of the bulk thermodynamics.



# Surface tension of liquids - complementing database

Thermodynamic database is needed also for calculation of surface tension of various systems (salts, oxides and liquid alloys) based on Butler equation:

$$\sigma = \sigma_1 + (1/A_1)(G_1^{E,s} - G_1^E) + (RT/A_1) \ln ((1-x_2^s)/(1-x_2))$$

$$\sigma = \sigma_2 + (1/A_2)(G_2^{E,s} - G_2^E) + (RT/A_2) \ln ((x_2^s)/(x_2))$$

Solving these equations we get values of  $\sigma$  and  $x_2^s$  for every value of  $x_2$

The superficial areas of pure liquid components  $A_1$ ,  $A_2$ , the surface tension of pure liquid components  $\sigma_1$ ,  $\sigma_2$  and partial excess Gibbs energies in the bulk  $G_1^E$ ,  $G_2^E$ , and in the surface  $G_1^{E,s}$ ,  $G_2^{E,s}$  have to be known.

$A_1 = 1.091 N_A^{1/3} V_1^{2/3}$  and similarly  $A_2 = 1.091 N_A^{1/3} V_2^{2/3}$  ( $N$  is Avogadro's number and  $V$  molar volume).

It is supposed that  $G_1^{E,s}/G_1^E = G_2^{E,s}/G_2^E = 0.83$  and then thermodynamic database for  $G_1^E$ ,  $G_2^E$  make us possible to calculate  $\sigma$  and  $x_2^s$  by simple computer program (<http://www.gsp.ipm.cz/kroupa/>) having complementary database for density and surface tension of pure components.

# Surface tension of liquids - example

R.Picha, J.Vrestal, A.Kroupa: CALPHAD 28 (2004) 141-146

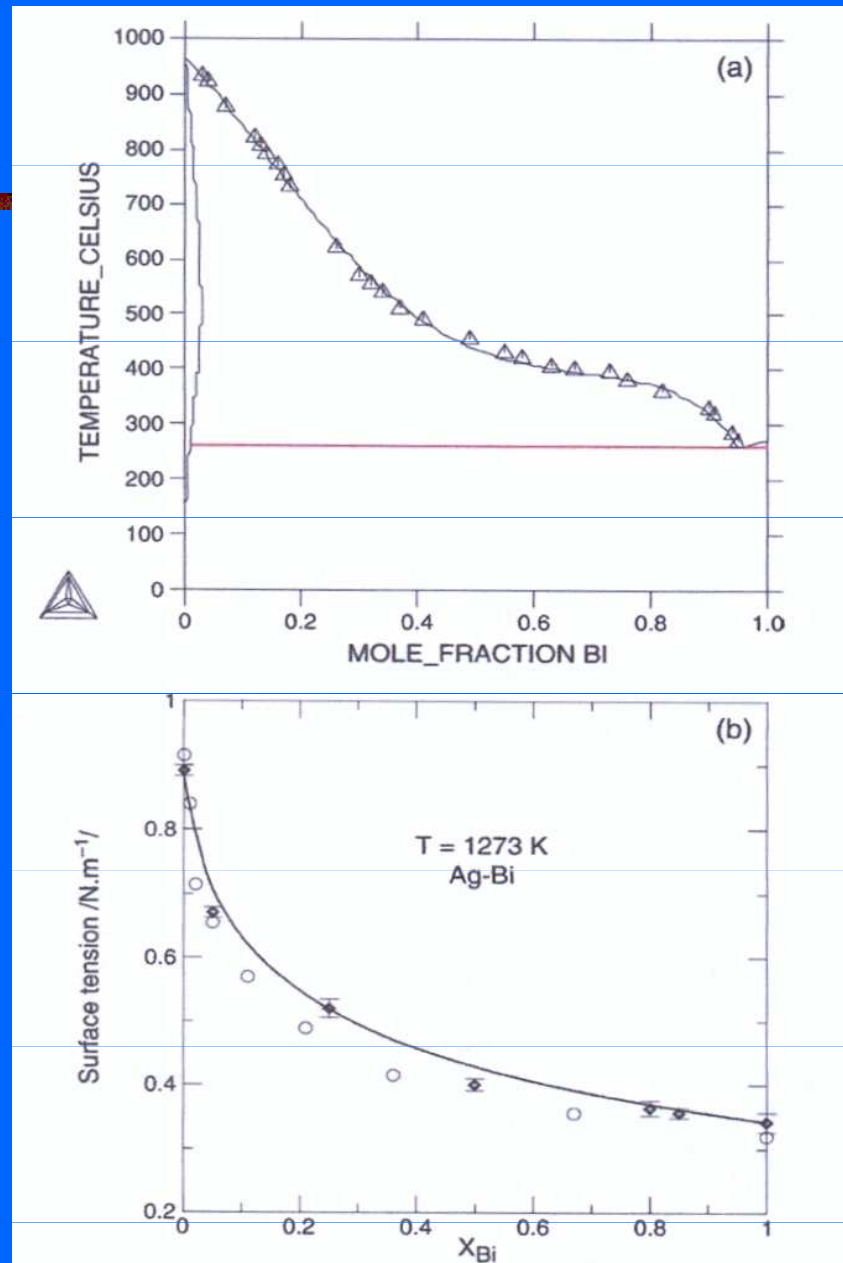


Fig. 1. (a) Phase diagram of the Ag-Bi system. Experiments from [25]. (b) Surface tension of the Ag-Bi system at 1273 K. Experiments from [12]—squares, [13]—circles-(1233 K).

# Nucleation in materials

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For the formation of the new phase in nucleation stage, the surface energy of the new phase is even more important than that for bulk phase.

Classical nucleation theory gives for critical radius of spherical particle of the new phase:

$$r_c = 2 \sigma V_m / \Delta G_m$$

(for  $r > r_c$ : spontaneous growth of nucleus)

Where  $\sigma$  is the surface energy,  $V_m$  is the molar volume of the new phase and  $\Delta G_m$  is the difference in Gibbs energy between the new and old phases („driving force“)

For solid phase, it is difficult to calculate  $\Delta G_m$  exactly. Only approximative calculations are available.

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# Examples using databases

## Multicomponent phase diagram calculations

High-speed steel, 4% Cr, 9% Mo, 1.5% W, 1%V, 8% Co (rest Fe), C-varying.  
Isopleth - reliability of lines is comparable with experimental determination – must be verified, but it helps to alloy design substantially

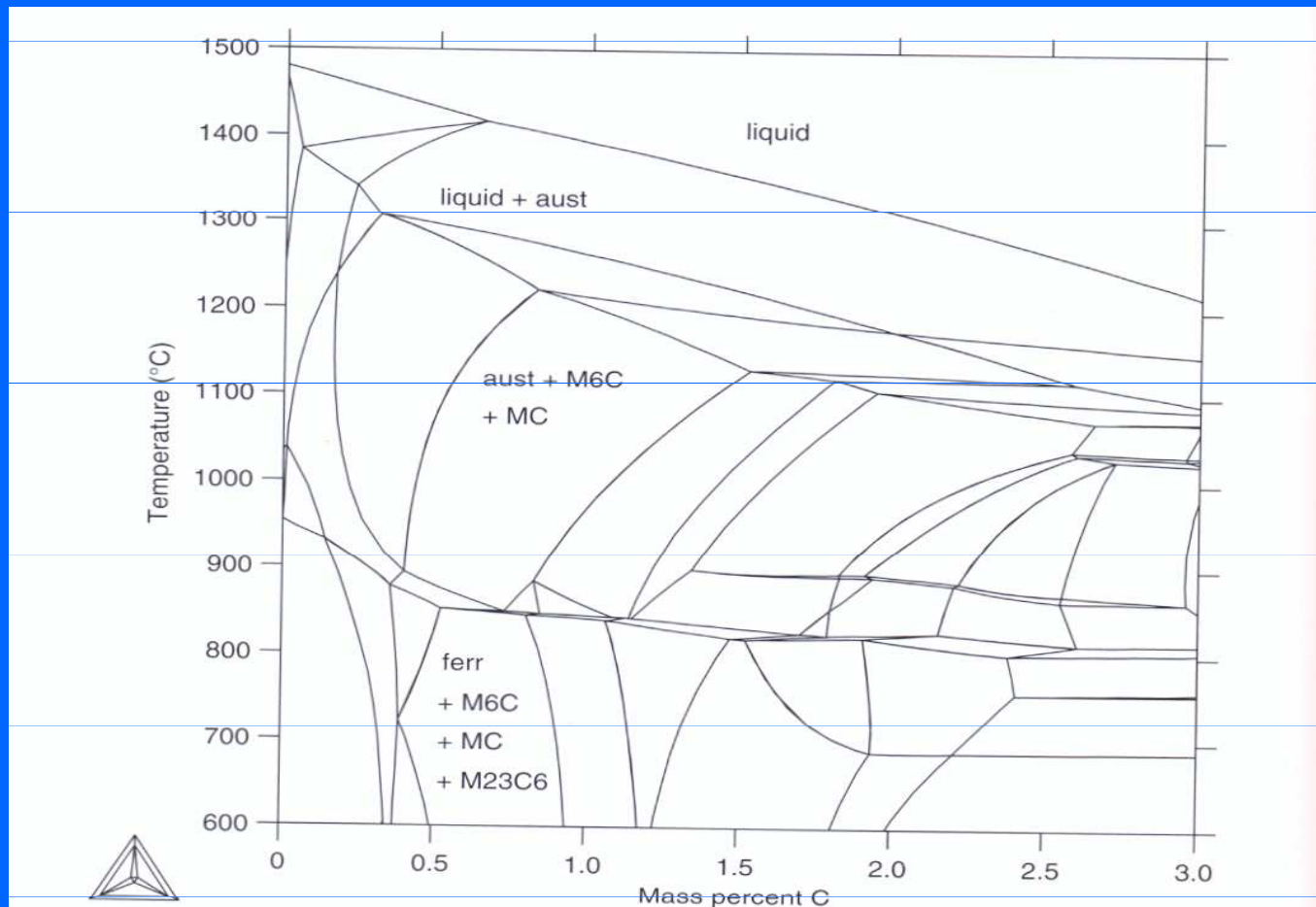


Figure 8.2 An isoplethal section of a high-speed steel. The lines indicate where a phase appears or disappears (zero-phase-fraction lines). The stable phases in some regions have been indicated; to write all of them on the figure would be too confusing.

