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

MIME 572

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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

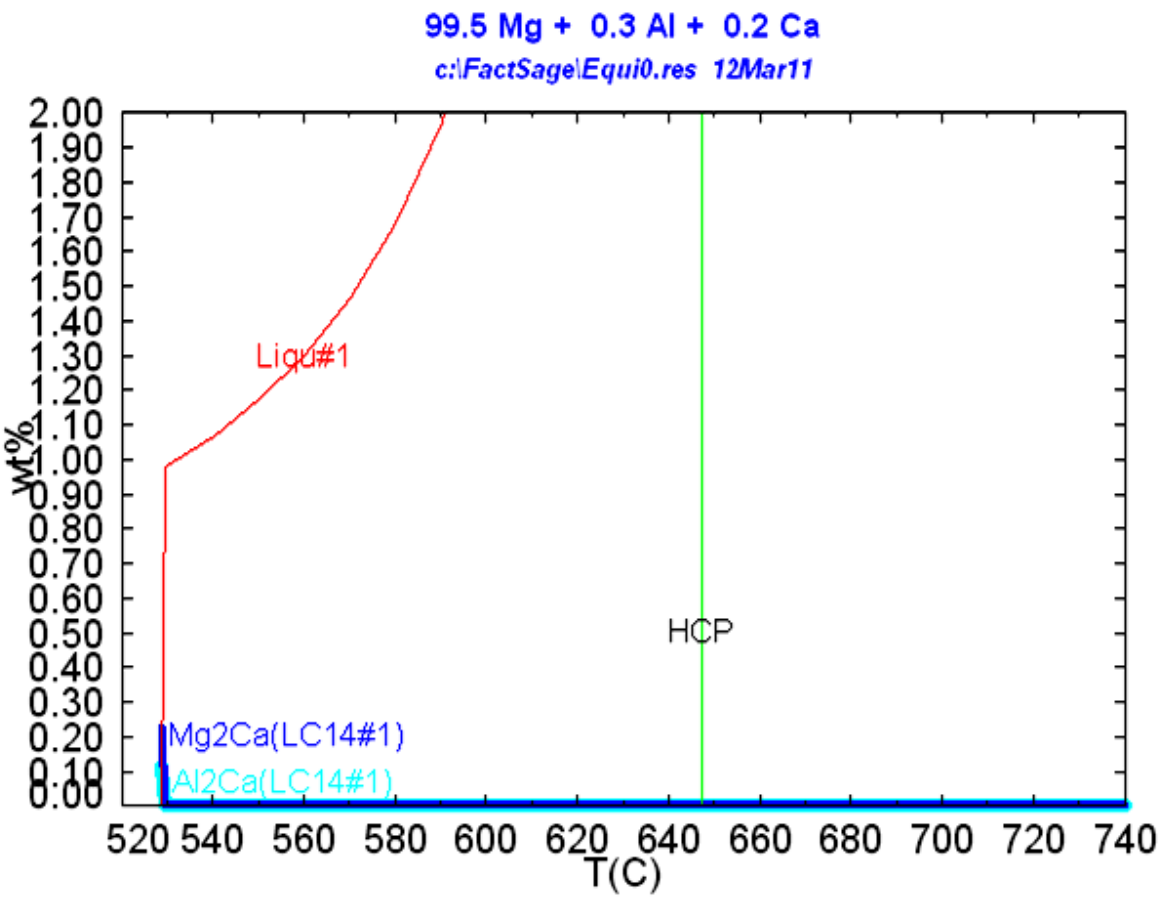
- Addition of Ca into Mg-Al alloys
  - Refinement of the microstructure --- Improvement of formability of sheets
  - Strengthening
  - Inexpensive alloy element comparing with the rare earth elements
  - Increase the ignition temperature --- Protecting the melting surface from oxidation
- Experimental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

