



# THERMODYNAMICS CALCULATION AND KINETICS MODELING OF PRECIPITATION OF MICRO- ALLOYED MG-AL-CA ALLOYS

**MIME 572**

**Student: Jing Su**

# Outline



- Objectives
- Background of my project
- Thermodynamics calculations
  - ▣ Scheil cooling diagrams of Mg-Al-Ca alloys
  - ▣ Equilibrium diagrams of Mg-Al-Ca alloys
- Kinetics modeling of precipitation
  - ▣ Classical theory of nucleation and growth
  - ▣ Selection of input parameters from literature
  - ▣ Calculation of input parameters by FactSage
  - ▣ TTT diagram of Mg-Al-Ca alloy
- Conclusion
- Reference

# Objectives



- To have a perspective of precipitates in as-cast Mg-Al-Ca alloys from Scheil cooling calculation by FactSage
- To acquire heat treatment temperatures for Mg-Al-Ca alloys from equilibrium calculation by FactSage
- To model the kinetics of precipitation during ageing treatment by using classical nucleation and growth theory



# Background of the project

- Addition of Ca into Mg-Al alloys
  - Refinement of the microstructure --- Improvement of formability of sheets
  - Strengthening
  - Inexpensive alloy element comparing with the rare earth elements
  - Increase the ignition temperature --- Protecting the melting surface from oxidation
- Experimental alloys

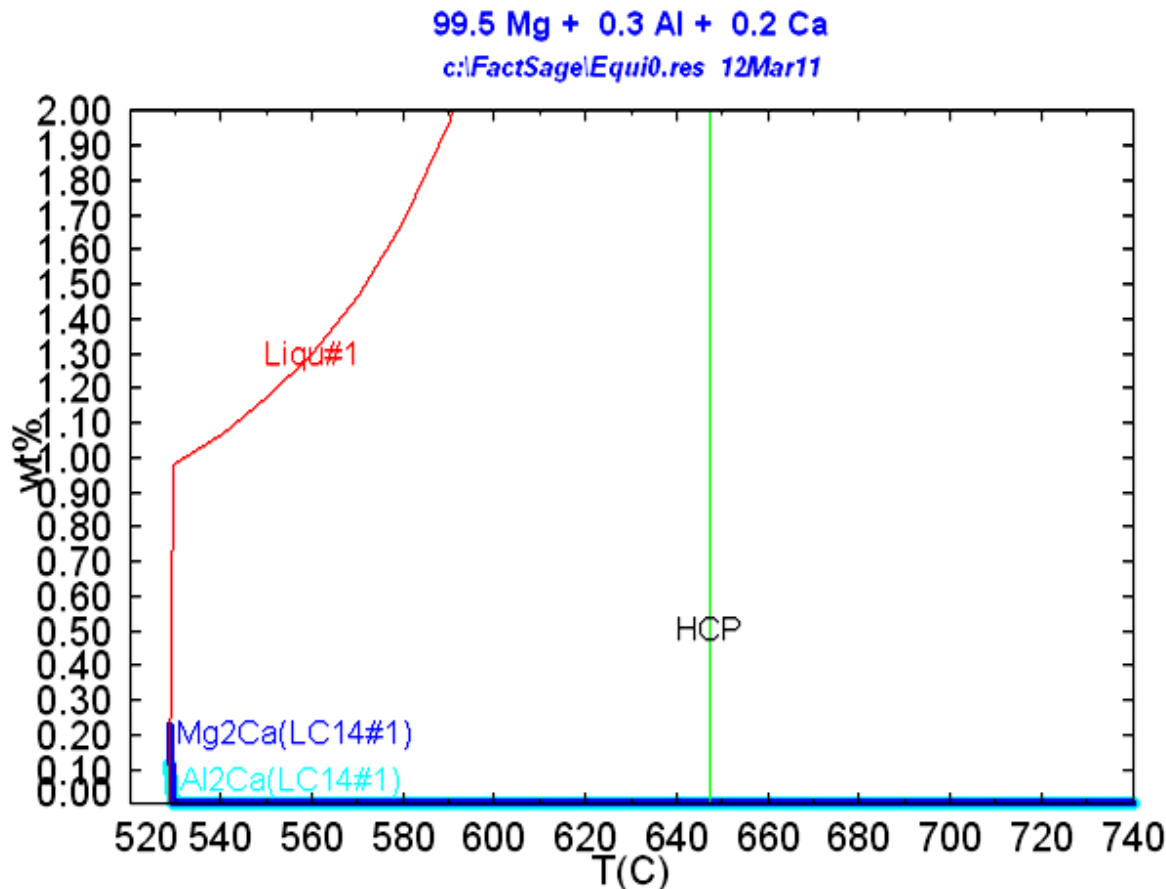
Table 1 Nominal compositions of two selected Mg-Al-Ca alloys

Alloy	Composition Range		
	Al (wt.%)	Ca (wt.%)	Mg (wt.%)
Alloy 1	0.1	0.5	Balance
Alloy 2	0.3	0.2	Balance



# Thermodynamics calculation

- Scheil cooling diagram of Mg-0.3Al-0.2Ca



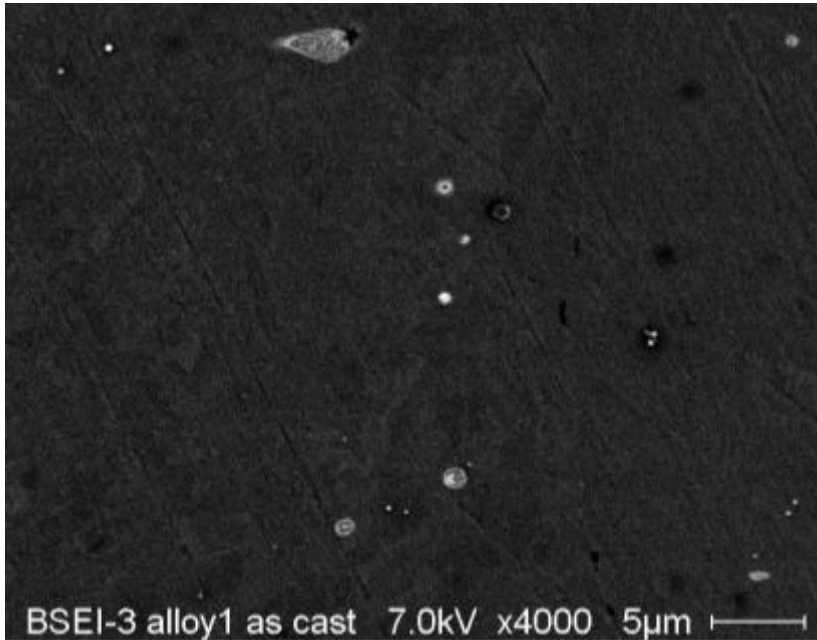
Scheil cooling  
↓  
Composition of as-cast alloys

Formation of Laves  
C14#1) phase:  
0.22wt% Mg<sub>2</sub>Ca  
0.11wt% Al<sub>2</sub>Ca

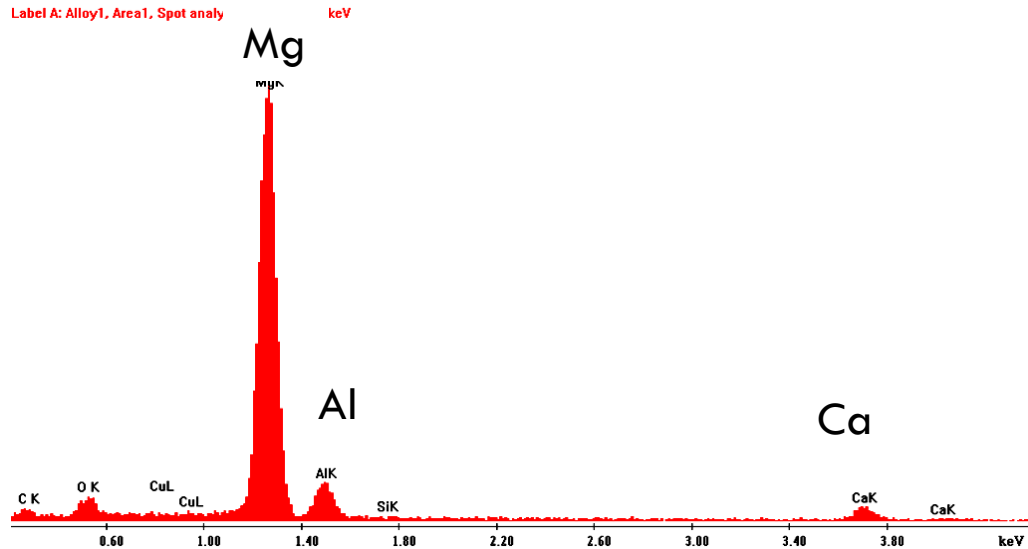
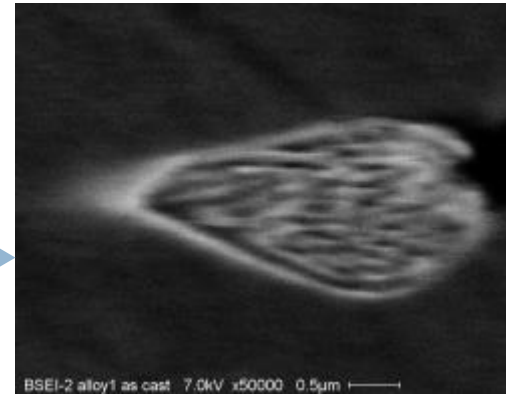