# Examples using databases – cont.

- A.Kroupa, J.Havránková, M.Coufalová, M.Svoboda, J.Vřešťál: Journal of Phase Equilibria 22 (2001) 312 – 323 – Improvement of thermodynamic description of carbides – important for long-term exploitation of that material (improved database for Fe-Cr-Mo-V-C system)

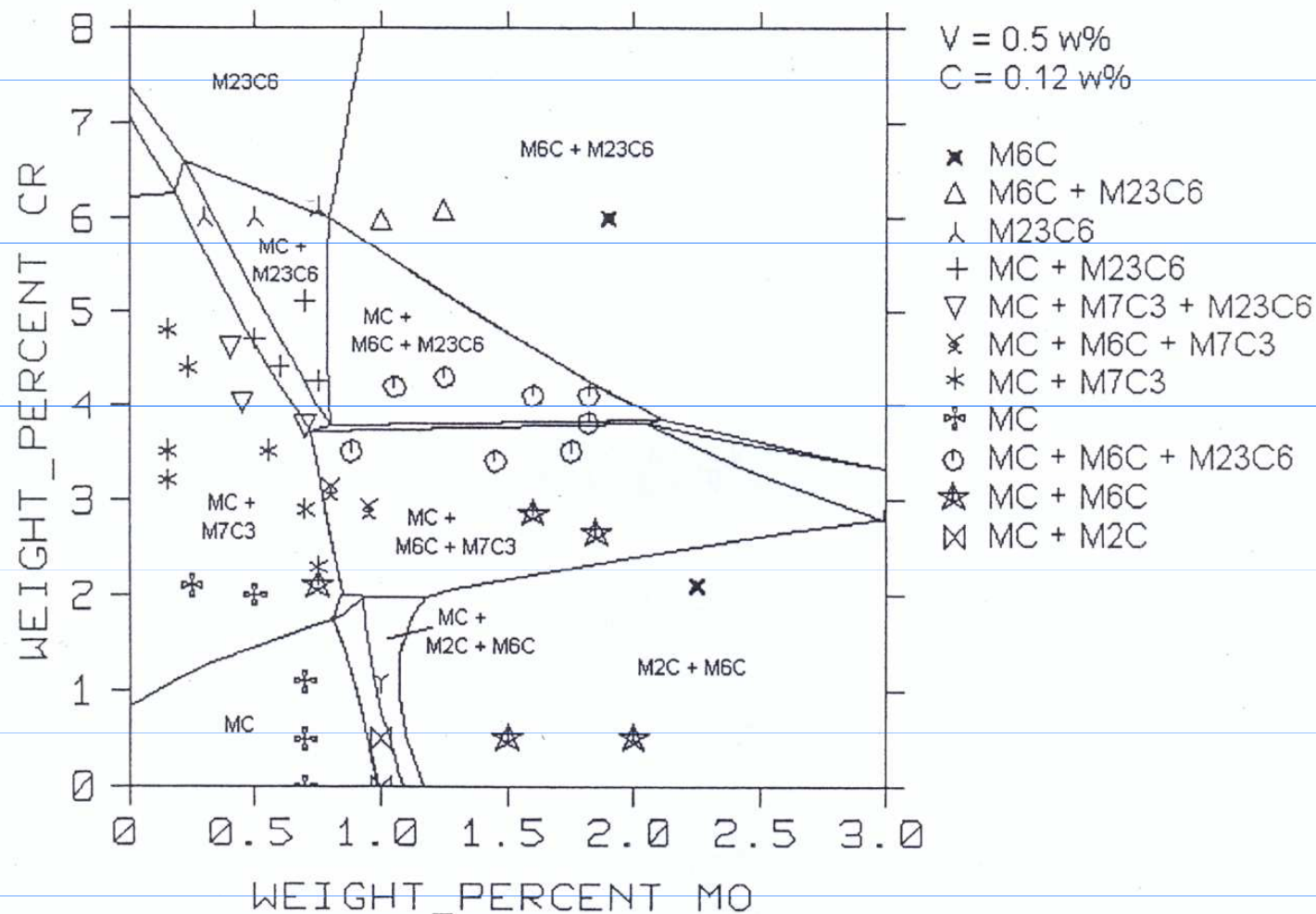
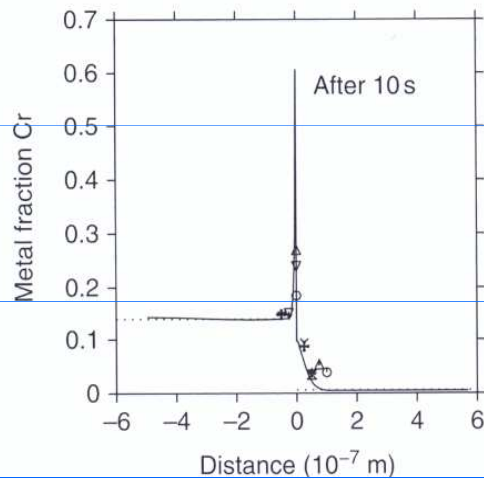


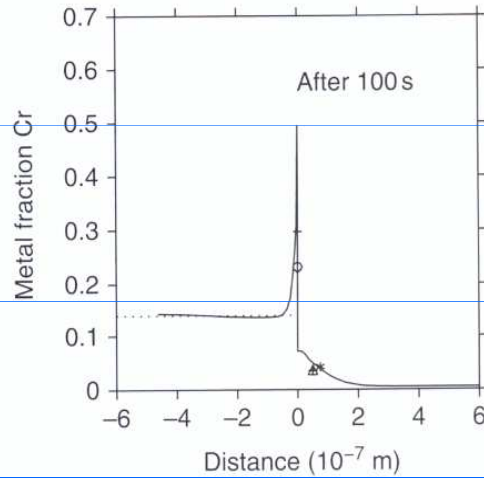
Fig. 3 Phase diagram of the Fe-Cr-Mo-V-C system at 973 K for 0.12 wt.% C and 0.5 wt.% V. Experimental results are taken from [1972And]

# Examples using databases – cont.

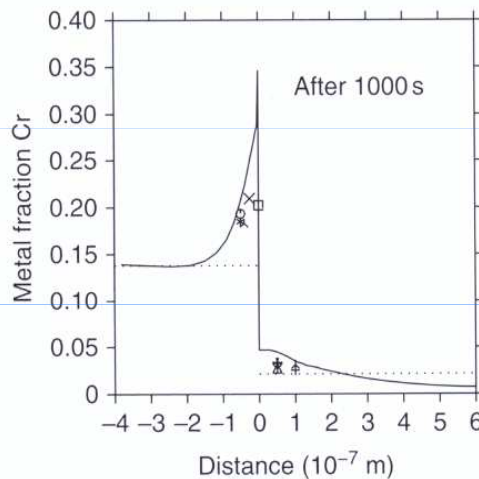
- Simulation of phase transformation by DICTRA: one dimensional diffusion problem solved using thermodynamic calculations of driving force for nucleation and thermodynamic factor for diffusion outside the stability range



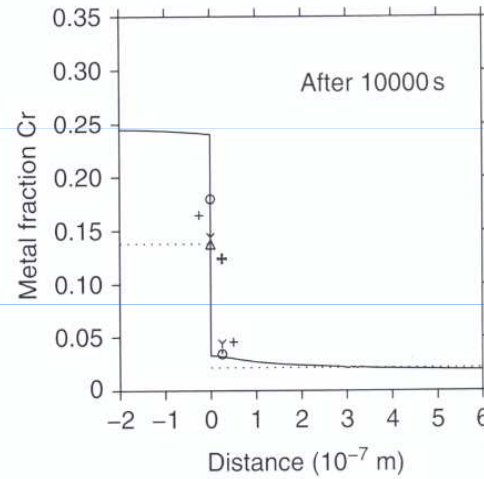
(a)



(b)



(c)



(d)

Dissolution of spherical cementite particle in an Fe-Cr-C austenite matrix during heating.

Assumption of local equilibrium at the interface (cementite surface)

Chromium has an effect of slowing down the transformation – dissolution of cementite particle in Fe-C system takes less than 1 sec.