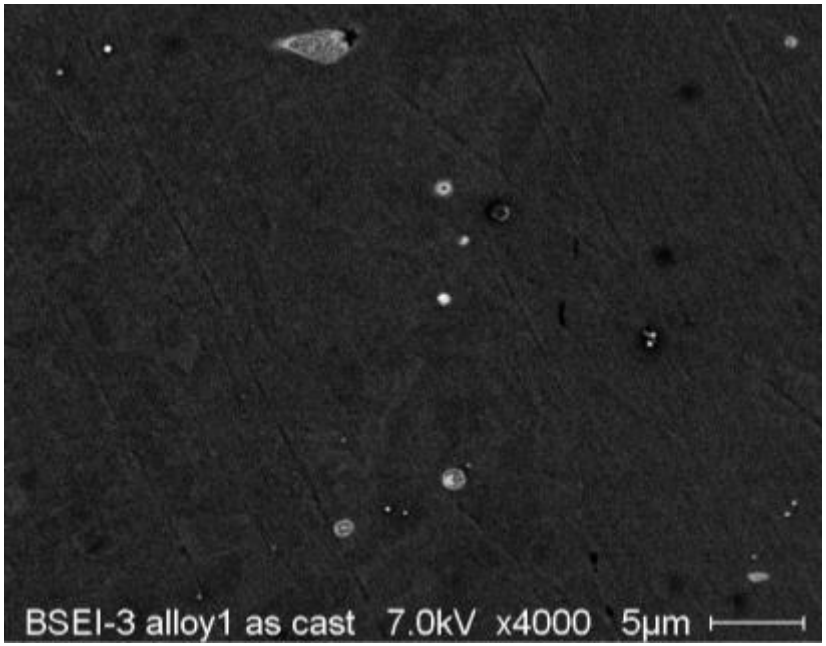
⇩

Composition of as-cast alloys

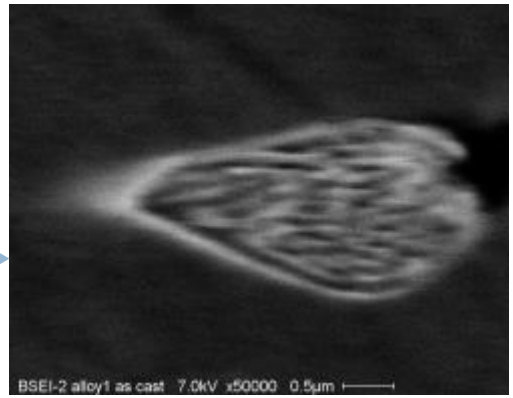
Formation of Laves C14#1) phase:
0.22wt% Mg2Ca
0.11wt% Al2Ca

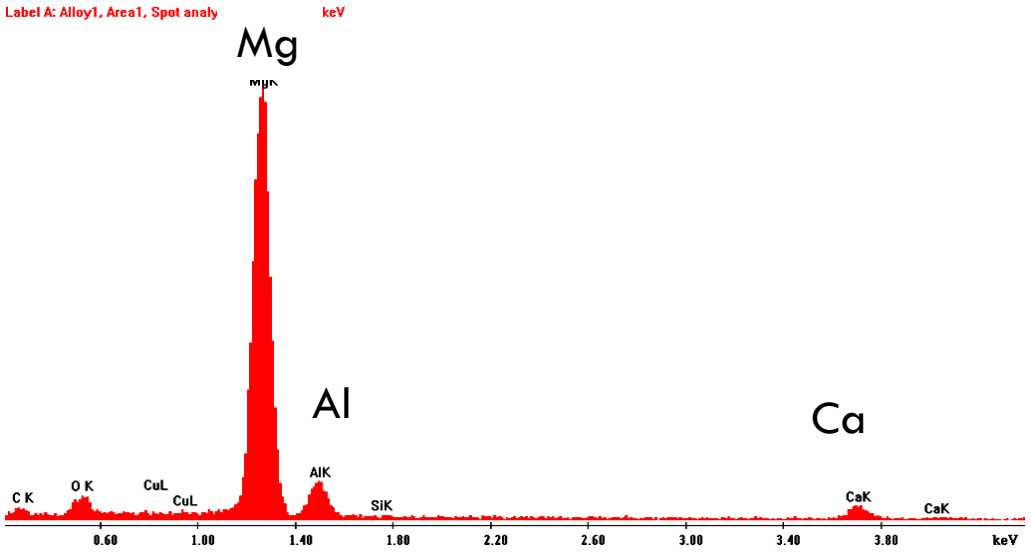
Thermodynamics calculation

- SEM results of Mg-0.3Al-0.2Ca



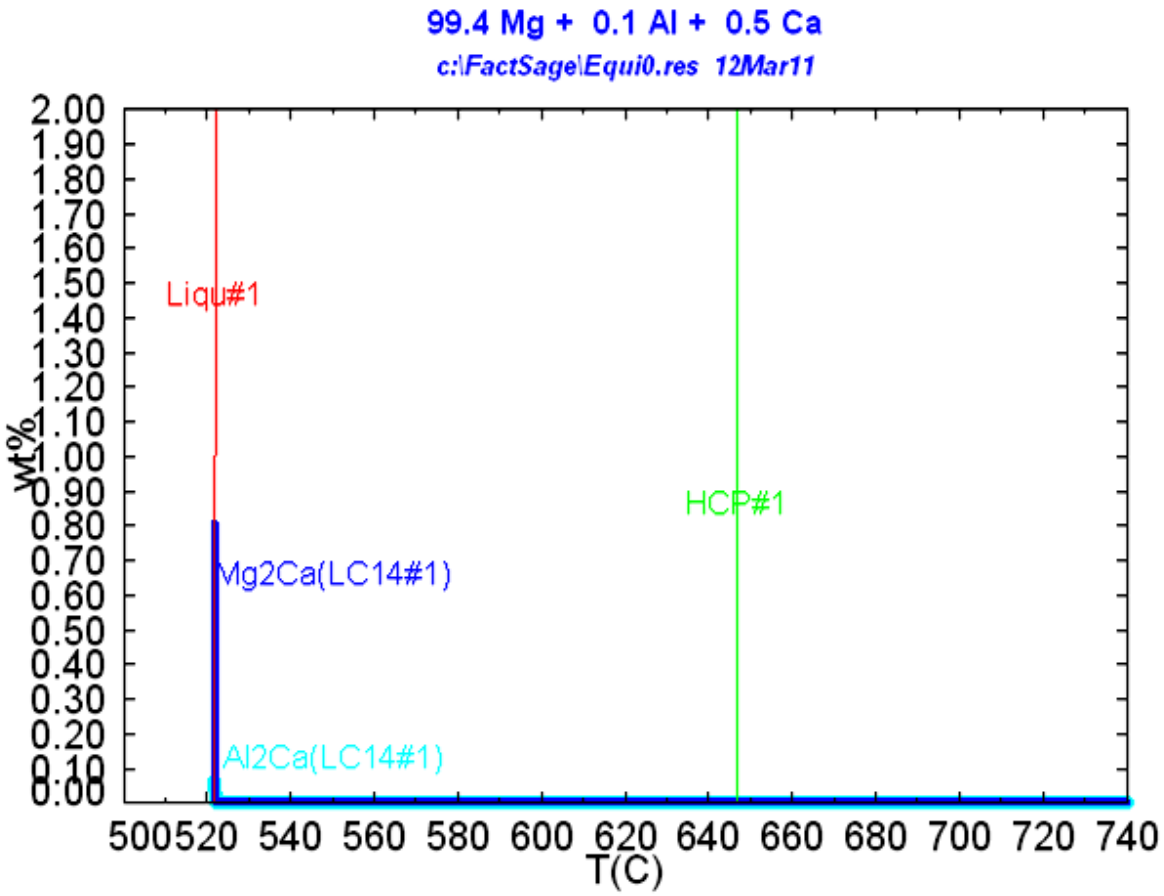
Higher Mag.