# Thermodynamics calculation

## SEM results of Mg-0.3Al-0.2Ca



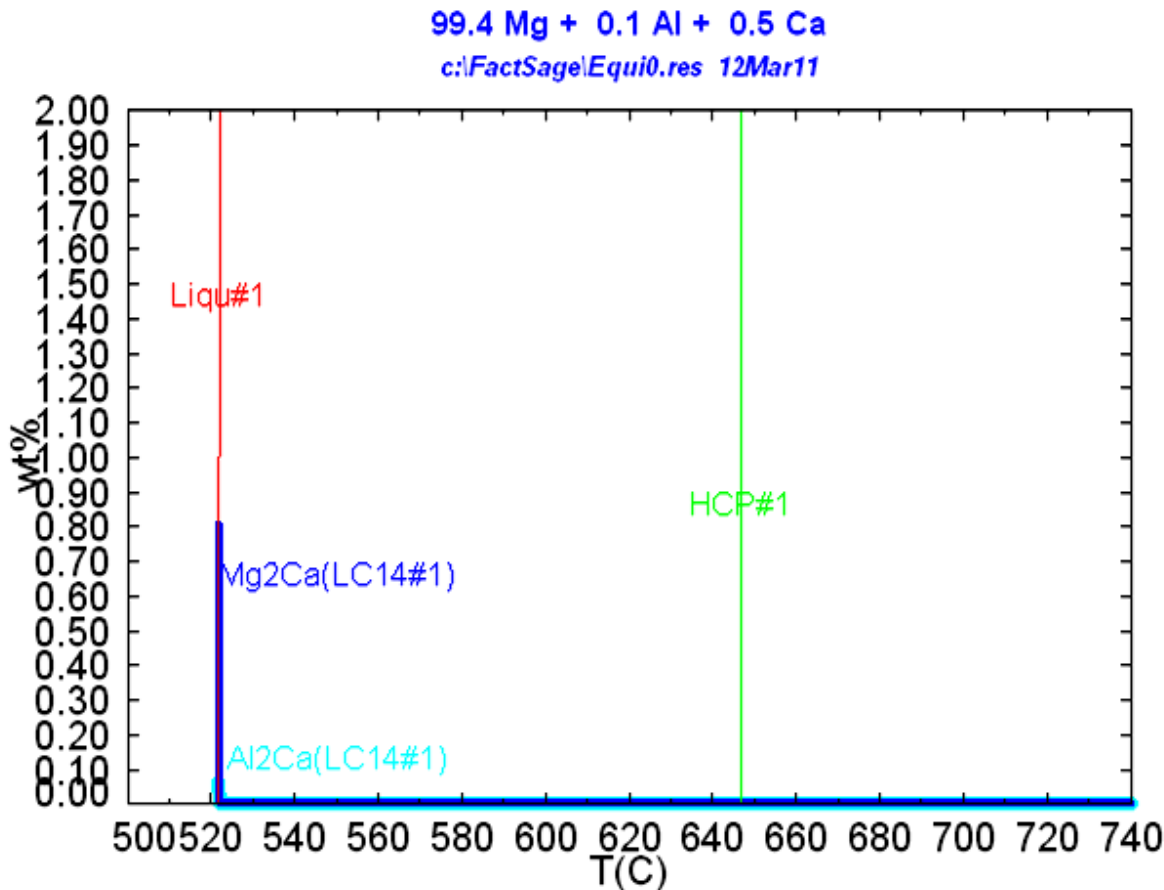
Higher  
Mag.  
→





# Thermodynamics calculation

- Scheil cooling diagram of Mg-0.1Al-0.5Ca

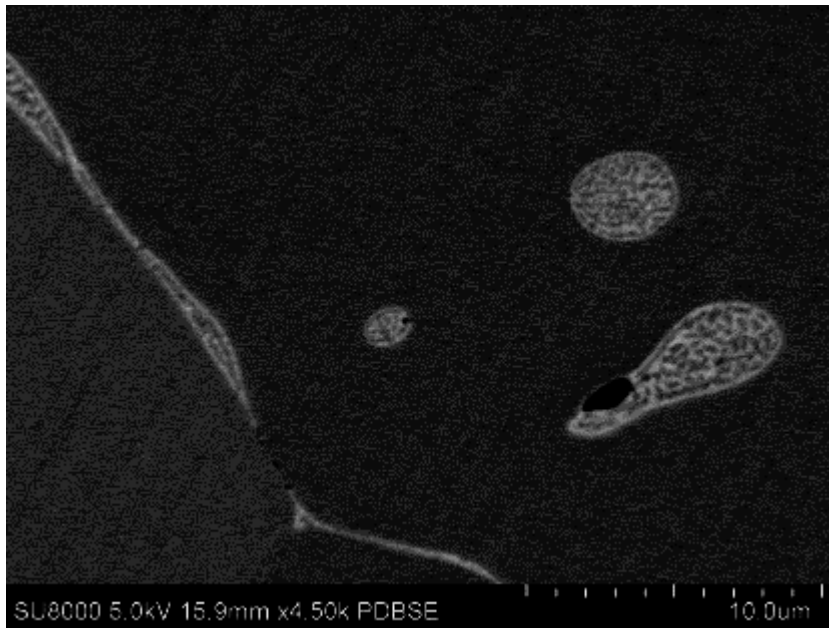


Formation of Laves  
C14#1 phase:  
0.8wt% Mg<sub>2</sub>Ca  
0.06wt% Al<sub>2</sub>Ca

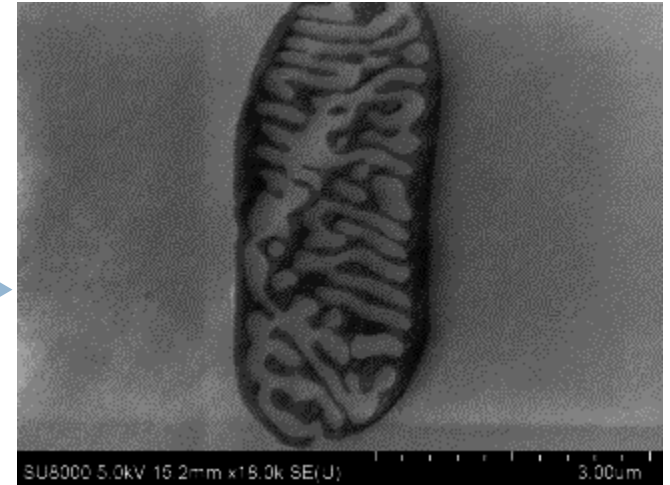


# Thermodynamics calculation

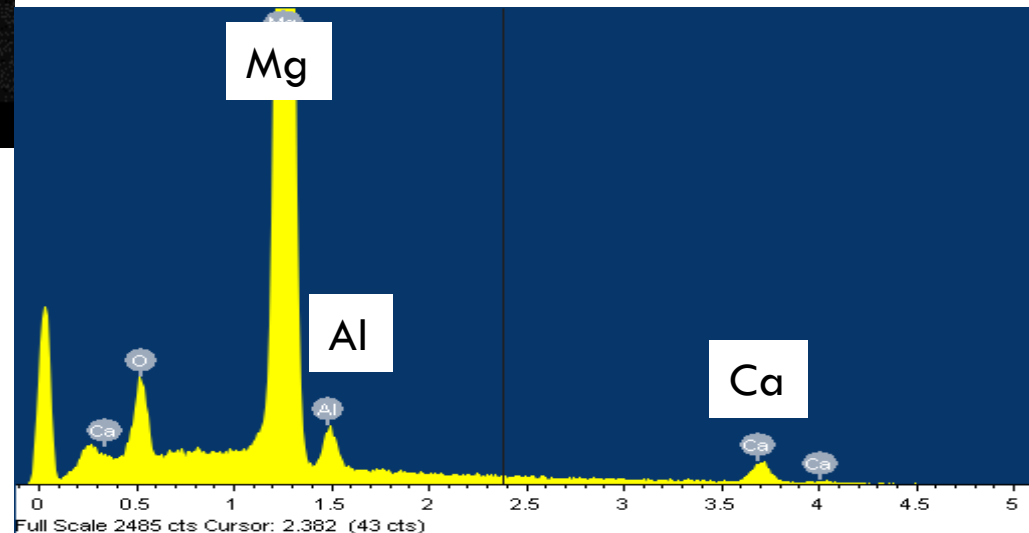
- SEM results of Mg-0.1Al-0.5Ca



Higher  
Mag.  
→



The precipitates in these two as-cast Mg-Al-Ca alloys are  $(Mg,Al)_2Ca$  and  $\alpha$ -Mg eutectic structure.



