

Thermo-Calc Software

TC-Prisma Online Training Course

April 15 - 16, 2025

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www.thermocalc.com

Day 1: TC-PRISMA (Precipitation Module)

09:00	Software Basics
09:30	Examples: Al alloys
10:20	Q & A
10:35	Theoretical Background: Nucleation
11:00	Examples: Cu alloys
11:45	Home assignment
11:50	Q & A

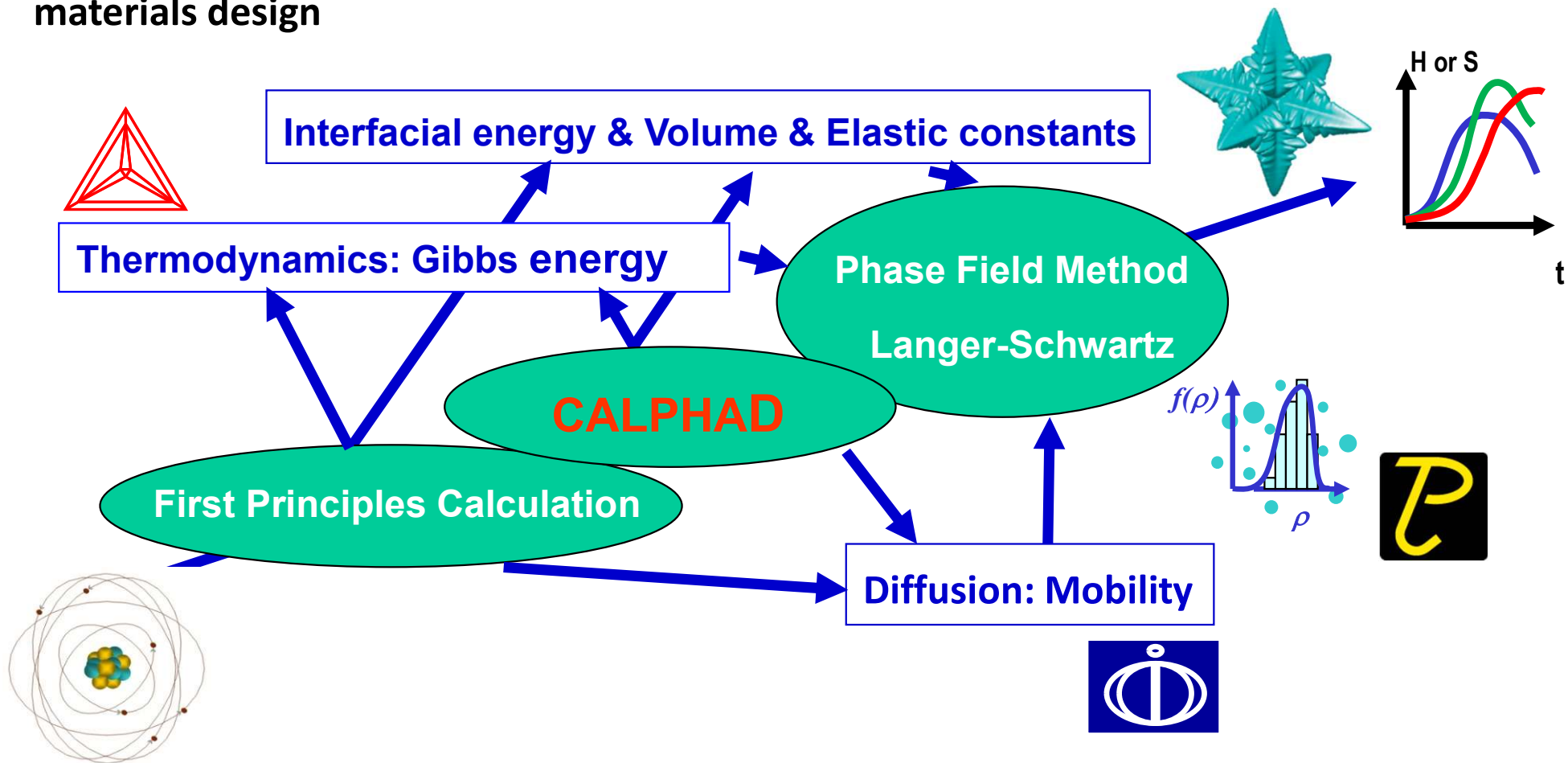
Day 2: TC-PRISMA (Precipitation Module)

09:00	Yesterday's home assignment
09:10	Theoretical Background: Growth Models
09:40	Examples: Ni alloys
10:30	Q & A
10:45	Examples: Steel
11:20	Example: Steel, Para-equilibrium models
11:50	Q & A

Software Basics

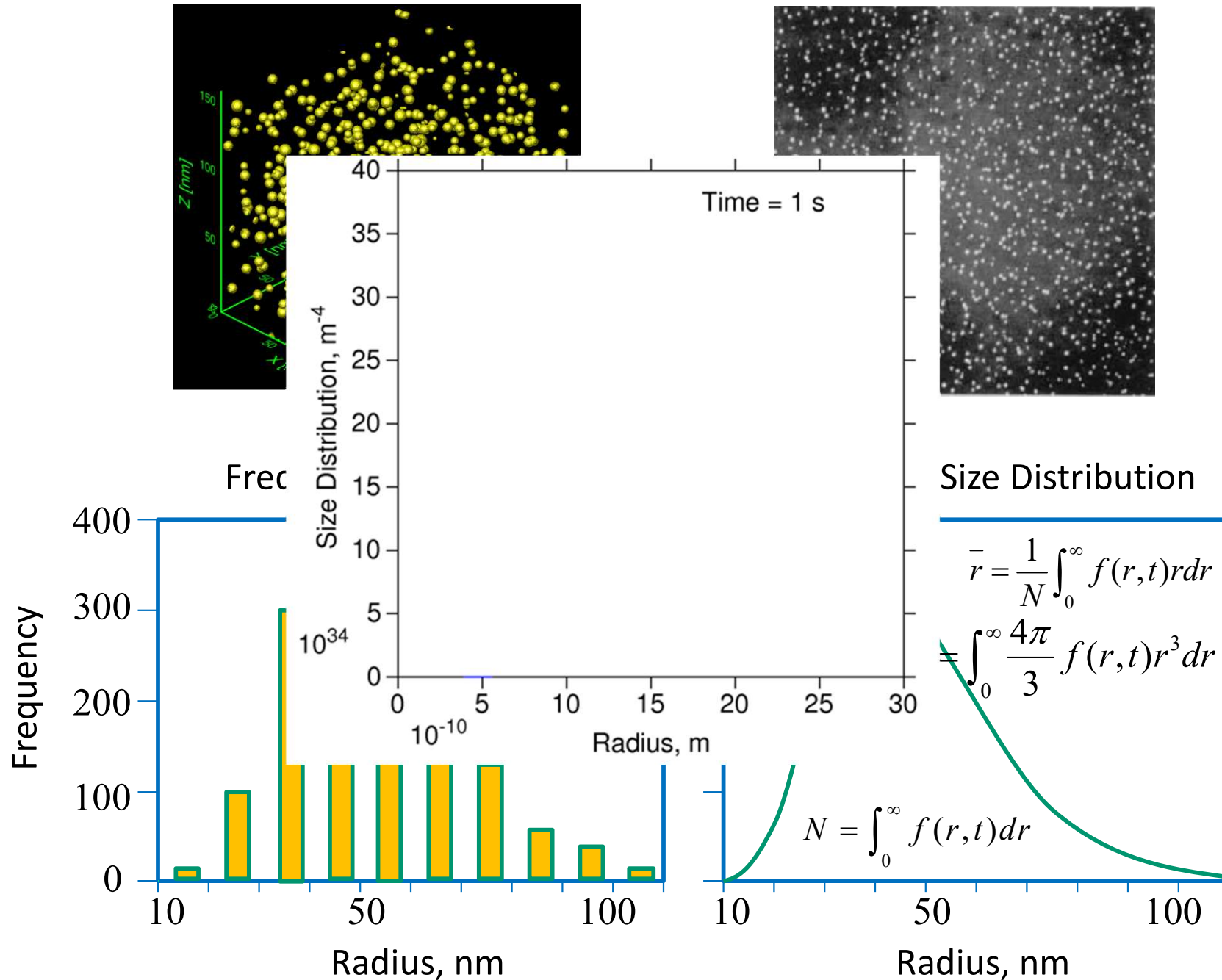
Introduction

CALPHAD method and CALPHAD-based tools play a central role in materials design



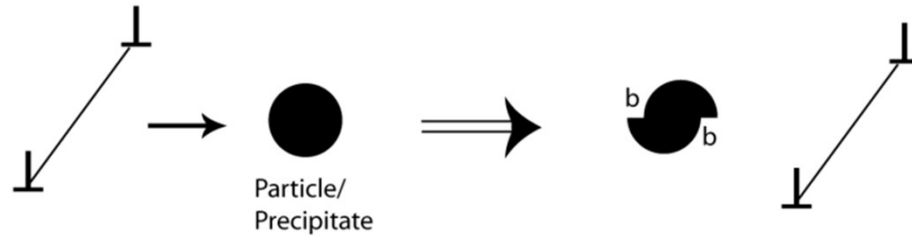
CALPHAD-type databases where each phase is described separately using models based on physical principles and model parameters assessed from experimental and ab initio data provide fundamental inputs for predicting microstructure evolution and materials properties.

Introduction - Precipitation

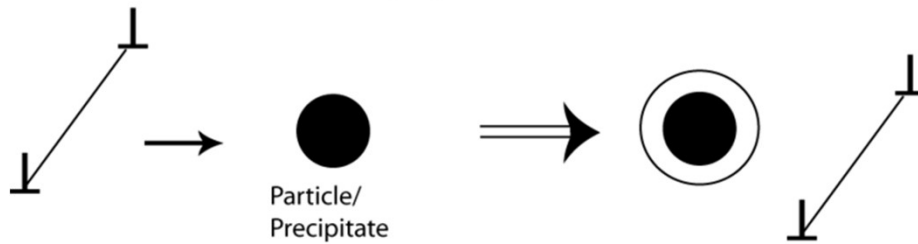


Introduction – Precipitation Hardening

Particle Cutting



Particle Looping

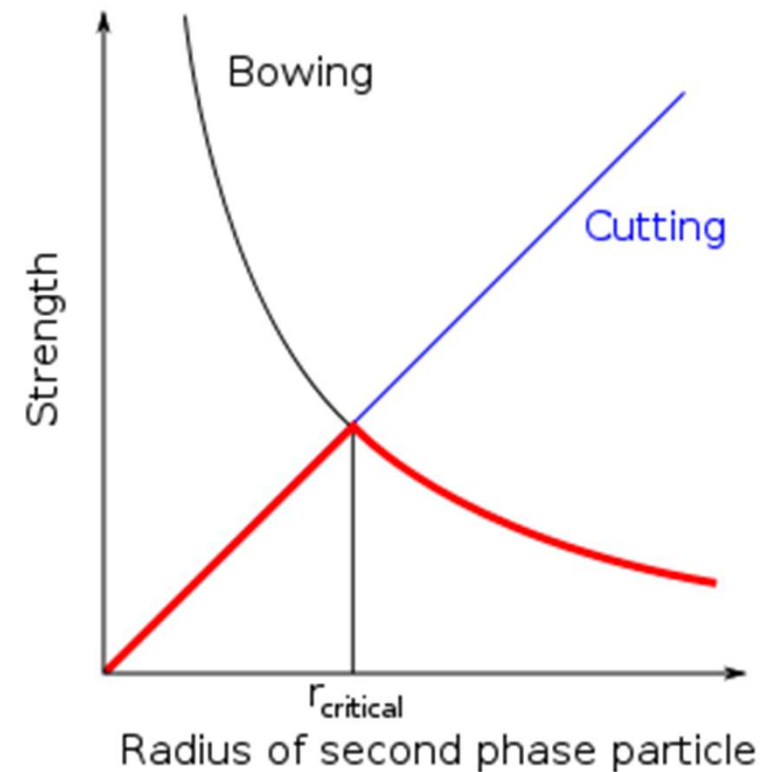


$$\tau = \frac{\pi r \sigma}{bL}$$

r : particle radius
 σ : interfacial energy
 b : Burgers vector
 L : particle spacing
 G : shear modulus

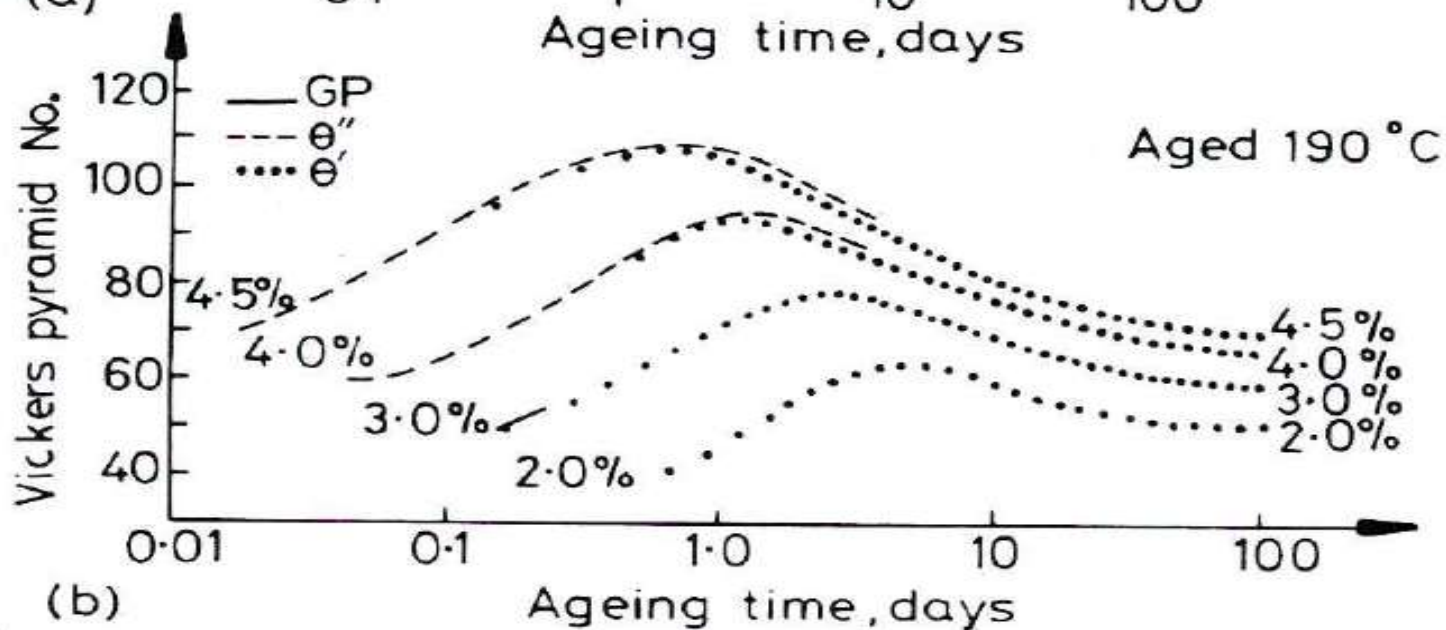
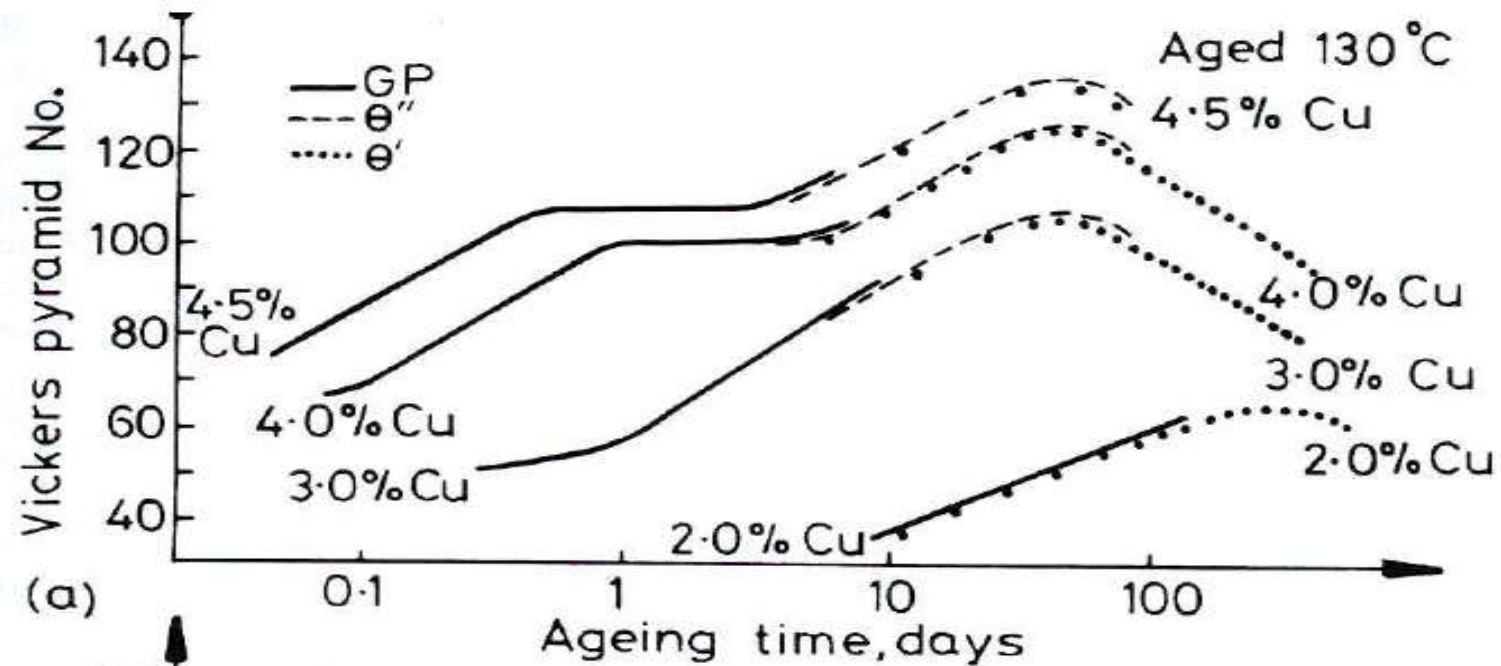
$$\tau = \frac{Gb}{L - 2r}$$

A Simple
Microstructure-Property Model



Precipitation hardening, Wikipedia

Precipitation Hardening



[1992, Porter and Easterling, Phase Transformation in metals and alloys]

Approaches to Multi-Particle Precipitation Modeling

- Continuum Models
 - Single-State Models (Volume Fraction or Particle Size)— JMAK Type Model, LSW Coarsening Theory
 - *Two-State Models (Number Particle Density and Particle Size)— LS (Langer-Schwartz) Theory, Cluster Dynamics*
 - Multi-State Models (+ Particle Morphology) — Diffuse Interface (Phase Field) Models, Sharp Interface (Level Set, Boundary Integral, etc.) Models
- Discrete Models
 - Atomistic Models — Kinetic Monte Carlo, Molecular Dynamics

Computational Cost

A vertical line with a downward-pointing arrowhead, indicating that computational cost increases from top to bottom.

TC-PRISMA A general computational tool for simulating kinetics of diffusion controlled multi-particle precipitation process in multi-component and multi-phase alloy systems. TC-PRISMA is based on Langer-Schwartz theory [1], and it adopts Kampmann-Wagner numerical (KWN) method [2] to compute the concurrent nucleation, growth, and coarsening of dispersed phase(s).

[1] Langer J, Schwartz A. Phys. Rev. A 1980;21:948-958.

[2] Wagner R, Kampmann R. Homogeneous Second Phase Precipitation. In: Haasen P, editor. Materials Science and Technology: A Comprehensive Treatment. Weinheim: Wiley-VCH, 1991. p. 213.

2011
Version 1.0

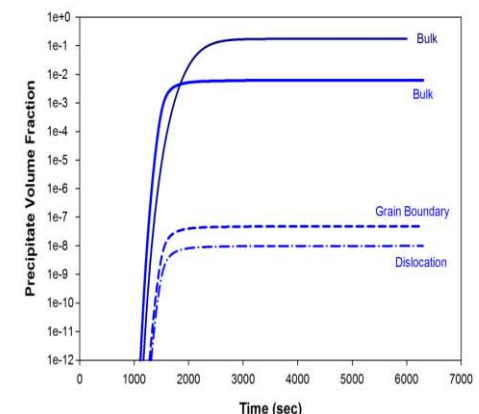
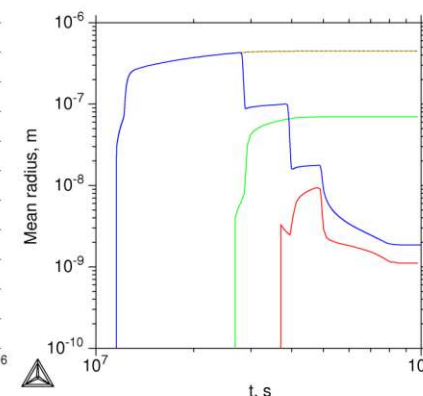
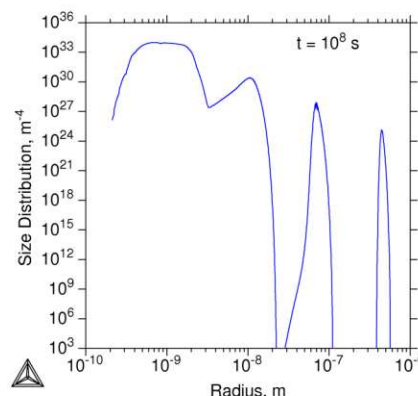
2013
Version 2.0

2016
Thermo-Calc
2016a

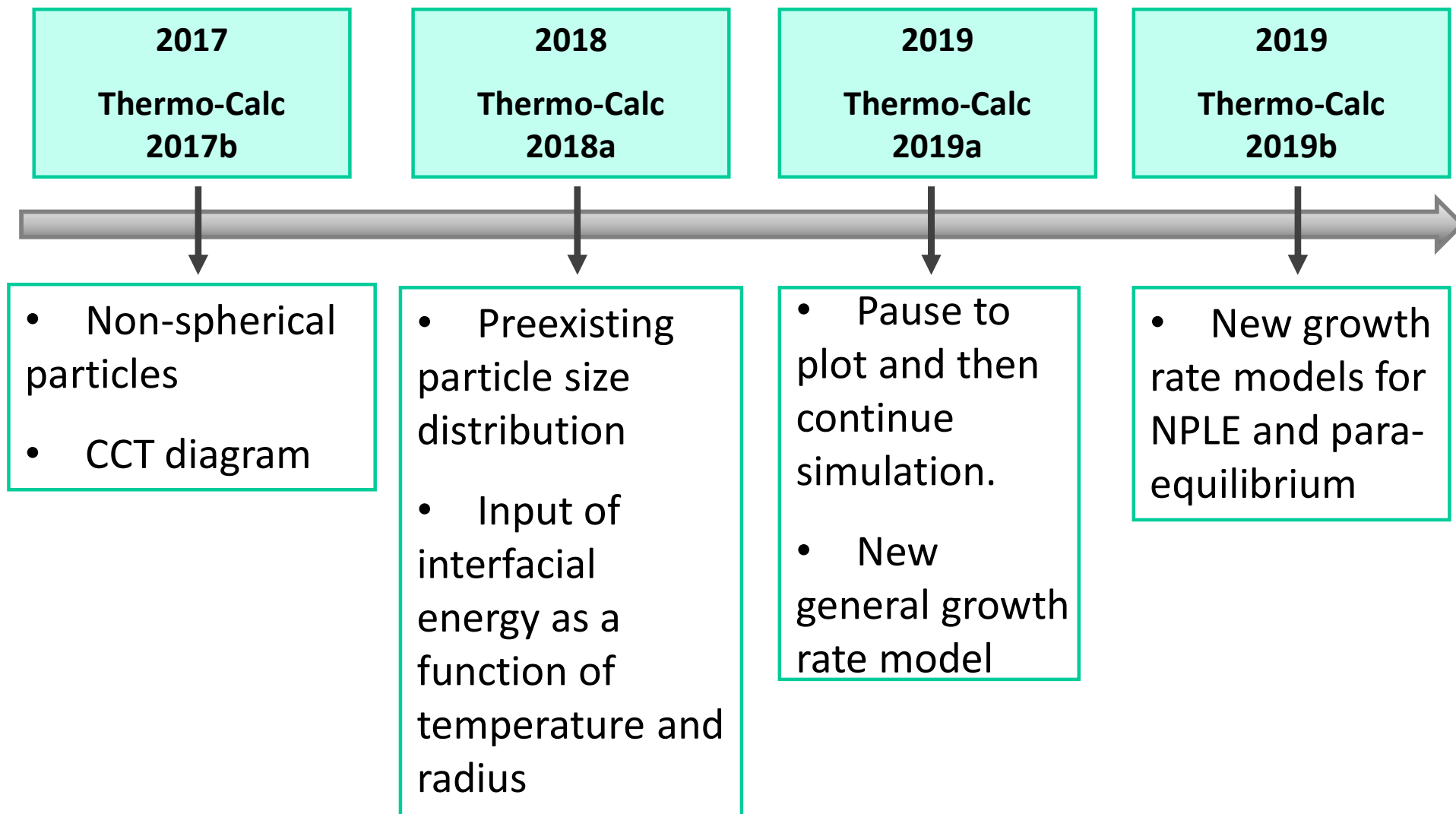
- Link to Thermo-Calc and DICTRA
- Multicomponent Nucleation and Growth
- Different Nucleation types
- Advanced Model for Cross Diffusion and High Supersaturation
- Highly Intuitive GUI