Thermodynamics calculation

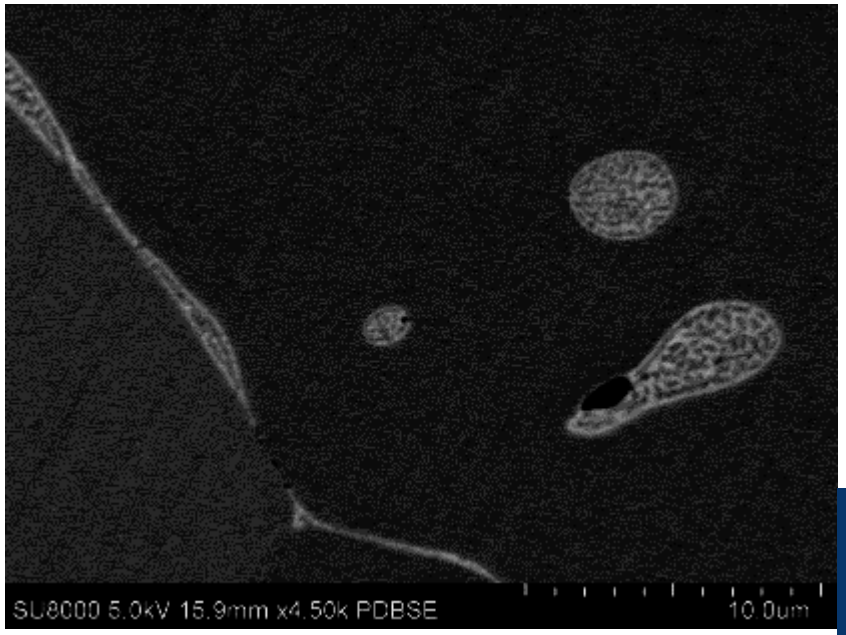
- Scheil cooling diagram of Mg-0.1Al-0.5Ca