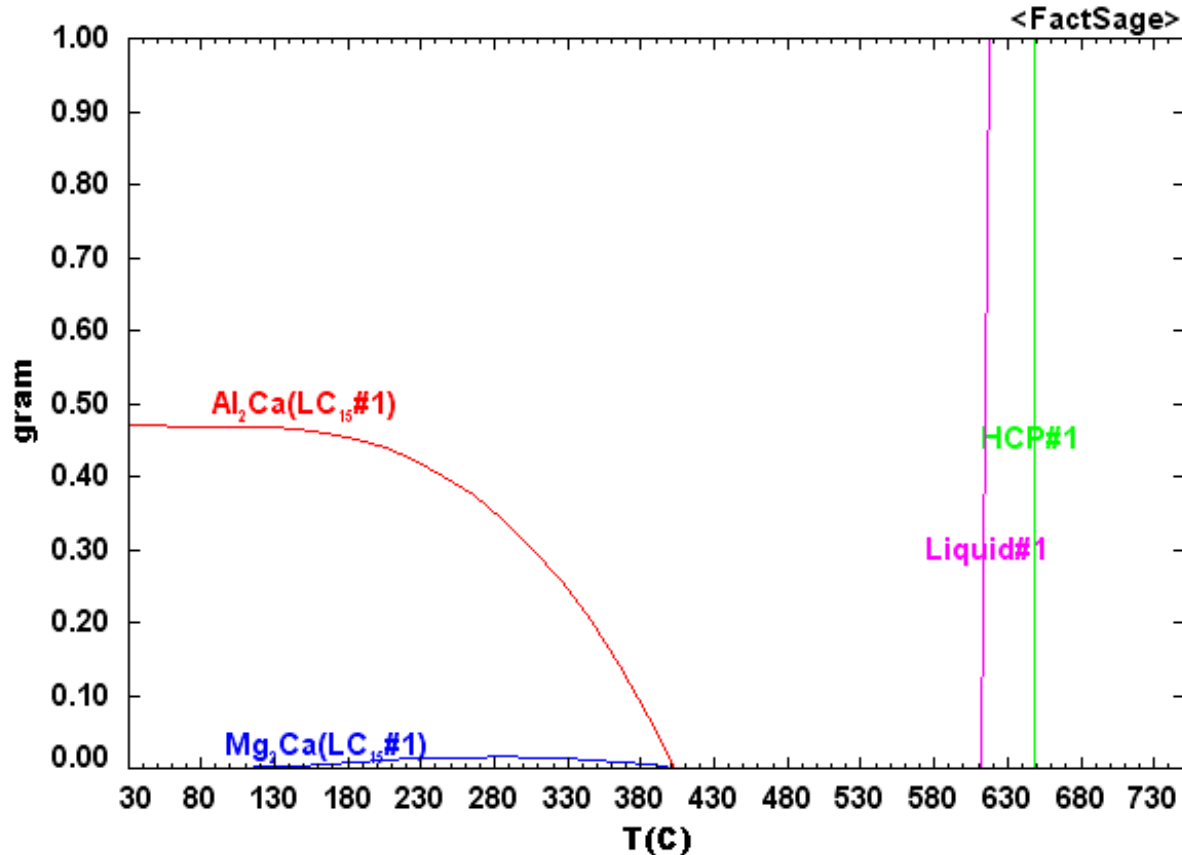




# Thermodynamics calculation

## Equilibrium diagrams of Mg-0.3Al-0.2Ca

99.5 Mg + 0.3 Al + 0.2 Ca



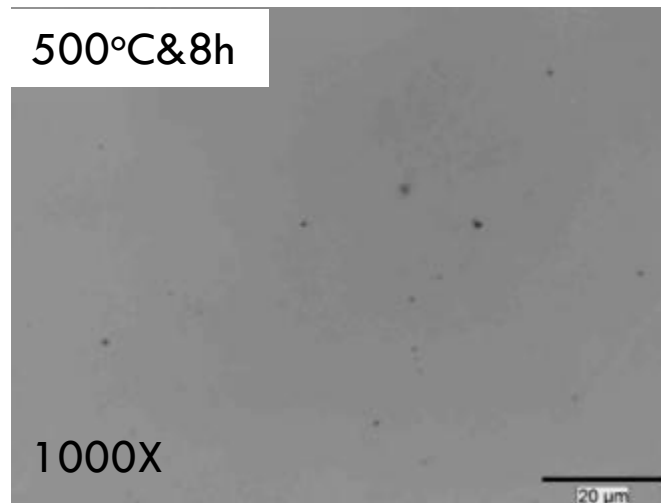
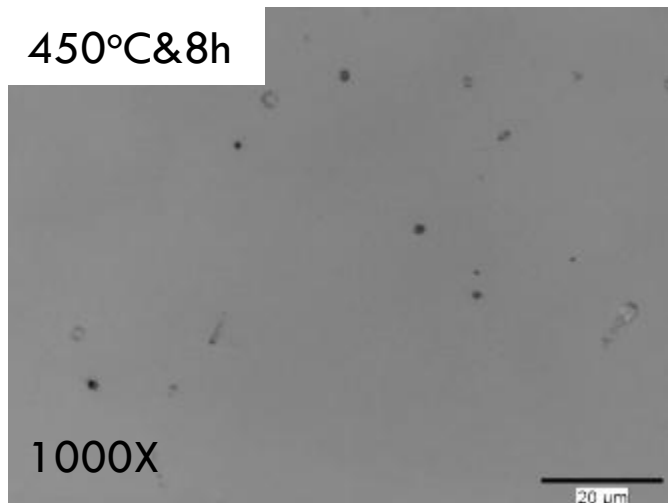
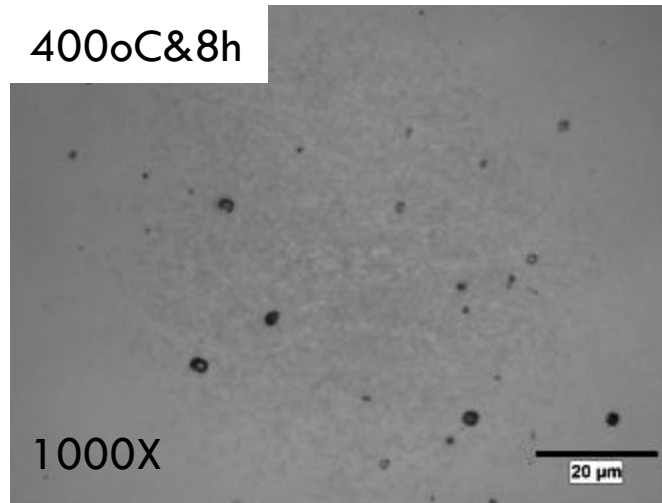
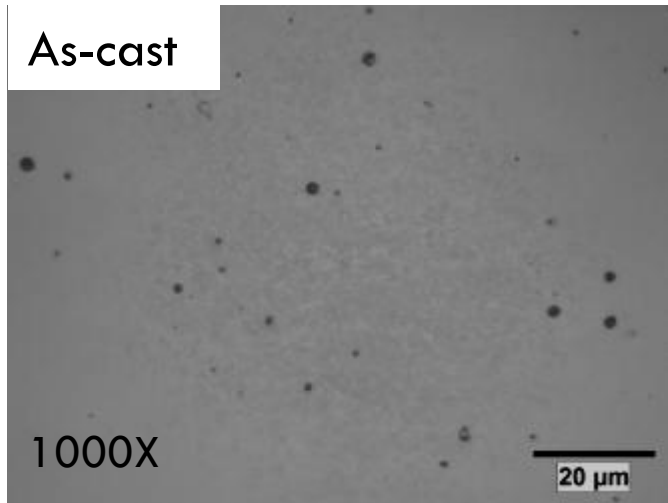
Precipitates in alloy 1  
are: Al<sub>2</sub>Ca(Laves 15)

Heat treatment  
temperature range:  
400-610°C



# Thermodynamics calculation

- Metallographic picture of solution heat treated Mg-0.1Al-0.5Ca alloy



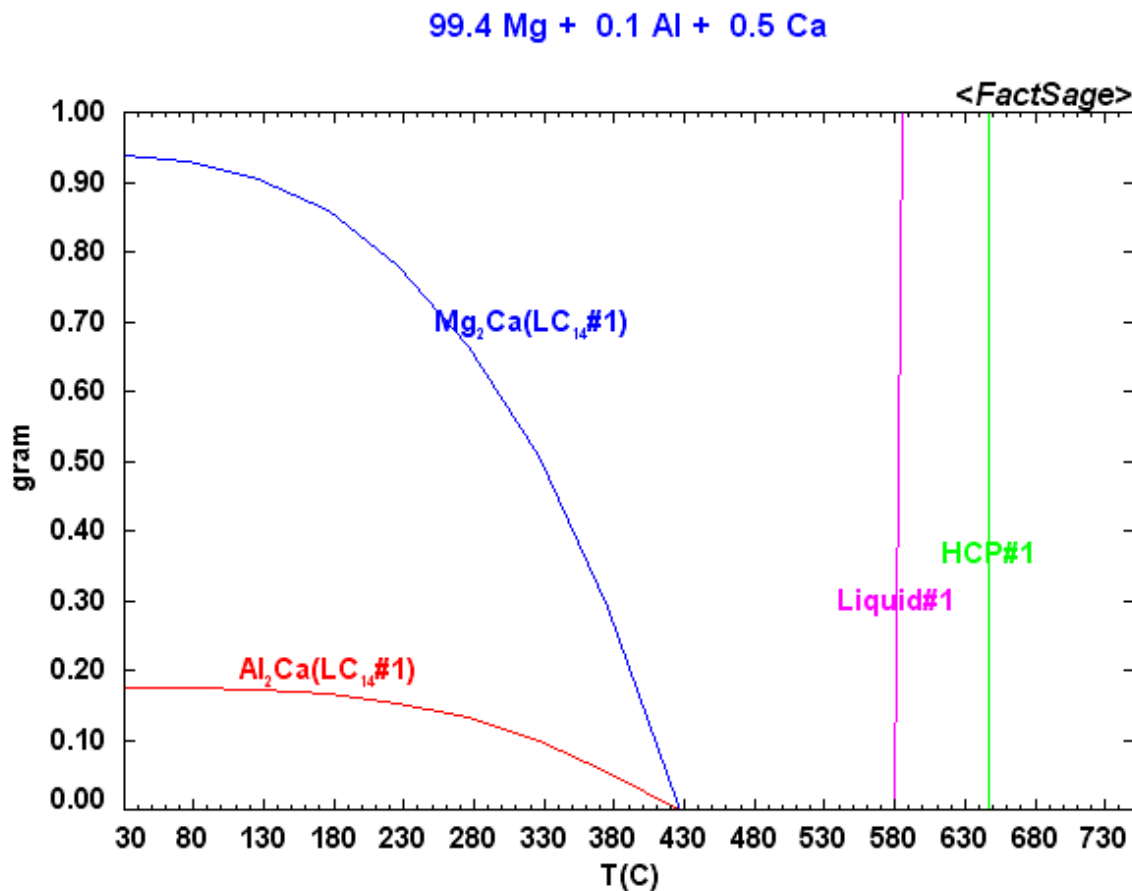
**FactSage:** Heat treatment temperature range: 430-580°C

**Experiment:** Precipitates are almost dissolved into matrix at 500°C for 8h.



# Thermodynamics calculation

- Equilibrium diagrams of Mg-0.1Al-0.5Ca



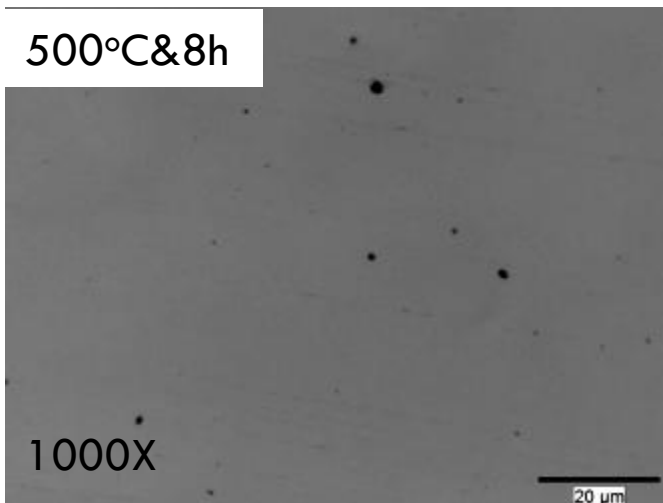
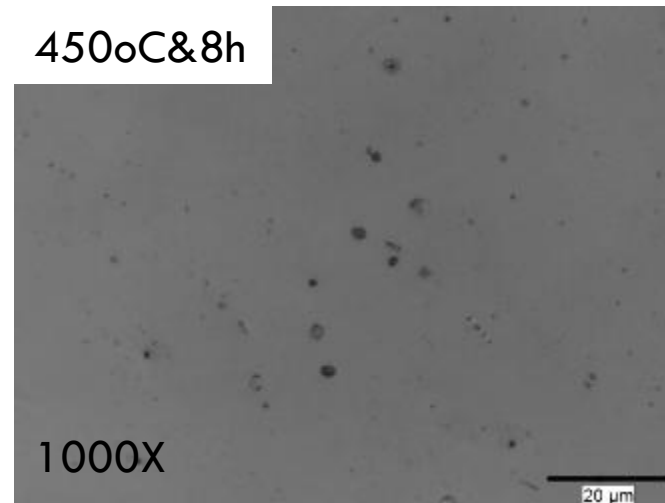
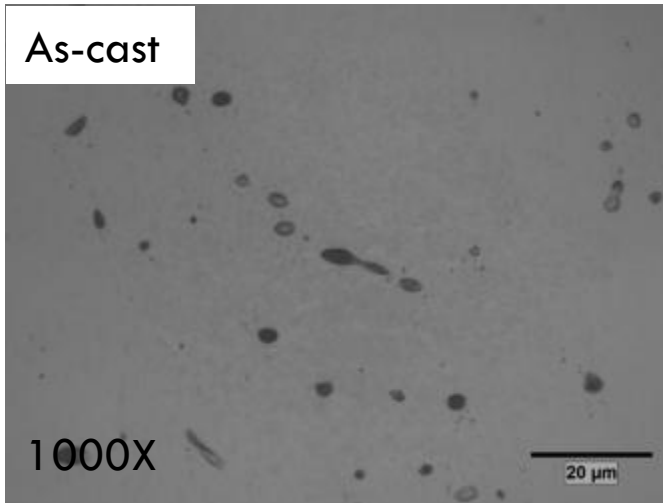
Precipitates in alloy 2  
are: Mg<sub>2</sub>Ca(Laves 14)