- Non-Isothermal Conditions
- Multi-Modal PSD Analysis
- Interfacial Energy Model

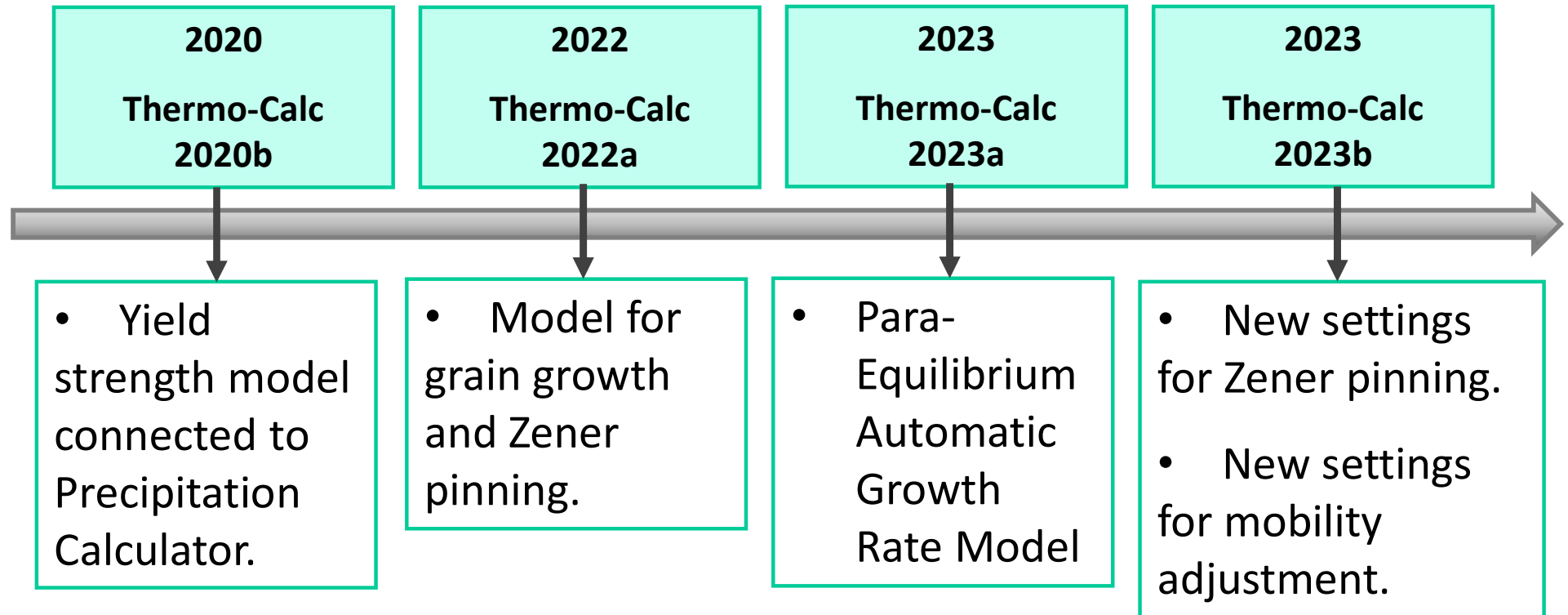
- Multiple Nucleation Types
- Wetting Angle for GB Precipitation
- Integration into Thermo-Calc
-



TC-PRISMA

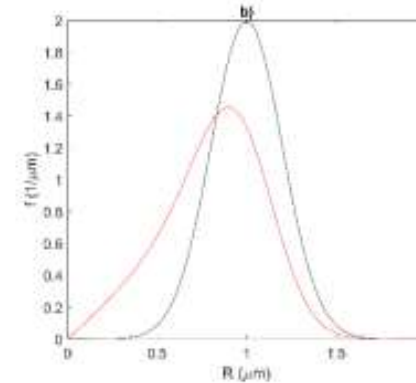
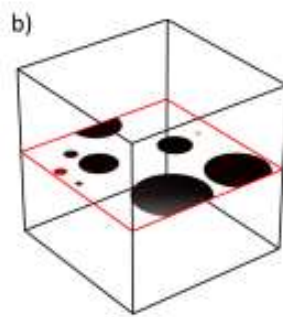
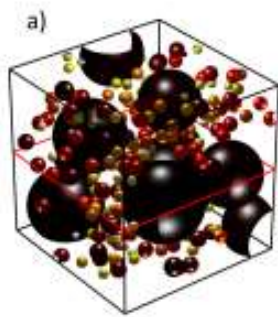


TC-PRISMA



2024: New in Thermo-Calc 2024a & 2024b

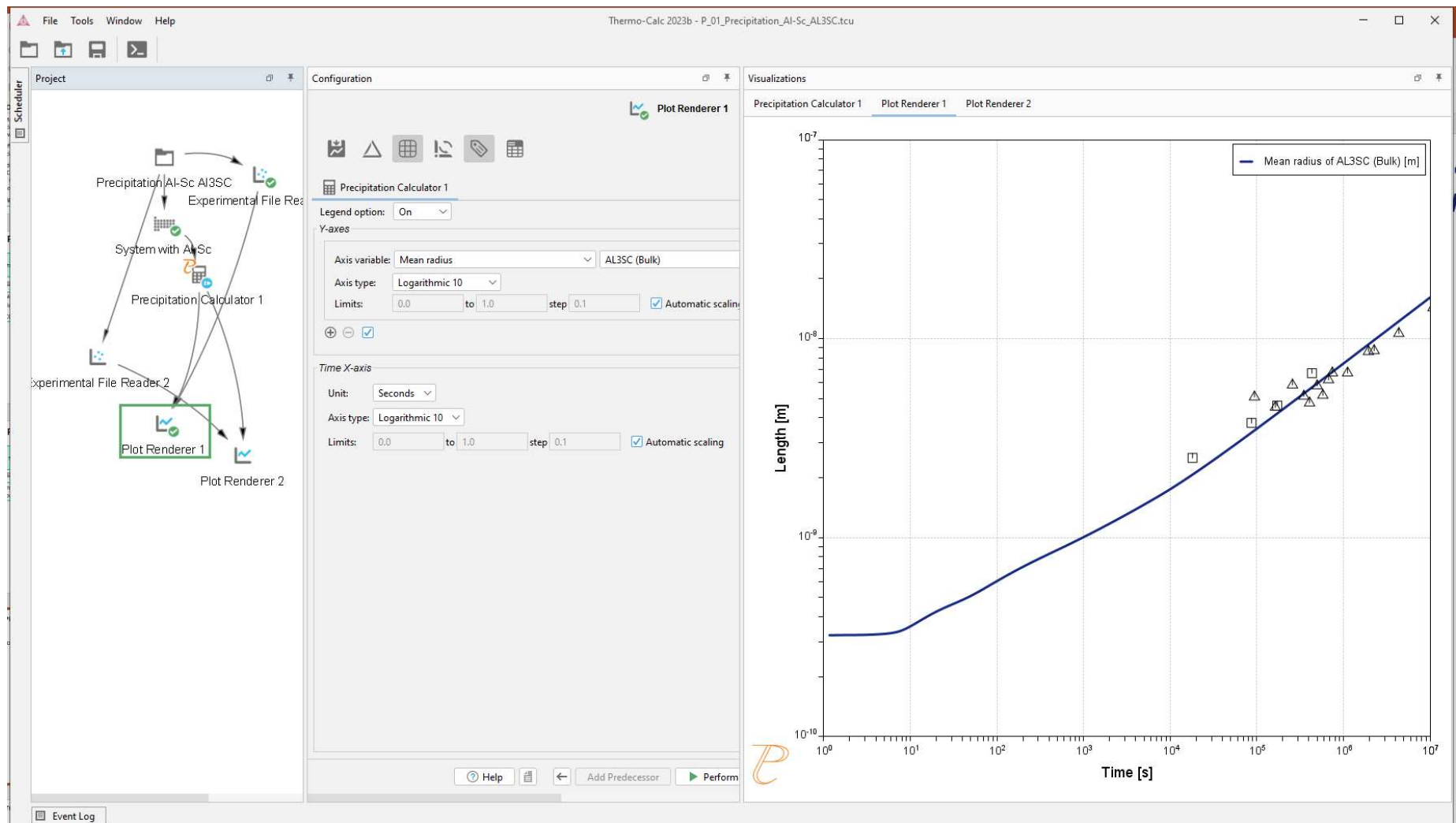
- Transforming 3D size distribution to 2D. New Example P16.



2025: New in Thermo-Calc 2025a

- Importing 1D and 2D size distribution and converting to 3D .
- New method to split calculated size distributions to identify statistics of individual populations.
- Improvements for simulations connected with AM Module.

Now formally known as Precipitation Simulation Module



Features:

- Concurrent nucleation, growth, and coarsening
- Multicomponent nucleation and growth models
- Account for different type of nucleation sites
- Treat cross diffusion and high supersaturation
- Estimation of multicomponent interfacial energy
- Non-spherical particles
- Para-equilibrium

- Integrated within Thermo-Calc
- Highly intuitive Graphic User Interface (GUI)
- Powered by Thermo-Calc and DICTRA calculation engine
- Linked to Thermo-Calc and DICTRA databases

TC-PRISMA vs DICTRA

DICTRA is for simulation of **D**iffusion **C**ontrolled **T**Ransformation in multicomponent system

- Single-phase problems: homogenization, carburization
- Moving boundary problems: solidification, dissolution, growth, and coarsening
- No nucleation, and no unified treatment to growth and coarsening
- For precipitation, good for detailed multicomponent analysis of composition profile evolution in diffusion zone

TC-PRISMA is for precipitation simulation with **multi-particle** interaction in multicomponent systems

- Unified treatment of nucleation, growth, dissolution, and coarsening of dispersed particles
- Not suitable for formation of non-dispersed high volume new phases

Introduction – TC-PRISMA

Input

- Thermodynamic data
- Kinetic data
- Alloy composition
- Temperature - Time
- Simulation time
- Property data
(Interfacial energy,
volume, etc.)
- Nucleation sites and
related microstructure
information

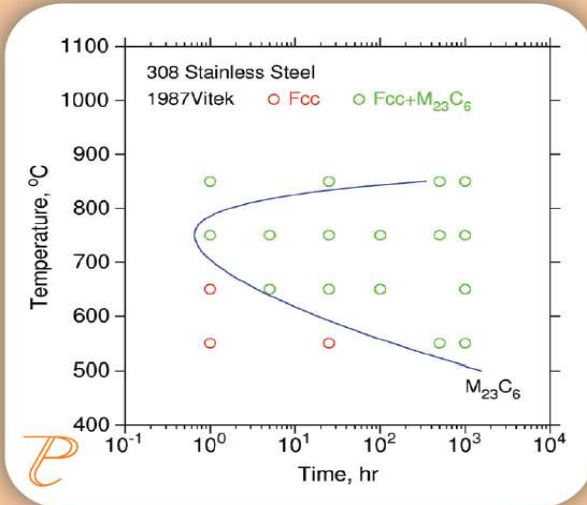
TC-PRISMA

Output

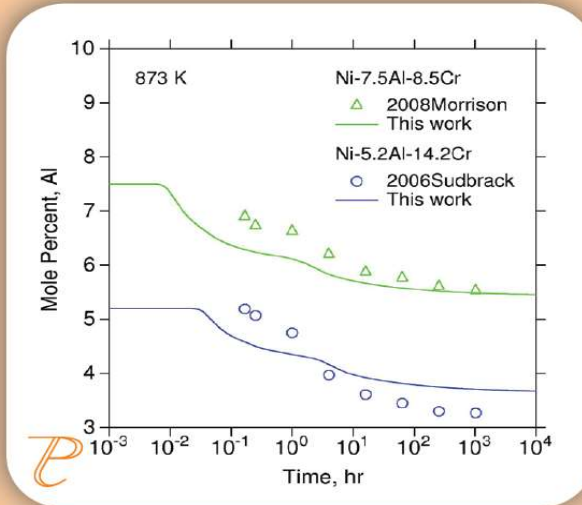
- Particle Size Distribution
- Number Density
- Average Particle Radius
- Volume Fraction
- Matrix composition
- Nucleation rate
- Critical radius
- Driving force
- Mean aspect ratio
- Aspect ratio distribution
- TTP/CCT diagrams
- Yield strength
- Grain size distribution

Introduction – TC-PRISMA

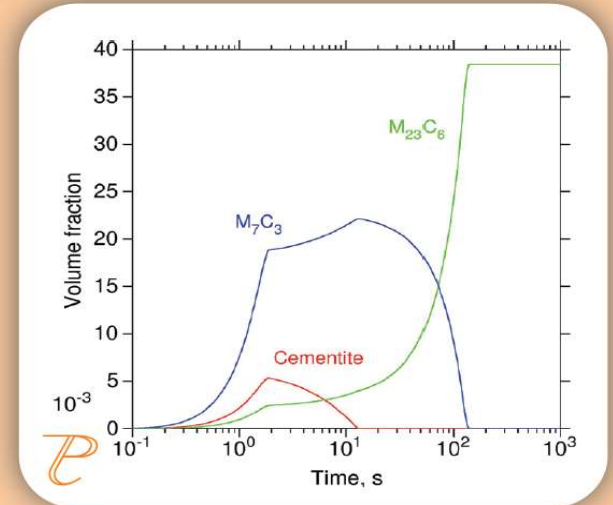
Example of results



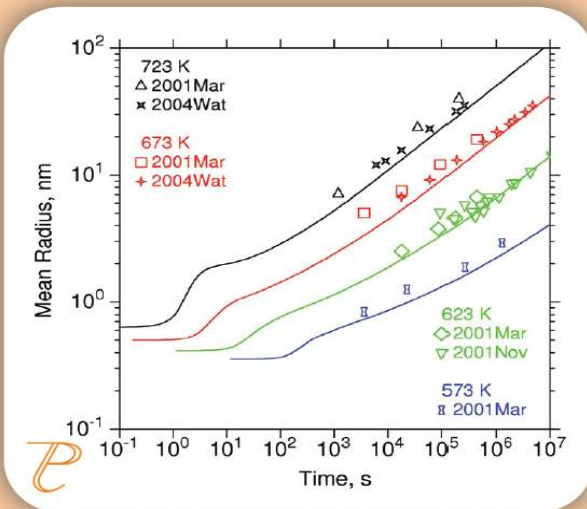
Time temperature precipitation of M₂₃C₆ in 308 stainless



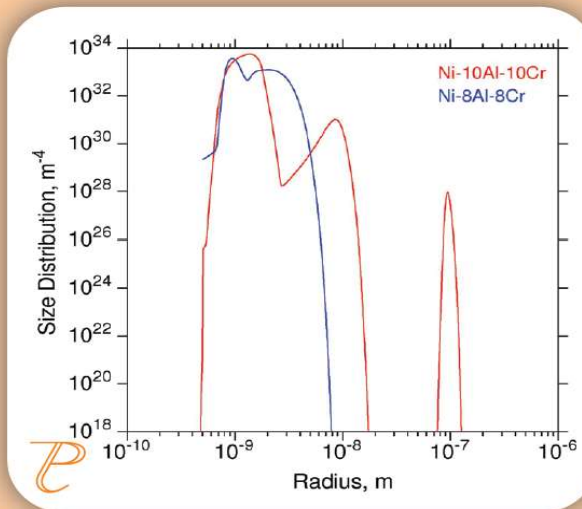
Average matrix composition vs time during precipitation



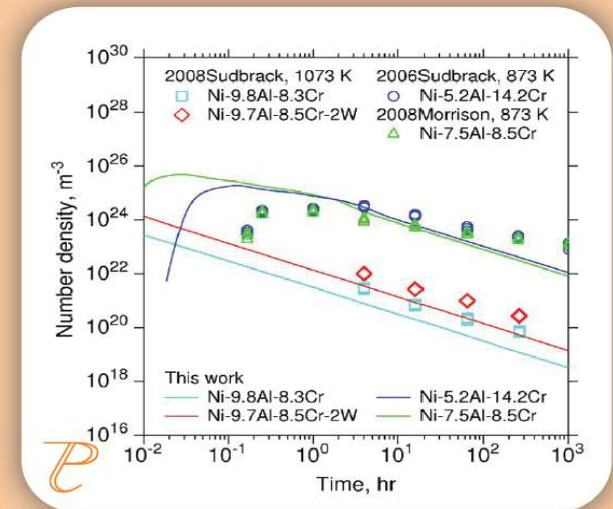
Precipitation of stable/metastable carbides in 12Cr steels



Mean radius of Al₃Sc precipitates vs time at various temperatures



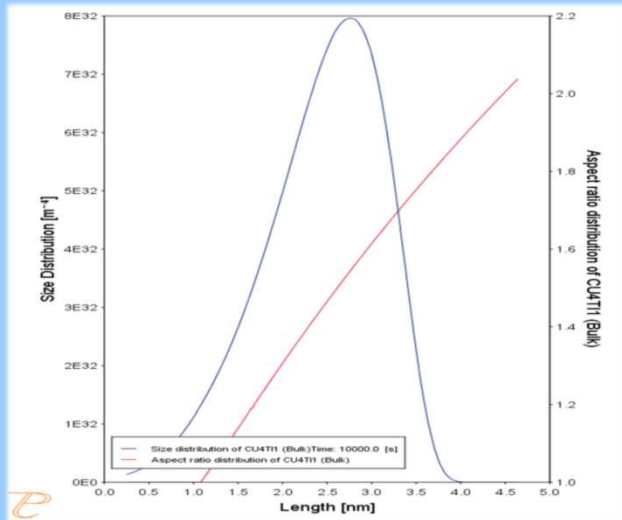
Multimodal size distribution of γ' during non-isothermal treatment



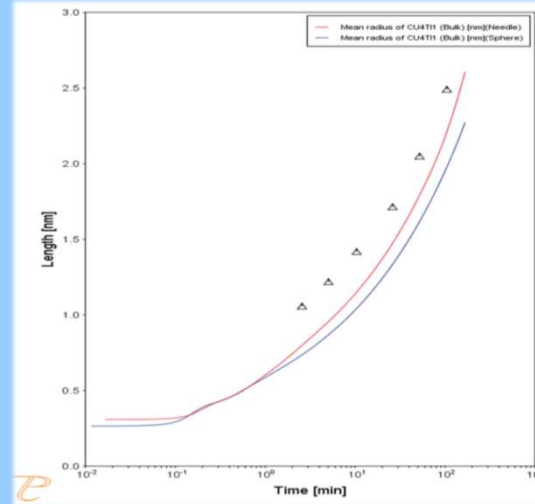
Number density of γ' vs time for various Ni-based superalloys