Formation of Laves C14#1phase:
0.8wt% Mg2Ca
0.06wt% Al2Ca

Thermodynamics calculation

- SEM results of Mg-0.1Al-0.5Ca



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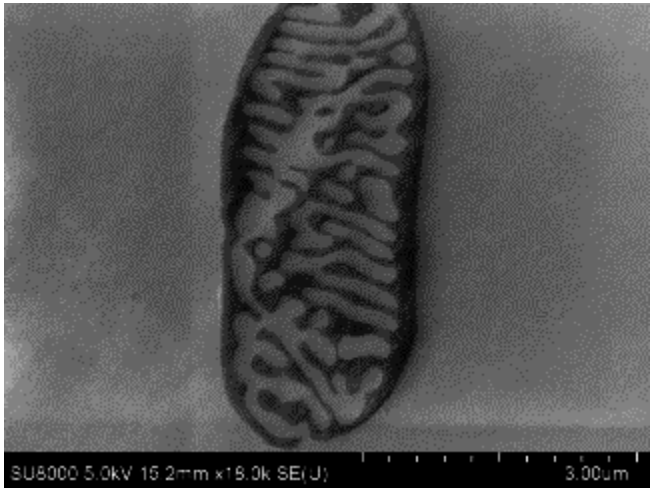
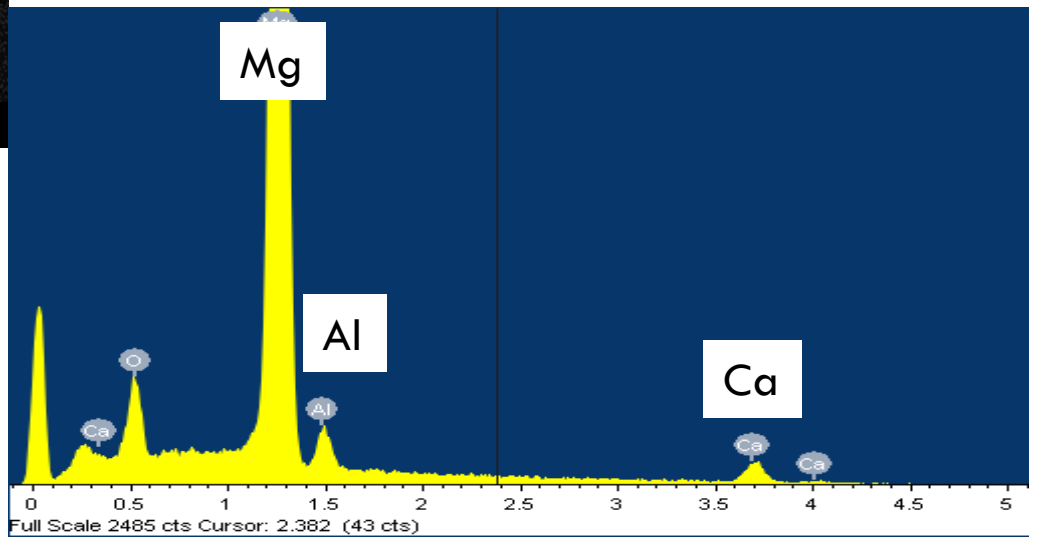
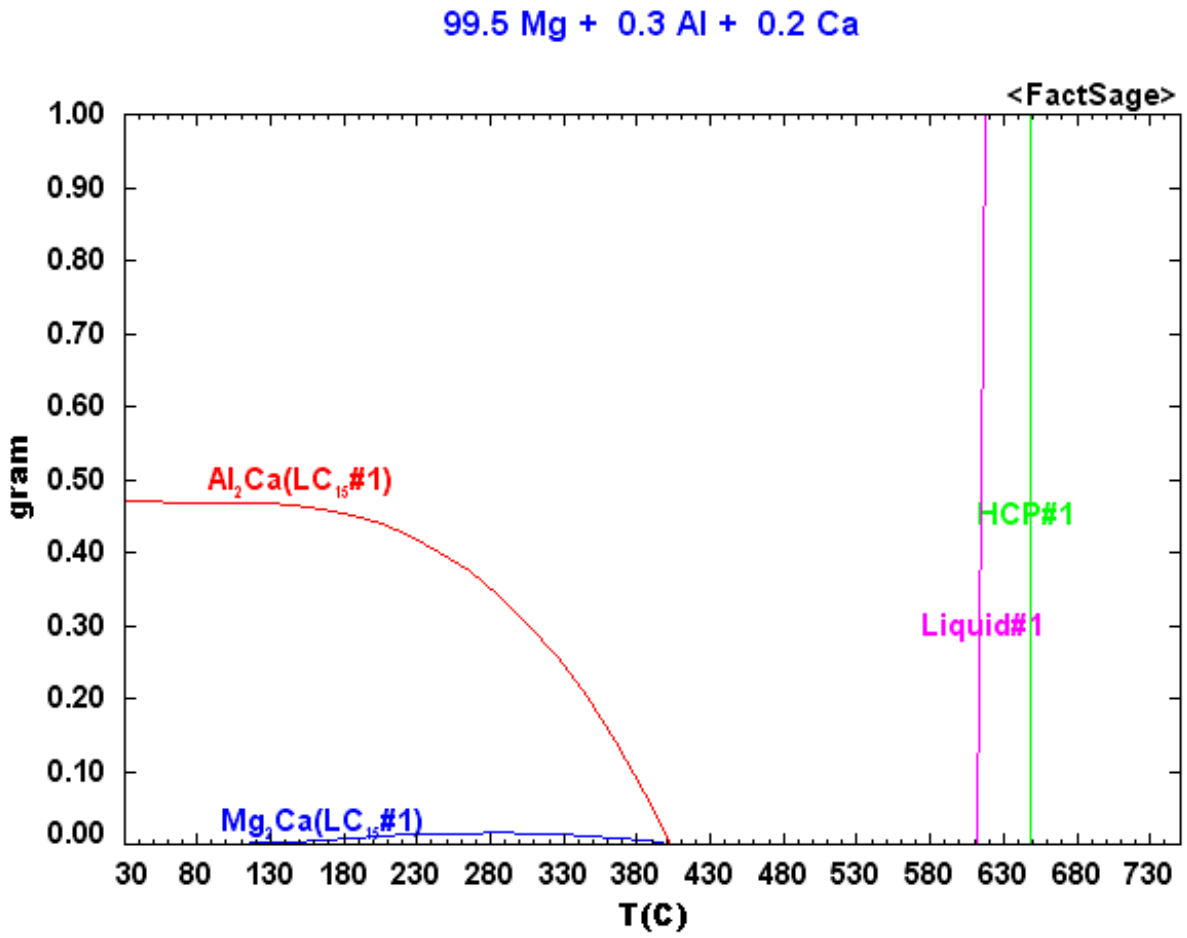


The precipitates in theses two as-cast Mg-Al-Ca alloys are $(Mg,Al)_2Ca$ and a-Mg eutectic structure.