Figure 8.3 Concentration profiles of Cr across the interface after various times. The origin of the horizontal axis is always at the interface.

# Examples using databases – cont.

Dissolution of cementite in Fe-Cr-C austenite

Independent thermodynamic assessment of Fe-Cr-C system and mobilities of Cr and C in austenite and cementite were needed

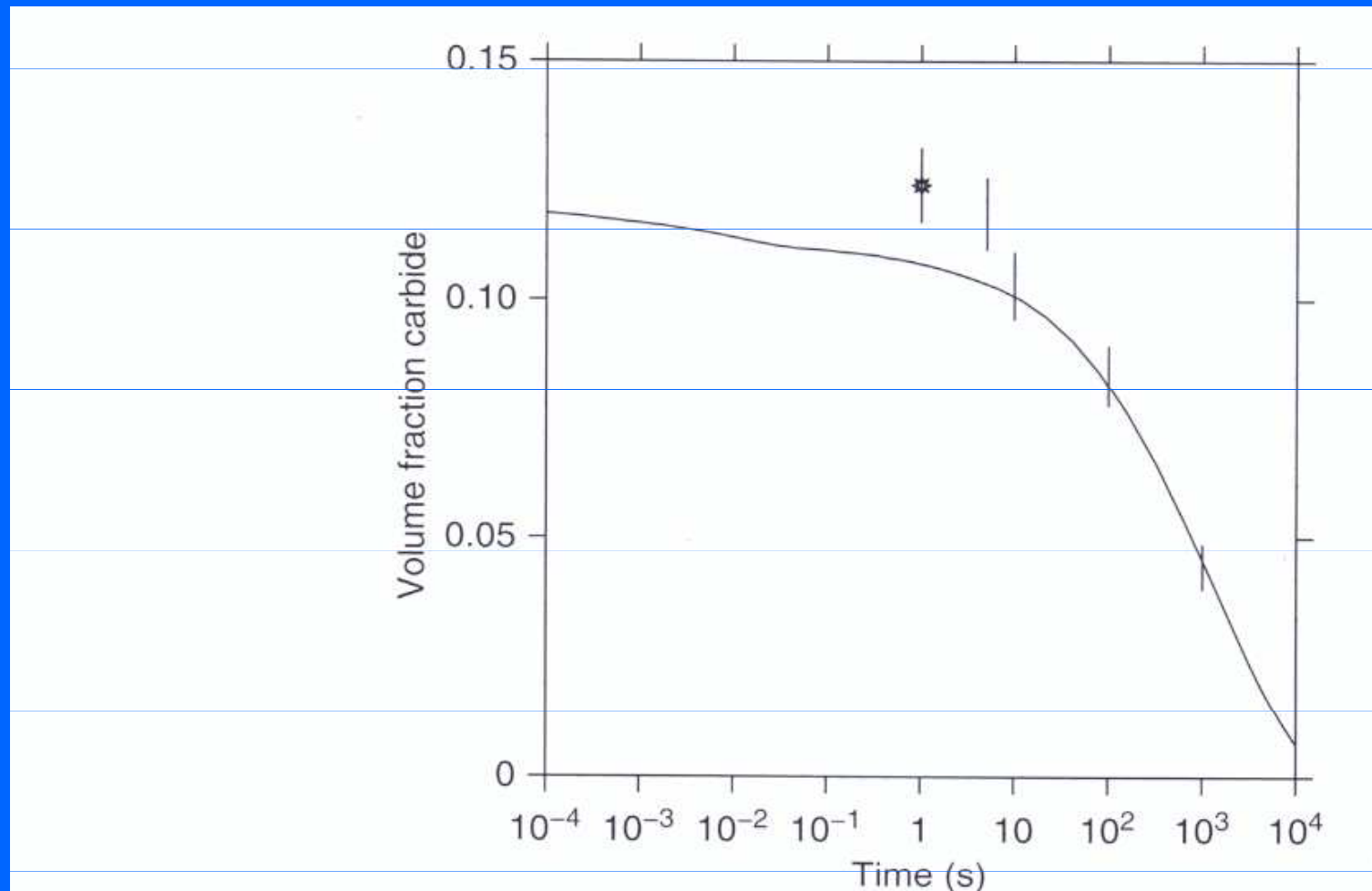


Figure 8.4 The volume fraction of carbide.

# Examples using databases – cont.

- Scheil (1942) - Gulliver (1913) solidification model:
- No diffusion in solid phase – liquid is assumed to be homogeneous

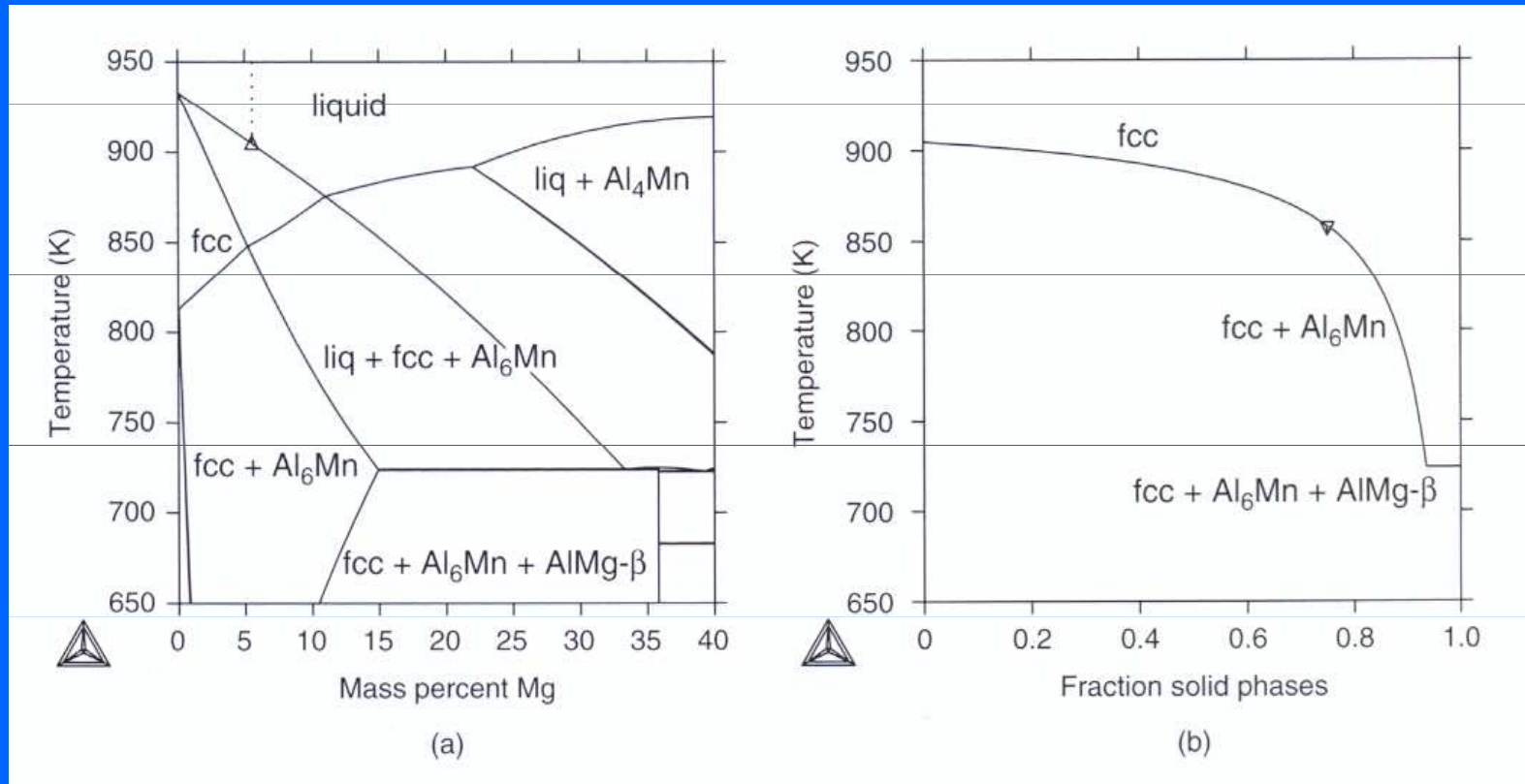


Figure 8.7 The phase diagram for Al-0.4Mn-Mg is shown in (a). A curve of the fraction of solid versus temperature from a Scheil-type solidification simulation is shown in (b).