Introduction – TC-PRISMA

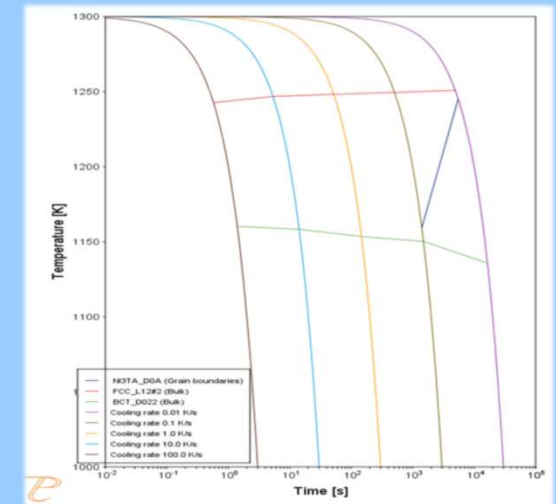
Example of results



**Size distribution and Aspect ratio
Distribution of Cu₄Ti needle-shaped
particles**

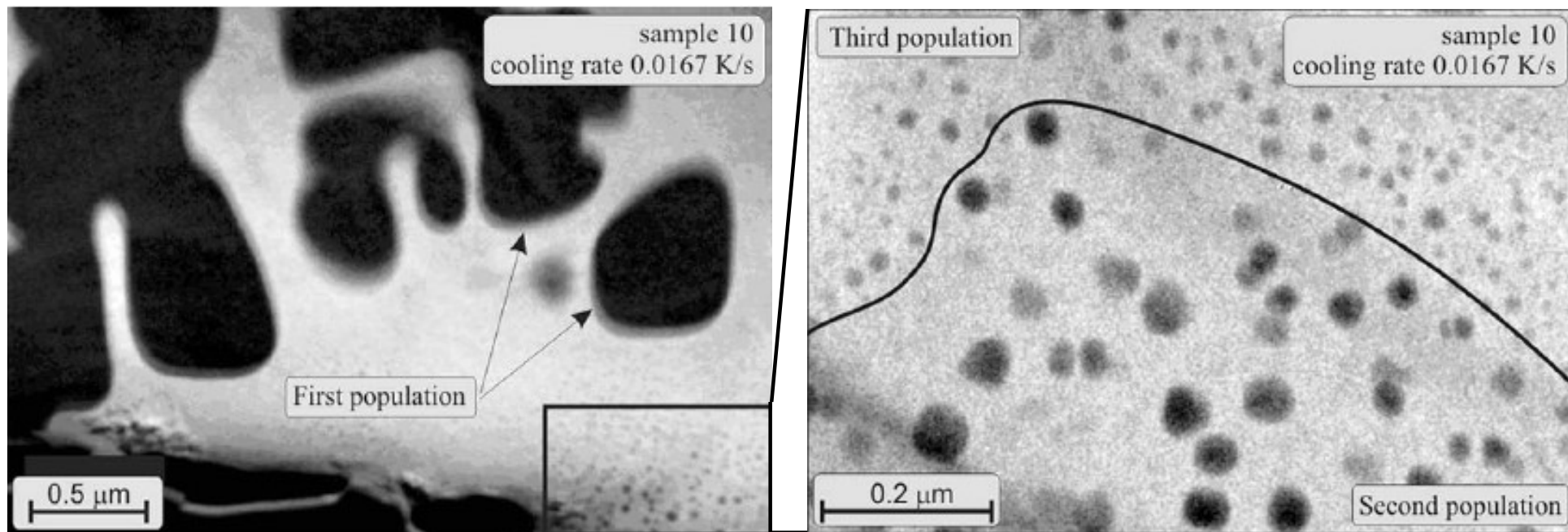


**Size of Cu₄Ti needle- and sphere-
shaped particles as a function of
time**



**CCT curves from 0.01 K/s to 100
K/s for different precipitates in a
Ni-superalloy**

Non-Isothermal Conditions



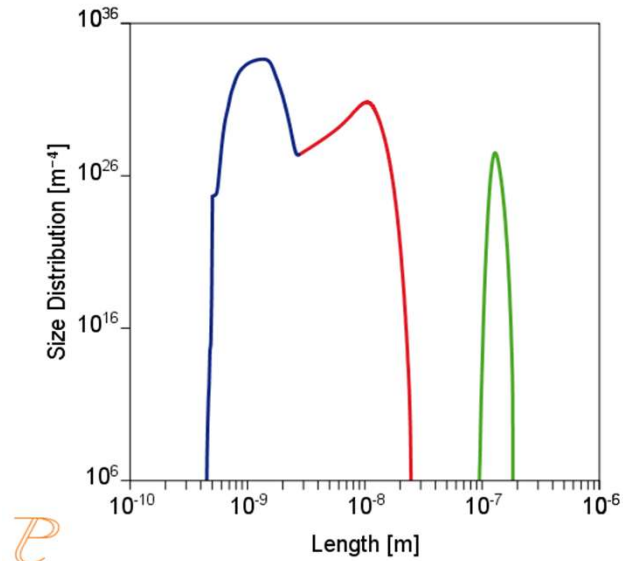
γ/γ' Microstructure in U720 Li

- Continuous cooling at 0.0167 K/s

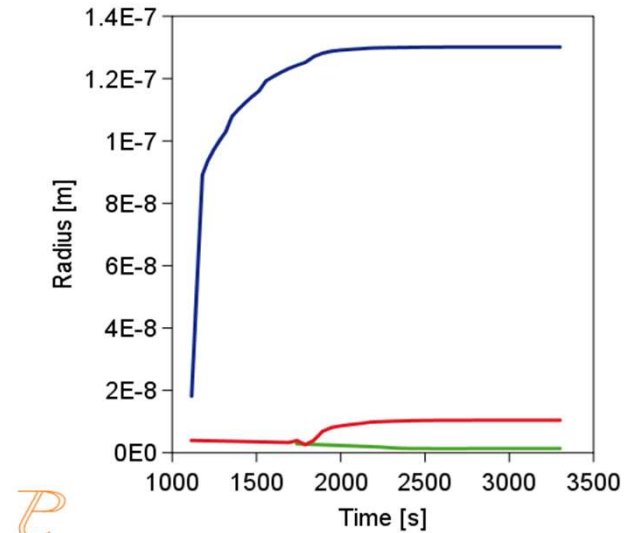
Introduction – TC-PRISMA

Multi-modal Distribution

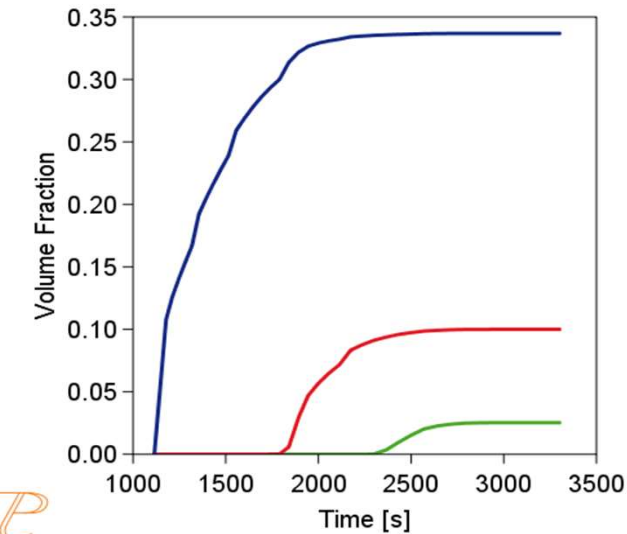
Particle Size Distribution



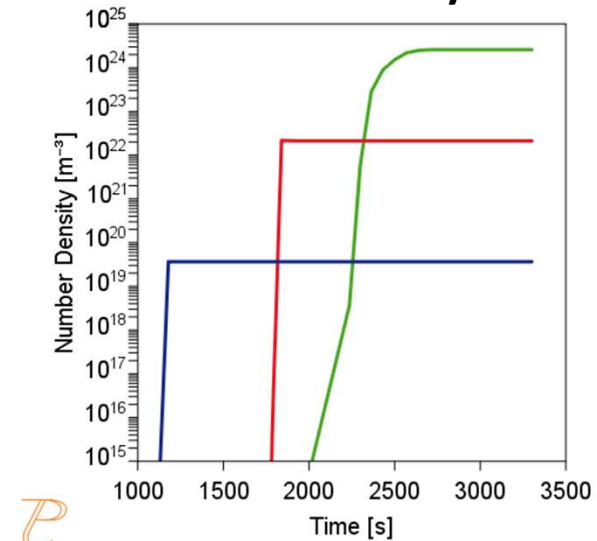
Mean Particle Size



Volume Fraction



Number Density



Compatibility of Databases

Thermodynamic Database	Kinetic Database
SSOL2, SSOL4, SSOL5, SSOL6, SSOL7, SSOL8	MOB2
TCFE5 and earlier versions	MOB2
TCHEA2, TCHEA3+4+5, TCHEA6+7	MOBHEA1, MOBHEA2, MOBHEA3
TCFE6, 7, 8, TCFE9, TCFE10, TCFE11, TCFE12, TCFE13+14	MOBFE1, 2, 3, 4, 5, 6, 7, MOBFE8
TTNI8 and earlier versions	MOBNI1
TCNI4, TCNI5, TCNI6*	MOBNI2*
TCNI7, TCNI8	MOBNI3, MOBNI4
TCNI9+TCNI10+TCNI11, TCNI12	MOBNI5, MOBNI6
TTAL8 and earlier versions	MOBAL1 and BISHOP
TCTI4, TCTI5	MOBTI4
TCAL1+2+3, TCAL4, TCAL5, TCAL6+7, TCAL8, TCAL9	MOBAL3,4,5, MOBAL6, MOBAL7, MOBAL8
TCMG1+2+3+TCMG4+TCMG5, TCMG6	MOBMG1, MOBMG2
TCCU1, TCCU2, TCCU3, TCCU4, TCCU5 + TCCU6	MOBCU1, 2, 3, 4, MOBCU5

* Pairing of TCNI6 and MOBNI2 is not possible for LIQUID phase.

TC-PRISMA Software Basics

Simulation – Setup



System

- ⌘ Databases
- ⌘ Matrix/Precipitate phases



Conditions

- ⌘ Composition
- ⌘ Type of simulation
- ⌘ Thermal Profile
- ⌘ Nucleation Sites



Additional Data

- ⌘ Interfacial Energies
- ⌘ Phase Boundary Mobility
- ⌘ Phase Energy Additions
- ⌘ Mobility Adjustment
- ⌘ Phase Molar Volumes
- ⌘ Wetting angle
- ⌘ Grain size/ shape
- ⌘ Dislocation density
- ⌘ Elastic Properties
- ⌘ Particle Morphology
- ⌘ Existing size distribution

Calculation Settings

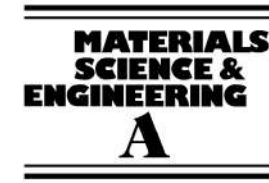
- ⌘ Numerical parameters
- ⌘ Growth Rate Model

Examples

Al Alloys



Materials Science and Engineering A318 (2001) 144–154



www.elsevier.com/locate/msea

Precipitation of Al_3Sc in binary Al–Sc alloys

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*Department of Materials Science and Engineering, School of Engineering and Applied Science, University of California, 405 Hilgard Avenue,
6531 Boelter Hall, Los Angeles, CA 90095, USA*

Received 21 September 2000; received in revised form 5 March 2001

Abstract

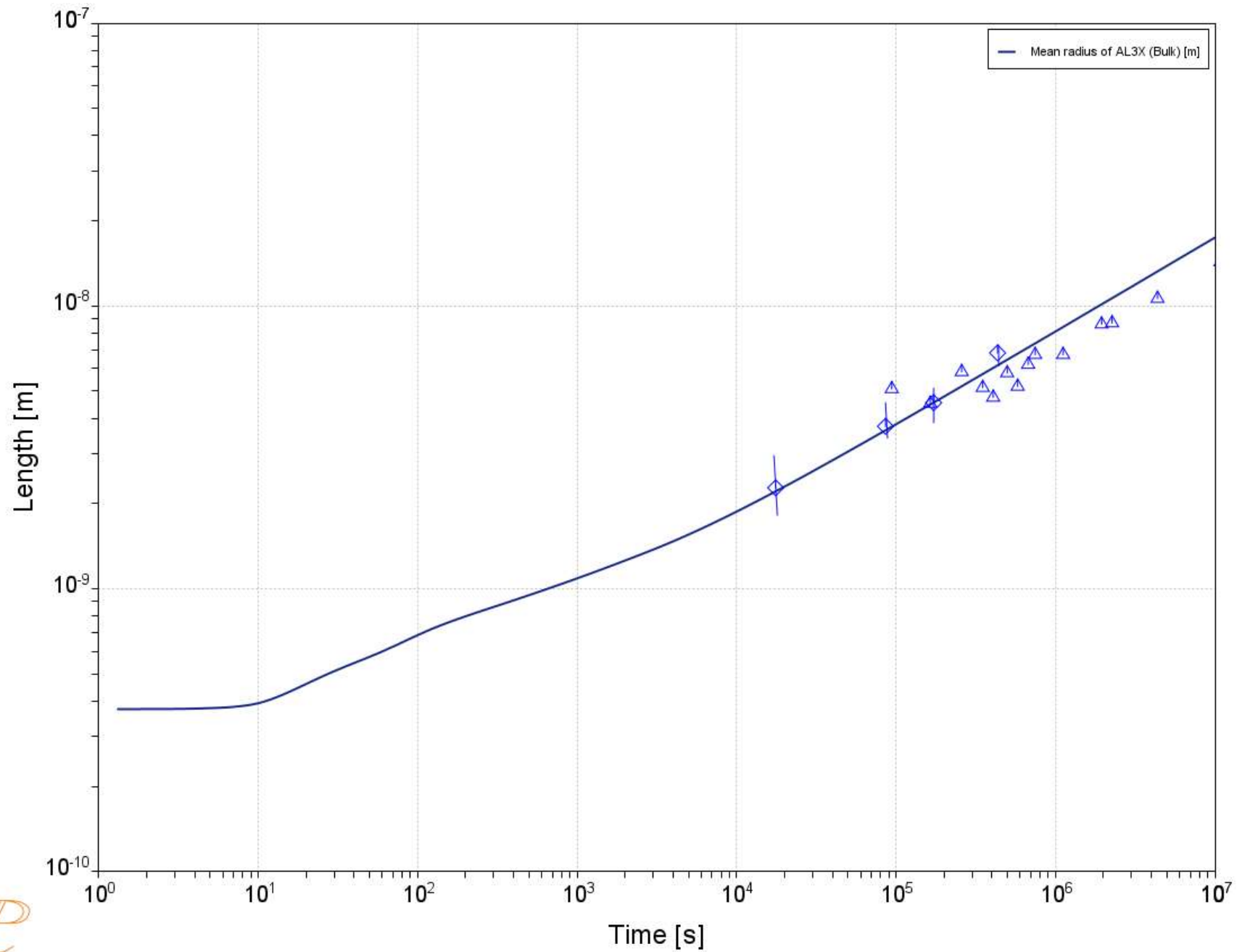
The precipitation of coherent Al_3Sc particles in Al–Sc alloys containing 0.06, 0.12 and 0.18 at.% Sc was investigated. The alloys were aged at 350°C for times up to 4663 h and the kinetics of particle growth, the particle size distributions and the evolution of particle morphology were measured and evaluated using transmission electron microscopy. Al_3Sc precipitates did not nucleate homogeneously in the most dilute alloy; this result was unexpected because 0.06 at.% Sc exceeds the solubility limit at 350°C. Persistent dislocation networks were observed in the alloy containing 0.12 at.% Sc under normal solution treatment conditions (e.g. 1 h at 600°C) and the dislocations acted as heterogeneous nucleation sites. The dislocations were ultimately eliminated using a very long solution treatment time of ~ 70 h near the melting temperature. Aging of both of the more concentrated alloys produced coherent precipitates. At short aging times the particles in the alloy containing 0.12% Sc were cauliflower-shaped and became spherical at longer times. At 4663 h some of the precipitates in this alloy were cuboidal, while others appear to have become semicoherent. The precipitates in this alloy were highly resistant to coarsening, and their size distributions were for the most part narrower than that predicted by the classical theory of Lifshitz, Slezov and Wagner (the LSW theory). The shapes of the precipitates in the alloy containing 0.18% Sc evolved from spherical to cuboidal with increasing aging time. The kinetics of growth of the precipitates in this alloy were consistent with the predictions of the LSW theory, the average size, $\langle r \rangle$, increasing with aging time, t , according to an equation of the type $\langle r \rangle^3 \simeq kt$. The experimentally measured rate constant, k , was in very good agreement with that calculated theoretically for this alloy. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Al–Sc; Precipitation; Coarsening; Microstructure; Kinetics

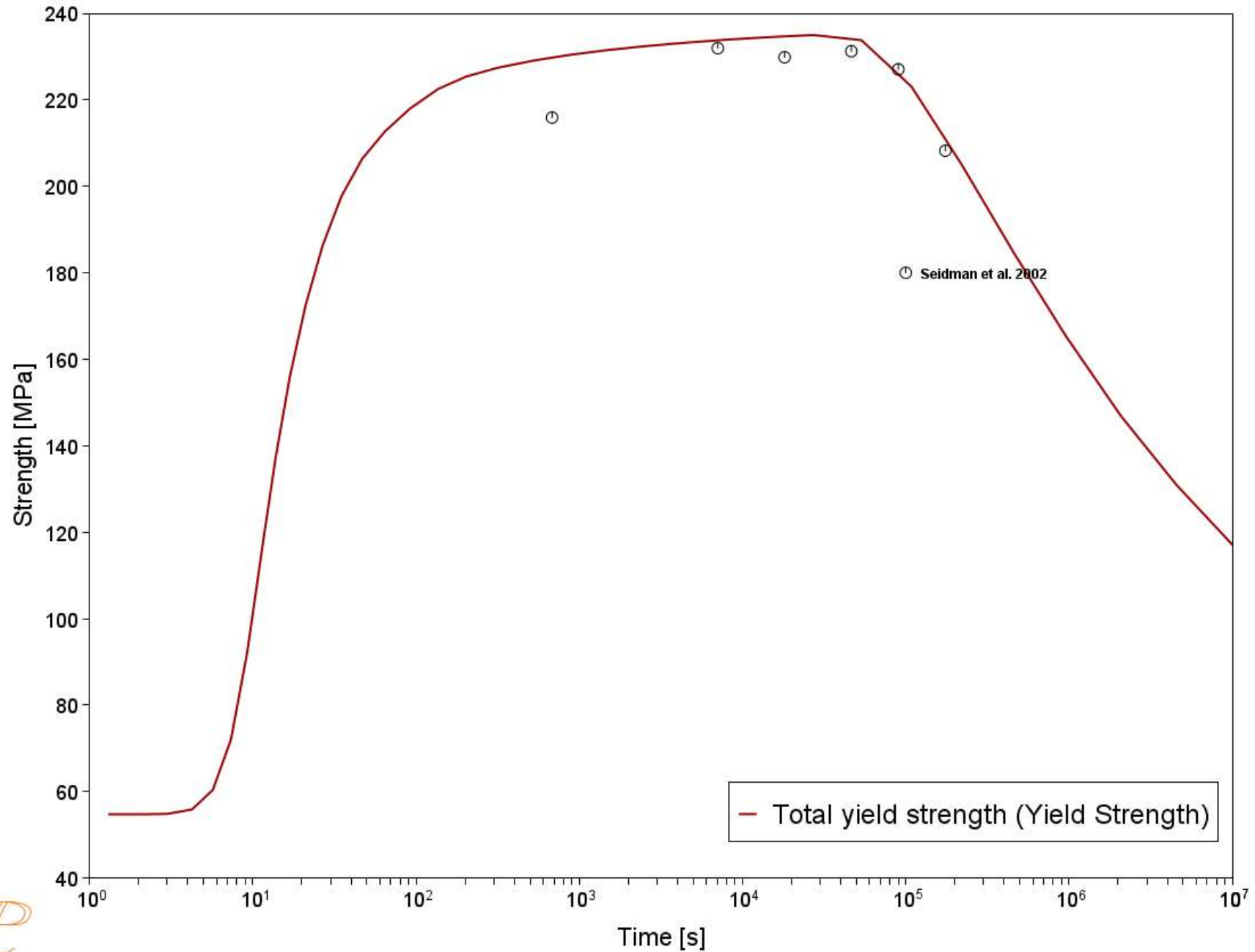
Example 1: Al - Sc Alloy

System	
Database package	TCAL9 + MOBAL8
Elements	Al, Sc
Matrix phase	Fcc_A1
Precipitate phase	Al ₃ Sc (= AL3X in database)
Conditions	
Composition	Al - 0.18 Sc (at.%)
Temperature	350 °C
Simulation time	1E7 s
Nucleation properties	Nucleation Site Type: Bulk
Data Parameters	
Interfacial Energy	Bulk: 0.074 J/m ²
Molar Volume (Matrix):	Fcc_A1: from database
Molar Volume (Precipitate):	Al ₃ Sc: from database

TC-PRISMA Example 1



P

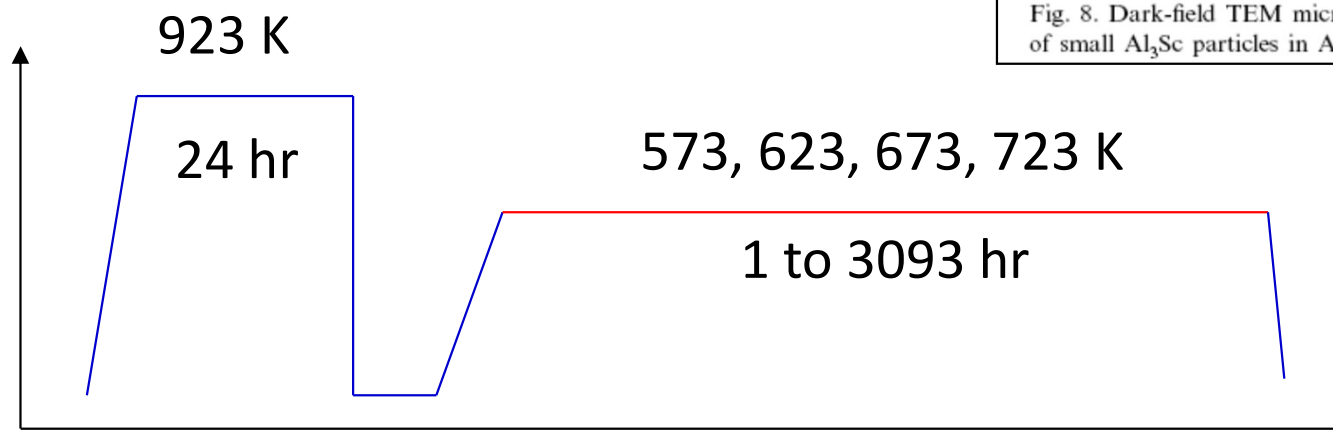
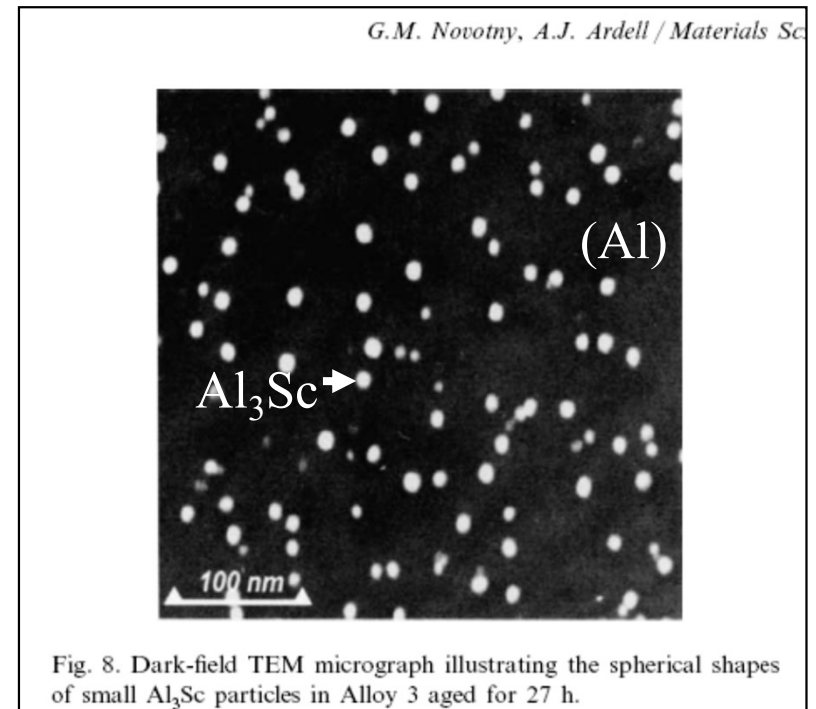


Application – Al-Sc Alloy

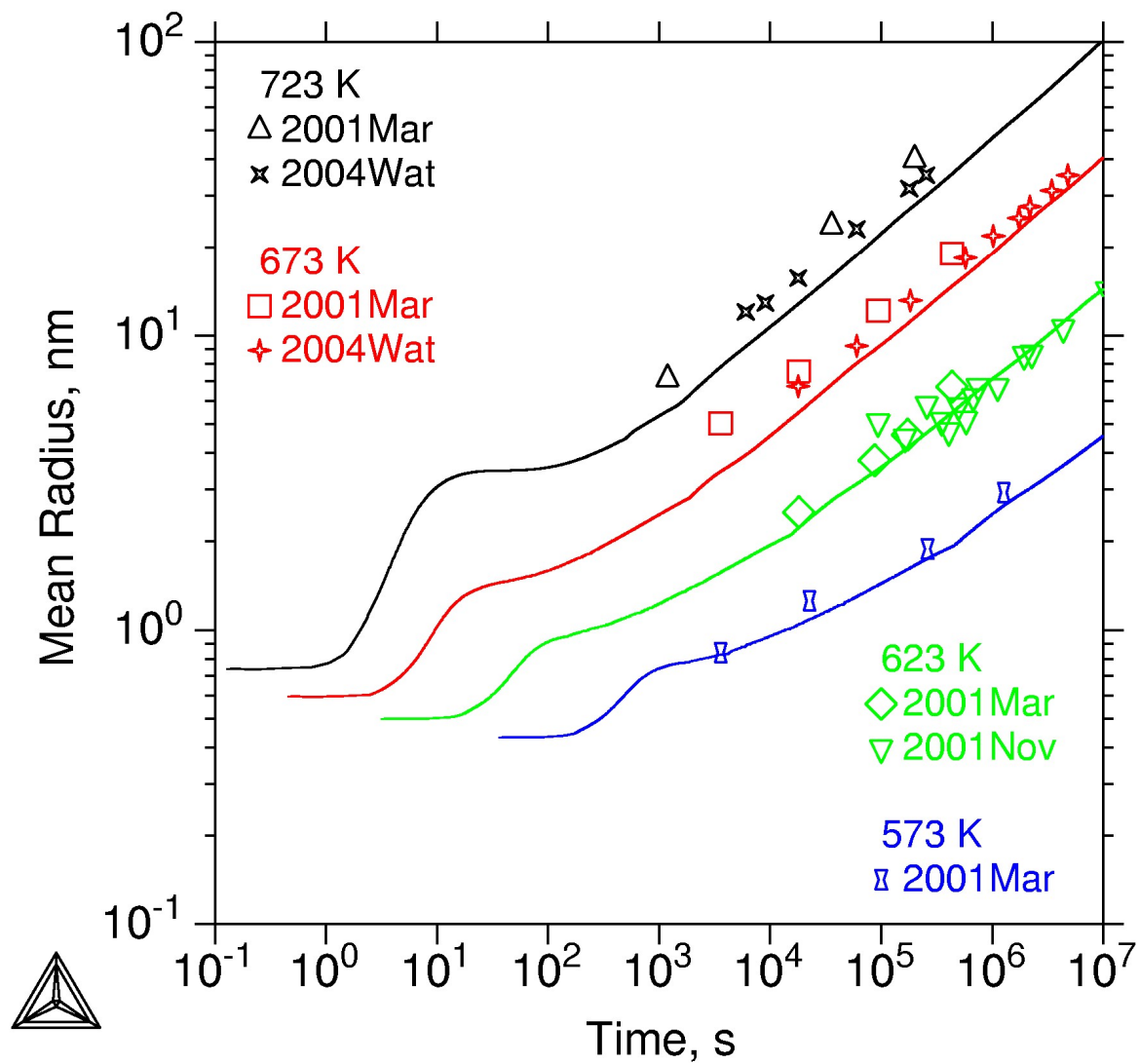
Novotny&Ardell, MSE, A318(2001)144; Marquis&Seidman, AM, 49(2001)1909;
Watanabe et al., MMT, 35A(2004)3003.