Thermodynamics calculation

- Equilibrium diagrams of Mg-0.3Al-0.2Ca

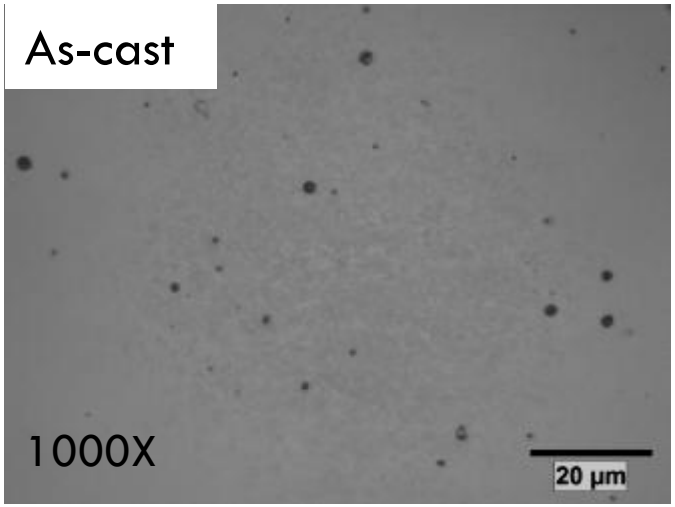


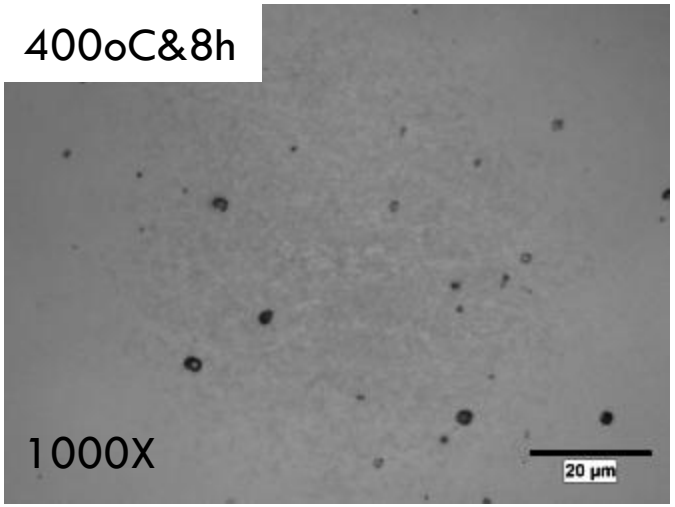
Precipitates in alloy 1 are: Al2Ca(Laves 15)

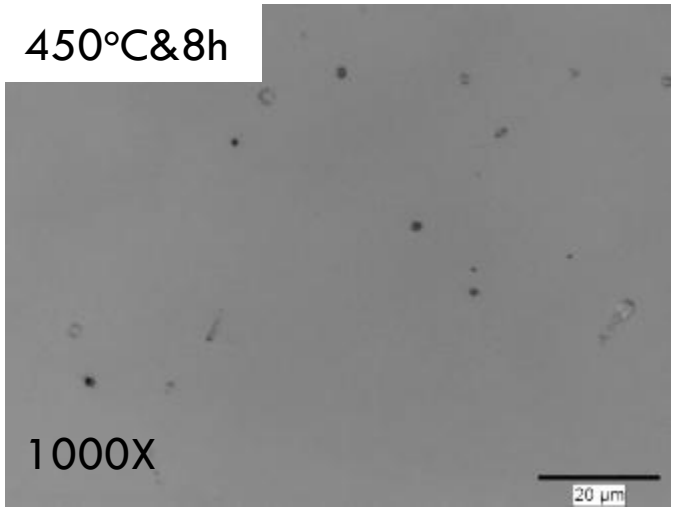
Heat treatment temperature range: 400-610°C