# Examples using databases – cont

**Phase field method:** simulation of phase transformation in two or three dimensions. Grid is imposed and the amounts of phases at each grid are calculated based on thermodynamics and kinetic data assumed not „sharp“, but „diffuse“ interface (MICRESS phase-field software – (<http://www.micress.de>), TQ Thermocalc interface (<http://www.thermocalc.com>), and COST-507 light-alloy database. (Al-5.5Mg-0.4Mn)

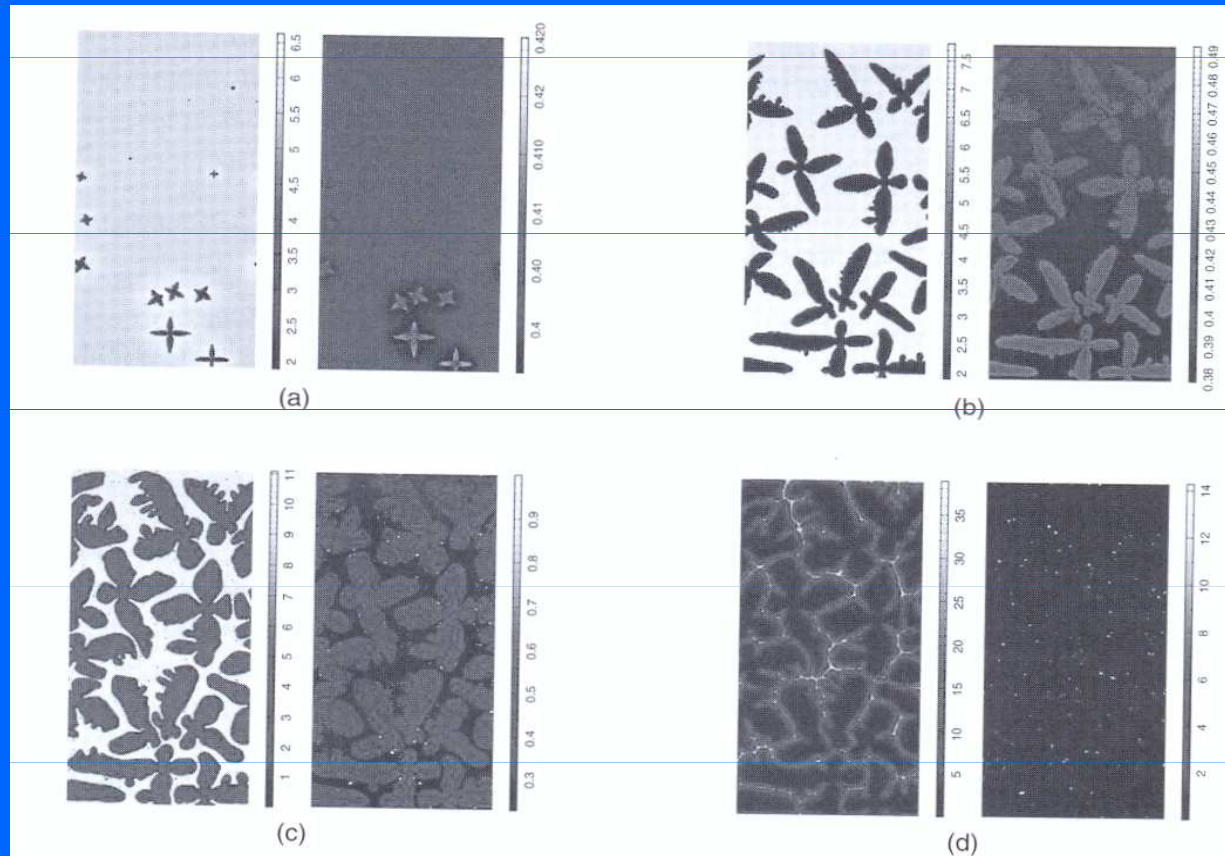


Figure 8.8 Steps in the phase-field-method simulation of the solidification. (a) Temperature just below liquidus after 1s, the Al dendrites have nucleated. (b) The Al dendrites have grown after 16 s. (c) The dendrites after 40 s and the Al<sub>6</sub>Mn phase has nucleated in the liquid. (d) The material is now completely solidified. The composition is displayed as a grayscale. The formation of the second solid phase in the liquid is shown in (c). In (d) the alloy is completely solid. Courtesy of Bernd Böttger.

# Examples using databases – cont.

Sigma phase in corrosion-resistant steel: Fe–20Cr–18Ni–6Mo–0.5Mn–0.7Cu–0.3Si–0.2N

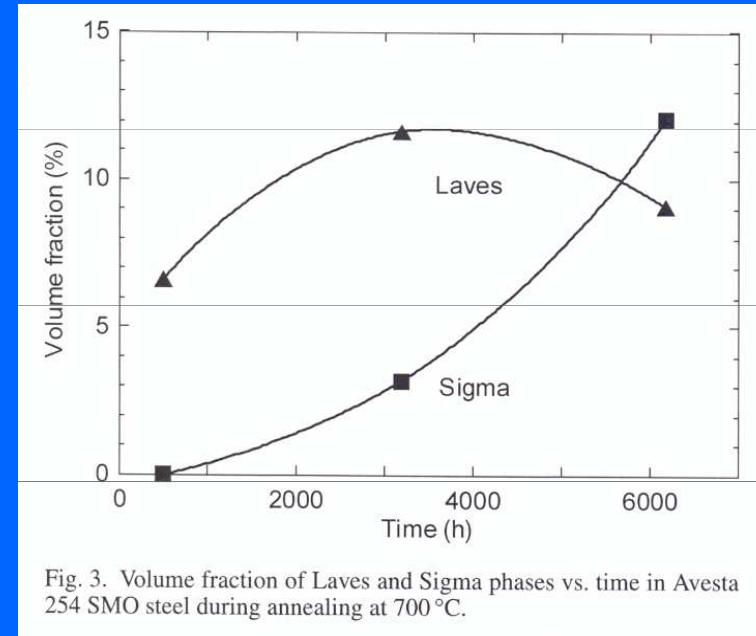
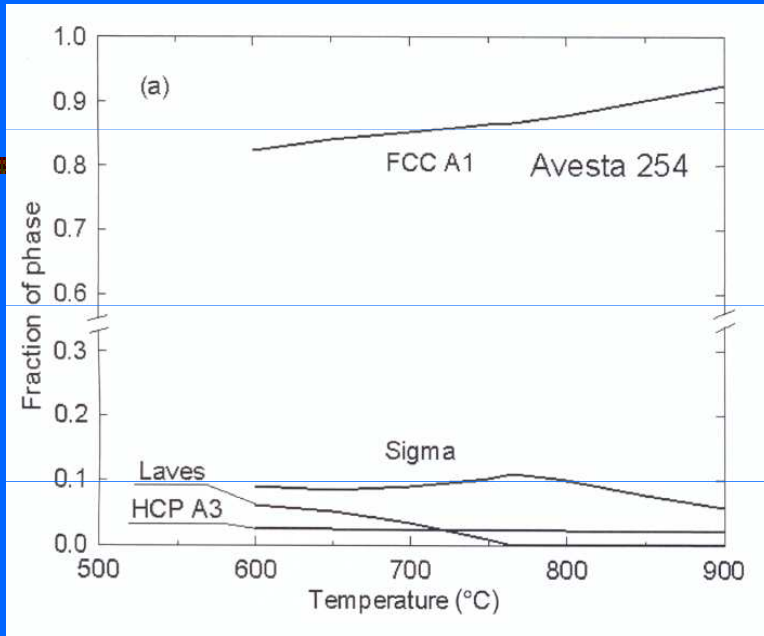


Fig. 3. Volume fraction of Laves and Sigma phases vs. time in Avesta 254 SMO steel during annealing at 700 °C.

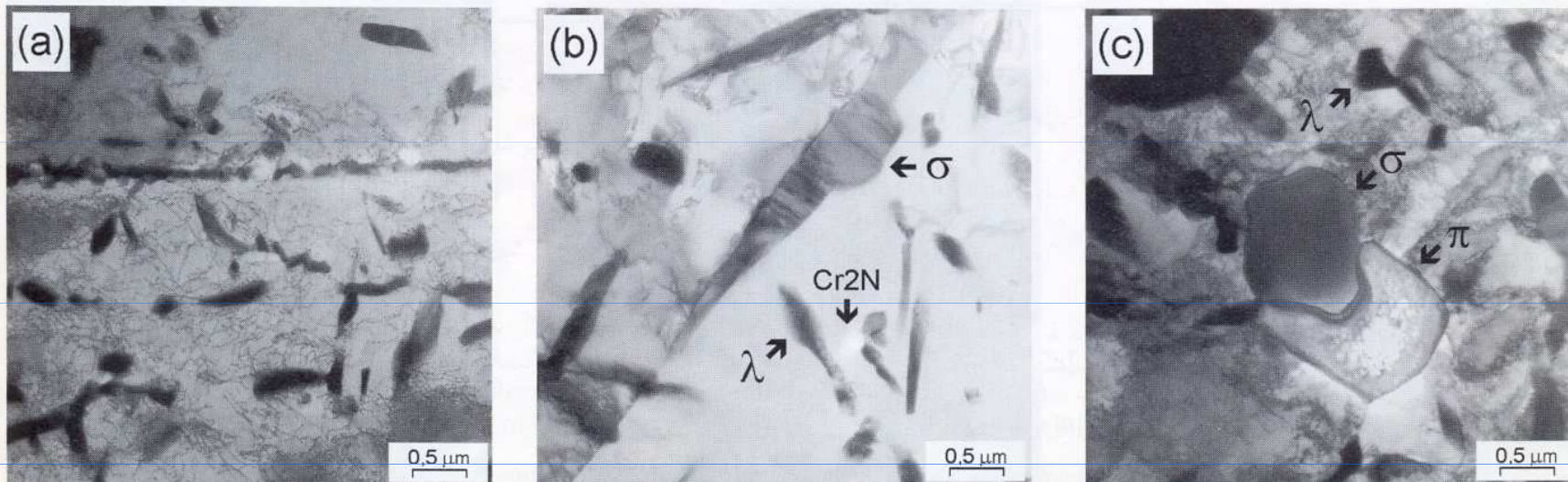


Fig. 2. TEM micrographs showing the microstructure of Avesta 254 SMO steel after annealing for (a) 500 h, (b) 3188 h and (c) 6170 h at 700 °C.