Al-0.18at%Sc and Al-0.17at%Sc

$$\sigma = 0.093 \text{ J/m}^2$$



Results – Al-Sc



Results – Al-Mg-Sc

Marquis & Seidman, Acta Mater. 53(2005)4259-4268.

Al-2.2at%Mg-0.12at%Sc

$$\sigma = 0.093 \text{ J/m}^2$$

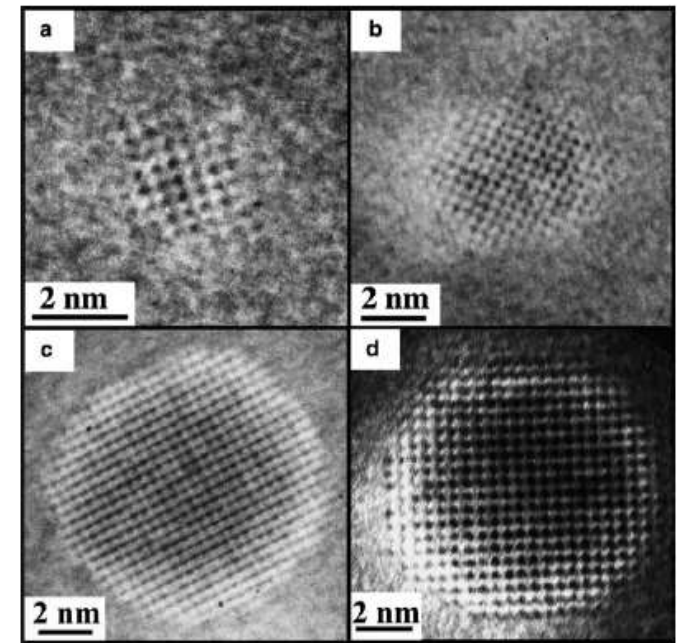
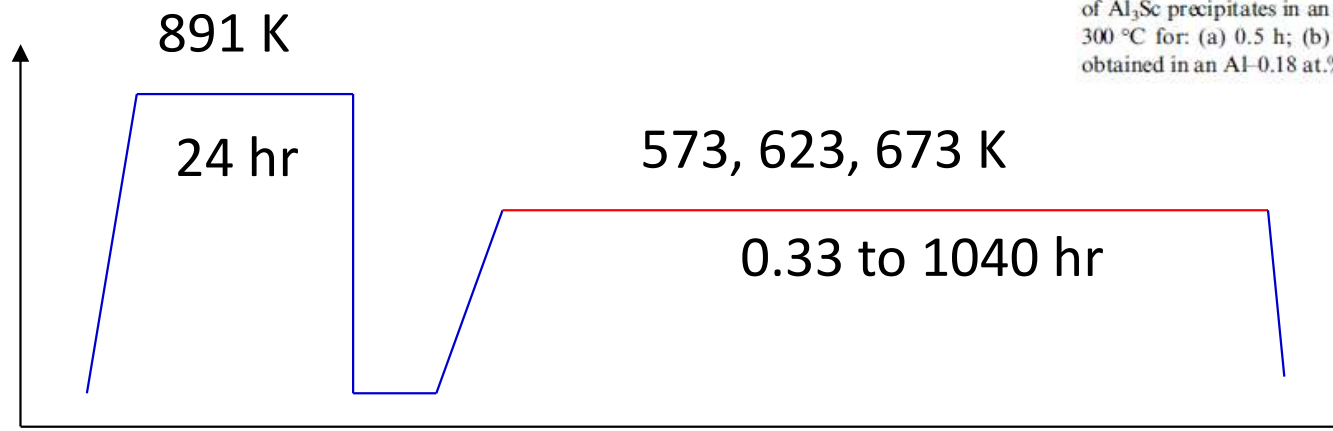
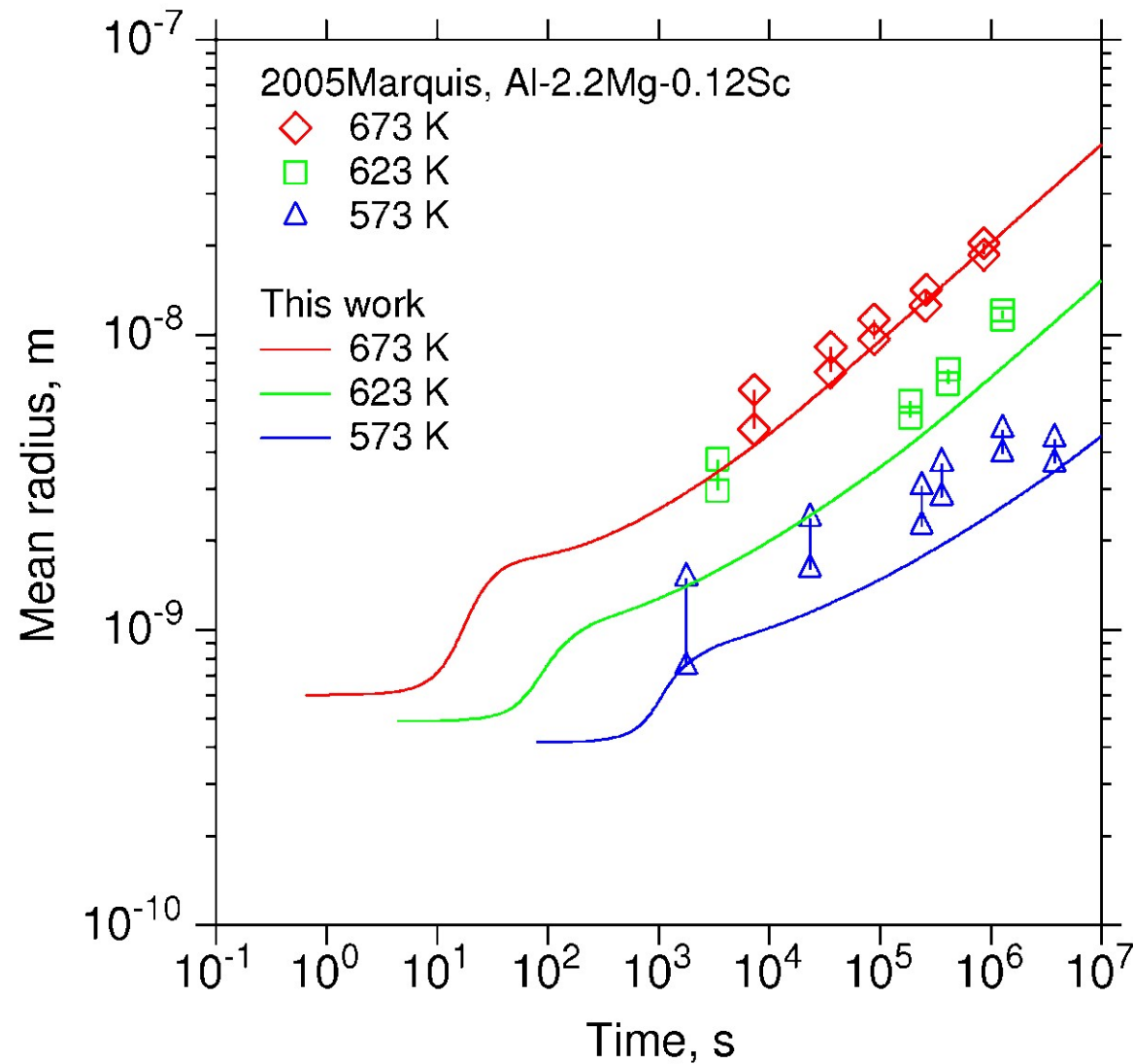


Fig. 3. High-resolution electron microscope images ([100] zone axis) of Al₃Sc precipitates in an Al-2.2 Mg-0.12 Sc at.% alloy after aging at 300 °C for: (a) 0.5 h; (b) 5 h; (c) 1040 h; and (d) Al₃Sc precipitate obtained in an Al-0.18 at.% Sc alloy after aging at 300 °C for 350 h [3].



Results – Al-Mg-Sc

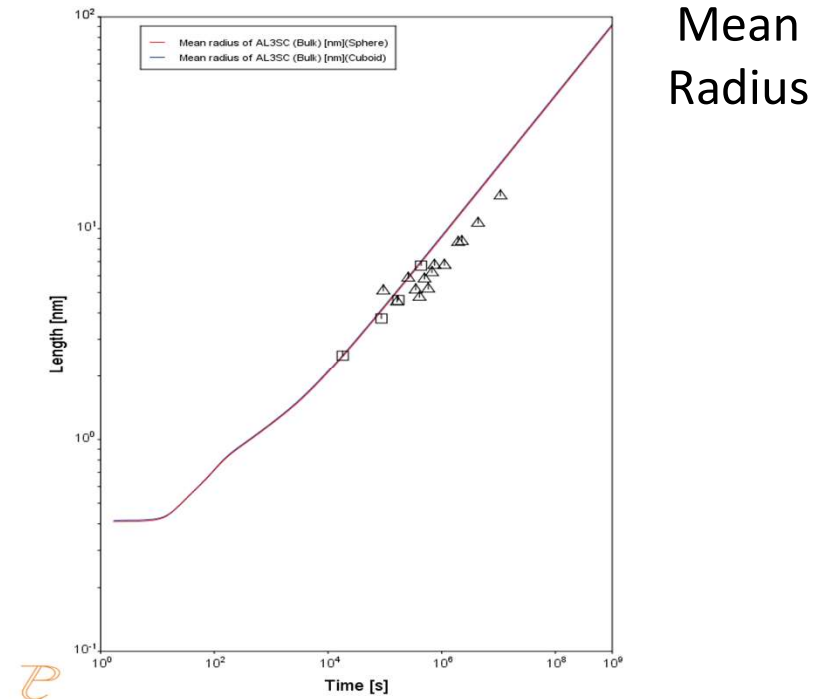
Same set of physical parameters as binary Al-Sc.



Example 2: Al-Sc Alloy

Precipitation of Al_3Sc from FCC

- Al-0.18at.% Sc
- Databases:
TCAL9+MOBAL8
- Misfit strain calculated from molar volume
- Default values for other parameters
- User defined interfacial energy:
 0.074 J/m^2
- $T = 350^\circ\text{C}$ for 1E9s



C_{11}	C_{12}	C_{44}
108.2 GPa	61.3 GPa	28.5 GPa

* J.K. Lee et al., Metall. Trans. A, 8(1977)963

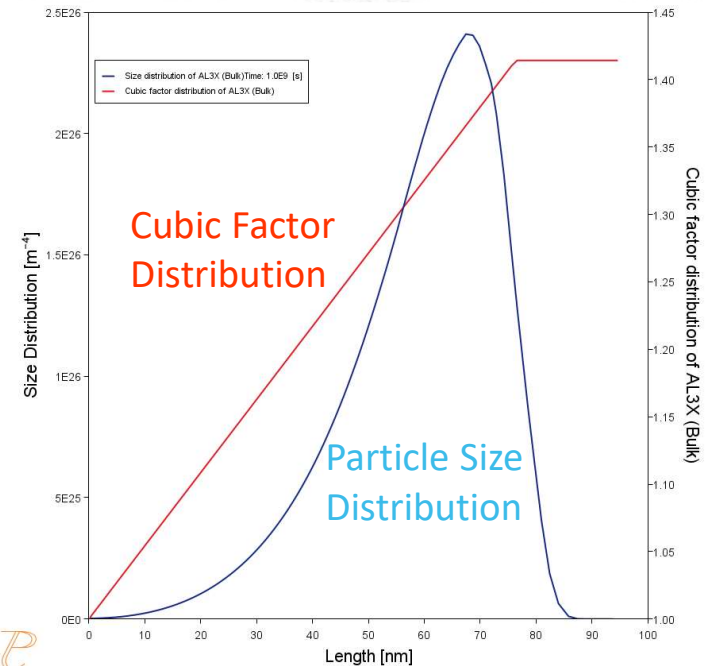
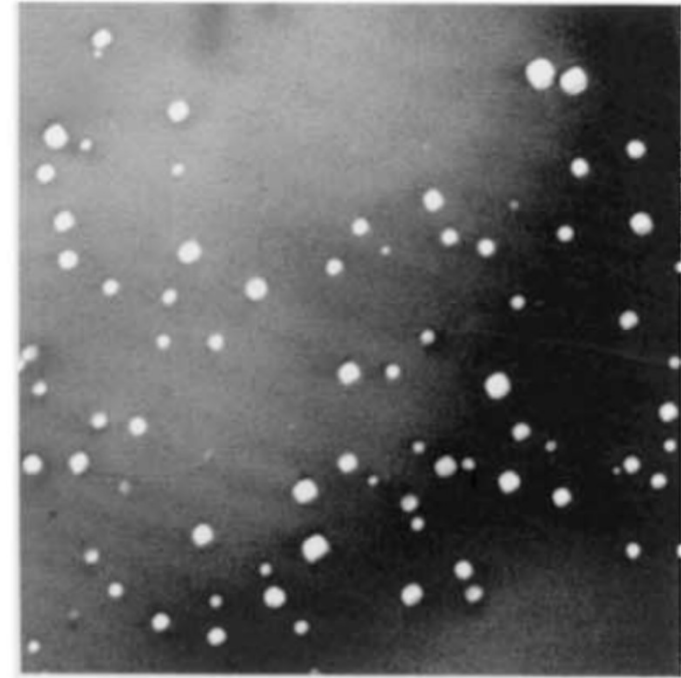
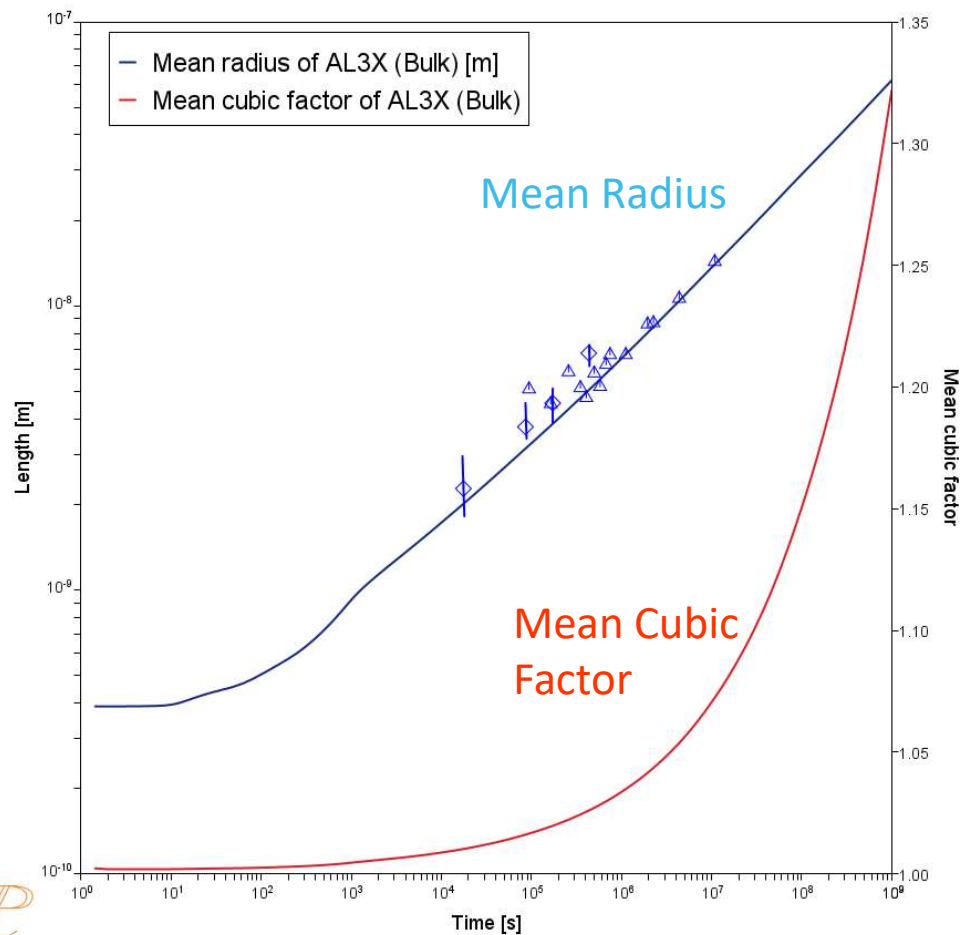
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Elements	Al, Sc
Matrix phase	Fcc_A1
Precipitate phase	Al ₃ Sc (= AL3X in database)
Conditions	
Composition	Al - 0.18 Sc (at.%)
Temperature	350 °C
Simulation time	1E7 s
Nucleation properties	Nucleation Site Type: Bulk
Data Parameters	
Interfacial Energy	Bulk: 0.074 J/m ²
Molar Volume (Matrix):	Fcc_A1: from database
Molar Volume (Precipitate):	Al ₃ Sc: from database

Allow transformation
from Spherical
to Cuboid morphology.

Example: Al-Sc Alloy

- Spherical to Cubic Shape with Increasing Particle Size



* TEM picture from G.M. Novotny and A.J. Ardell, *Mater. Sci. Eng. A318*(2001)144



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Acta Materialia 52 (2004) 591–600



www.actamat-journals.com

Loss in coherency and coarsening behavior of Al₃Sc precipitates

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6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan*

Received 18 August 2003; received in revised form 18 August 2003; accepted 29 September 2003

Abstract

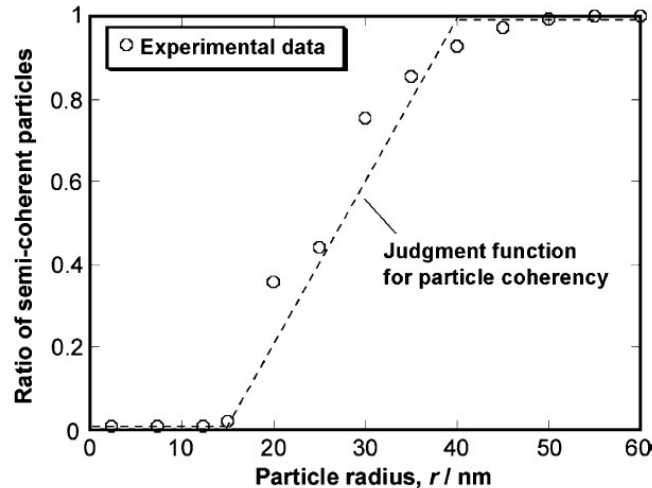
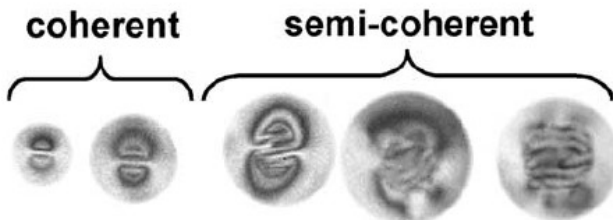
The coarsening behavior of the Al₃Sc particles in Al–0.2wt%Sc alloy at 673–763 K is studied on the basis of TEM observations with the numerical model. Emphasis is on the effects of coherent/semi-coherent transition of the particles. The radius for coherent/semi-coherent transition of the Al₃Sc particles is determined from TEM micrographs as 15–40 nm. The average particle radius, r_{ave} , of the Al₃Sc particles obeys the r_{ave}^3 growth law both in the coherent stage ($r_{\text{ave}} < 15$ nm) and semi-coherent stage ($r_{\text{ave}} > 40$ nm). However, in the intermediate stage, where coherent and semi-coherent particles coexist ($15 < r_{\text{ave}} < 40$ nm), coarsening is delayed and particle size distribution is broadened in the experiment and also in the calculation. These results are qualitatively understood in consideration of the different growth rates of individual particles in the intermediate stage.

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Example 3 – Al Alloys

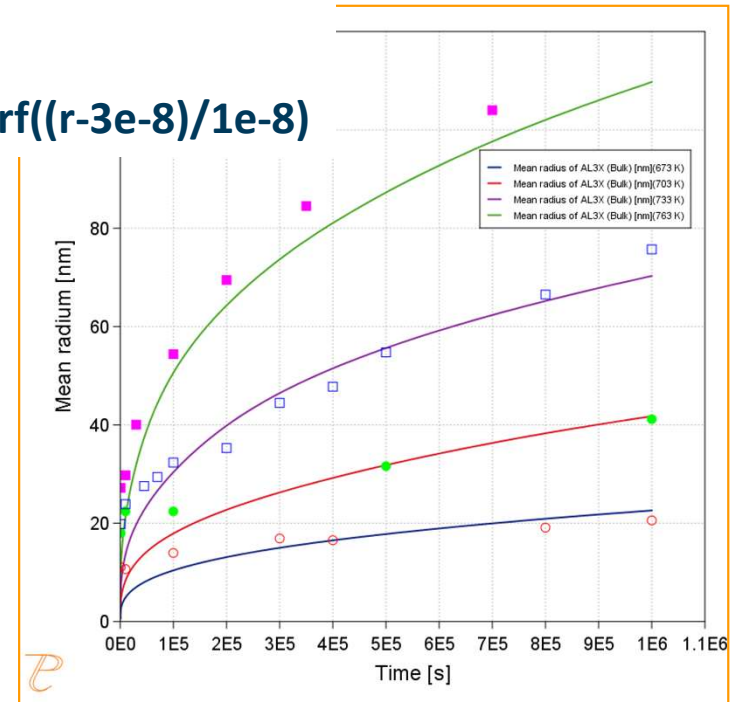
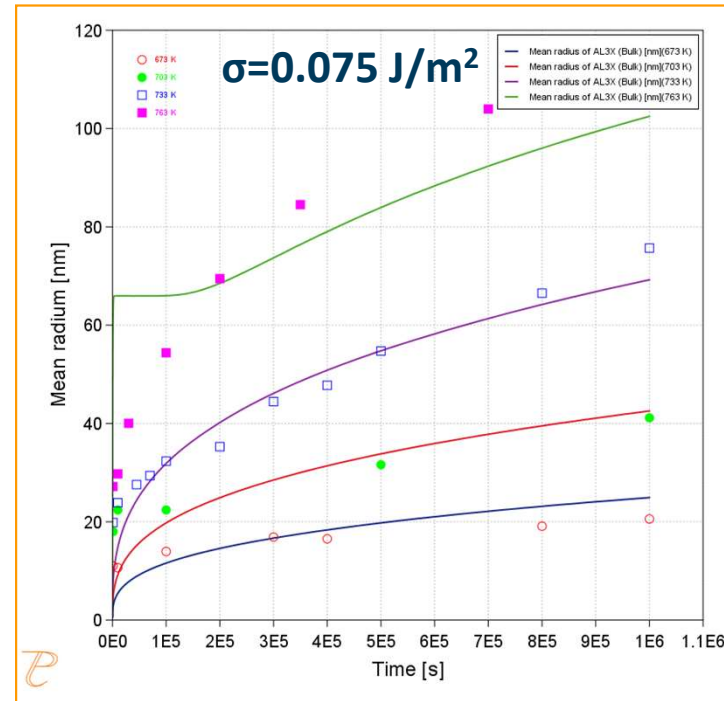
□ $\sigma=0.075 \text{ J/m}^2$ using
TCAL9 +MOBAL8

○ Al-0.12 at.% Sc, solution
treated at 640 °C for 2 h.