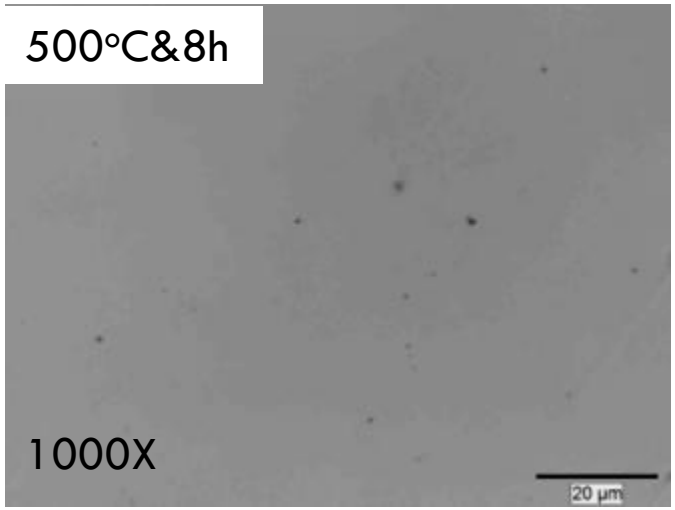
Thermodynamics calculation

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







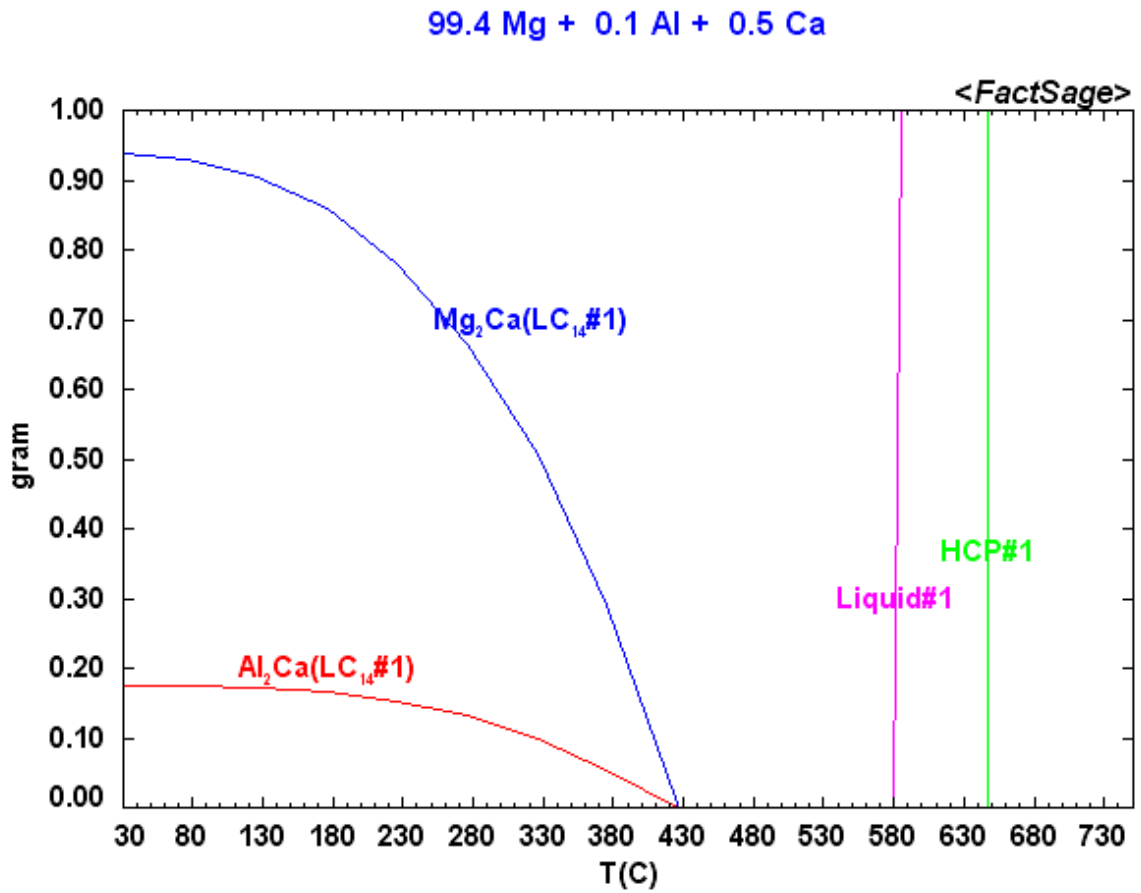


FactSage: Heat treatment temperature range: 430-580°C

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

Thermodynamics calculation

- Equilibrium diagrams of Mg-0.1Al-0.5Ca

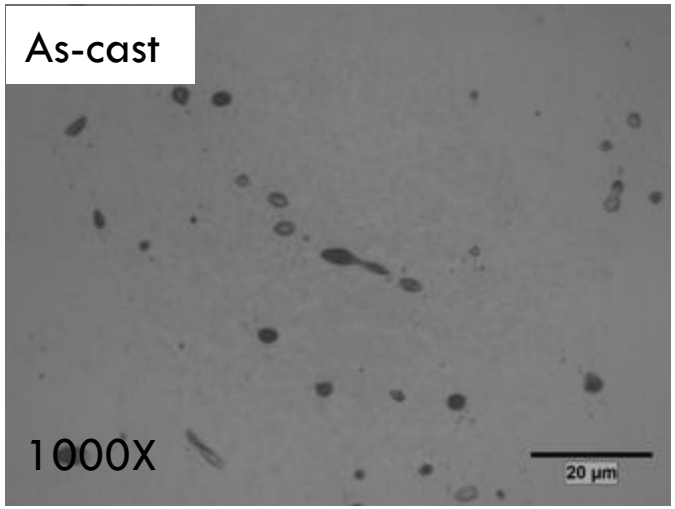


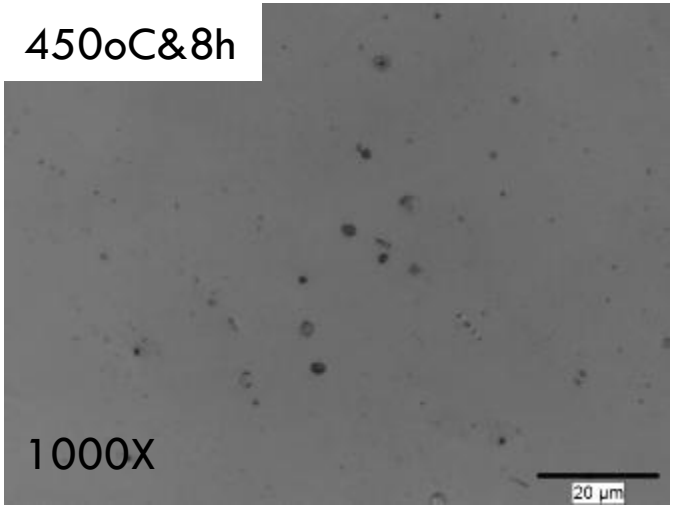
Precipitates in alloy 2 are: Mg2Ca(Laves 14)