Heat treatment  
temperature range:  
430-580°C



# Thermodynamics calculation

- Metallographic picture of solution heat treated Mg-0.1Al-0.5Ca alloy



**FactSage:** Heat treatment temperature range: 430-580°C

**Experiment:** Precipitates are almost dissolved into matrix at 500oC for 8h.

# Kinetics

## — Classical nucleation and growth theory



### □ Nucleation

Nucleation rate: (Kampmann and Wagner Equation)

$$\left. \frac{dN}{dt} \right|_{\text{nucl}} = N_0 Z \beta^* \exp\left(-\frac{\Delta G^*}{kT}\right) \exp\left(-\frac{\tau}{t}\right)$$

$N_0$  -- the number of nucleation site per unit volume;

$$N_0 = 3 / (4 \times 3.14 \times R^{*3})$$

$\Delta G^*$  -- the energy required to form a critical nucleus of radius  $R^*$

$$\Delta G^* = \frac{16}{3} \pi \frac{\gamma^3}{\Delta g^2} \quad R^* = -\frac{2\gamma}{\Delta g}$$

$Z$  -- the Zeldovich factor

$\beta^*$  -- the condensation rate of solute atoms in a cluster of critical size  $R^*$

# Kinetics



## — Classical nucleation and growth theory

### □ Nucleation

$$Z = \frac{v_{\text{at}}^{\text{P}}}{2\pi R^{*2}} \sqrt{\frac{\gamma}{k_{\text{B}}T}}$$

$v_{\text{at}}^{\text{P}}$  -- the mean atomic volume within precipitates  
 $\gamma$  -- the specific interfacial energy

$$\beta^* = \frac{4\pi R^{*2}DX}{a^4}$$

$D$  -- diffusion coefficient of solute atoms  
 $X$  -- the matrix mean solute atom fraction  
 $a$  -- the lattice parameter of matrix

In multi-component precipitates, the addition of condensation characteristic times for each atomic species  $i$  gives:

$$\beta^* = \frac{4\pi R^{*2}}{a^4} \left( \sum_i \frac{1}{D_i X_i} \right)^{-1}$$

$$\tau = 4 / (2\pi\beta^* Z^2)$$

$\tau$  -- incubation time for nucleation



# Kinetics

## — Classical nucleation and growth theory

### □ Growth

$$\left. \frac{d\bar{R}}{dt} \right|_{\text{growth}} = \frac{D}{\bar{R}} \frac{X - X^i(\bar{R})}{\alpha X^P - X^i(\bar{R})} + \frac{1}{N} \frac{dN}{dt} \left( R_{k_B T}^* - \bar{R} \right)$$

$X_p$  -- mole fraction of precipitates

$X$  -- mean solute mole fraction in the matrix

$X_i$  -- equilibrium solute mole fraction at the precipitate/matrix interface

$\bar{R}$  -- mean radius of precipitates

$D$  -- diffusion coefficient

$\alpha$  -- the ratio of matrix to precipitates atomic volumes (mean volume per atom)

$$\alpha = v_{\text{at}}^M / v_{\text{at}}^P$$

$v_{\text{at}}^P$  -- the mean atomic volume within precipitates

$v_{\text{at}}^M$  -- the mean atomic volume within matrix

# Kinetics

## — Classical nucleation and growth theory



### □ Another equation for growth

$$\frac{dR}{dt} = \frac{D}{R} \frac{C - C_{eq} \exp(R_0/R)}{1 - C_{eq} \exp(R_0/R)} + \frac{1}{N} \frac{dN}{dt} \left( \alpha \frac{R_0}{\ln(C/C_{eq})} - R \right)$$

D -- diffusion coefficient

R -- radius of precipitates

C -- the current solute concentration of the

$C_{eq}$  -- equilibrium solute concentration of the matrix

$\alpha$  -- The numerical factor  $\alpha$  in equation accounts for the fact that nucleated precipitates can grow only if their radius is slightly larger than the nucleation radius. The precise value of  $\alpha$  is of no consequence on the results of the model. It was taken  $\alpha = 1.05$  in the following.

$$R_0 = 2\gamma v_{at}^P / (k_B T)$$





# Kinetics

## — Classical nucleation and growth theory

### □ Coarsen

When the mean radius of precipitates is much larger than the critical radius  $R^*$ , equations describing pure growth are valid:

$$\begin{cases} \left. \frac{dR}{dt} \right|_{\text{growth}} = \frac{D}{R} \frac{C - C_{\text{eq}} \exp(R_0/R)}{1 - C_{\text{eq}} \exp(R_0/R)} \\ \left. \frac{dN}{dt} \right|_{\text{growth}} = 0. \end{cases}$$

When the mean radius and the critical radius are equal, the conditions for the standard LSW law are fulfilled :

$$\begin{cases} \left. \frac{dR}{dt} \right|_{\text{coars}} = \frac{4}{27} \frac{C_{\text{eq}}}{1 - C_{\text{eq}}} \frac{R_0 D}{R^2} \\ R = R^* = \frac{R_0}{\ln(C/C_{\text{eq}})} \end{cases}$$

The rate of variation of the density of precipitates in pure coarsening:

$$\left. \frac{dN}{dt} \right|_{\text{coars}} = \frac{4}{27} \frac{C_{\text{eq}}}{1 - C_{\text{eq}}} \frac{R_0 D}{R^3} \left[ \frac{R_0 C}{R(1 - C)} \left( \frac{3}{4\pi R^3} - N \right) - 3N \right].$$

$$\rightarrow \begin{cases} \frac{dR}{dt} = (1 - f_{\text{coars}}) \left. \frac{dR}{dt} \right|_{\text{growth}} + f_{\text{coars}} \left. \frac{dR}{dt} \right|_{\text{coars}} \\ \frac{dN}{dt} = f_{\text{coars}} \left. \frac{dN}{dt} \right|_{\text{coars}} \end{cases}$$

# Kinetics

## —For ternary alloy application



### □ Nucleation

- The addition of an extra component leads considerably to the complexity in obtaining a rigorous solution for the nucleation rate.
- Unlike in the binary case, in a multi-component system, there are multiple pathways across the nucleation energy barrier, and which path is followed depends on both kinetic and thermodynamic factors. Although this problem has been solved rigorously for simple systems, the solution is mathematically complex and does not account for solute depletion.
- It is difficult to justify this level of complexity given the large uncertainty in the predicted nucleation rate that arises from a lack of accurate knowledge of the interfacial energy.

# Kinetics

## —For ternary alloy application



### □ Growth

- Calculating the growth rate of each precipitate requires a knowledge of the interfacial compositions. Local equilibrium is maintained at the interface as growth and dissolution occur.
- In a binary system the interfacial compositions are uniquely defined by a single tie line on the phase diagram. In the ternary case, there is an additional degree of freedom, and for any temperature there are a whole series of tie lines that lead to local equilibrium at the interface.

# Kinetics

—For ternary alloy application



## □ Assumptions

- For the binary precipitates ( $Mg_2Ca$ ) with matrix element (Mg) in ternary alloys, the important simplification is that the ternary nature of the alloy is not taken into account, the alloy is considered to be pseudo-binary, with an equivalent solute having its own equilibrium concentration and diffusion constant.
- For the binary precipitates ( $Al_2Ca$ ) without matrix element (Mg), the growth rate depends on the element with lower diffusivity.

# Kinetics

## – Input parameters



### □ Input parameters

	Alloy 1	Alloy2
Weight percentage	Mg-0.3Al-0.2Ca	Mg-0.1Al-0.5Ca
Mole percentage	0.9961Mg-0.0027Al- 0.0012Ca	0.9961Mg-0.0009Al- 0.003Ca
Mole fraction of matrix	0.9961	0.9961
Mole fraction of solute element	Al-0.0027 Ca-0.0012	Ca-0.003
Atomic ratio solute element 1 in compound	(Precipitates--Al <sub>2</sub> Ca) 2	(Precipitates--Mg <sub>2</sub> Ca) 2
Atomic ratio solute element 2 in compound	(Precipitates--Al <sub>2</sub> Ca) 1	(Precipitates--Mg <sub>2</sub> Ca) 1
Molar volume of compound (m <sup>3</sup> /mol)	4.6*10 <sup>-5</sup>	4.93*10 <sup>-5</sup>



# Kinetics

## – Selection of input parameters from literature

- Selection of input parameters from literature
- Inter-diffusivity of Ca in Mg

$$D = D_0 \exp\left(\frac{-Q}{RT}\right)$$

- Diffusion coefficient ( $D_0$  is the pre-exponential factor ( $\text{m}^2/\text{s}$ ),  $Q$  is the activation energy of diffusion ( $\text{J}/\text{mol}$ ),  $R$  is the gas constant ( $8.3145$ ),  $T$  is the absolute temperature)
- $T_1$  is chosen as the melting point of calcium ( $1111\text{K}$ ),  $D_{T_1}$  is estimated to be  $10^{-12}$  ( $\text{m}^2/\text{s}$ ),  **$Q$  is approximated as  $166 \text{ kJ}/\text{mol}$ .**

$$\frac{D_{T_2}}{D_{T_1}} = \exp\left[\frac{-Q}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]\right]$$

- At  $505^\circ\text{C}$ , this gives  $D_{T_2} = 4.62 \times 10^{-16}$  ( $\text{m}^2/\text{s}$ ) for the diffusion of calcium in magnesium.
- **$D_0 = 6.8 \times 10^{-5} \text{ J}/\text{m}^2$**



# Kinetics

## – Selection of input parameters from literature

- Selection of input parameters from literature
  - Inter-diffusivity of Al in Mg
    - An activation energy (Q) for diffusion of **125 kJ/mol** and A pre-exponential (D0) of  **$4 \times 10^{-4} \text{ m}^2/\text{s}$**

Table I. Parameters and Values Used in the Calculations

Parameter	Description	Value Used	Reference
$l/t$	length-to-thickness ratio of $\text{Mg}_{17}\text{Al}_{12}$ lath	10	this work
$l/w$	length-to-width ratio of $\text{Mg}_{17}\text{Al}_{12}$ lath	4	this work
$d$	hcp Mg matrix grain size	100 $\mu\text{m}$	estimate from 61
$G_p$	shear modulus of $\text{Mg}_{17}\text{Al}_{12}$	32.6 GPa	10, 11
$G_m$	shear modulus of hcp matrix	17.2 GPa	10, 11
$D_0^{\text{Al}}$	pre-exponential for Al diffusion in hcp Mg	$4 \cdot 10^4 \text{ m}^2/\text{s}$	this work
$Q^{\text{Al}}$	activation energy for Al diffusion in hcp	125 kJ/mol	this work
$\nu$	Poisson's ratio	0.35	60
$M$	Taylor factor	5	this work
$b$	Burgers vector for basal slip in hcp Mg	0.32 nm	11, 60
$a_0$	lattice parameter of hcp Mg	0.32 nm	11, 60
$\sigma_0$	intrinsic lattice strength in hcp Mg	11 MPa	60
$k$	Hall–Petch parameter	0.37 ( $\text{MPa m}^{1/2}$ )	60
$C$	coefficient for solid solution strengthening	197 ( $\text{MPa. at.}^{-2/3}$ )	61
$\sigma^{\text{coarsening}}$	$\text{Mg}_{17}\text{Al}_{12}$ /hcp interfacial energy extracted from plate tip radii assuming maximum growth rate hypothesis	0.43 ( $\text{J/m}^2$ )	this work
$\sigma_{\text{eff}}^{\text{nucleation}}$	'Effective' $\text{Mg}_{17}\text{Al}_{12}$ /hcp interfacial energy used for the nucleation of $\text{Mg}_{17}\text{Al}_{12}$	0.114 ( $\text{J/m}^2$ )	this work



# Kinetics

– Selection of input parameters from literature

- Selection of input parameters from literature
  - Calculation of diffusivity of Ca in Mg and Al in Mg with different temperature

temperature	Diffusivity(Ca-Mg)	Diffusion (Al-Mg)
473	3.17052E-23	6.29E-18
493	1.7571E-22	2.28E-17
513	8.52075E-22	7.49E-17
533	3.67029E-21	2.25E-16
553	1.42249E-20	6.24E-16
573	5.01561E-20	1.61E-15
593	1.62437E-19	3.91E-15
613	4.87239E-19	8.93E-15
633	1.3635E-18	1.94E-14

The diffusivity of Ca in Mg is almost  $10^4$  smaller than that of Al in Mg, so the growth of  $Al_2Ca$  depends on the diffusivity of Ca.