Error function

$$\sigma=0.075+0.011*\text{erf}((r-3\text{e-}8)/1\text{e-}8)$$



□ Size dependence of interfacial energy

- Due to coherency loss

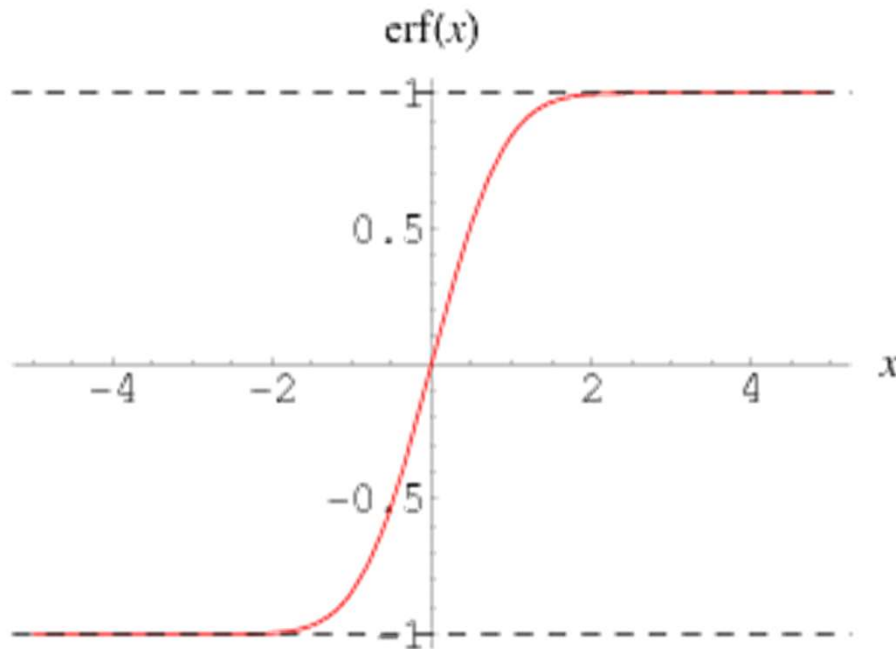
Example 3: Al - Sc Alloy

System	
Database package	TCAL9 + MOBAL8
Elements	Al, Sc
Matrix phase	FCC_A1
Precipitate phase	Al ₃ Sc (= AL3X in database)
Conditions	
Composition	Al - 0.12 Sc (at.%)
Temperature	673, 703, 733 and 763 K
Simulation time	1E7 s
Nucleation properties	Nucleation Site Type: Bulk
Data Parameters	
Interfacial Energy	Bulk: $0.075 + 0.011 * \text{erf}((r - 3e-8)/1e-8)$
Molar Volume (Matrix):	Fcc_A1: from database
Molar Volume (Precipitate):	Al ₃ Sc: from database

Example 3 – Al Alloys

The error function, $\text{erf}(x)$, is used to input the size dependent interfacial energy in this example. Below is a diagram to remind us of its properties.

$\text{Erf}(x)$ can also be used as a simple solution to binary diffusion problems, and can be used to smooth out step-like composition-input profiles in DICTRA. The sharpness of the the step-like profile can be set by the user.



$$\sigma = 0.075 + 0.011 * \text{erf}((r - 3e-8)/1e-8)$$

Image from:
<http://mathworld.wolfram.com/Erf.html>

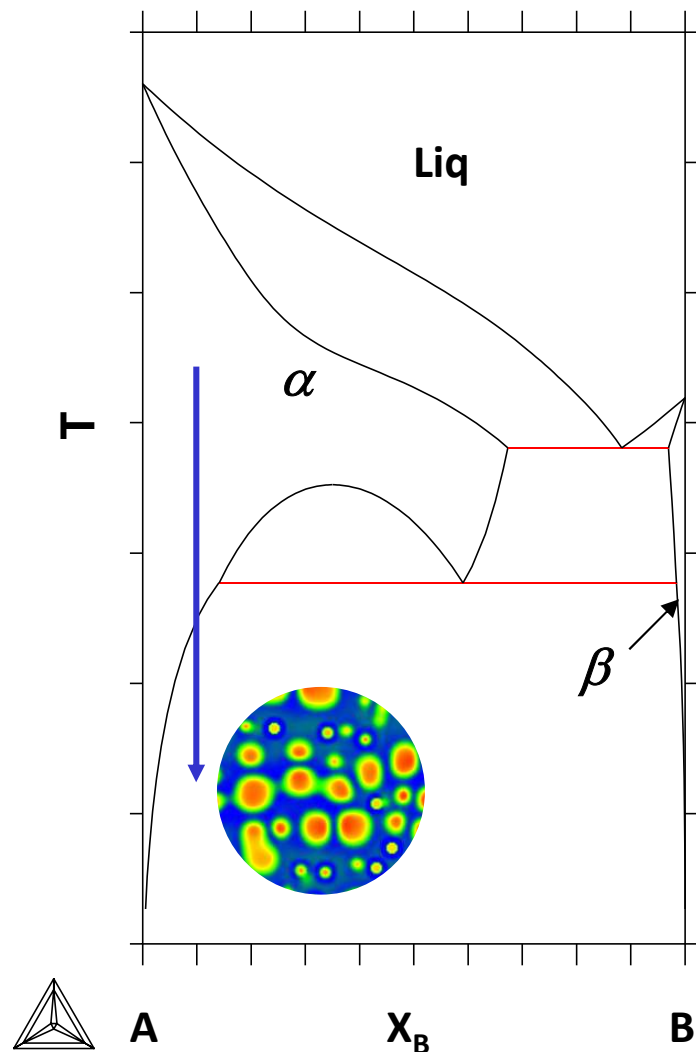
Q & A

Theory: Nucleation

Models and Model Parameters

LS (Langer-Schwartz) and KWN (Kampmann and Wagner Numerical) Approach

$$J = \int_{r^*}^{\infty} j(r) dr$$



Continuity equation

$$\frac{\partial f(r,t)}{\partial t} = - \frac{\partial}{\partial r} [\nu(r) f(r,t)] + j(r,t)$$

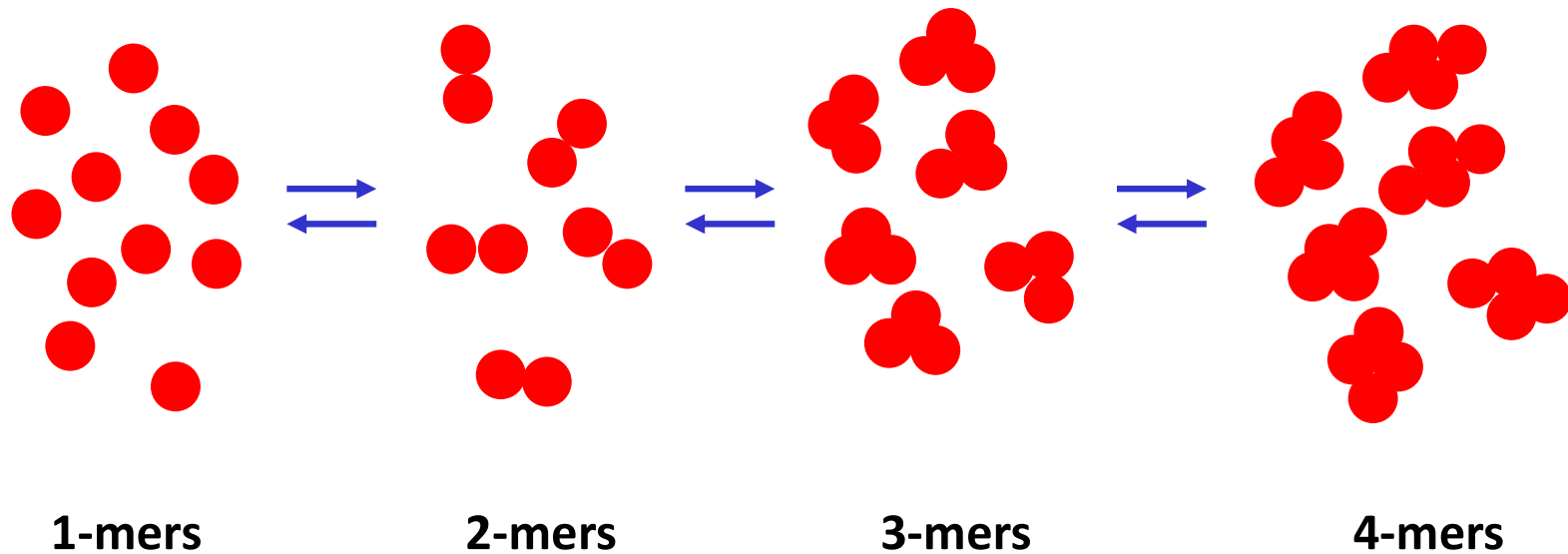
$$C_0^\alpha = C^\alpha + (C^\beta - C^\alpha) \int_0^\infty \frac{4\pi}{3} f(r,t) r^3 dr$$

Mass balance



Models: Nucleation Rate

Classic Nucleation Theory (CNT)



$$\frac{\partial N_{n,t}}{\partial t} = \frac{\partial}{\partial n} \left[\beta(n) \frac{\partial N_{n,t}}{\partial n} \right] + \frac{\partial}{\partial n} \left[N_{n,t} \frac{\beta(n)}{kT} \frac{\partial \Delta G_n}{\partial n} \right]$$

Zeldovich–Frenkel equation

Models: Nucleation Rate

Classical Nucleation Theory (CNT)

$$J(t) = J_s \exp\left(-\frac{\tau}{t}\right)$$

J : nucleation rate

J_s : steady state nucleation rate

τ : incubation time

$$J_s = Z\beta^* N \exp\left(\frac{-\Delta G^*}{kT}\right)$$

N : potential nucleation sites

Z : Zeldovich Factor

β^* : molecular attachment rate

$$\Delta G^* = \frac{16\pi\sigma^3 V_m^2}{3\Delta G_m^2}$$

σ : interfacial energy of matrix/precipitate

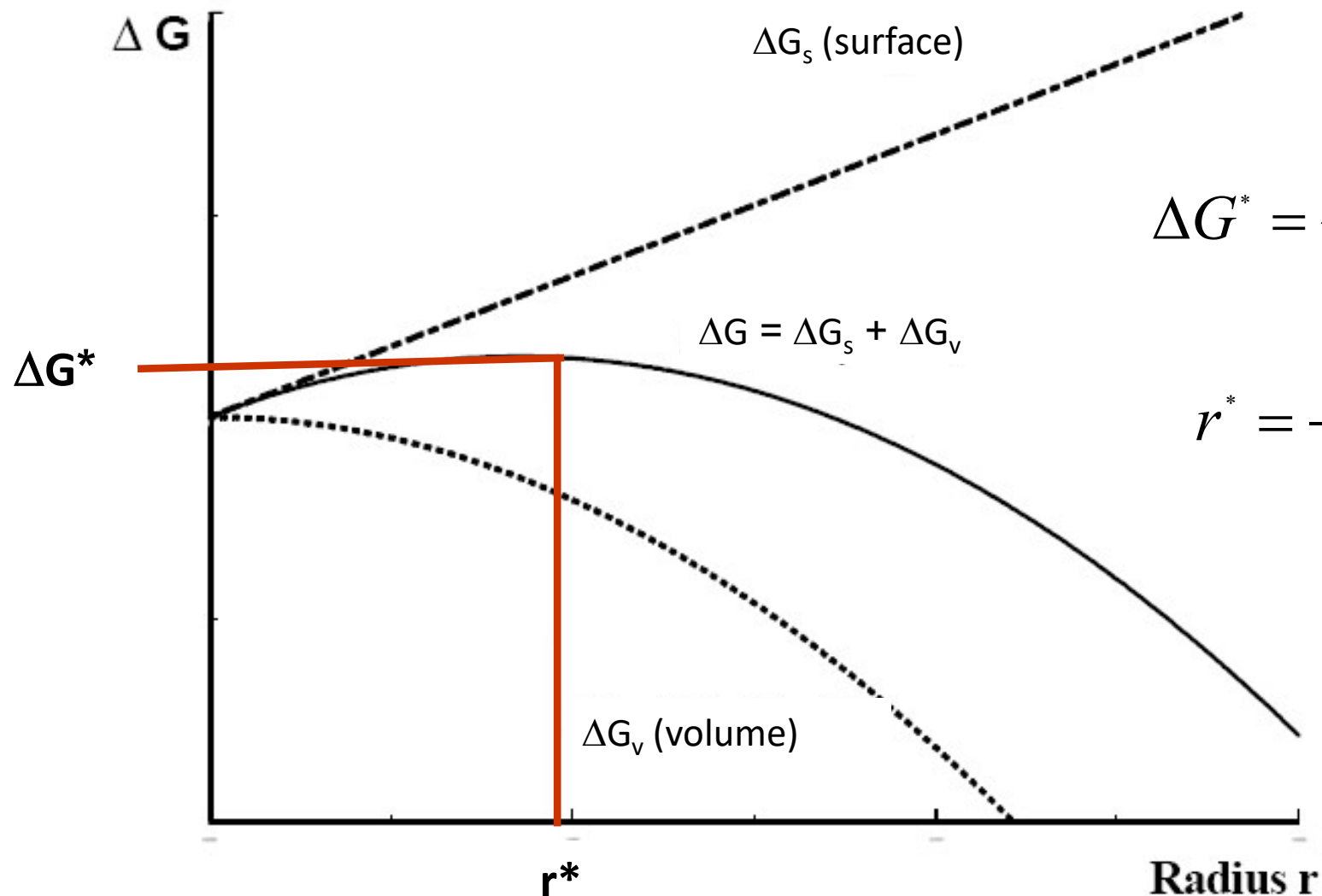
V_m : molar volume of precipitate phase

ΔG_m : driving force for nucleation

ΔG^* : energy barrier for nucleation

Models: Nucleation Rate

ΔG^* and r^*



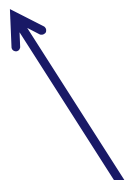
$$\Delta G^* = \frac{16\pi\sigma^3 V_m^2}{3\Delta G_m^2}$$

$$r^* = -\frac{2\sigma V_m}{\Delta G_m}$$

Models: Nucleation Rate

τ - incubation time

$$\tau = \frac{1}{\Theta Z^2 \beta^*}$$

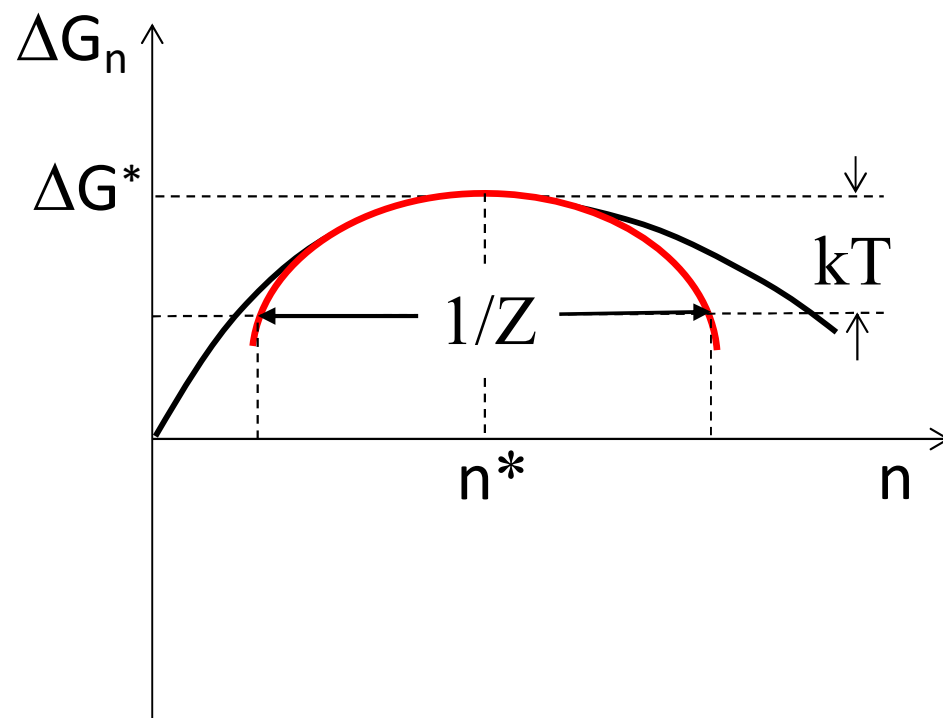
$$\tau = \frac{1}{2Z^2 \beta^*}$$


Θ : constant (depending on assumptions/model derivation)
Z: Zeldovich Factor
 β^* : attachment kinetics

- used in TC-PRISMA
- based on : Feder et al.; Advances in Physics 15 (1966)111-178

Models: Nucleation Rate

Zeldovich factor (thermodynamic):
accounts for deviation of steady-state concentration of critical nuclei with size n^* from equilibrium concentration



$$Z = \left\{ \frac{-1}{2\pi kT} \left(\frac{\partial^2 \Delta G_n}{\partial n^2} \right)_{n^*} \right\}^{1/2}$$

- Corresponds to curvature of ΔG_n
- Higher curvature leads to higher probability for super-critical nuclei to survive

β^* - molecular attachment rate

$$\beta^* = \frac{4\pi r^{*2} XD}{a^4} \quad \text{binary}$$

$$\beta^* = \frac{4\pi r^{*2}}{a^4} \left[\sum_{i=1}^n \frac{\left(X_i^{\beta/\alpha} - X_i^{\alpha/\beta} \right)^2}{X_i^{\alpha/\beta} D_i} \right]^{-1}$$

$4\pi r^{*2}$: surface of critical nucleus

a : lattice spacing

D_i : diffusion coefficients in matrix

Svoboda J, Fischer FD, Fratzl P, Kozeschnik E. Materials science and engineering a 2004;385:166-174.

Models: Nucleation Rate

Classic Nucleation Theory (CNT)

From grain size, dislocation density, etc

$$J(t) = J_s \exp\left(-\frac{\tau}{t}\right) \quad J_s = Z\beta^* N \exp\left(\frac{-\Delta G^*}{kT}\right)$$

$$Z = \frac{V_m^\beta}{2\pi N_A r^{*2}} \sqrt{\frac{\sigma}{kT}} \quad \beta^* = \frac{4\pi r^{*2}}{a^4} \left[\sum_{i=1}^n \frac{(X_i^{\beta/\alpha} - X_i^{\alpha/\beta})^2}{X_i^{\alpha/\beta} D_i} \right]^{-1}$$

2004Svoboda

Interfacial energy, Volume

$$r^* = -\frac{2\sigma V_m^\beta}{\Delta G_m^{\alpha \rightarrow \beta}} \quad \Delta G^* = \frac{16\pi\sigma^3 V_m^2}{3\Delta G_m^2} \quad \tau = \frac{1}{2Z^2\beta^*}$$

Models: Nucleation Rate

ΔG_m : driving force for nucleation

Nuclear Composition—A Factor of Interest in Nucleation*

Nucleation in the solid state is a very complicated process. Therefore, theoretical investigations in this field deal with simplified models. Some factors are examined while other factors are neglected. A factor that is usually neglected is the uncertainty of the nucleus composition. It is not necessarily true that the nuclei which form most readily have the composition appropriate for the precipitate, when equilibrium has been established. In the present note this point will be examined, on the assumption that many other factors can be neglected.

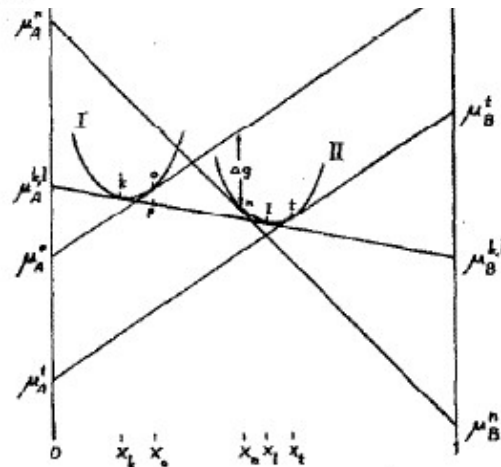


FIGURE 1. Free-energy diagram. The point *o* represents the parent phase. x_t is the thermodynamically most favourable nuclear composition.

MATS HILLERT

Metallografiska Institutet
Stockholm, Sweden

764 ACTA METALLURGICA, VOL. 1, 1953

tension the nucleus should exhibit a composition between that of the parent phase and that of the equilibrium precipitate. In the present paper a thermodynamic treatment will be carried out under the assumption that the surface tension of the nuclei is independent of composition.

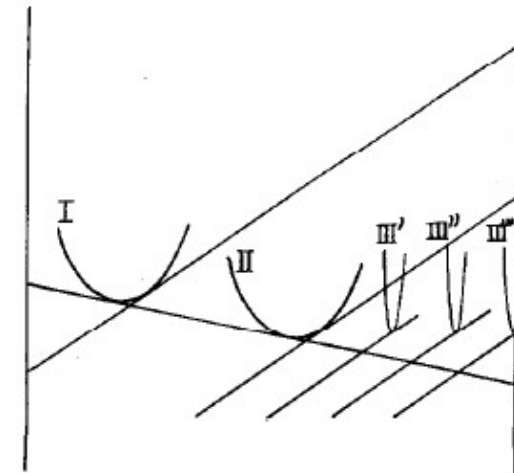
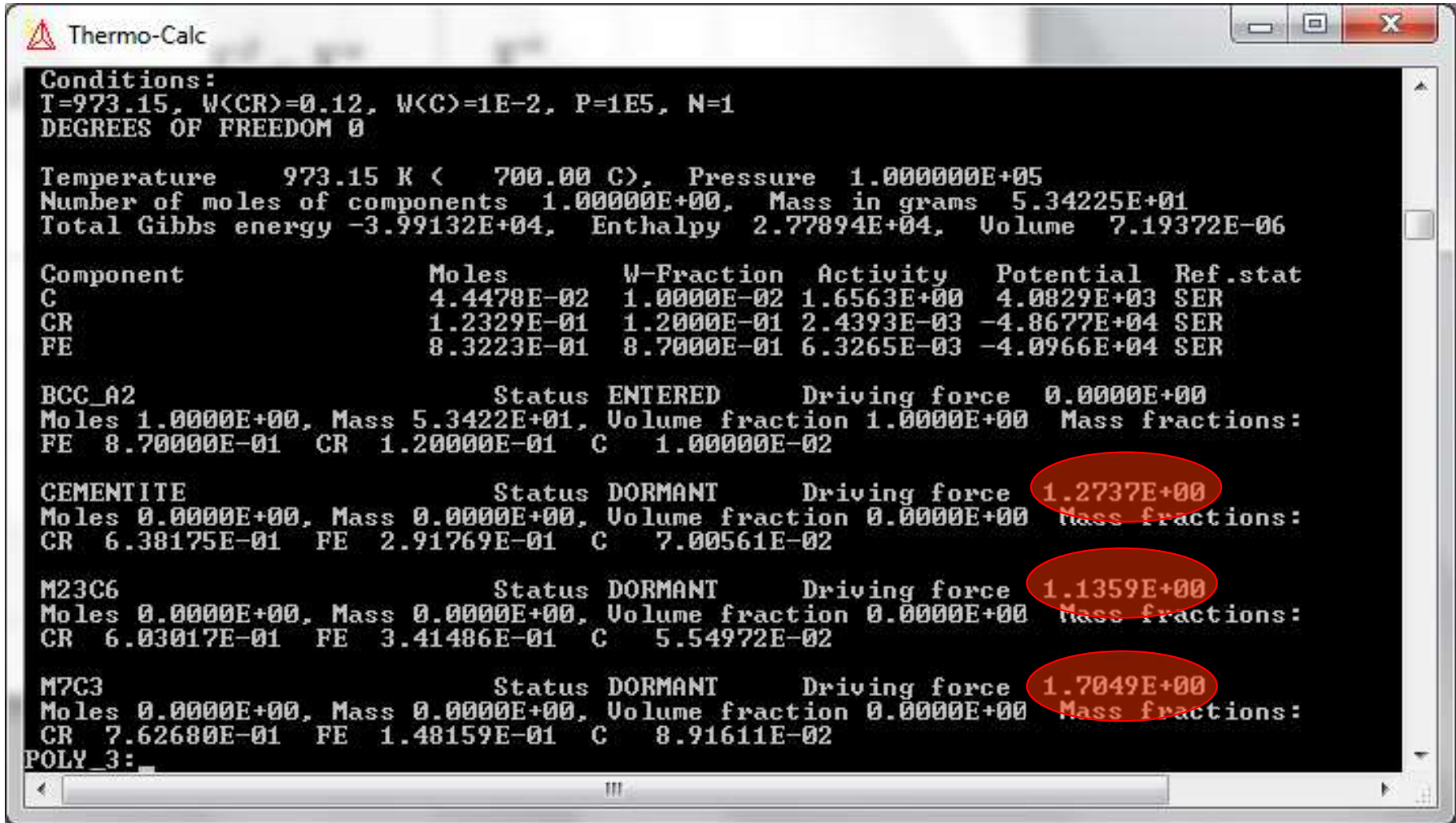


FIGURE 2. Free-energy diagram. The point *o* represents the parent phase. Phase III becomes more favored the more to the right it lies.