# Examples using databases – cont.

## ■ Solder database – Ag-Cu-Sn (SAC) solder – phase relations

A.Dinsdale, A.Watson, A.Kroupa, J.Vrestal, A.Zemanova, J.Vizdal: Atlas of Phase Diagrams for Lead-Free Soldering. COST office 2008

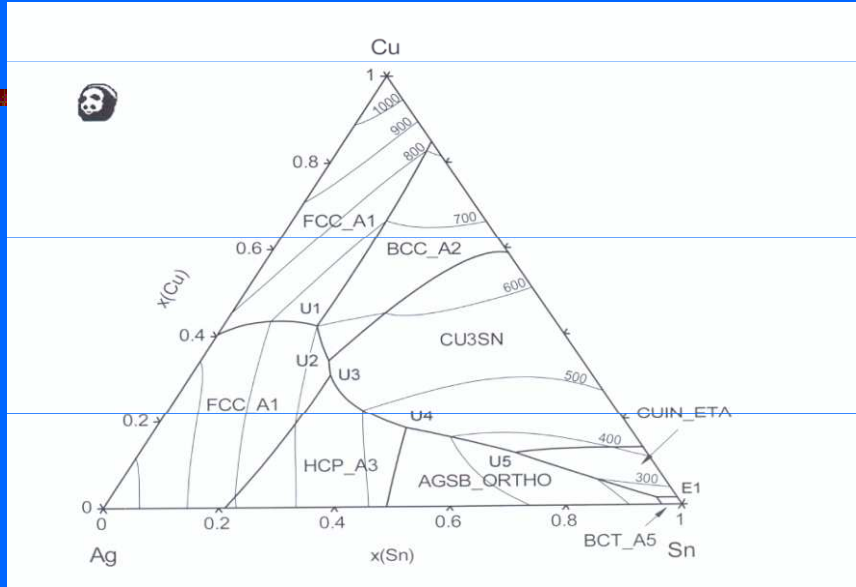


Fig. 106: Liquidus projection of the Ag-Cu-Sn system

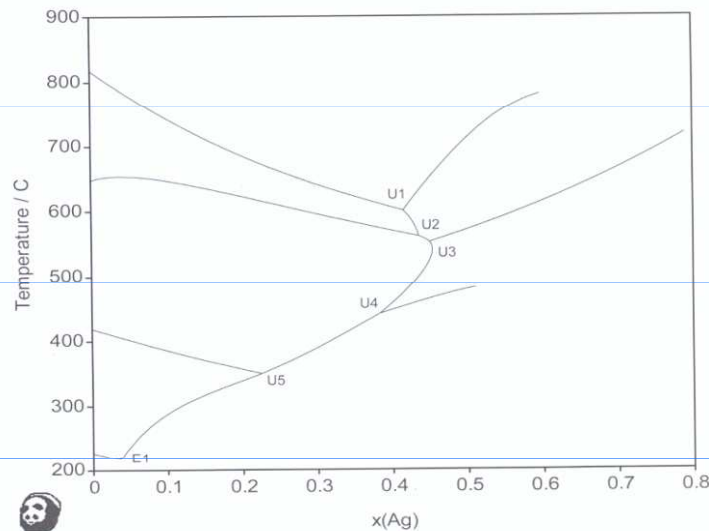


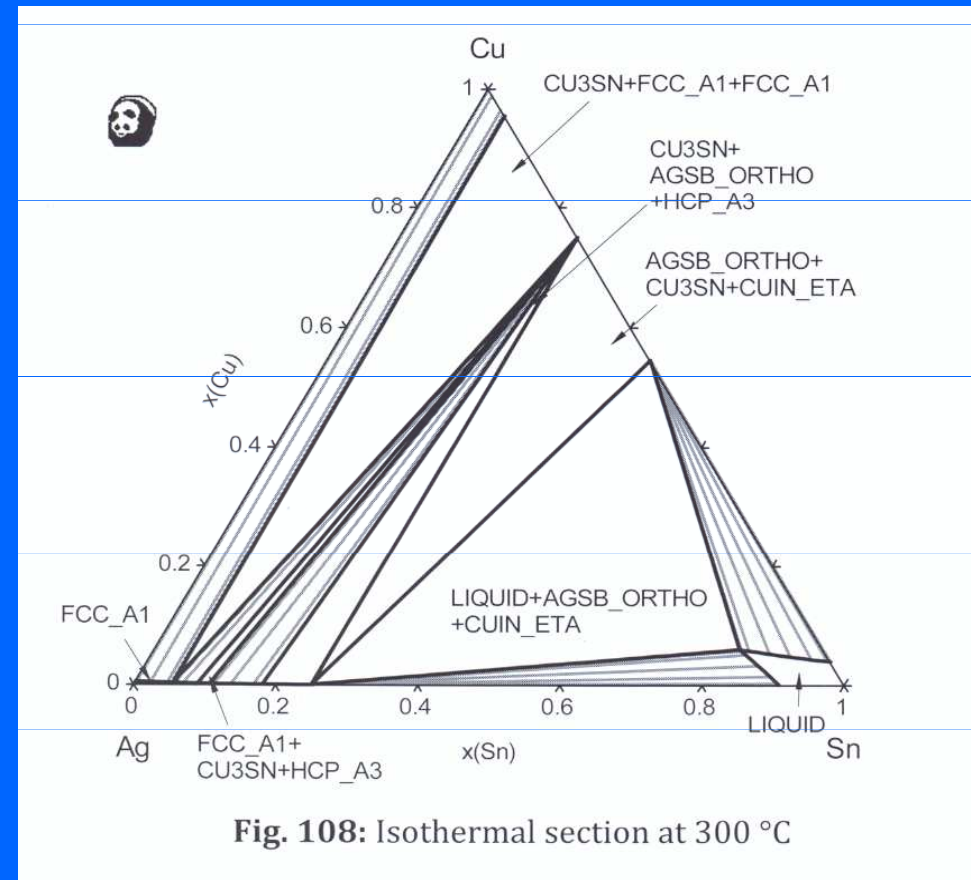
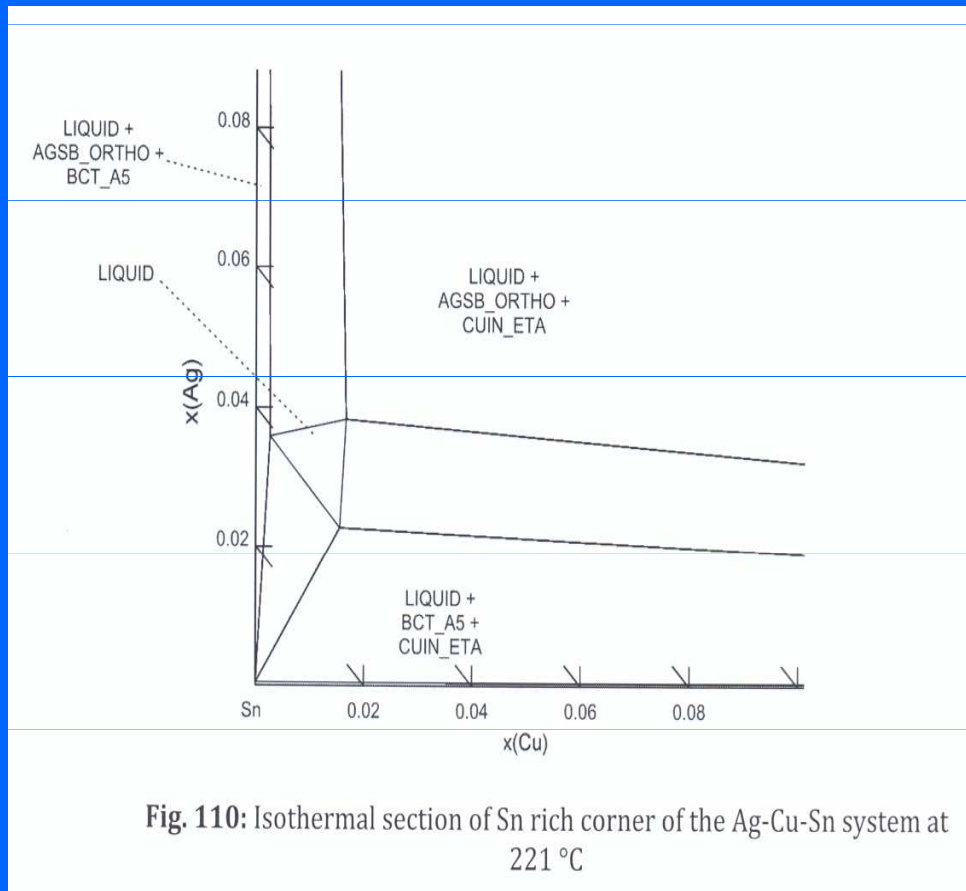
Fig. 107: Liquidus lines in the Ag-Cu-Sn system projected onto the T-  $x(\text{Ag})$  plane