# Kinetics



– Selection of input parameters from literature

## □ Selection of input parameters from literature

### □ Inter-facial energy

- $\text{MgZn}_2$ :  $65 \pm 18 \text{ mJ/m}^2$
- $\text{Mg}_2\text{Sn}$ :  $410 \pm 120 \text{ mJ/m}^2$
- $\text{Mg}_2\text{Sn}$  particles are plate-like and mainly equiaxed in the  $\alpha$ -Mg-matrix while precipitates of  $\text{MgZn}_2$  have a needle-like shape and are semi-coherent during almost all stages of growth and coarsening
- The low value of interface surface energy is in line with the coherent interface between  $\text{MgZn}_2$  precipitates and Mg-matrix. A rather large value is indicative of incoherent interfaces between  $\text{Mg}_2\text{Sn}$ -particles and Mg.
- $\text{Mg}_{17}\text{Al}_{12}$ :  $114 \text{ mJ/m}^2$  (Literature)
- Assume  $\text{Mg}_2\text{Ca}$ (hcp—coherent with matrix(Mg))--  $50 \text{ mJ/m}^2$
- Assume  $\text{Al}_2\text{Ca}$ (fcc—incoherent with matrix(Mg))--  $100 \text{ mJ/m}^2$

# Kinetics

## —Calculation input parameters from FactSage



- Formation energy of the precipitate
  - $\Delta G = \Delta G^0 + RT \ln K$
  - $\Delta G^0$  -- Standard formation energy of precipitates— from FactSage
    - $2\text{Mg (hcp)} + \text{Ca (fcc)} = \text{Mg}_2\text{Ca(s)}$
    - $2\text{Al (fcc)} + \text{Ca (fcc)} = \text{Al}_2\text{Ca(s)}$
  - $K = 1 / (a(\text{Mg})^2 + a(\text{Ca})^1)$
  - $a$  -- Activity of elements – from Factsage
- Mean atomic volume of precipitates
  - $v_{\text{at}}^{\text{P}} = V / ((x+y) * 1000 * 6.02 * 10^{23})$
  - $V$ —Mole volume--from FactSage
- Solute concentration at the interface of precipitates and matrix
  - —from FactSage

# Kinetics



## —Calculation input parameters from FactSage

- Activity of solute element

The screenshot shows the 'Reactants - Equilib' window in FactSage 6.2. The window title is 'F Reactants - Equilib'. The menu bar includes 'File', 'Edit', 'Table', 'Units', 'Data', 'Search', and 'Help'. The toolbar contains icons for file operations and a calculator. The main area displays a table with columns: 'Mass(mol)', 'Species', 'Phase', 'T(K)', 'P(total)\*\*', 'Stream#', and 'Data'. The table contains three rows of data for Mg, Al, and Ca. A 'Next >>' button is located at the bottom center. The status bar at the bottom shows 'FactSage 6.2', 'Compound: 1/20 databases', and 'Solution: 1/16 databases'. There is also an 'Initial Conditions' checkbox at the bottom right of the main area.

Mass(mol)	Species	Phase	T(K)	P(total)**	Stream#	Data
0.9961	Mg				1	
+ 0.0009	Al				1	
+ 0.003	Ca				1	

Initial Conditions

Next >>

FactSage 6.2    Compound: 1/20 databases    Solution: 1/16 databases

# Kinetics



## —Calculation input parameters from FactSage

### □ Activity of solute element

Equilib: last system

File Units Parameters Help

T(K) P(atm) Energy(J) Mass(mol) Vol(litre)

Reactants (3)

0.9961 Mg + 0.0009 Al + 0.003 Ca

Products

Compound species

gas  ideal  real 0

aqueous 0

pure liquids 0

\* pure solids 3

suppress duplicates apply

\* - custom selection species: 3

Target

- none -

Estimate T(K): 1000

Mass(mol): 0

Solution species

*	+	Base-Phase	Full Name
		FTlite-Liqu	Liquid
		FTlite-FCC	FCC_A1
I		FTlite-HCP	HCP_A3
		FTlite-BCC	BCC_A2
		FTlite-LC14	Laves_C14
		FTlite-LC15	Laves_C15
		FTlite-LC36A	ALaves_C36
		FTlite-LC36B	BLaves_C36

Legend

I - immiscible 1  Show  all  selected

species: 6

solutions: 2 Select

Final Conditions

<A>	<B>	T(K)	P(atm)	Product H(J)
		473 713 20	1	

10 steps  Table 13 calculations

Equilibrium

normal

transitio

predom

FactSage 6.2

+	Code	Species	Data	Phase	T	V	Activity
+	4	Mg(s)	FTlite	hcp_a3		V	0.9961
	5	Mg(s2)	FTlite	hcp_zn			0.9817
	6	Mg(s3)	FTlite	fcc_a1		V	0.7159
	7	Mg(s4)	FTlite	bcc_a2			0.7601
	8	Mg(s5)	FTlite	cbcc_a12			0.6583
	9	Mg(s6)	FTlite	cub_a13			0.6148
+	10	Al(s)	FTlite	fcc_a1		V	2.7806E-03
	11	Al(s2)	FTlite	hcp_a3			1.3697E-03
	12	Al(s3)	FTlite	hcp_zn			1.3697E-03
	13	Al(s4)	FTlite	cbcc_a12			9.0539E-04
	14	Al(s5)	FTlite	bcc_a2			9.0545E-04
	15	Al(s6)	FTlite	cub_a13			7.8604E-04
	16	Al(s7)	FTlite	bct_a5			9.0545E-04
	17	Al(s8)	FTlite	diamond_a4			7.5359E-05
	18	Al30Mg23(s)	FTlite	epsilon		V	4.1656E-65
+	19	Ca(s)	FTlite	fcc_a1			5.7942E-03
	20	Ca(s2)	FTlite	bcc_a2			5.7904E-03
	21	Ca(s3)	FTlite	hcp_a3			4.8955E-03
	22	Mg2Ca(s)	FTlite	laves_c-14			0.6685
	23	Al2Ca(s)	FTlite	cf24-laves_c15			9.6200E-02
	24	Al4Ca(s)	FTlite	ti10-i4/mmm			1.5853E-06
	25	Al3Ca8(s)	FTlite	ap22_(ca8in3)			2.2385E-15
	26	Al14Ca13(s)	FTlite	solid_monoclinic			1.4808E-19
	27	Ca4Al3Mg(s)	FTlite	pbcm			5.1961E-06

# Kinetics



## —Calculation input parameters from FactSage

- Activity of solute element

**F Results - Equilib 473 K (page 1/13)**

Output Edit Show Pages

T(K) P(atm) Energy(J) Mass(mol) Vol(litre)

473 K | 493 K | 513 K | 533 K | 553 K | 573 K | 593 K | 613 K | 633 K | 653 K | 673 K | 693 K | 713 K

```
STREAM CONSTITUENTS      AMOUNT/mol
Mg                        9.9610E-01
Al                        9.0000E-04
Ca                        3.0000E-03

PHASE: HCP_A3#1
      EQUIL AMOUNT  MOLE FRACTION  ACTIVITY
      mol
Al      9.0000E-04  9.0000E-04  1.7002E-03
Ca      3.0000E-03  3.0000E-03  2.2426E-03
Mg      9.9610E-01  9.9610E-01  9.9610E-01
TOTAL:  1.0000E+00  1.0000E+00  1.0000E+00
PHASE: HCP_A3#2
      EQUIL AMOUNT  MOLE FRACTION  ACTIVITY
      mol
Al      0.0000E+00  9.0000E-04  1.7002E-03
Ca      0.0000E+00  3.0000E-03  2.2426E-03
Mg      0.0000E+00  9.9610E-01  9.9610E-01
TOTAL:  0.0000E+00  1.0000E+00  1.0000E+00

      EQUIL AMOUNT  ACTIVITY
      mol
Mg_hcp_a3(s)  0.0000E+00  9.9610E-01
Al_fcc_al(s)  0.0000E+00  5.5176E-03
Ca_fcc_al(s)  0.0000E+00  2.7704E-03
*****

      J.K-1      J      J.K-1      J      dm3
*****
      2.68936E+01  4.51985E+03  4.48161E+01  -1.66782E+04  1.42569E-02

Lattice parameters for HCP_A3#1:
a/nm = 0.32258
c/nm = 0.52540
```



# Kinetics

## —Calculation input parameters from FactSage

- Standard formation energy

The screenshot shows the 'Reactants - Equilib' window in FactSage 6.2. The window title is 'Reactants - Equilib'. The menu bar includes 'File', 'Edit', 'Table', 'Units', 'Data Search', and 'Help'. The toolbar contains icons for file operations and a 'Next >>' button. The main area displays a table of reactant input parameters. The table has columns for 'Mass(mol)', 'Species', 'Phase', 'T(K)', 'P(total)\*\*', and 'Stream# Data'. The first row shows 2 moles of Mg in the 'solid-1 hcp\_a3' phase at 473 K and 1 atm. The second row shows 1 mole of Ca in the 'solid-1 fcc\_a1' phase at 473 K and 1 atm. A checkbox for 'Initial Conditions' is checked. The status bar at the bottom shows 'FactSage 6.2', 'Compound: 1/20 databases', and 'Solution: 1/16 databases'.