Models: Nucleation Rate

ΔG_m : driving force for nucleation



```
Thermo-Calc

Conditions:
T=973.15, W<CR>=0.12, W<C>=1E-2, P=1E5, N=1
DEGREES OF FREEDOM 0

Temperature 973.15 K ( 700.00 C), Pressure 1.000000E+05
Number of moles of components 1.00000E+00, Mass in grams 5.34225E+01
Total Gibbs energy -3.99132E+04, Enthalpy 2.77894E+04, Volume 7.19372E-06

Component      Moles      W-Fraction  Activity   Potential  Ref.stat
C               4.4478E-02  1.0000E-02  1.6563E+00  4.0829E+03  SER
CR             1.2329E-01  1.2000E-01  2.4393E-03  -4.8677E+04  SER
FE             8.3223E-01  8.7000E-01  6.3265E-03  -4.0966E+04  SER

BCC_A2          Status ENTERED      Driving force  0.0000E+00
Moles 1.0000E+00, Mass 5.3422E+01, Volume fraction 1.0000E+00  Mass fractions:
FE 8.70000E-01 CR 1.20000E-01 C 1.00000E-02

CEMENTITE       Status DORMANT      Driving force  1.2737E+00
Moles 0.0000E+00, Mass 0.0000E+00, Volume fraction 0.0000E+00  Mass fractions:
CR 6.38175E-01 FE 2.91769E-01 C 7.00561E-02

M23C6           Status DORMANT      Driving force  1.1359E+00
Moles 0.0000E+00, Mass 0.0000E+00, Volume fraction 0.0000E+00  Mass fractions:
CR 6.03017E-01 FE 3.41486E-01 C 5.54972E-02

M7C3            Status DORMANT      Driving force  1.7049E+00
Moles 0.0000E+00, Mass 0.0000E+00, Volume fraction 0.0000E+00  Mass fractions:
CR 7.62680E-01 FE 1.48159E-01 C 8.91611E-02
POLY_3:
```

Models: Nucleation Rate

Homogeneous nucleation

So far all nucleation theory slides have dealt with homogeneous nucleation of spherical nuclei. Additions to the models must be made in order to take into account:

- Heterogenous nucleation
- Elastic strain energy, resulting in other precipitate shapes

Models: Nucleation Rate

N - Available Nucleation Sites

Homogeneous Nucleation: $N_h = N_A / V_m^\alpha$

Heterogeneous Nucleation - Grain boundaries, edges, corners:

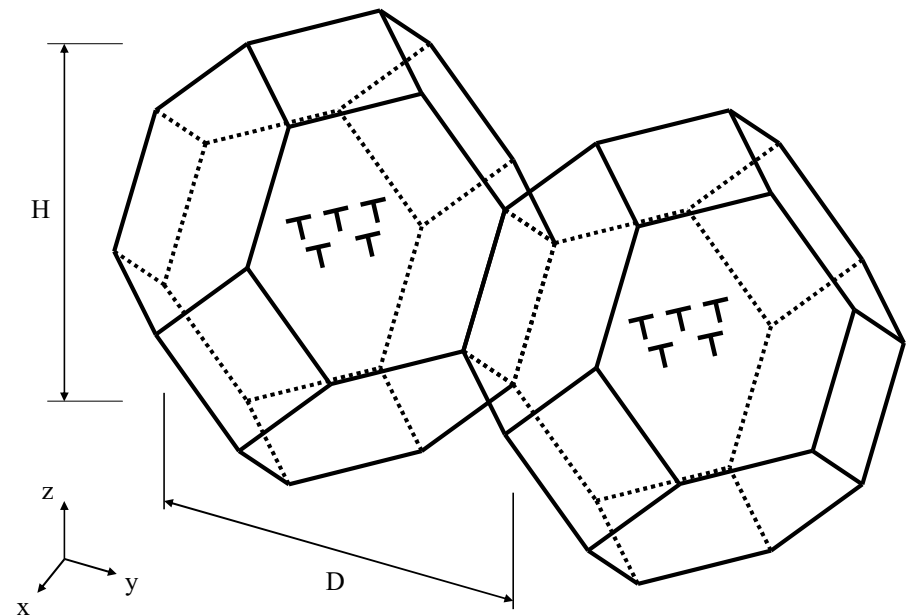
$$\rho_2 = \frac{6\sqrt{1+2A^2} + 1 + 2A}{4A} D^{-1}$$

$$\rho_1 = 2 \frac{\sqrt{2} + 2\sqrt{1+A^2}}{A} D^{-2}$$

$$\rho_0 = \frac{12}{A} D^{-3}$$

$$N_i = \rho_i \left(\frac{N_A}{V_m^\alpha} \right)^{i/3} \quad (i = 2, 1, 0)$$

Aspect Ratio $A=H/D$



Dislocations

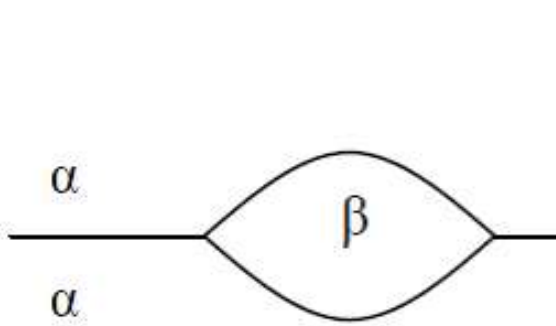
$$N_d = \rho_d \left(\frac{N_A}{V_m^\alpha} \right)^{1/3}$$

Tetrakaidecahedron approximation of grains

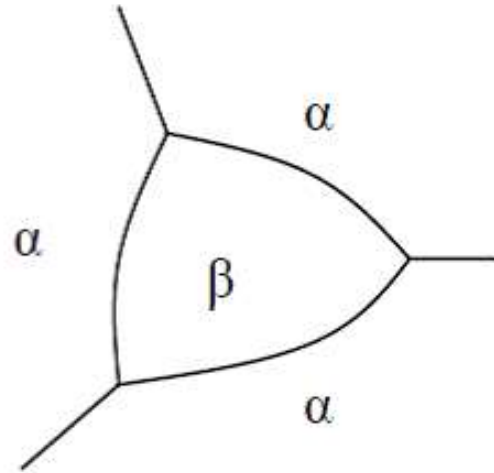
$A=1$, J. Cahn, Acta Metall. 4(1956)449

Models: Heterogenous Nucleation

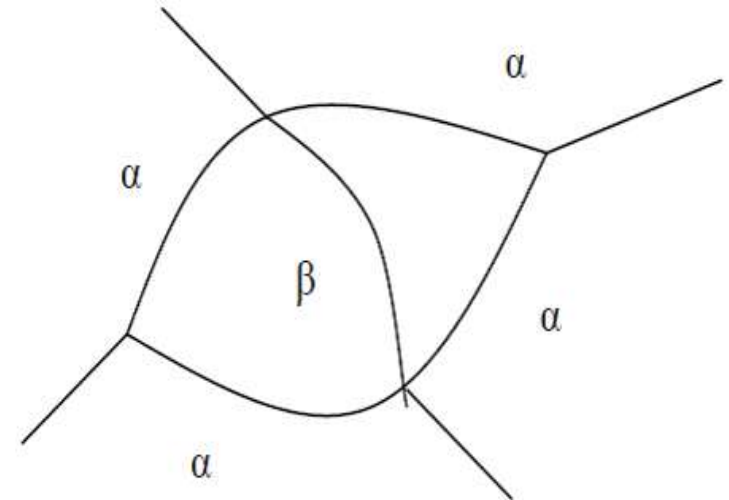
Wetting Angles for Grain Boundary Precipitation



Grain Boundary*
(Two-Grain Junction)



Grain Edge*
(Three-Grain Junction)

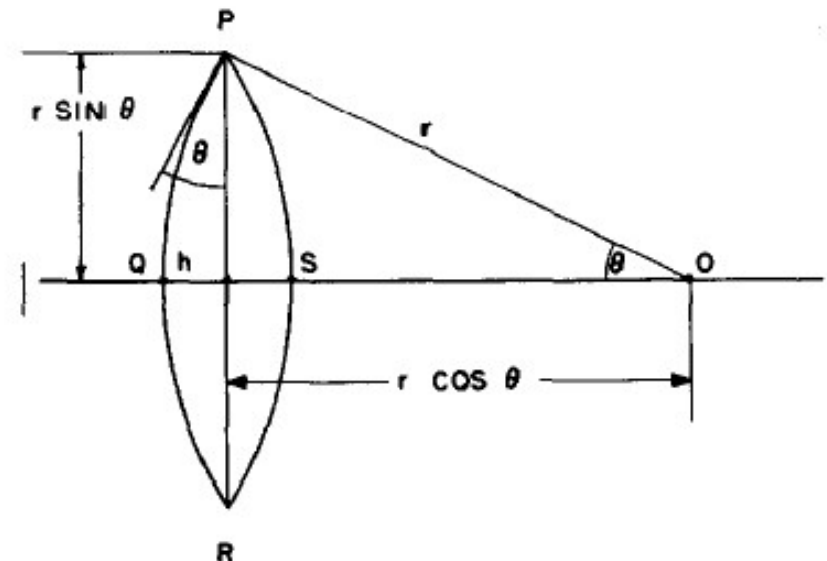


Grain Corner*
(Four-Grain Junction)

* Images taken from L. Zang,
<http://www.eng.utah.edu/~lzang/images/lecture-13.pdf>

Wetting Angle** **(Two-Grain Junction)**

** Image taken from P. Clemm and J. Fisher, Acta Metallurgica, 3(1)70-73



Models: Heterogenous Nucleation

Shape Factors

Eliminated GB Area	Surface Area of Nuclei	Volume of Nuclei	Wetting Angle
$A_{\alpha\alpha} = ar^2$	$A_{\alpha\beta} = br^2$	$V = cr^3$	$k = \cos \theta = \frac{\sigma_{\alpha\alpha}}{2\sigma_{\alpha\beta}}$

Effects of Wetting Angle

Activation Energy	$W = \frac{4}{27} \frac{\sigma_{\alpha\beta}^3 V_m^2}{(\Delta G_m^{\alpha \rightarrow \beta})^2} \frac{(b - 2ak)^3}{c^2}$
Critical Radius	$r^* = - \frac{2(b - 2ak)\sigma_{\alpha\beta} V_m}{3c\Delta G_m^{\alpha \rightarrow \beta}}$
Zeldovitch Factor	$Z = Z_b \sqrt{\frac{3c}{4\pi}}$
Molecular Attachment Rate	$\beta^* = \frac{br^2 XD}{a^4}$
Nucleation Site Density	$A_{\text{reduction}} = an\bar{r}^2$

The expression of a , b , and c for grain boundary (two-grain junction), grain edge (three-grain junction) and grain corner (four-grain junction) can be found in the paper by P. Clemm and J. Fisher, Acta Metallurgica, 3(1) 70-73.

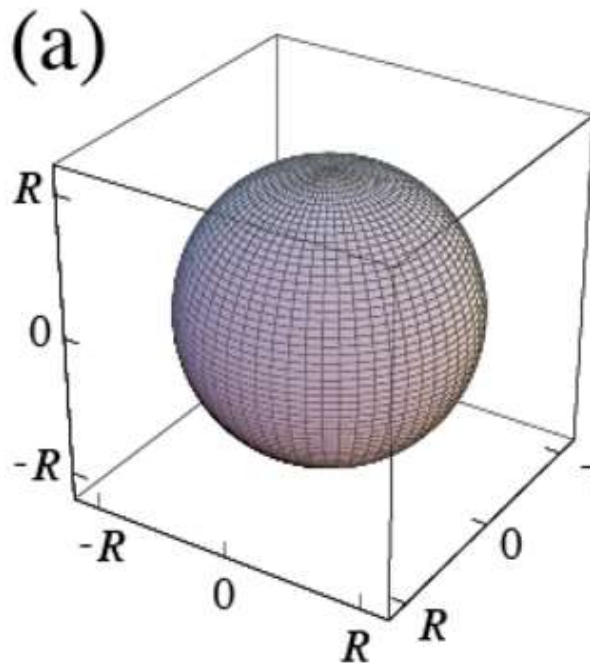
Precipitate Shapes

Elastic strain energy will change the shape of the nucleating particles.

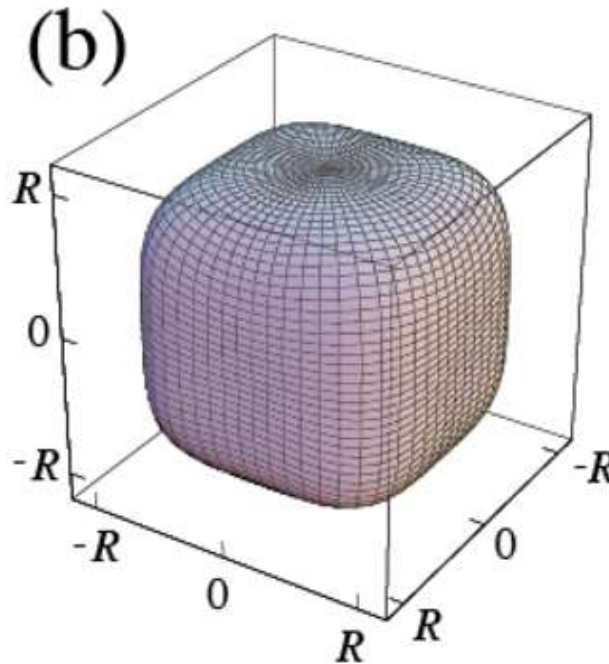
Cuboid (SuperSphere*)

K. Wu, Q. Chen, P. Mason, J Phase Eq. Diffus. 39(2018)571-583.

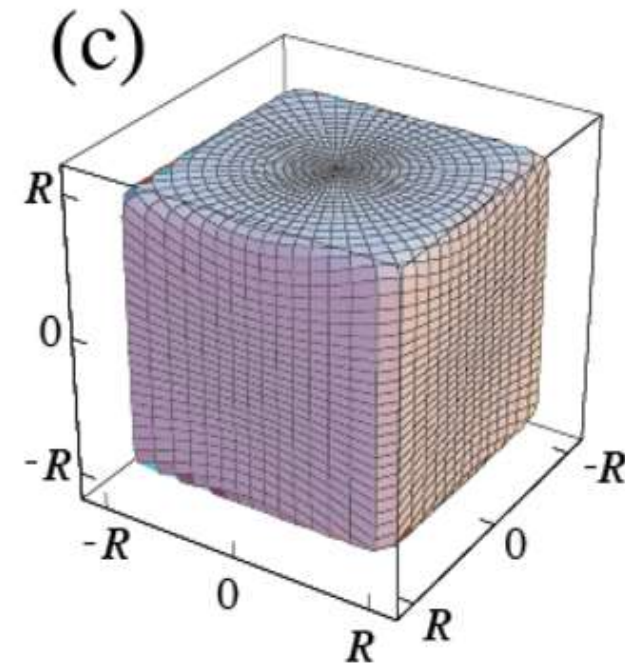
$$\left| \frac{x}{R} \right|^p + \left| \frac{y}{R} \right|^p + \left| \frac{z}{R} \right|^p = 1 \quad (p \geq 2) \quad \eta = 2^{\frac{p-2}{2p}}$$



$$p = 2(\eta = 1)$$



$$p = 4(\eta = 1.19)$$



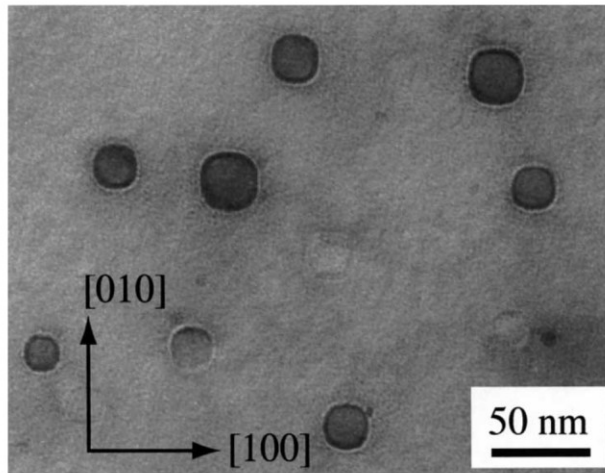
$$p = 20(\eta = 1.37)$$

*Susumu Onaka, *Symmetry* **2012**, 4(3), 336-343

Precipitate Shapes

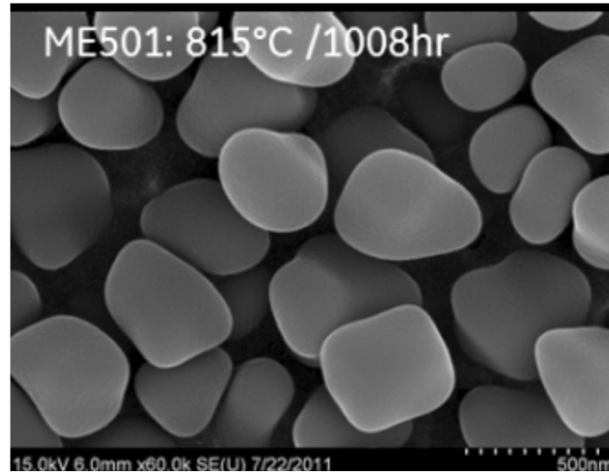
Cuboid (SuperSphere)

CoCr in (Cu)

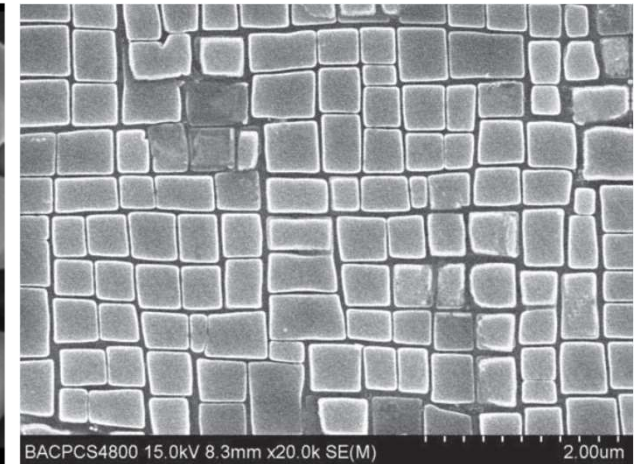


S. Onaka et al., Mater Sci & Engr, A347 (2003) 42 – 49.

γ' Phase in Ni-based Superalloys



A. Powell et al., Superalloys 2016, p. 189-196



J.R. Li et al., Superalloys 2016, p.57-63

- Alloy chemistry and heat treatment have profound effect on particle morphologies
- Precipitate shape is related to size and atomic misfit
- Precipitate shape is determined automatically by the ratio of interfacial energy/elastic energy

Precipitate Shapes

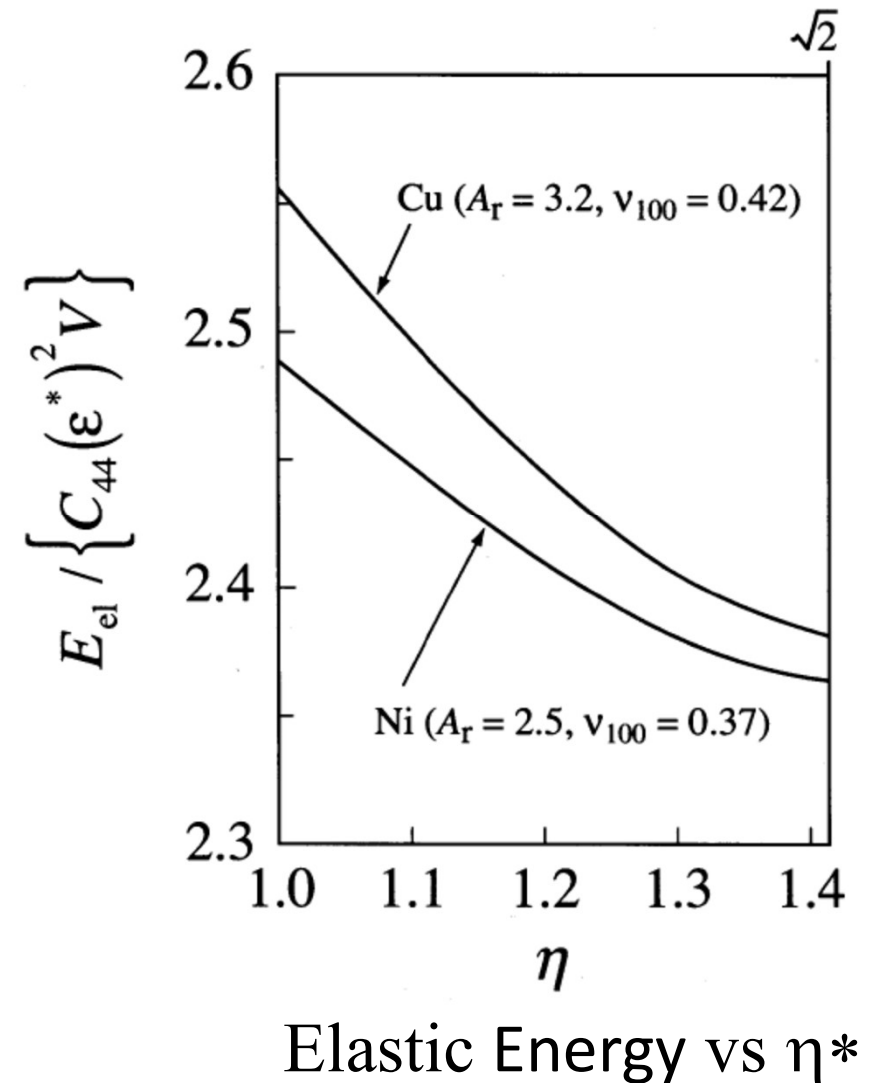
Cuboid (SuperSphere)

➤ Elastic Energy

- Elastically Cubic System
- Strain from Atomic Misfit
- Assumption of Linear Relation up to $\eta=1.35$
- Elastic Energy of Spherical and Cubic Particles from Khachaturyan's Treatment**

➤ Particle Shape

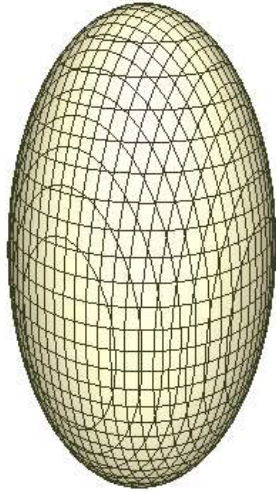
- Determined by Minimization of Combined Interfacial Energy and Elastic Strain Energy



* S. Ontaka et al., *Mater. Sci. Eng.* A347(2003)42

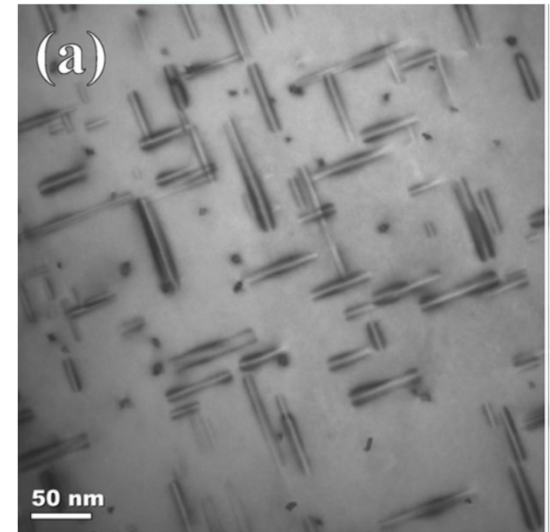
** A.G. Khachaturyan, *Theory of Structural Transformation in Solids*

Precipitate Shapes



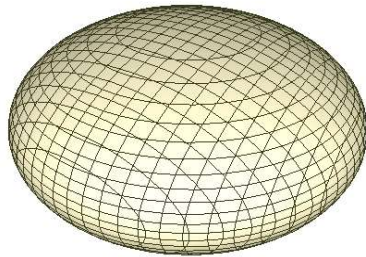
**Needle
(Prolate Spheroid)**

$$\frac{x_1^2}{r^2} + \frac{x_2^2}{r^2} + \frac{x_3^2}{l^2} \leq 1 \quad l > r$$



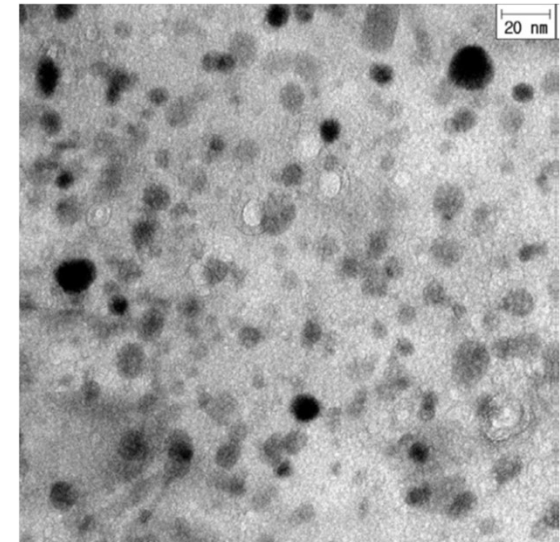
β'' phase in Al-Mg-Si Alloy

F.A.Martinsen et al., *Acta Materialia* 60(2012)6091-6101



**Plate
(Oblate Spheroid)**

$$\frac{x_1^2}{l^2} + \frac{x_2^2}{l^2} + \frac{x_3^2}{r^2} \leq 1 \quad l > r$$



η' phase in Al-7075 Alloy

M.H.Shaeri et al., *Materials and Design* 57(2014)250-257

- Faster Growth
- Interfacial Energy Anisotropy
- Shape Determined by Ratio of Interfacial Energy/ Elastic Energy