# Examples using databases – cont.

## ■ Solder database – Ag-Cu-Sn (SAC) solder – phase relations

A.Dinsdale, A.Watson, A.Kroupa, J.Vrestal, A.Zemanova, J.Vizdal:

Atlas of Phase Diagrams for Lead-Free Soldering. COST office 2008



# Examples using databases – cont.

Solder database – prediction of ternary diagram based on binary data and verification of it by experiment, Bi-Sb-Sn:Manasijevič D.,Vřešťál J.,Minič D.,Kroupa A.,Živkovič D.,Živkovič Ž.: Journal of Alloys and Compounds 438 (2007)150-157

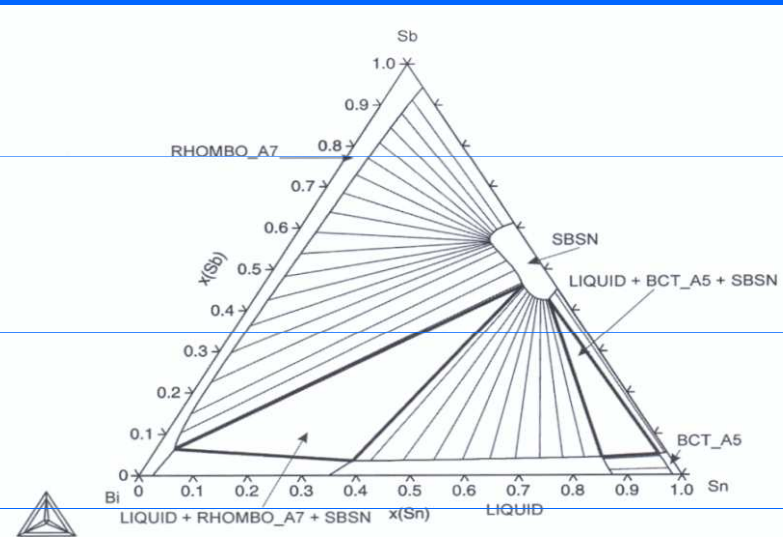


Fig. 176: Isothermal section at 200 °C

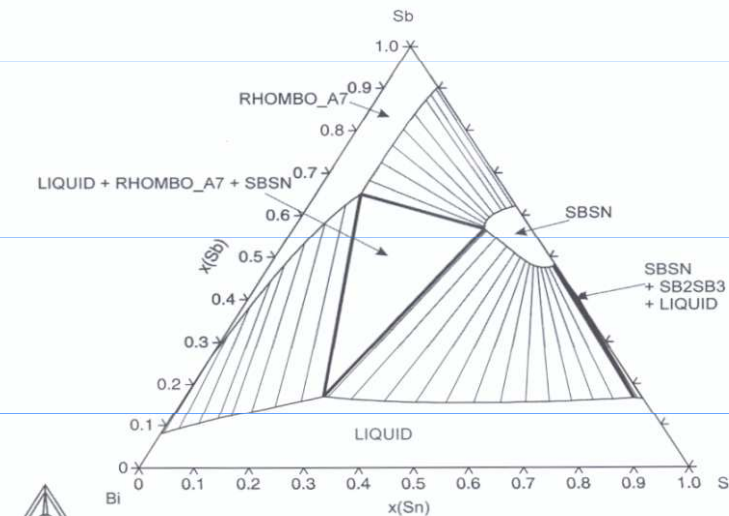
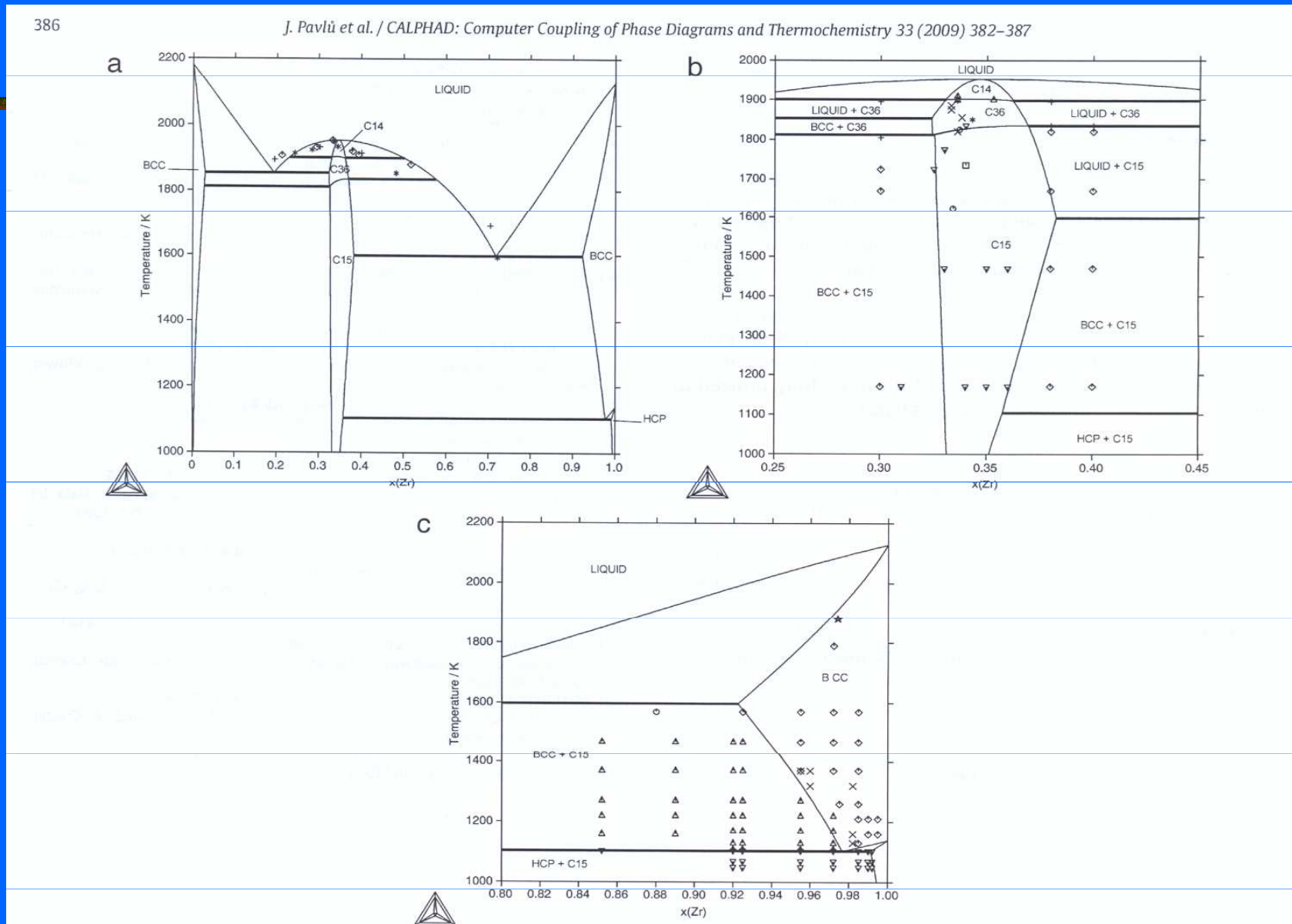


Fig. 177: Isothermal section at 300 °C

# Examples using databases – cont.

- Laves phases database for aircraft engines. System Cr-Zr.

(Special separate database)