Mass(mol)	Species	Phase	T(K)	P(total)**	Stream# Data
2	Mg	solid-1 hcp_a3	473	1	1
+ 1	Ca	solid-1 fcc_a1	473	1	1

Initial Conditions

Next >>

FactSage 6.2    Compound: 1/20 databases    Solution: 1/16 databases

# Kinetics



## —Calculation input parameters from FactSage

- Standard formation energy

Equilib: last system

Reactants (2): 2 Mg + Ca (473K,s1,#1) (473K,s1,#1)

Products:

+	Code	Species	Data	Phase	T	V	Activity
	3	Mg(s)	FTlite	hcp_a3		V	
	4	Mg(s2)	FTlite	hcp_zn			
	5	Mg(s3)	FTlite	fcc_a1		V	
	6	Mg(s4)	FTlite	bcc_a2			
	7	Mg(s5)	FTlite	cbcc_a12			
	8	Mg(s6)	FTlite	cub_a13			
	9	Ca(s)	FTlite	fcc_a1			
	10	Ca(s2)	FTlite	bcc_a2			
	11	Ca(s3)	FTlite	hcp_a3			
+	12	Mg2Ca(s)	FTlite	laves_c-14			

Legend: immiscible 1

Equilibrium: normal (selected), normal + transitions, transitions only, predominant

Calculate >>

# Kinetics



## —Calculation input parameters from FactSage

- Standard formation energy

```
F Results - Equilib 473 K
Output Edit Show Pages
[Icons] T(K) P(atm) Energy(J) Mass(mol) Vol(litre) [Icons]

2 Hg + Ca =
(473,1,sl,#1) (473,1,sl,#1)

0.00000 mol Laves_C14#1
(473.00 K, 1 atm, a=0.99999)
( 1.0000 Hg2Ca V)

+ 0.00000 mol Laves_C14#2
(473.00 K, 1 atm, a=0.99999)
( 1.0000 Hg2Ca V)

+ 1.0000 mol Hg2Ca_laves_c-14
(88.688 gram, 1.0000 mol, 4.9271E-02 litre, 1.8000 gram/cm3)
(473.00 K, 1 atm, Sl, a=1.0000)

The cutoff concentration has been specified to 1.0000E-75

2 product species identified with "V" are modeled with an equation of state

*****
DELTA H DELTA G DELTA V DELTA S DELTA Cp
(J) (J) (litre) (J/K) (J/K)
*****
-3.39775E+04 -3.01364E+04 -4.81077E-03 -8.12064E+00 1.31473E-01
*****
H G V S Cp
(J) (J) (litre) (J/K) (J/K)
*****
-3.39775E+04 -3.01364E+04 -4.81077E-03 -8.12064E+00 1.31473E-01
```



# Kinetics



## —Calculation input parameters from FactSage

- Mean atomic volume of precipitates

The screenshot shows the 'Reactants - Equilib' window in FactSage. The interface includes a menu bar (File, Edit, Table, Units, Data Search, Help) and a toolbar with icons for file operations and calculation. The main area contains a table for defining reactants with columns for Mass(mol), Species, Phase, T(K), P(total)\*\*, Stream#, and Data. Two reactants are listed: Mg and Ca. The 'Initial Conditions' checkbox is unchecked. A 'Next >>' button is located at the bottom of the window. The status bar at the bottom indicates 'FactSage 6.2' and shows the number of databases searched for compounds (1/20) and solutions (1/16).

Mass(mol)	Species	Phase	T(K)	P(total)**	Stream#	Data
2	Mg				1	
+ 1	Ca				1	

Initial Conditions

Next >>

FactSage 6.2    Compound: 1/20 databases    Solution: 1/16 databases

# Kinetics



## —Calculation input parameters from FactSage

- Mean atomic volume of precipitates

**Menu - Equilib: last system**

File Units Parameters Help

T(K) P(atm) Energy(J) Mass(mol) Vol(litre)

Reactants [2]

2 Mg + Ca

Products

Compound species

- gas  ideal  real 0
- aqueous 0
- pure liquids 0
- \*  pure solids 1
- suppress duplicates apply
- \* - custom selection

Solution species

*	+	Base-Phase	Full Name
		FTlite-Liqu	Liquid
		FTlite-FCC	FCC_A1
		FTlite-HCP	HCP_A3
		FTlite-BCC	BCC_A2
I		FTlite-LC14	Laves_C14
		FTlite-LC15	Laves_C15
		FTlite-LC36?	?Laves_C36

Legend

I - immiscible 1

Show  all  selected

species: 4

solutions: 2

Custom Solutions

- fixed activities
- ideal solutions
- activity coefficients

Pseudonyms

apply  List ...

include molar volumes

Total Species (max 1500) 5

Total Solutions (max 40) 2

Equilibrium

- normal  normal + transitions
- transitions only  open
- predominant

Calculate >>

+	Code	Species	Data	Phase	T	V	Activity
	3	Mg(s)	FTlite	hcp_a3		V	
	4	Mg(s2)	FTlite	hcp_zn			
	5	Mg(s3)	FTlite	fcc_a1		V	
	6	Mg(s4)	FTlite	bcc_a2			
	7	Mg(s5)	FTlite	cbcc_a12			
	8	Mg(s6)	FTlite	cub_a13			
	9	Ca(s)	FTlite	fcc_a1			
	10	Ca(s2)	FTlite	bcc_a2			
	11	Ca(s3)	FTlite	hcp_a3			
+	12	Mg2Ca(s)	FTlite	laves_c-14			1.000

T(K) P(atm) Product H(J)

473 1

1 calculation

# Kinetics



## —Calculation input parameters from FactSage

- Mean atomic volume of precipitates

```
F Results - Equilib 473 K
Output Edit Show Pages
T(K) P(atm) Energy(J) Mass(mol) Vol(litre)

2 Hg + Ca =
0.00000 mol Laves_C14#1
(473.00 K, 1 atm, a=0.99999)
( 1.0000 Hg2Ca V)
+ 0.00000 mol Laves_C14#2
(473.00 K, 1 atm, a=0.99999)
( 1.0000 Hg2Ca V)
+ 1.0000 mol Hg2Ca_laves_c-14
(88.688 gram, 1.0000 mol, 4.9271E-02 litre, 1.8000 gram/cm3)
(473.00 K, 1 atm, Sl, a=1.0000)

The cutoff concentration has been specified to 1.0000E-75
2 product species identified with "V" are modeled with an equation of state
.....
H C V S Cp
(J) (J) (litre) (J/K) (J/K)
.....
-2.02199E+04 -8.40810E+04 4.92711E-02 1.35013E+02 8.19252E+01
.....
Total mass/gram = 88.688
System density/gram/cm3 = 1.8000
.....
```

Mean atomic volume of precipitates(AxBy):  
 $V_{df}^P = \frac{V}{(x+y) \times 1000 \times 6.02 \times 10^{-23}}$

# Kinetics



## —Calculation input parameters from FactSage

- Mean atomic volume of matrix

The screenshot shows the 'Reactants - Equilib' window in FactSage 6.2. The window title is 'Reactants - Equilib'. The menu bar includes 'File', 'Edit', 'Table', 'Units', 'Data Search', and 'Help'. The toolbar contains icons for file operations and a calculator. The main area displays a table with columns: 'Mass(mol)', 'Species', 'Phase', 'T(K)', 'P[total]\*\*', and 'Stream#'. The table contains three rows of data:

Mass(mol)	Species	Phase	T(K)	P[total]**	Stream#
0.9961	Mg				0
0.0009	Al				1
0.003	Ca				1

At the bottom right of the table area, there is a checkbox labeled 'Initial Conditions' which is currently unchecked. Below the table area is a 'Next >>' button. The status bar at the bottom shows 'FactSage 6.2', 'Compound: 1/20 databases', and 'Solution: 1/16 databases'.

# Kinetics



## —Calculation input parameters from FactSage

- Mean atomic volume of matrix

Equilib: last system

File Units Parameters Help

T(K) P(atm) Energy(J) Mass(mol) Vol(litre)

Reactants (3)

0.003 Ca + 0.9961 Mg + 0.0009 Al

Products

Compound species: gas 0, ideal 0, real 0, aqueous 0, pure liquids 0, pure solids 3

Solution species

*	+	Base-Phase	Full Name
		FTlite-Liqu	Liquid
		FTlite-FCC	FCC_A1
I		FTlite-HCP	HCP_A3
		FTlite-BCC	BCC_A2
		FTlite-LC14	Laves_C14
		FTlite-LC15	Laves_C15
		FTlite-LC36A	ALaves_C36
		FTlite-LC36B	BLaves_C36

Legend: I - immiscible 1

Equilibrium:  normal,  normal + transitions,  transitions only,  predominant

Calculate >>

+	Code	Species	Data	Phase	T	V	Activity
*	4	Mg(s)	FTlite	hcp_a3		V	0.9961
	5	Mg(s2)	FTlite	hcp_zn			0.9799
	6	Mg(s3)	FTlite	fcc_a1		V	0.6261
	7	Mg(s4)	FTlite	bcc_a2			0.7226
	8	Mg(s5)	FTlite	cbcc_a12			0.6106
	9	Mg(s6)	FTlite	cub_a13			0.5665
*	10	Al(s)	FTlite	fcc_a1		V	3.1694E-03
	11	Al(s2)	FTlite	hcp_a3			1.4274E-03
	12	Al(s3)	FTlite	hcp_zn			1.4274E-03
	13	Al(s4)	FTlite	cbcc_a12			8.7517E-04
	14	Al(s5)	FTlite	bcc_a2			8.7523E-04
	15	Al(s6)	FTlite	cub_a13			7.4947E-04
	16	Al(s7)	FTlite	bct_a5			8.7523E-04
	17	Al(s8)	FTlite	diamond_a4			8.5888E-05
	18	Al30Mg23(s)	FTlite	epsilon		V	1.4163E-62
*	19	Ca(s)	FTlite	fcc_a1		V	5.0325E-03
	20	Ca(s2)	FTlite	bcc_a2			4.9496E-03
	21	Ca(s3)	FTlite	hcp_a3			4.2173E-03
	22	Mg2Ca(s)	FTlite	laves_c-14			1.071
	23	Al2Ca(s)	FTlite	cf24-laves_c15			0.4692
	24	Al4Ca(s)	FTlite	b10-i4/mmm			1.1750E-05
	25	Al3Ca8(s)	FTlite	ap22_(ca8n3)			1.9897E-14
	26	Al14Ca13(s)	FTlite	solid_monoclin			6.8635E-15
	27	Ca4Al3Mg(s)	FTlite	pbcm			5.4880E-05