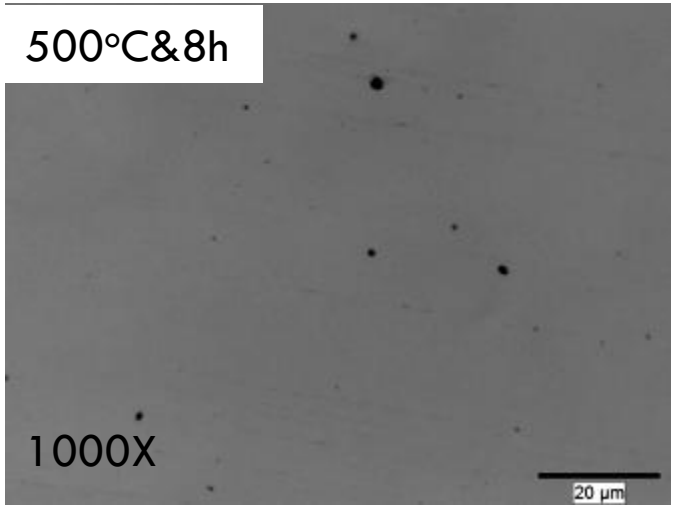
Heat treatment temperature range: 430-580°C

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 disolved into matrix at 500oC for 8h.

Kinetics

—Classical nucleation and growth theory

- Nucleation

Nucleation rate: (Kampmann and Wagner Equation)

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

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

$N_0=3/(4\times3.14\times R^{*3})$

ΔG^* -- the energy required to form a critical nucleus of radius R*

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

Z -- the Zeldovich factor

β* --the condensation rate of solute atoms in a cluster of critical size R *

Kinetics

—Classical nucleation and growth theory

- Nucleation

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

V^{P}_{at} -- the mean atomic volume within precipitates

γ -- 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:

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

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

τ -- incubation time for nucleation

Kinetics
—Classical nucleation and growth theory

- Growth

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

Xp -- mole fraction of precipitates

X -- mean solute mole fraction in the matrix

Xi -- equilibrium solute mole fraction at the precipitate/matrix interface

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

D -- diffusion coefficient

α -- the ratio of matrix to precipitates atomic volumes (mean volume per atom)

$$\alpha = v^M_{at} / v^P_{at}$$

v^P_{at} -- the mean atomic volume within precipitates

v^M_{at} -- 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

α -- The numerical factor a 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 a is of no consequence on the results of the model. It was taken a= 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:

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

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

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

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

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

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

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 (Mg2Ca) 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 (Al2Ca) without matrix element (Mg), the growth rate depends on the element with lower diffusivity.

Kinetics
– Input parameters

- Input parameters

	Alloy 1	Allloy2
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--Al2Ca) 2	(Precipitates--Mg2Ca) 2
Atomic ratio solute element 2 in compound	(Precipitates--Al2Ca) 1	(Precipitates--Mg2Ca) 1
Molar volume of compound (m^3/mol)	$4.6*10^{-5}$	$4.93*10^{-5}$

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 (m2/s), Q is the activation energy of diffusion (J/mol), R is the gas constant(8.3145), T is the absolute temperature)
  - T_1 is chosen as the melting point of calcium (1111K), D_{T1} is estimated to be 10^{-12} (m2/s), Q is approximated as 166 kJ/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°C, this gives $D_{T2}= 4.62\times10^{-16}$(m2/s) for the diffusion of calcium in magnesium.
  - $D_0=6.8\times10^{-5}$ J/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 4×10^{-4} m^2/s

Table I. Parameters and Values Used in the Calculations

Parameter	Description	Value Used	Reference
l/t	length-to-thickness ratio of $Mg_{17}Al_{12}$ lath	10	this work
l/w	length-to-width ratio of $Mg_{17}Al_{12}$ lath	4	this work
d	hcp Mg matrix grain size	100 μm	estimate from 61
G_p	shear modulus of $Mg_{17}Al_{12}$	32.6 GPa	10, 11
G_m	shear modulus of hcp matrix	17.2 GPa	10, 11
D_o^{Al}	pre-exponential for Al diffusion in hcp Mg	$4\cdot10^4$ m^2/s	this work
Q^{Al}	activation energy for Al diffusion in hcp	125 kJ/mol	this work
ν	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_o	lattice parameter of hcp Mg	0.32 nm	11, 60
σ_o	intrinsic lattice strength in hcp Mg	11 MPa	60
k	Hall–Petch parameter	0.37 (MPa $m^{1/2}$)	60
C	coefficient for solid solution strengthening	197 (MPa. $at.^{-2/3}$)	61
$\sigma^{coarsening}$	$Mg_{17}Al_{12}$/hcp interfacial energy extracted from plate tip radii assuming maximum growth rate hypothesis	0.43 (J/m^2)	this work
$\sigma_{eff}^{nucleation}$	'Effective' $Mg_{17}Al_{12}$/hcp interfacial energy used for the nucleation of $Mg_{17}Al_{12}$	0.114 (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-I	Diffusion (Al-M r
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 Al2Ca depends on the diffusivity of Ca.