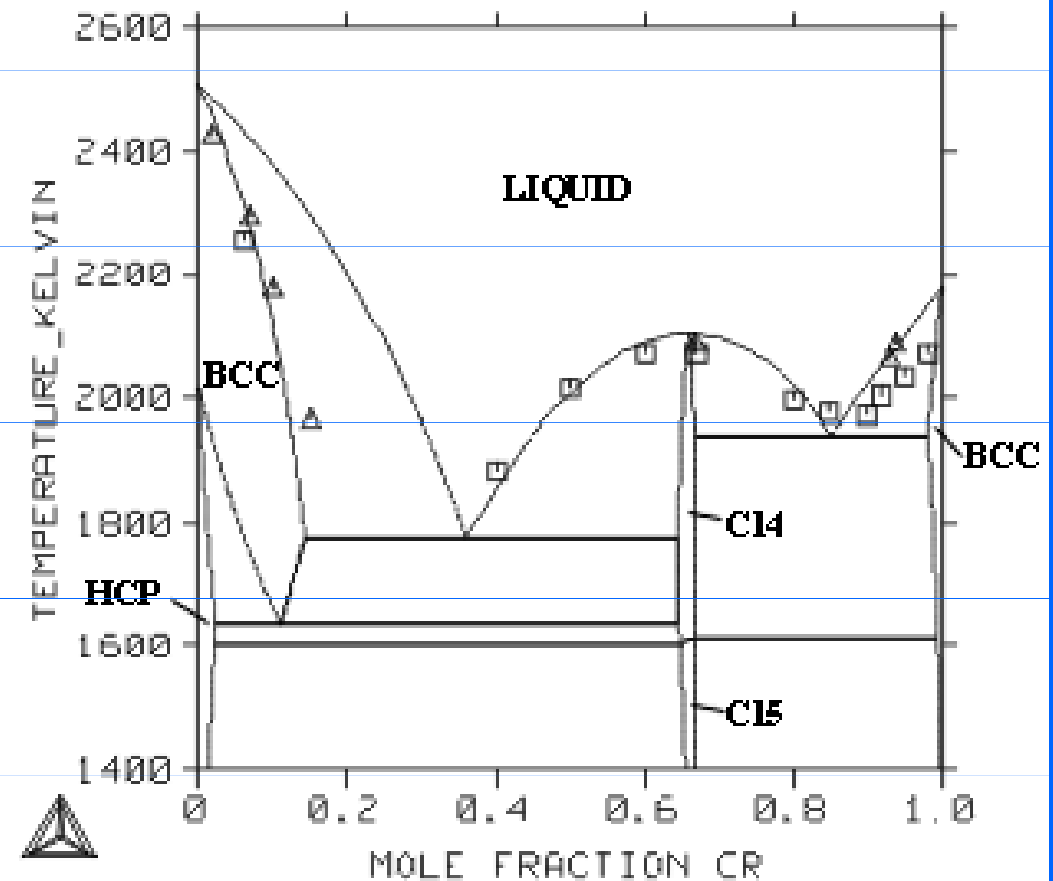
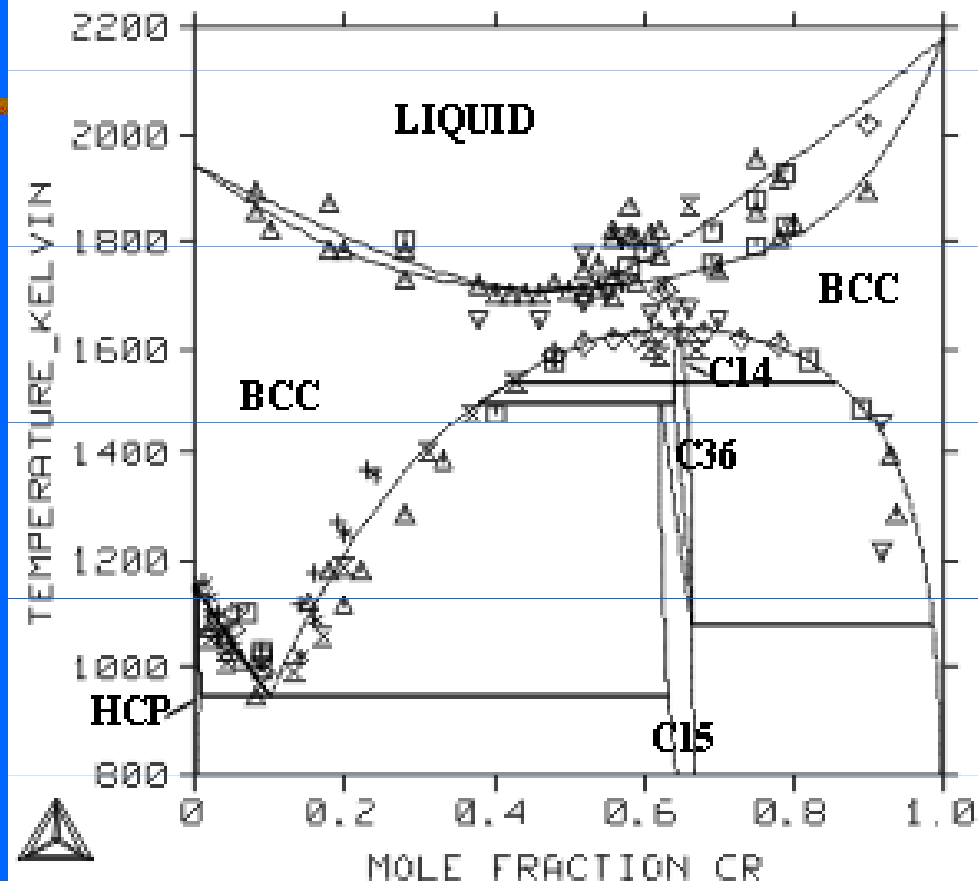
**Fig. 1.** Comparison of the phase diagram of Cr-Zr system calculated in this work with corresponding experimental data. (a) Phase diagram Cr-Zr. (b) Region of stability of Laves phases. (c) The Zr-rich region. Experimental points from various authors are: (a) Liquidus: ★ [8], ◇ [10], + [11]; (b) 3 phases: + [11], 2 phases: ◇ [11], C15: ○ [10], ▽ [11], □ [12], C36: × [11], ★ [12], C14: △ [10]; (c) Solidus: ★ [6], (BCC-Zr + C15): △ [6], ○ [7] (HCP-Zr + C15): ▽ [6] BCC-Zr: ◇ [6], × [9].

# Examples using databases – cont.

(Vrestal J.: CALPHAD XXXVIII Prague 2009, Book of abstracts)  
(Special separate database)

**Cr-Ti**

**Cr-Hf**



Experiments: original sources in (Zhuang 2000)

(Carlson 1968) – squares

(Svechnikov 1965) – triangles

W. Zhuang, J. Shen, Y. Liu, L. Ling, S. Shang, Y. Du, J.C. Schuster, Z. Metallkde 91 (2000) 121

O.N. Carlson, D.G. Alexander, J. Less-Common Metals 15 (1968) 361

V.N. Svechnikov, A.K. Shurin, G.P. Dmitrijeva, Prevrashchen Faz., AN Ukr.SSR 1965 159

# Thermodynamic models of phases

■ BCC: 2 \ 1 3

■ HCP: 2 \ 1 0.5

■ Liquid: 1 \ 1

■ Laves\_C14: 2 \ 2 1 or 3 \ 4 6 2

■ Laves\_C15: 2 \ 2 1

■ Laves\_C36: 2 \ 2 1 or 3 \ 8 12 4 (simplified)

## ■ Assignment of lattice sites in models

■ Sublattice	1	2	3
■ Laves_C14	4f	6h	2a (Cr)
■ Laves_C15	8a	16d	(two sublattice model)
■ Laves_C36	4e, 4f	6g, 6h	4f (Cr)

**Ab initio values (NEW) for  $\Delta H^\circ(T=0K)$  for Cr-Ti and Cr-Hf Laves phases C14, C15, C36 vs. SER phases (all combinations) – not changed in assessment – thermodynamic data!**



# Parameter values of solution phases: Cr-Ti, Cr-Hf (in J/mol of atoms) – adjusted to experimental data

## Cr-Ti

[Zhuang 2000]

BCC

$$L^0 = 11824$$

$$L^1 = 5012$$

HCP

$$L^0 = 25500$$

Liquid

$$L^0 = -992$$

$$L^1 = 1811$$

## Cr-Hf

[Yang 2008]

$$L^0 = 42847.5 - 12 * T$$

$$L^1 = 12064$$

$$L^0 = 43774 + 0.64729 * T$$

$$L^1 = 15000$$

$$* L^0 = -30000 + 8 * T$$

$$* L^1 = 3800$$

\* this work

Liquid phase Cr-Hf: Miedema's guess:  $L^{0,H} = -9000$  (J/mol of atoms), Tanaka's rule:  $L^H/L^S = 1150$  K

# Contribution of vibrational heat capacity and vibrational entropy to the Gibbs energy – influence of temperature

$$G = \Delta H_o + \int_0^T \Delta C_p \cdot dT - T \int_0^T (\Delta C_p / T) \cdot dT$$

$$\Delta H_o = E_o^L - E_o^{SER} \quad (0 \text{ K})$$

$$\Delta C_p = C_p^L - C_p^{SER} = a + bT$$

$$G = \Delta H_o + T(a - b - a \ln T) + (b/2)T^2$$

(assume:  $b = 0$ ,  $\Delta C_p = a$ )

$$G \cong \Delta H_o + Ta(1 - \ln T)$$

**New: (  $\Delta C_p(T - T \ln T)$  – adjusted)**

# How to calculate vibrational contribution to heat capacity?

## New: Contribution of heat capacity

- -  $\Delta C_p^{L-SER}$  is more positive for less stable C14 than for more stable (at 0 K) C15
- - Term  $\Delta C_p^{L-SER} (T-T\ln T)$  at higher temperature stabilises less stable structures.
- - The origin of this **heat capacity** is more probably vibrational (not configurational) –  
(**it may be calculated from vibrational data – phonon spectra**)
- Programmes calculating phonon spectra:
  - ABINIT – NL – free
  - PHONON – PL - commercial
  - MEDEA – US - commercial

# Parameter values of Laves phases (in J/mol of comp.)

## Cr-Ti system - 3 sublattices for C14 and C36 Laves phases

(**adjusted values are in red** - correspond to the contribution of vibrational entropy and vibrational heat capacity)