# Kinetics



## —Calculation input parameters from FactSage

- Mean atomic volume of matrix

```
F Results - Equilib 473 K
Output Edit Show Pages
T(K) P(atm) Energy(J) Mass(mol) Vol(litre)

+ 0.00000 mol Mg_hcp_a3 V
  (473.00 K, 1 atm, S1, a=0.99610)

+ 0.00000 mol Al_fcc_al V
  (473.00 K, 1 atm, S1, a=5.5176E-03)

+ 0.00000 mol Ca_fcc_al V
  (473.00 K, 1 atm, S1, a=2.7704E-03)

The cutoff concentration has been specified to 1.0000E-75

8 product species identified with "V" are modeled with an equation of state

*****
      H          G          V          S          Cp
      (J)        (J)        (litre)    (J/K)      (J/K)
*****
  4.51985E+03 -1.66782E+04 1.42569E-02 4.48161E+01 2.68936E+01

Total mass/gram = 24.355
System density/gram/cm3 = 1.7083

-----

T = 473.00 K
P = 1.00000E+00 atm
V = 1.42569E-02 dm3

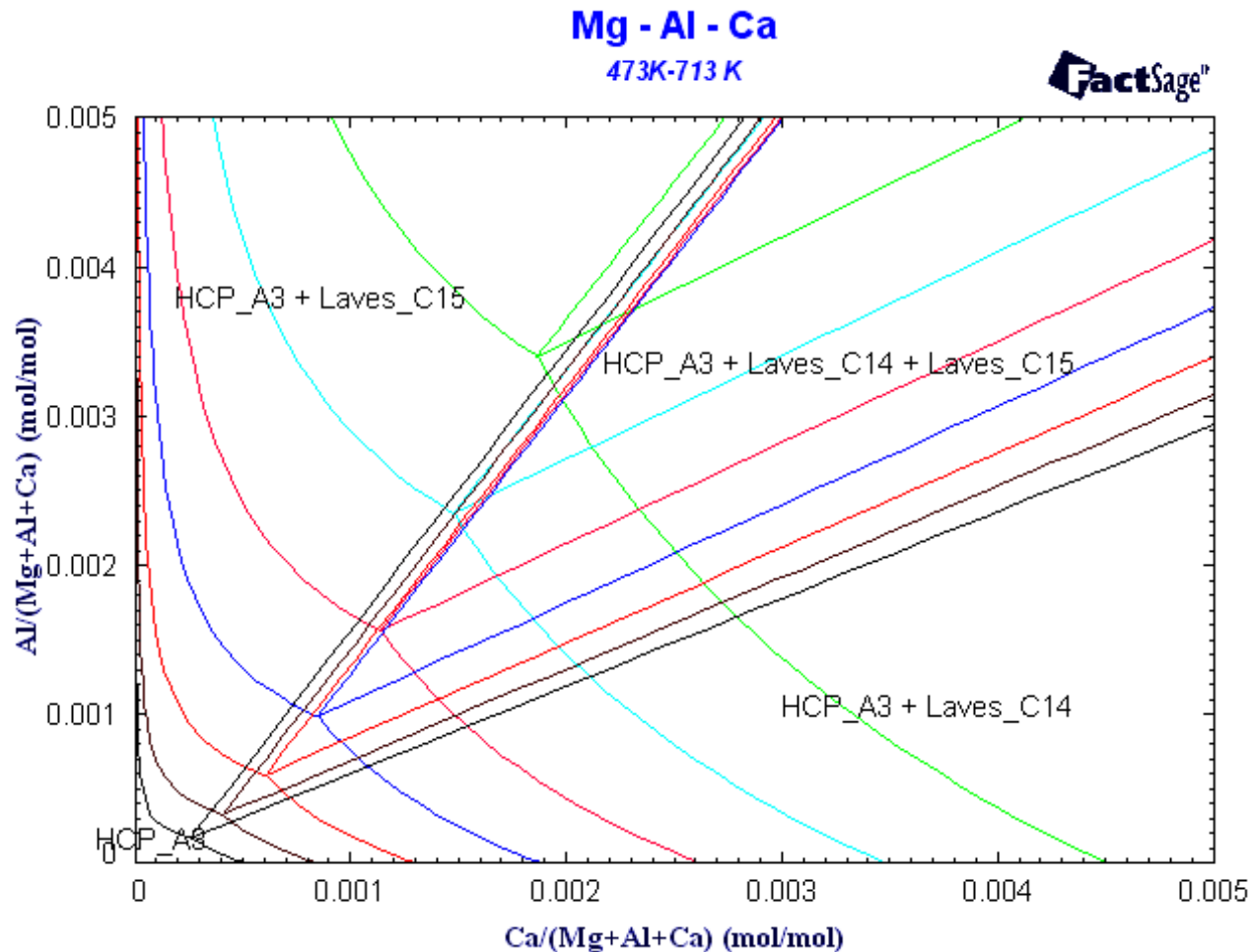
STREAM CONSTITUENTS      AMOUNT/mol
```



# Kinetics

—Calculation input parameters from FactSage

- Equilibrium concentration at the matrix/precipitates interface



# Kinetics



—Calculation input parameters from FactSage

- Equilibrium concentration at the matrix/precipitates interface

The screenshot shows the 'Reactants - Equilib' window in FactSage. The window title is 'Reactants - Equilib'. The menu bar includes 'File', 'Edit', 'Table', 'Units', 'Data', 'Search', and 'Help'. The toolbar contains icons for file operations and a calculator. The main area displays a table with columns: 'Mass(mol)', 'Species', 'Phase', 'T(K)', 'P(total)\*\*', and 'Stream#'. The table contains three rows of data:

Mass(mol)	Species	Phase	T(K)	P(total)**	Stream#
0.9961	Mg				0
+ 0.0009	Al				1
+ 0.003	Ca				1

At the bottom right of the table area, there is a checkbox labeled 'Initial Conditions' which is currently unchecked. Below the table area is a 'Next >>' button. The status bar at the bottom of the window shows 'FactSage 6.2', 'Compound: 1/20 databases', and 'Solution: 1/16 databases'.



# Kinetics



## —Calculation input parameters from FactSage

- Equilibrium concentration at the matrix/precipitates interface

Equilib: last system

File Units Parameters Help

T(K) P(atm) Energy(J) Mass(mol) Vol(litre)

Reactants (3)  
0.9961 Mg + 0.0009 Al + 0.003 Ca

Products

Compound species  
 gas  ideal  real 0  
 aqueous 0  
 pure liquids 0  
 pure solids 1  
 suppress-duplicates apply  
\* - custom selection species: 1

Solution species

*	+	Base-Phase	Full Name
		FTlite-Liqu	Liquid
		FTlite-FCC	FCC_A1
I		FTlite-HCP	HCP_A3
		FTlite-BCC	BCC_A2
I		FTlite-LC14	Laves_C14
		FTlite-LC15	Laves_C15
		FTlite-LC36A	ALaves_C36
		FTlite-LC36B	BLaves_C36

Legend  
I - immiscible 2  Show  all  selected  
species: 18   
solutions: 4

Target  
- none -  
Estimate T(K): 1000  
Mass(mol): 0

Final Conditions

<A>	<B>	T(K)	P(atm)	Product H(J)
		473 713 20	1	

10 steps  Table  13 calculations

Equilibri  
 normal  
 transiti  
 predon

FactSage 6.2

+	Code	Species	Data	Phase	T	V	Activity
	4	Mg(s)	FTlite	hcp_a3		V	0.9996
	5	Mg(s2)	FTlite	hcp_zn			0.9760
	6	Mg(s3)	FTlite	fcc_a1		V	0.5750
	7	Mg(s4)	FTlite	bcc_a2			0.5650
	8	Mg(s5)	FTlite	cbcc_a12			0.4455
	9	Mg(s6)	FTlite	cub_a13			0.4021
	10	Al(s)	FTlite	fcc_a1		V	4.4935E-04
	11	Al(s2)	FTlite	hcp_a3			1.3847E-04
	12	Al(s3)	FTlite	hcp_zn			1.3847E-04
	13	Al(s4)	FTlite	cbcc_a12			6.1727E-05
	14	Al(s5)	FTlite	bcc_a2			6.1734E-05
	15	Al(s6)	FTlite	cub_a13			4.9885E-05
	16	Al(s7)	FTlite	bct_a5			6.1734E-05
	17	Al(s8)	FTlite	diamond_a4			1.2178E-05
	18	Al30Mg23(s)	FTlite	epsilon		V	1.7059E-84
	19	Ca(s)	FTlite	fcc_a1			3.3449E-04
	20	Ca(s2)	FTlite	bcc_a2			3.0375E-04
	21	Ca(s3)	FTlite	hcp_a3			2.7077E-04
+	22	Mg2Ca(s)	FTlite	laves_c-14			0.7112
	23	Al2Ca(s)	FTlite	cf24-laves_c15			0.2540
	24	Al4Ca(s)	FTlite	ti10-i4/mmm			2.5617E-07
	25	Al3Ca8(s)	FTlite	ap22_(ca8in3)			3.1327E-21
	26	Al14Ca13(s)	FTlite	solid_monoclinic			9.1571E-23
	27	Ca4Al3Mg(s)	FTlite	pbcn			1.3691E-07

# Kinetics



## —Calculation input parameters from FactSage

- Equilibrium concentration at the matrix/precipitates interface

F Results - Equilib 473 K (page 1/13)

Output Edit Show Pages

T(K) P(atm) Energy(J) Mass(mol) Vol(litre)

473 K | 493 K | 513 K | 533 K | 553 K | 573 K | 593 K | 613 K | 633 K | 653 K | 673 K | 693 K | 713 K

0.9961 Mg + 0.0009 Al + 0.003 Ca =

0.99208 mol HCP\_A3#1  
(24.118 gram, 0.99208 mol, 1.4084E-02 litre, 1.7124 gram/cm3)  
(473.00 K, 1 atm, a=1.0000)

( 7.3152E-05	Al	V
+ 3.6267E-04	Ca	V
+ 0.99956	Mg	V)

System component	Mole fraction	Mass fraction
Ca	3.6267E-04	5.9789E-04
Al	7.3152E-05	8.1188E-05
Mg	0.99956	0.99932

Lattice parameter a/nm = 0.32241  
Lattice parameter c/nm = 0.52374  
c/a = 1.6244

+ 0.00000 mol HCP\_A3#2  
(473.00 K, 1 atm, a=1.0000)

( 7.3152E-05	Al	V
+ 3.6267E-04	Ca	V
+ 0.99956	Mg	V)

System component	Mole fraction	Mass fraction
Ca	3.6267E-04	5.9789E-04
Al	7.3152E-05	8.1188E-05
Mg	0.99956	0.99932

+ 2.6402E-03 mol Laves\_C14#1  
(0.23637 gram, 2.6402E-03 mol, 1.3418E-04 litre, 1.7615 gram/cm3)