Precipitate Shapes

➤ Interfacial Energy Anisotropy*

$$\frac{\sigma_l}{\sigma_r} = \frac{l}{r} = \alpha$$

➤ Elastic Strain Energy

- Elastically Isotropic or Cubic Systems
- First Approximation: Elastically Homogenous
- Eshelby's Theory**

➤ Particle Shape

- Determined by Minimization of Combined Interfacial Energy and Elastic Energy
- User-Defined, Fixed Value

Needle (Prolate Spheroid)

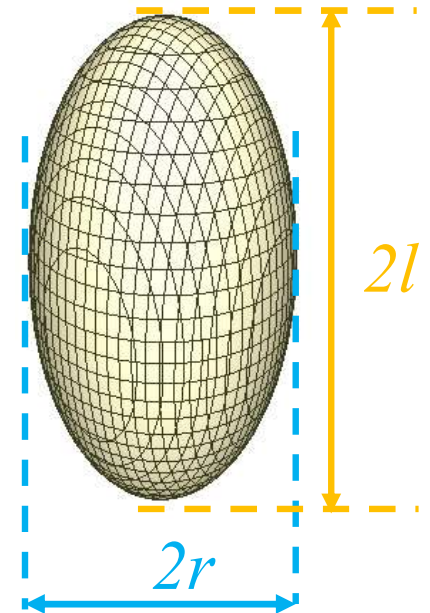
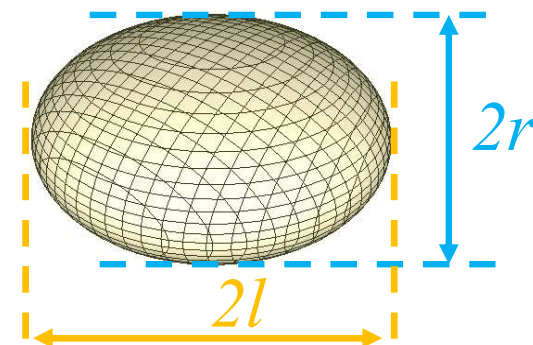


Plate (Oblate Spheroid)



* C.A. Johnson, *Surf. Sci.* 3(1965)429

** J.D. Eshelby, *Pro. Roy. Soc. A*, 241(1957)376

Precipitate Shapes

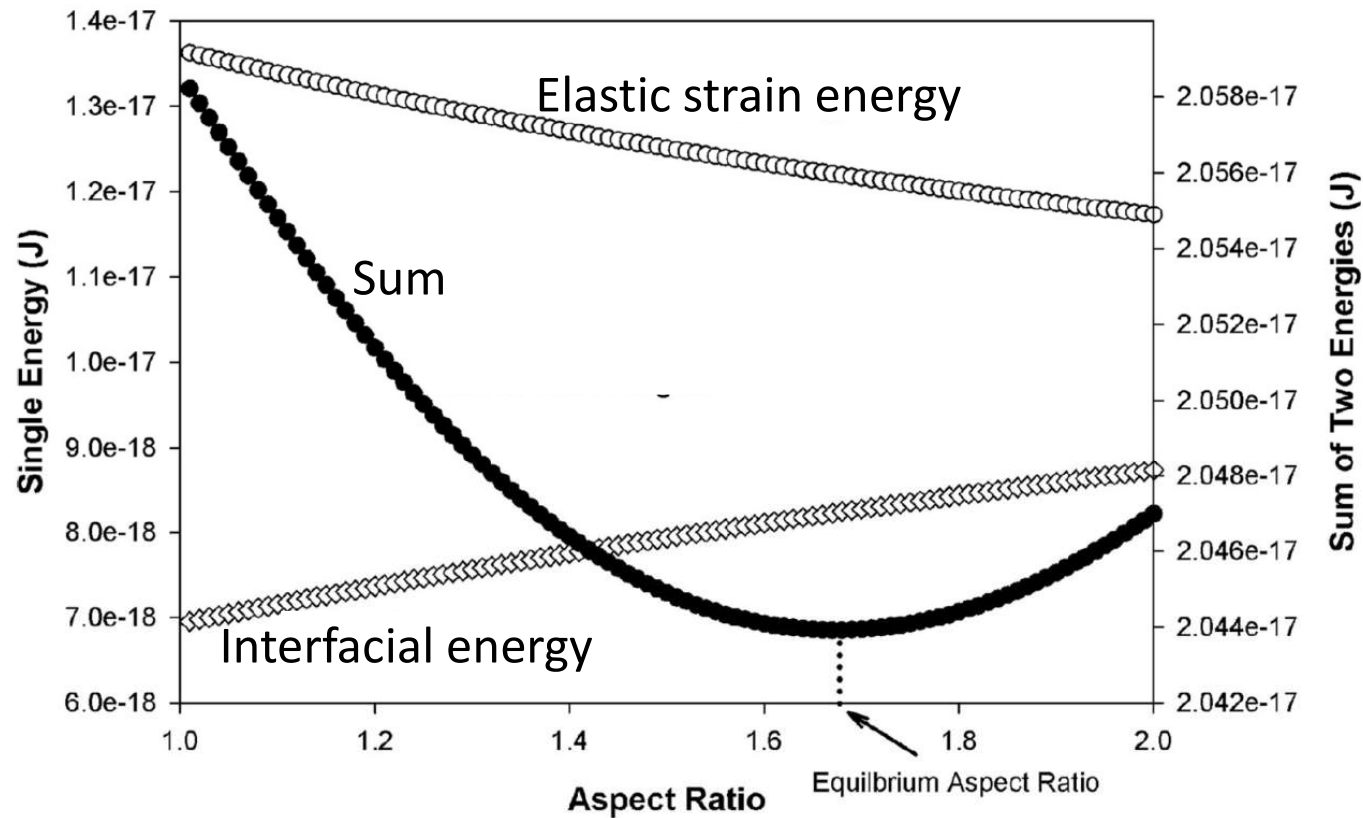


Fig. 1 The calculated elastic strain energy and interfacial energy (with scales displaying on left Y-axis), and the sum of the two energies (with scale displaying on right Y-axis) as function of aspect

ratio for a Cu_4Ti particle. The volume of the particle is equal to a sphere with radius of 4 nm. The minimum of the summed energy determines the equilibrium aspect ratio

Examples

Cu-Ti

TC-PRISMA Examples

Example, Cu-Ti Alloy:

Precipitation of Cu_4Ti from FCC (Kampmann et al 1987)

Precipitation Kinetics in Metastable Solid Solutions – Theoretical Considerations and Application to Cu-Ti Alloys

R. Kampmann, H. Eckerlebe, and R. Wagner

GKSS-Forschungszentrum, Institut für Physik
D-2054 Geesthacht, FR Germany

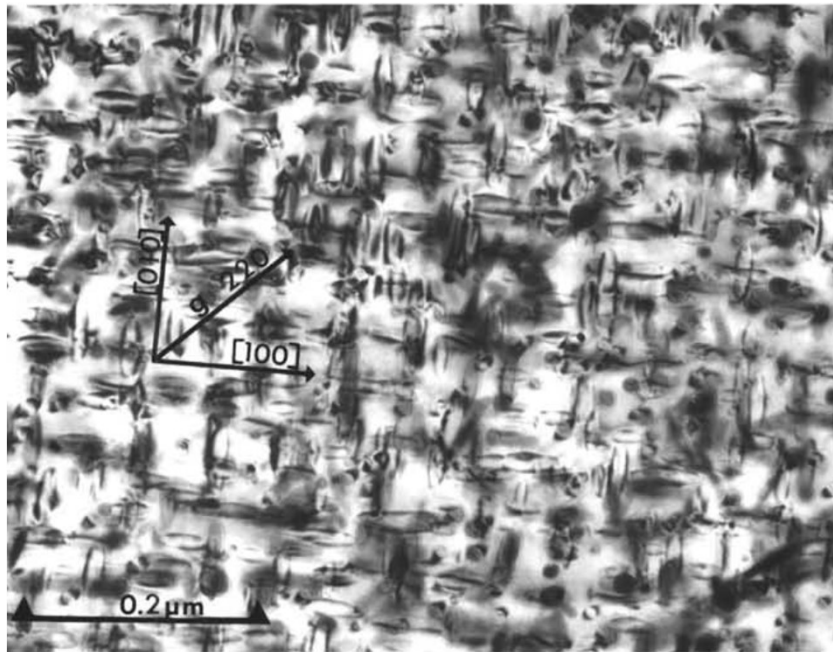
ABSTRACT

Cu-2.9 at.% Ti single crystals were homogenized at various temperatures ($780^\circ\text{C} \leq T_H \leq 960^\circ\text{C}$) and quenched. Subsequent isothermal aging at 350°C led to phase separation, the kinetics of which have been followed by employing small-angle neutron scattering (SANS). According to complementary transmission electron and analytical field ion microscopy studies, the resulting transformation products of this first order phase transition are stoichiometrically ordered ellipsoidal Cu_4Ti particles, the aspect ratio of which changes with aging time (t) as revealed by two-dimensional SANS-detection. In the early stages of phase separation, the decomposition kinetics are strongly influenced by the quenching rate via quenched-in excess vacancies. During aging the structure factor $S(\kappa, t)$ develops a maximum, the height (S_m) of which increases and the position (κ_m) of which decreases with t . Neither $S_m(t)$ nor $\kappa_m(t)$ follow a power law as predicted by several recent theories on spinodal decomposition. On the other hand, the time evolution of the mean Ti-rich cluster size (\bar{R}), their number density (N_v), and the supersaturation (Δc) as inferred from the SANS-data and the diffuse Laue-scattering, are well predicted by a precipitation model which describes nucleation, growth and coarsening as competing processes.

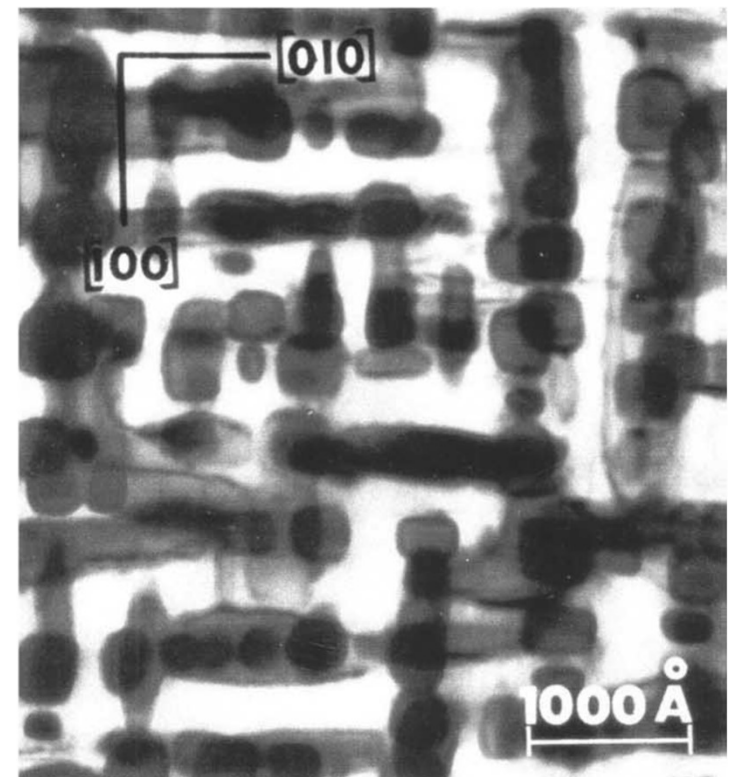
TC-PRISMA Examples

Example, Cu-Ti Alloy:

Precipitation of Cu_4Ti
from FCC



Cu-1wt.%Ti, 500°C, 100min



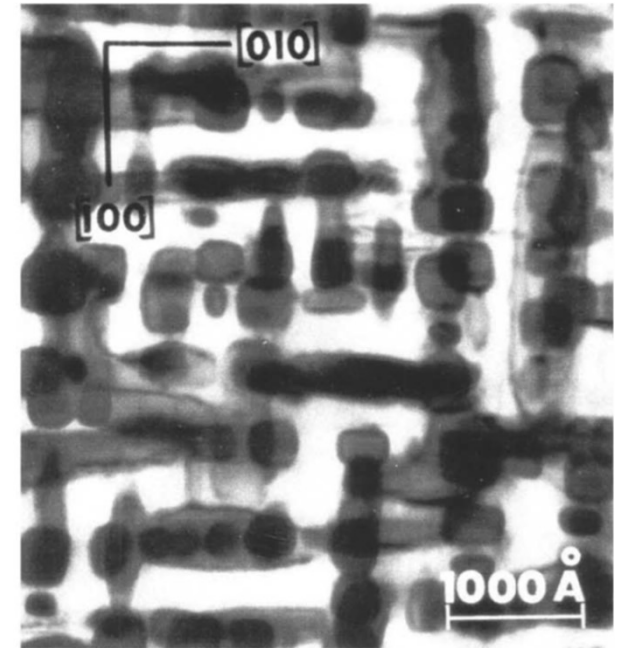
Cu-4wt.%Ti, 500°C, 2000min

Precipitation of Cu_4Ti from FCC

- Needle shape
- Tetragonal body-center D1a
- Coherent with matrix with a tetragonal misfit*

$$\epsilon_{11} = \epsilon_{22} = 0.022 \quad [100]_{\text{FCC}}, [010]_{\text{FCC}}$$

$$\epsilon_{33} = 0.003 \quad [001]_{\text{FCC}}$$



Cu_4Ti precipitates in a Cu-Ti Alloy

Image taken from W.A.Soffa and D.E. Laughlin, *Prog. Mater. Sci.* 49(2004)347

* C. Borchers, *Phil. Mag.*, 79(1999)537

Example Cu-Ti Alloy

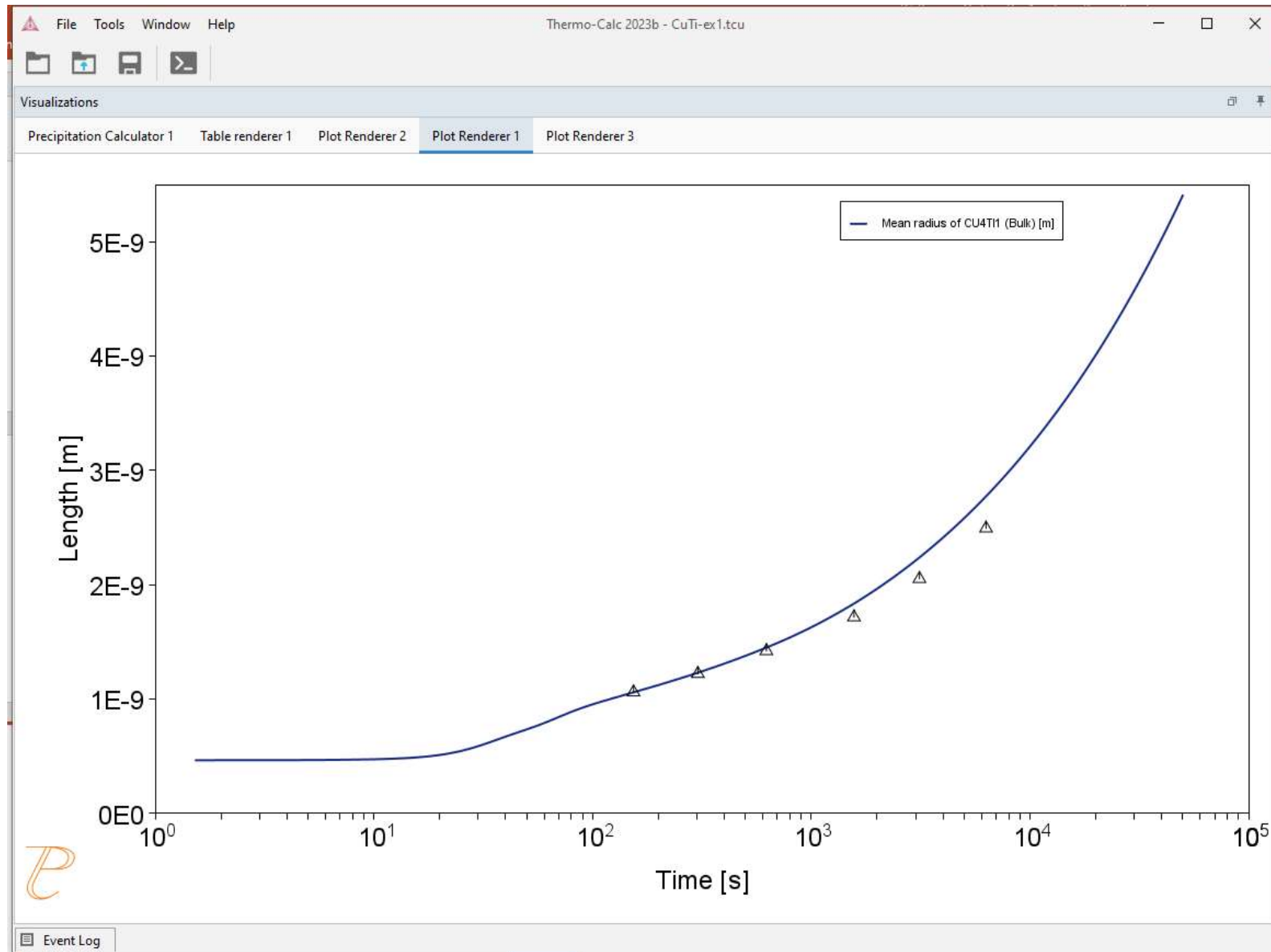
Precipitation of Cu_4Ti from FCC (Cu)
(Kampmann et al 1987) . They estimated
 $D = 2.5 \cdot 10^{-19} \text{ m}^2/\text{s}$ after solution treatment and
quenching. Compare with our calculated D value.

Composition	Cu - 1.9 Ti (at. %)
Temperature	350 °C
Simulation time	1E4 s
Nucleation Site Type	Bulk
Interfacial Energy	0.067 J/m ²
Mobility Adjustment	100
Molar volume of Phases	Database values

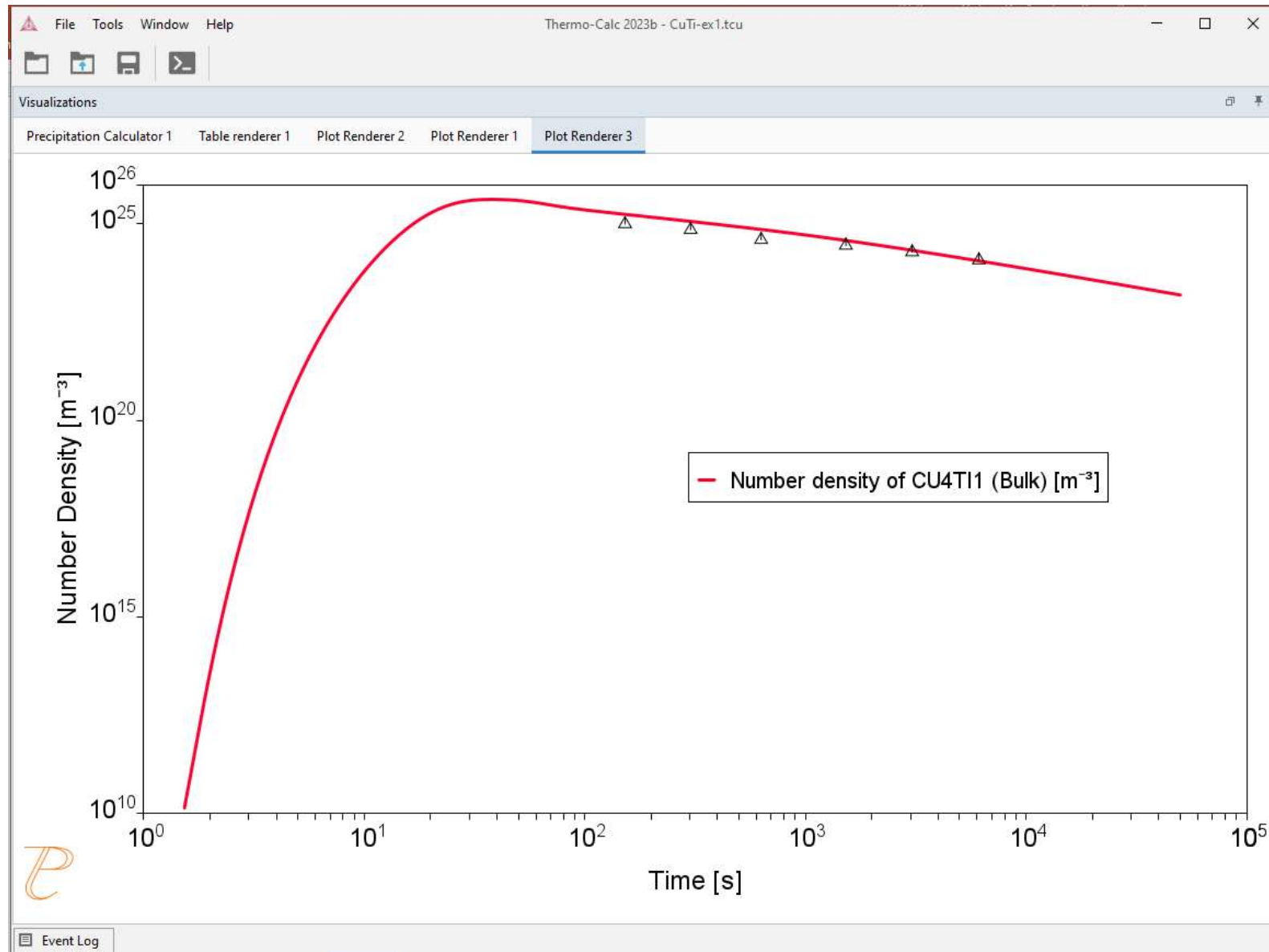
Cu-Ti Example 1

System	
Database package	TCCU6 + MOBCU5
Elements	Cu, Ti
Matrix phase	FCC_A1
Precipitate phase	Cu ₄ Ti
Conditions	
Composition	Cu - 1.9 Ti (at. %)
Temperature	350 °C
Simulation time	5E4 s
Nucleation properties	Nucleation Site Type: Bulk
Data Parameters	
Interfacial Energy	Bulk: 0.067 J/m ²
Molar Volume (Matrix):	FCC: Database
Molar Volume (Precipitate):	Cu ₄ Ti: Database
Mobility Adjustment Factor	+100

Cu-Ti Example 1



Cu-Ti Example 1



Cu-Ti Example 2 – needle shape

System	
Database package	TCCU6 + MOBCU5
Elements	Cu, Ti
Matrix phase	FCC_A1
Precipitate phase	Cu ₄ Ti
Conditions	
Composition	Cu - 1.9 Ti (at. %)
Temperature	350 °C
Simulation time	1E5 s
Nucleation properties	Nucleation Site Type: Bulk
Data Parameters	
Interfacial Energy	0.067 J/m ²
Molar Volume (Matrix):	Database
Molar Volume (Precipitate):	Database
Mobility Adjustment Factor	+100

Select the
General Growth
Rate Model.