**ab initio calculated values are in blue** – not changed during optimization

C14	G(Cr:Cr:Cr):	<b>343598</b>	+ 12*GHSERCR
	G(Cr:Ti:Cr):	<b>-101605</b> <b>-3.15*T + 3.15*T*ln(T)</b>	+ 8*GHSERCR + 4*GHSERTI
	G(Cr:Cr:Ti):	<b>425552</b>	+ 6*GHSERTI + 6*GHSERCR
	G(Cr:Ti:Ti):	<b>151040</b>	+ 2*GHSERCR + 10*GHSERTI
	L(Cr:Ti:Cr,Ti;0):	<b>-20000</b>	
C15	G(Cr:Cr):	<b>81877</b>	+ 3*GHSERCR
	G(Cr:Ti):	<b>-30486</b> <b>-1.412*T + 1.412*T*ln(T)</b>	+ 2*GHSERCR + GHSERTI
	G(Ti:Cr):	<b>171806</b>	+ 2*GHSERTI + GHSERCR
	G(Ti:Ti):	<b>96780</b>	+ 3*GHSERTI
	L(Cr:Cr,Ti;0):	<b>-57900</b>	
C36	G(Cr:Cr:Cr):	<b>333020</b>	+ 12*GHSERCR
	G(Cr:Ti:Cr):	<b>-114138</b> <b>-4.427*T + 4.427*T*ln(T)</b>	+ 8*GHSERCR + 4*GHSERTI
	G(Cr:Cr:Ti):	<b>444722</b>	+ 6*GHSERTI + 6*GHSERCR
	G(Cr:Ti:Ti):	<b>161657</b>	+ 2*GHSERCR + 10*GHSERTI
	L(Cr:Ti:Cr,Ti;0):	<b>-32200</b>	

# Parameter values of Laves phases (in J/mol of comp.)

## Cr-Hf system - 3 sublattices for C14 and C36 Laves phases

(**adjusted values are in red** - correspond to the contribution of vibrational entropy and vibrational heat capacity)

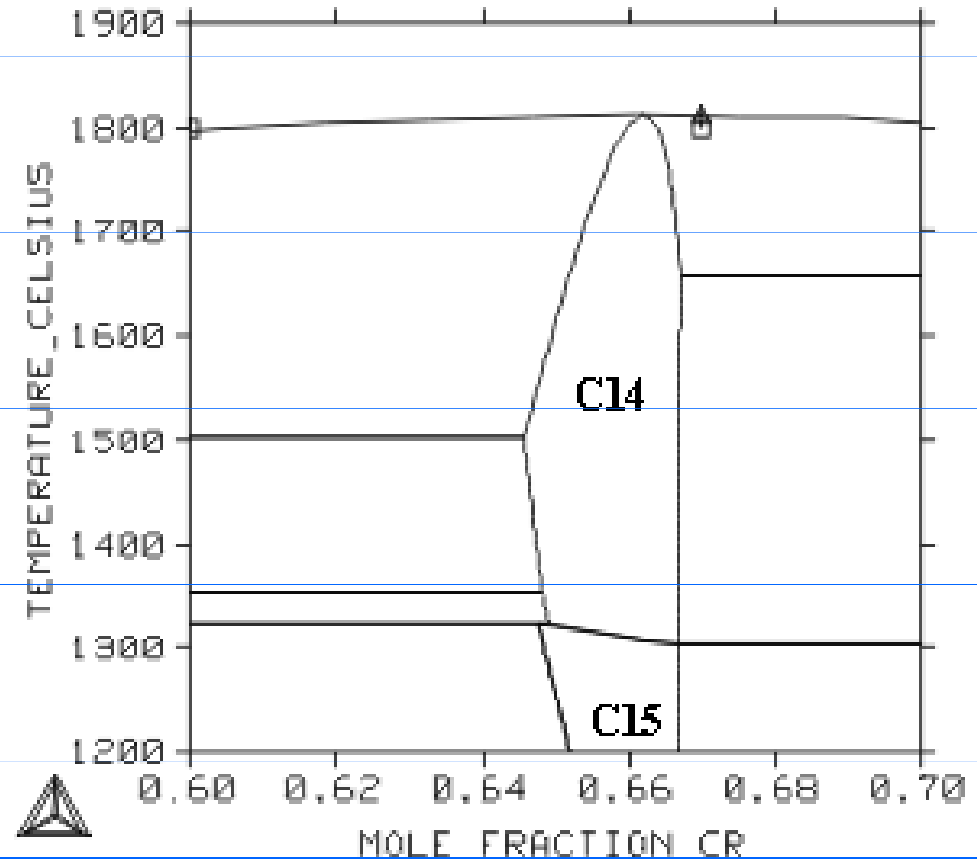
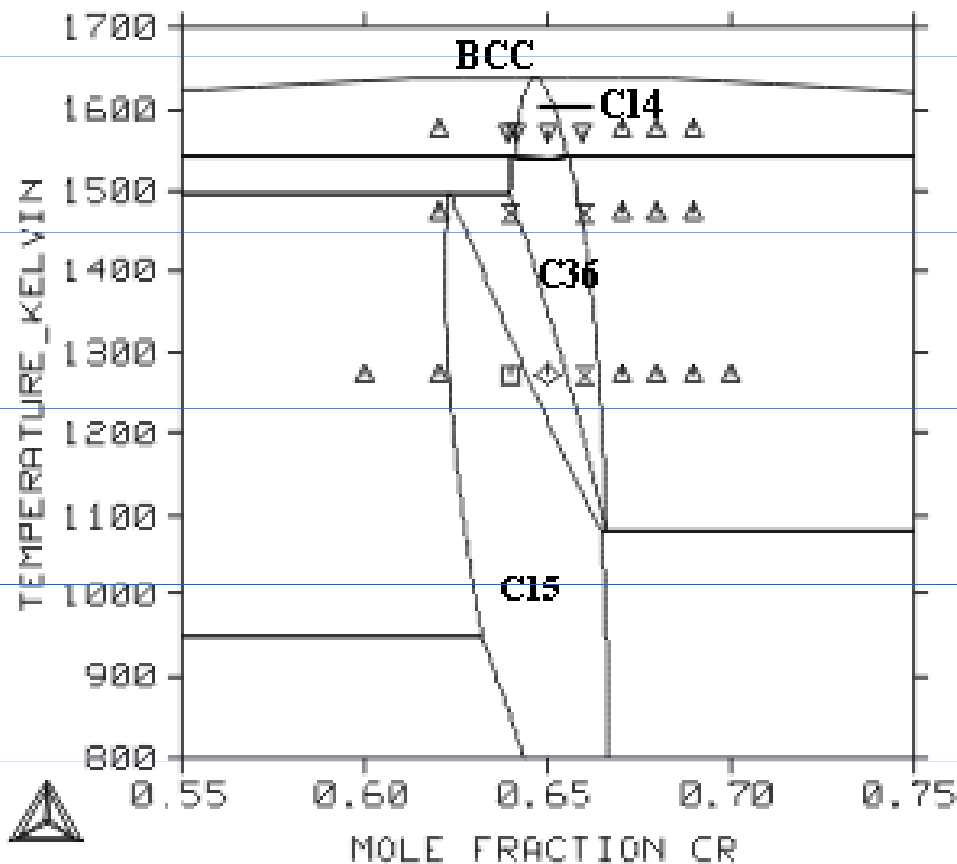
ab initio calculated values are in blue – not changed during optimization

C14	G(Cr:Cr:Cr):	343598	+ 12*GHSECR
	G(Cr:Hf:Cr):	-104379 -2.70*T + 2.70*T*ln(T)	+ 8*GHSECR + 4*GHSEHF
	G(Cr:Cr:Hf):	566979	+ 6*GHSEHF + 6*GHSECR
	G(Cr:Hf:Hf):	231990	+ 2*GHSECR + 10*GHSEHF
	L(Cr:Hf:Cr,Hf;0):	-10000	
C15	G(Cr:Cr):	81877	+ 3*GHSECR
	G(Cr:Hf):	-31130 -0.185*T + 0.185*T*ln(T)	+ 2*GHSECR + GHSEHF
	G(Hf:Cr):	310380	+ 2*GHSEHF + GHSECR
	G(Hf:Hf):	114000	+ 3*GHSEHF
	L(Cr:Cr,Hf;0):	-21000	
C36	G(Cr:Cr:Cr):	333020	+ 12*GHSECR
(prediction)	G(Cr:Hf:Cr):	-116208 -1.72*T + 1.72*T*ln(T)	+ 8*GHSECR + 4*GHSEHF
	G(Cr:Cr:Hf):	597242	+ 6*GHSEHF + 6*GHSECR
	G(Cr:Hf:Hf):	234827	+ 2*GHSECR + 10*GHSEHF
	L(Cr:Hf:Cr,Hf;0):	-15000	

# Assessment results – Cr-rich region

Cr-Ti

Cr-Hf



Experiments:

(Chen 1995) triangles up, diamond – 2 phase field

Other symbols – single phase fields

(Zhuang 2000) points for  $x_{Cr}=0.6$  and  $0.7$

Chen, K.C., Allen, S.M., Livingstone, J.D.:

Mater. Res. Symp. Proc. 364 (1995) 1401

(Carlson 1968) – squares

(Svechnikov 1965) – triangles

# Conclusion

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## Calphad method

is physically based semiempirical method of calculations of phase diagram on thermodynamic bases.

It represents valuable tool for prediction of stable state of materials which enable us to do prediction of their properties and scientific materials design.

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# Questions for learning

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1. Explain the term „compatibility“ of database
  2. Explain the rules which have to be kept in preparing the database
  3. Explain the use of thermodynamic database for calculation of diffusion phenomena and in phase field method
  4. Explain the use of thermodynamic database for calculation of surface tension of binary and higher-order systems, for nucleation processes and for stability of nanomaterials
  5. Describe process of management and updating of databases
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