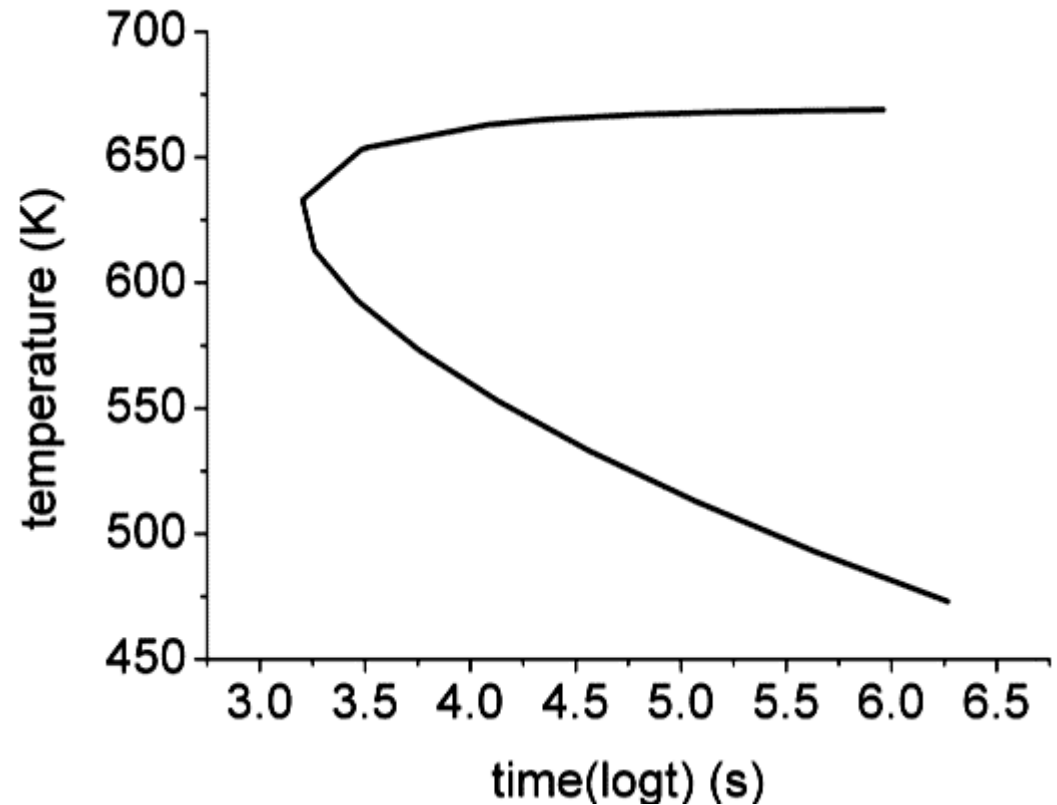
# Kinetics

## –Results (TTT diagram)



Alloy 1: Mg-0.0027Al-0.0012Ca---Al<sub>2</sub>Ca precipitates

time	logt	temperature
1.85E+06	6.26788	473
4.30E+05	5.63328	493
1.17E+05	5.06712	513
3.68E+04	4.56601	533
1.35E+04	4.12892	553
5.73E+03	3.75826	573
2.90E+03	3.46194	593
1.82E+03	3.25964	613
1.59E+03	3.20258	633
3.01E+03	3.47909	653
3.26E+03	3.51312	654
1.20E+04	4.08008	663
2.25E+04	4.35139	665
6.30E+04	4.799	667
1.54E+05	5.18765	668
9.15E+05	5.96156	669



**The incubation time of alloy 1 is 1590 seconds (26.5minutes) at 633K (360oC).**

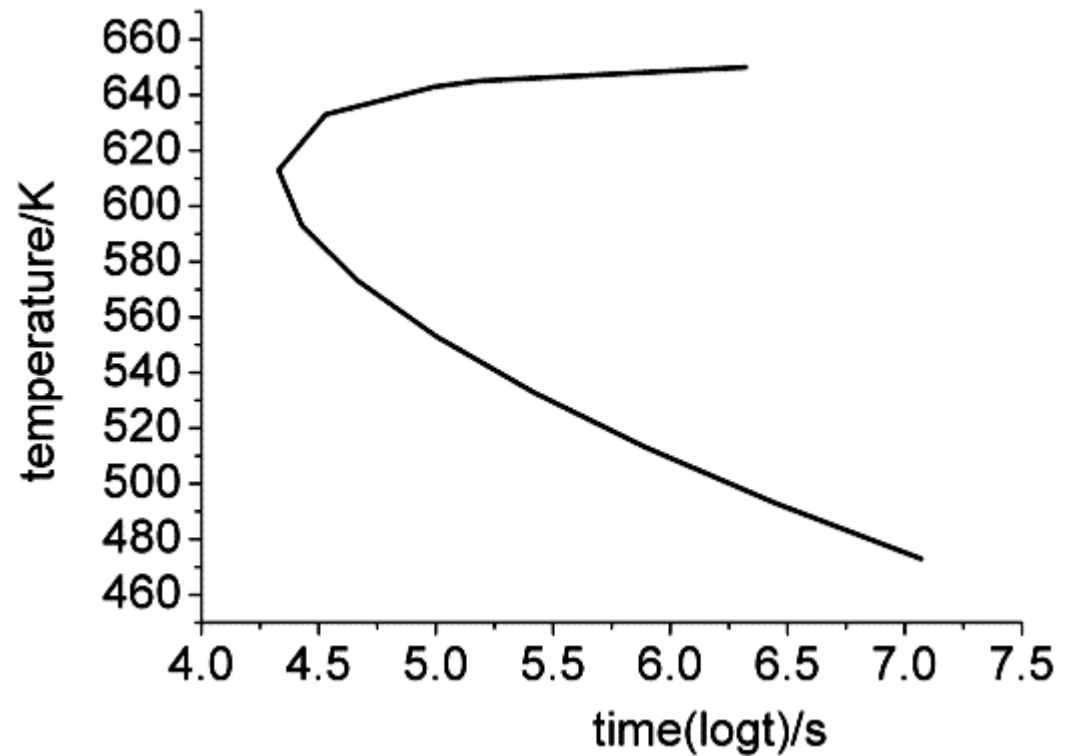
# Kinetics

–Results (TTT diagram)



Alloy 2: Mg-0.0009Al-0.003Ca---Mg<sub>2</sub>Ca precipitates

time	logt	temperature
1.18E+07	7.070508	473
2.81E+06	6.448068	493
7.88E+05	5.896791	513
2.60E+05	5.414602	533
1.01E+05	5.002745	553
4.65E+04	4.667882	573
2.68E+04	4.427599	593
2.13E+04	4.327799	613
3.38E+04	4.529422	633
9.87E+04	4.99448	643
1.53E+05	5.184327	645
2.10E+06	6.322184	650



**The incubation time of alloy 2 is 21300 second (5.9 hours) at 613K (340oC).**



# Discussion

- The incubation time of alloy 1 is 26.5 minutes at 633K (360°C). However, the incubation time of alloy 2 is 5.9 hours at 613K (340°C).

- Effects on the incubation time

$$\tau = 4 / (2\pi\beta^*Z^2).$$

- Incubation time has an inverse relationship with Z factor and  $\beta^*$ .
- Effect of diffusivity and interfacial energy on  $\beta^*$  and Z factor

$$\beta^* = \frac{4\pi R^{*2}DX}{a^4} \quad Z = \frac{v_{at}^P}{2\pi R^{*2}} \sqrt{\frac{\gamma}{k_B T}} \quad R^* = -\frac{2\gamma}{\Delta g}$$

- $\beta^* \propto DX\gamma^2/\Delta g^2$  and  $Z \propto -\Delta g/\gamma^{3/2} \Rightarrow \beta^*Z^2 \propto DX/\gamma^{1/2}$
- Increasing of  $\gamma$  decreases Z, while increasing of  $\gamma$  increases  $\beta^*$ . Increasing of D increases  $\beta^*$ .
- Higher diffusivity, higher concentration of solute element and lower interfacial energy results in lower incubation time.



# Discussion

- Effect of interfacial energy on incubation time

For example:

Mg-0.0009Al-0.003Ca

If interfacial energy changes from  $50\text{mJ/m}^2$  to  $10\text{mJ/m}^2$ , the Z factor will increase almost  $10^1$  and  $\beta^*$  will decrease  $10^2$ , and then the incubation time will reduce near  $10^1$ .

interfacial energy	Beta star	Z factor	time	logt	temperature
5.00E-02	1.90E-05	2.39E-02	5.88E+07	7.769478	473
5.00E-02	1.33E-04	1.84E-02	1.40E+07	7.147038	493
5.00E-02	8.47E-04	1.38E-02	3.94E+06	6.595761	513
5.00E-02	4.98E-03	9.92E-03	1.30E+06	6.113572	533
5.00E-02	2.79E-02	6.73E-03	5.03E+05	5.701715	553
5.00E-02	1.55E-01	4.20E-03	2.33E+05	5.366852	573
5.00E-02	9.04E-01	2.29E-03	1.34E+05	5.126569	593
5.00E-02	6.25E+00	9.79E-04	1.06E+05	5.026769	613
5.00E-02	7.54E+01	2.23E-04	1.69E+05	5.228392	633
5.00E-02	5.78E+02	4.72E-05	4.94E+05	5.69345	643
5.00E-02	1.08E+03	2.78E-05	7.64E+05	5.883297	645
5.00E-02	2.37E+04	1.60E-06	1.05E+07	7.021154	650

interfacial energy	Beta star	Z factor	time	logt	temperature
1.00E-02	7.59E-07	2.67E-01	1.18E+07	7.070508	473
1.00E-02	5.33E-06	2.06E-01	2.81E+06	6.448068	493
1.00E-02	3.39E-05	1.54E-01	7.88E+05	5.896791	513
1.00E-02	1.99E-04	1.11E-01	2.60E+05	5.414602	533
1.00E-02	1.12E-03	7.52E-02	1.01E+05	5.002745	553
1.00E-02	6.20E-03	4.70E-02	4.65E+04	4.667882	573
1.00E-02	3.62E-02	2.57E-02	2.68E+04	4.427599	593
1.00E-02	2.50E-01	1.09E-02	2.13E+04	4.327799	613
1.00E-02	3.02E+00	2.50E-03	3.38E+04	4.529422	633
1.00E-02	2.31E+01	5.28E-04	9.87E+04	4.99448	643
1.00E-02	4.33E+01	3.10E-04	1.53E+05	5.184327	645
1.00E-02	9.49E+02	1.79E-05	2.10E+06	6.322184	650

# Discussion



- Effect of interfacial energy on Zeldovich factor
  - ▣ Increasing of interfacial energy decreases the Z factor.
  - ▣ The Zeldovich factor is often called the Zeldovich non-equilibrium factor. The actual concentration of clusters of size is smaller than the equilibrium concentration, and many supercritical clusters decay back to smaller sizes. The actual nucleation rate is therefore smaller and Z corrects for these effects.
  - ▣ The dimensionless term is often called the Zeldovich factor and has a magnitude typically near  $10^{-1}$ .
  - ▣ From previous example, when the interfacial energy of  $Mg_2Ca$  is either  $50\text{mJ/m}^2$  or  $10\text{mJ/m}^2$ , the Z factor will be from  $10^{-2}$  to  $10^{-6}$  or from  $10^{-1}$  to  $10^{-5}$ . The value of Z factor could be the factor to introduce error in the calculation of incubation time.

# Summary



- The precipitates in as-cast microstructure is eutectic structure with  $(Mg,Al)_2Ca$  and  $\alpha$ -Mg. So Scheil cooling gives good prediction of composition of precipitates in as-cast structure.
- The equilibrium calculation gives good prediction of heat treatment temperature range.
- From kinetics modeling of precipitation, the incubation time of alloy 1 is 26.5minutes at 633K (360°C). However, the incubation time of alloy 2 is 5.9 hours at 613K (340°C) .



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**Thank You !**

**Questions & Comments**