Cu-Ti Example 2 – needle shape

Precipitation of Cu_4Ti from FCC

- Cu-1.9at.% Ti
- Databases:
TCCU6+MOBCU5 (or demo-DB)
- User-input misfit strain

ϵ_{11}	ϵ_{22}	ϵ_{33}
0.022	0.022	0.003

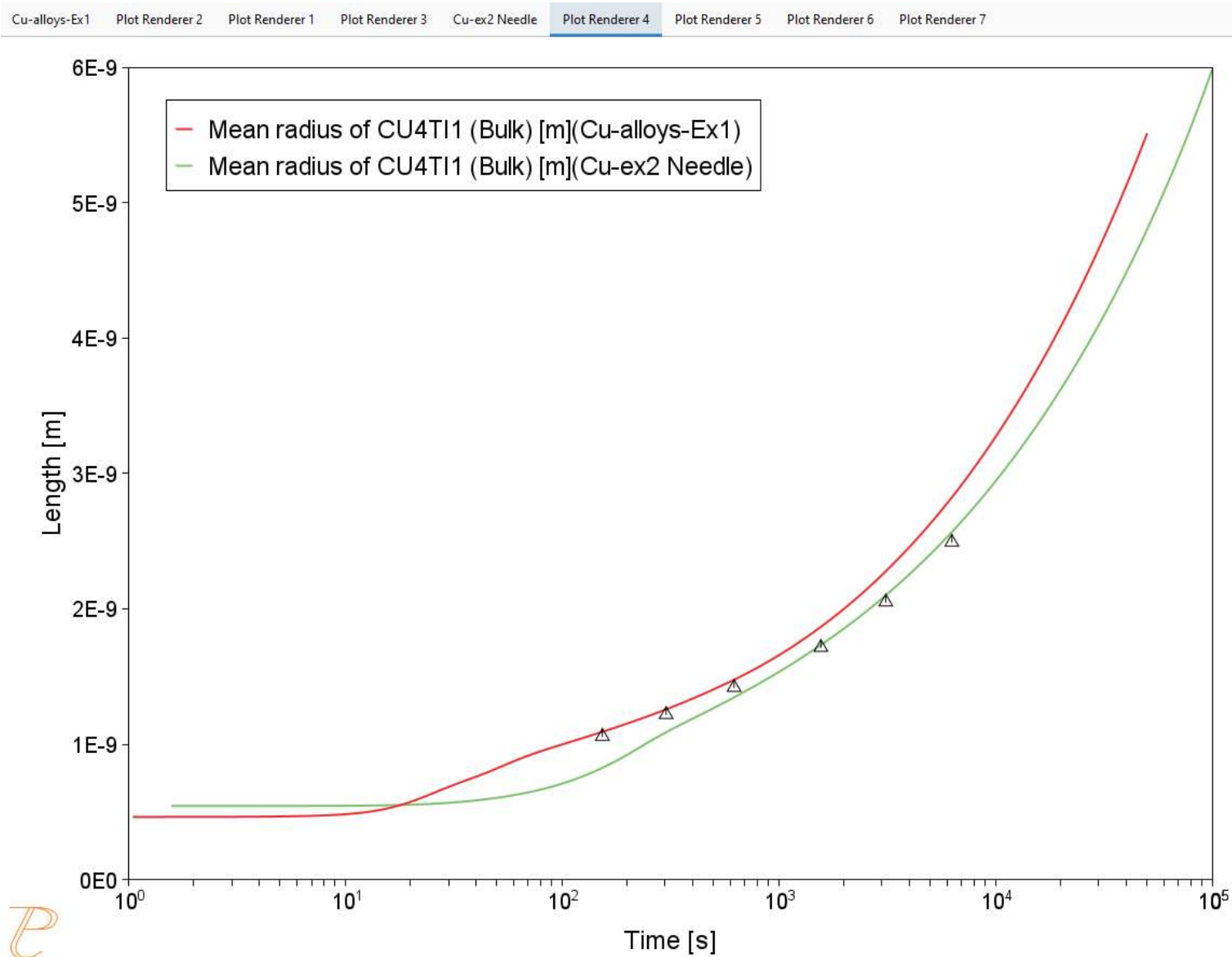
* C. Borchers, *Phil. Mag.*, 79(1999)537

C_{11}	C_{12}	C_{44}
168.4 GPa	121.4 GPa	75.4 GPa

* J.K. Lee et al., *Metall. Trans. A*, 8(1977)963

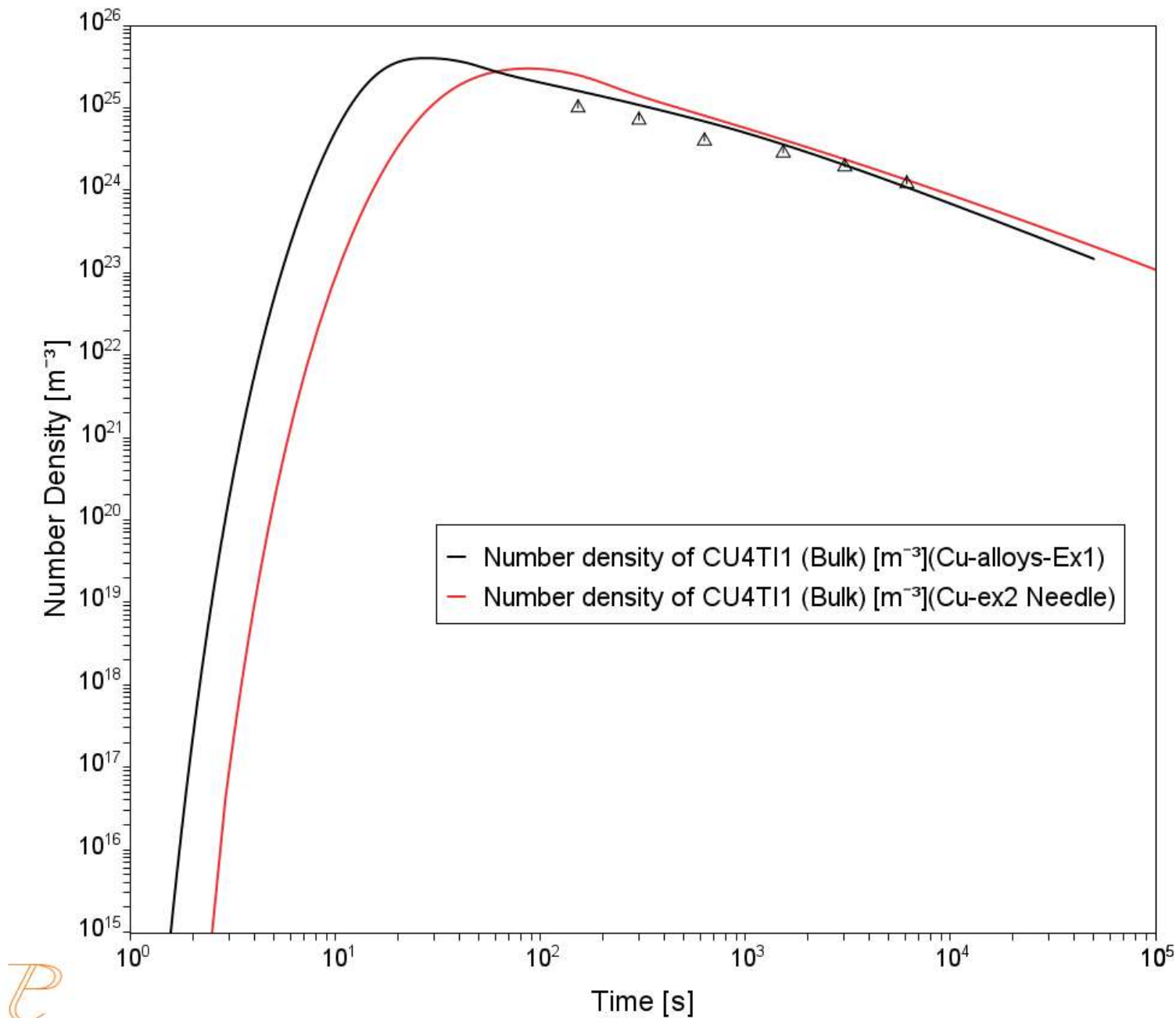
- Default values for other parameters

Cu-Ti Example 2 – needle shape

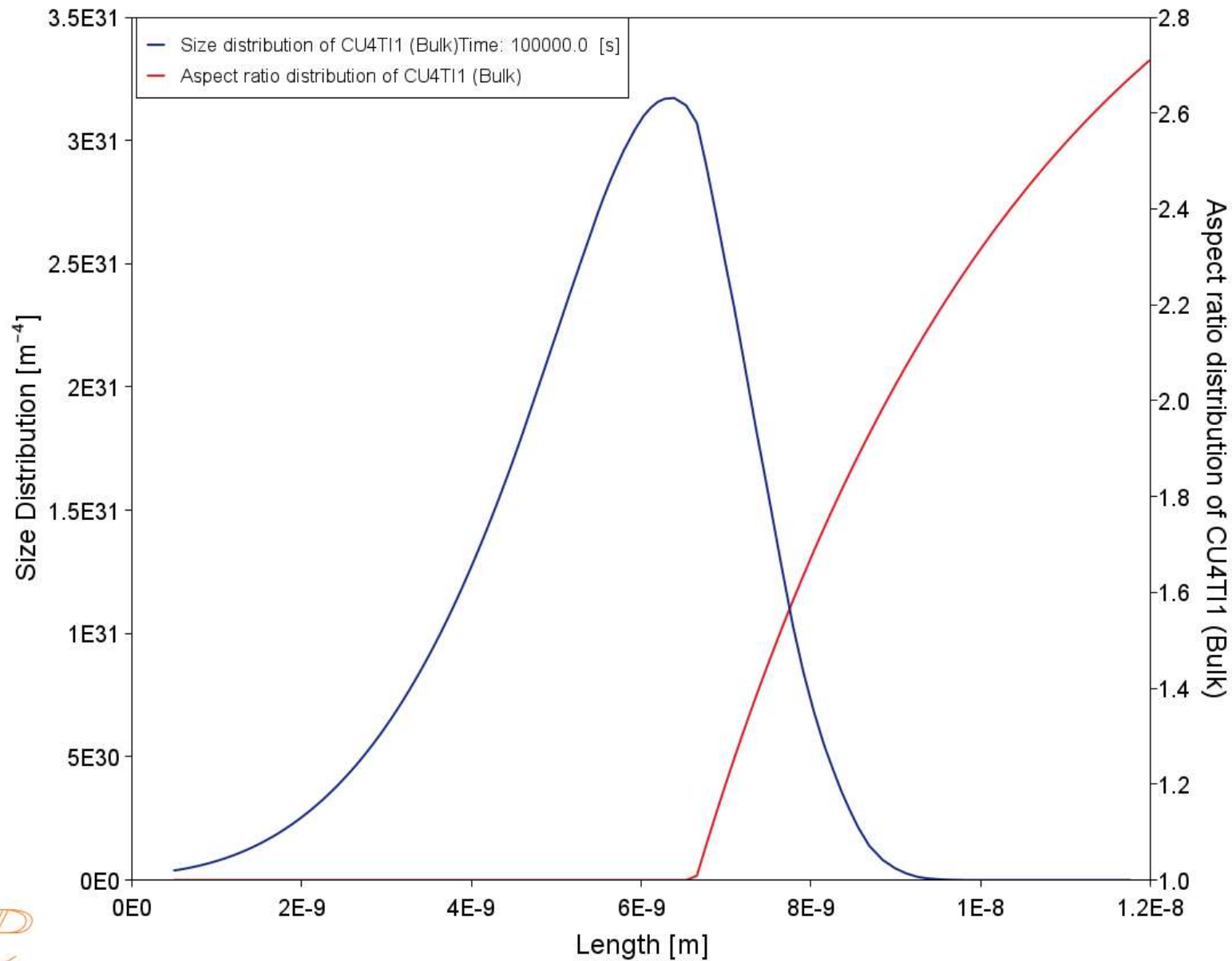


P

Cu-Ti Example 2 – needle shape



Cu-Ti Example 2 – needle shape



P

Cu-Ti Example 3 – TTP diagram

System	
Database package	CUDEMO + MCODEMO
Elements	Cu, Ti
Matrix phase	FCC_A1
Precipitate phase	CU4TI1
Conditions – TTT diagram	
	- Phase fraction = 0.001
Composition	Cu - 1.9 Ti (at. %)
Temperature	200 °C - 560 °C, $\Delta=10$ °C
Max annealing time	1E7 s
Nucleation properties	Nucleation Site Type: Bulk
Data Parameters	
Interfacial Energy	0.067
Molar Volume (Matrix):	Database
Molar Volume (Precipitate):	Database
Mobility Adjustment Factor	+100

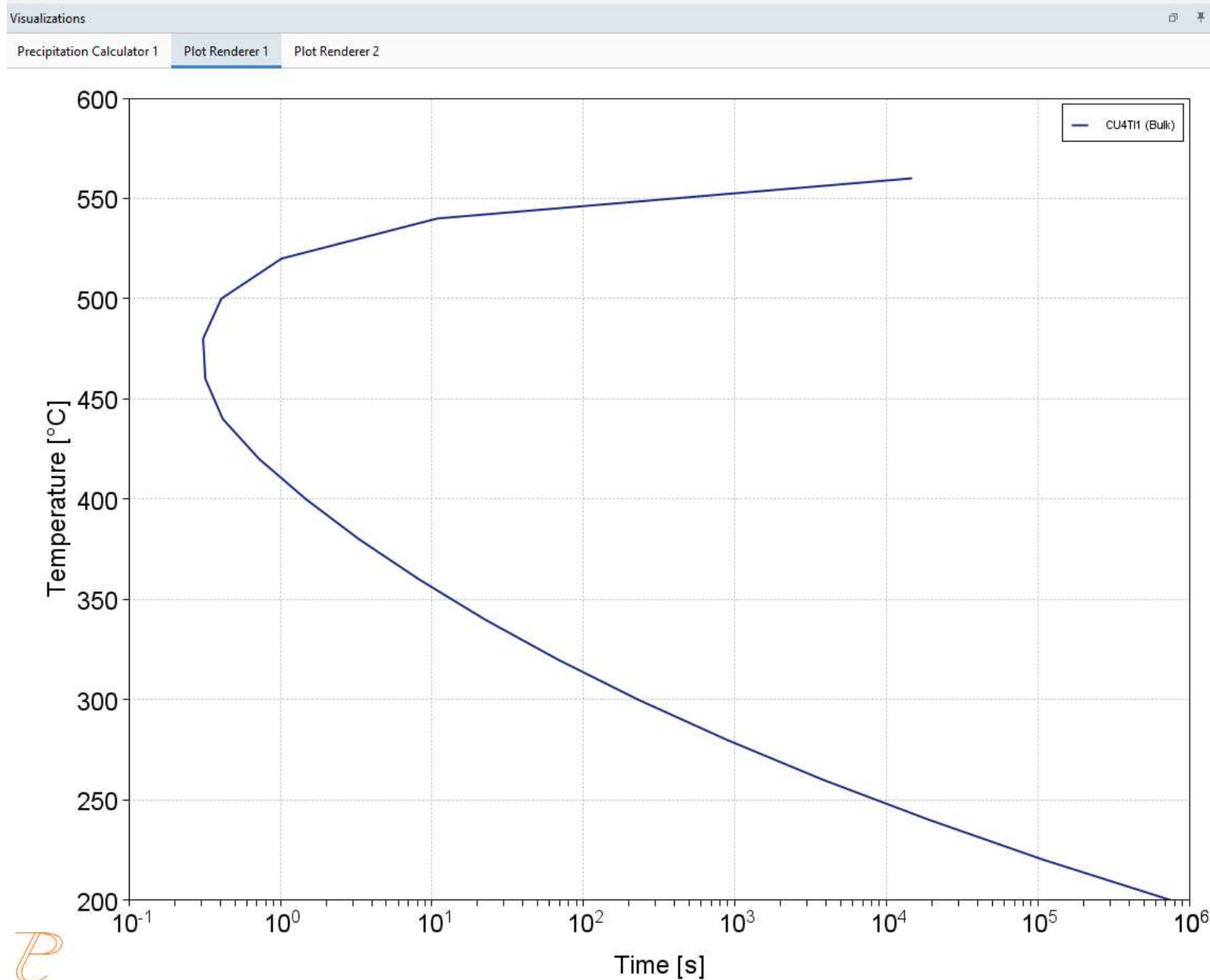
Set Options:

Number of grid points: 15

Maximum number of grid points: 20

Minimum number of grid points: 10

Cu-Ti Example 3 – TTP diagram



Home assignment: Al - Zr Alloy

J MATER RES TECHNOL. 2018;7(1):66–72



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Original Article

Precipitation hardening in dilute Al-Zr alloys



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ARTICLE INFO

Article history:

Received 6 April 2017

Accepted 15 May 2017

Available online 26 June 2017

Keywords:

Aluminum alloys

Age hardening

Precipitation hardening
mechanisms

Al₃Zr

ABSTRACT

The aim of this study was to investigate the effect of solute content (hiperperitectic Al-0.22 wt.%Zr and hiperperitectic Al-0.32 wt.%Zr) on the precipitation hardening and microstructural evolution of dilute Al-Zr alloys isothermally aged. The materials were conventionally cast in a muffle furnace, solidified in a water-cooled Cu mold and subsequently heat-treated at the temperature of 650 K (377 °C) for 4, 12, 24, 100 and 400 h. Mechanical characterization was performed at room temperature, using a microhardness tester and microstructural characterization was carried out on a Transmission Electron Microscope – TEM. The observed microhardness values increased during isothermal aging, due to the precipitation of nanometer-scale Al₃Zr L1₂ particles. Peak strength was achieved within 100 h of aging. After aging for 400 h, microhardness values presented a slight decrease for both alloys, thus indicating overaging due to the coalescence of precipitates. Microhardness values increased with solute content, due to the precipitation of a higher number density of finer precipitates. After 400 h of heat-treating, coalescence was higher for the alloy with lower solute content and, also, the presence of antiphase boundaries – APBs, planar faults associated with the L1₂ to D0₂₃ structural transition, were observed. Comparing theoretical calculations of the increment in strength due to precipitation strengthening with experimental results, it was observed that their values are in reasonable agreement. The Orowan dislocation looping mechanism takes place during precipitation hardening for both alloys in the peak hardness condition.

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Home assignment: Al - Zr Alloy

System	
Database package	ALDEMO + MALDEMO (or TCAL9+MOBAL8)
Elements	Al, Zr, Si, (Fe is optional if TCAL9 used)
Matrix phase	FCC_A1
Precipitate phase	Al ₃ Sc (= AL3X in TCAL9)
Conditions	
Composition	Al - 0.23 Zr – 0.05 Si (- 0.1 Fe) (wt.%)
Temperature	650 K
Simulation time	500 hours
Nucleation properties	Nucleation Site Type: Bulk
Data Parameters	
Interfacial Energy	Calculated
Molar Volume (Matrix):	Fcc_A1: from database
Molar Volume (Precipitate):	Al ₃ Sc: from database

Home assignment: Al - Zr Alloy

The aim of this assignment is not only to simulate the precipitation treatment of this alloy, but to compare its simulated hardness (HV) with experimental data from the paper.

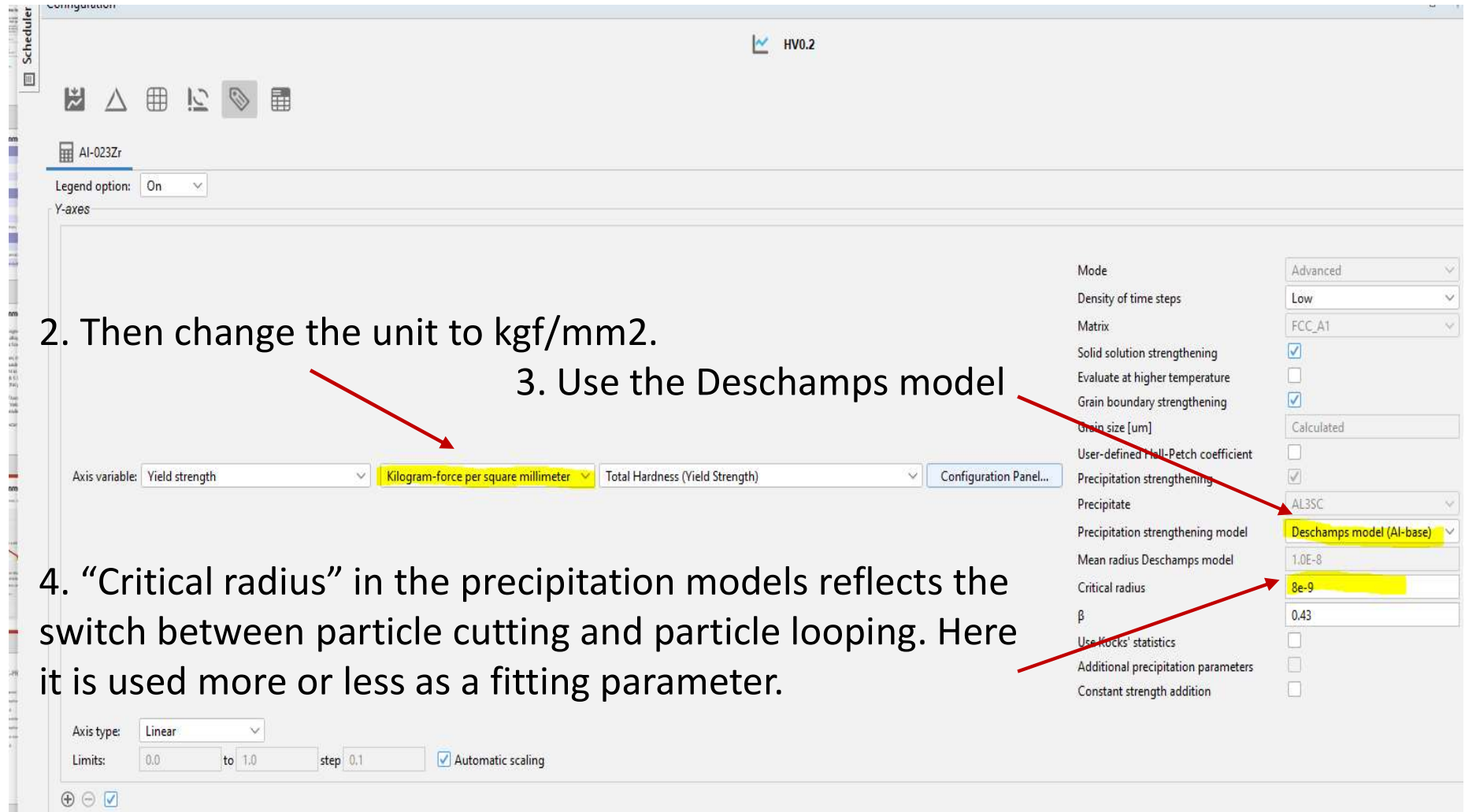
Following the paper, it is not the most stable Al-Zr phase that forms during the first several hundred hours of heat treatment. The most stable phase is called AL3ZR_D023 in TCAL and will probably become stable after even longer time at high T. Instead another phase of the same chemistry, AL3X, precipitates first (this phase is called AL3SC in ALDEMO).

The calculation of hardness in TC-Prisma is based on the same principle as the calculation of Yield strength. The selection and setting of parameters is done in the Plot renderer after the precipitation calculation, see next slide.

Use the experimental file "Souza_data.exp" for comparison with your result.

Home assignment: Al - Zr Alloy

1. In the Plot renderer, select Yield Strength as Y-axis variable.



2. Then change the unit to kgf/mm².

3. Use the Descamps model

4. “Critical radius” in the precipitation models reflects the switch between particle cutting and particle looping. Here it is used more or less as a fitting parameter.

Configuration window for Al-023Zr alloy, showing the Y-axis variable set to Yield strength, the unit set to Kilogram-force per square millimeter, and the Precipitation strengthening model set to Descamps model (Al-base). The Critical radius is set to 8e-9.

Axis variable: Yield strength | Kilogram-force per square millimeter | Total Hardness (Yield Strength) | Configuration Panel...

Axis type: Linear | Limits: 0.0 to 1.0 step 0.1 | Automatic scaling

Mode: Advanced | Density of time steps: Low | Matrix: FCC_A1 | Solid solution strengthening: ☒ | Evaluate at higher temperature: ☐ | Grain boundary strengthening: ☒ | Grain size [um]: Calculated | User-defined Hall-Petch coefficient: ☐ | Precipitation strengthening: ☒ | Precipitate: AL3SC | Precipitation strengthening model: Descamps model (Al-base) | Mean radius Descamps model: 1.0E-8 | Critical radius: 8e-9 | β : 0.43 | Use Kocks' statistics: ☐ | Additional precipitation parameters: ☐ | Constant strength addition: ☐

Q & A