Kinetics

– Selection of input parameters from literature

- Selection of input parameters from literature
  - Inter-facial energy
    - $MgZn_2$: 65±18 mJ/m^2
    - Mg_2Sn: 410±120 mJ/m^2
    - Mg_2Sn particles are plate-like and mainly equiaxed in the a-Mg-matrix while precipitates of $MgZn_2$ 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 $MgZn_2$ precipitates and Mg-matrix. A rather large value is indicative of incoherent interfaces between Mg_2Sn-particles and Mg.
    - $Mg_{17}Al_{12}$:114 mJ/m^2 (Literature)
  - Assume Mg_2Ca(hcp—coherent with matrix(Mg))-- 50mJ/m^2
  - Assume Al_2Ca(fcc—incoherent with matrix(Mg))--100mJ/m^2

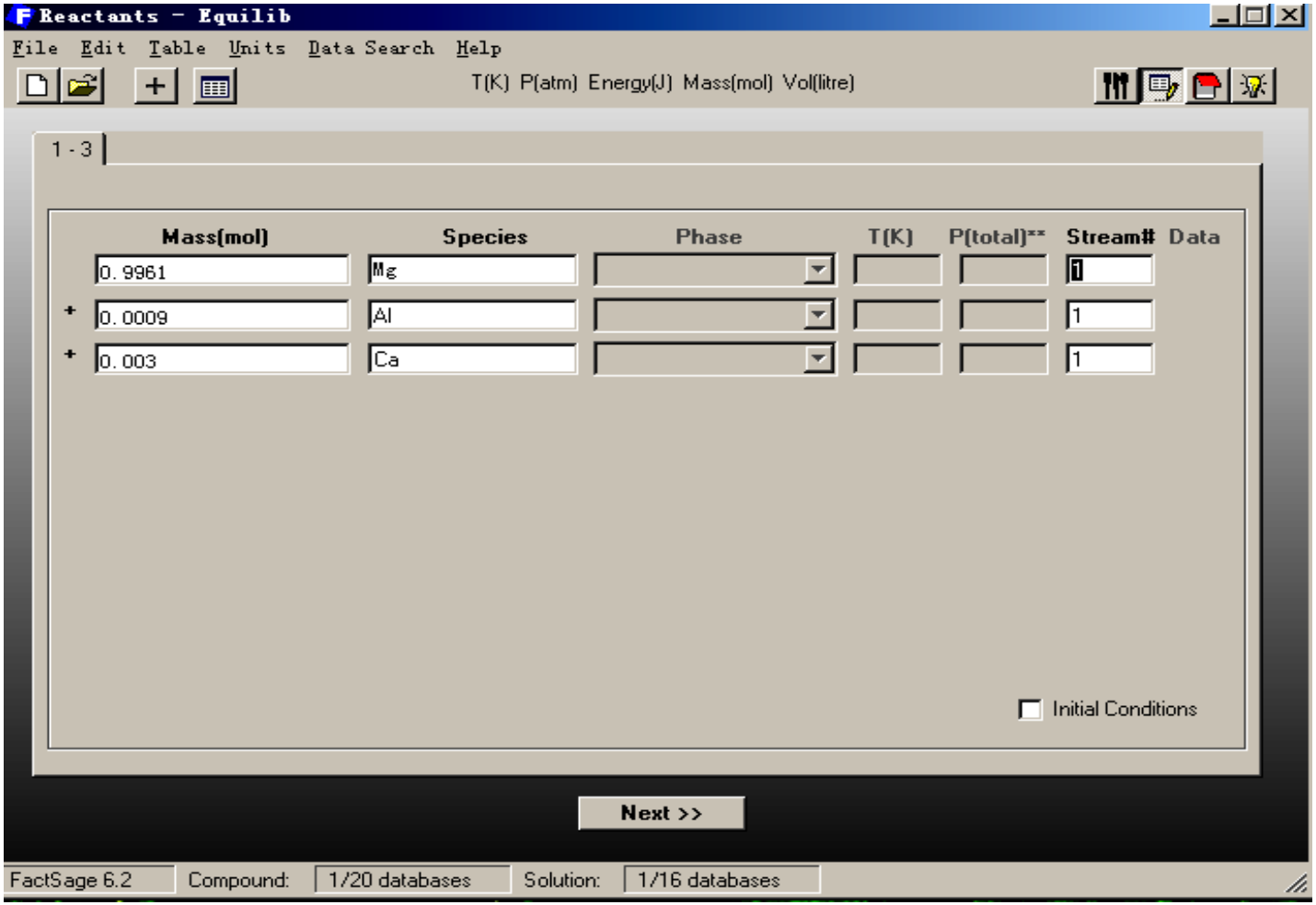
Kinetics
—Calculation input parameters from FactSage

- Formation energy of the precipitate
  - $\Delta G = \Delta G^0 + RT\ln K$
  - ΔG^0 -- Standard formation energy of precipitates– from FactSage
    - 2Mg (hcp) +Ca (fcc)= Mg2Ca(s)
    - 2Al (fcc) + Ca (fcc)= Al2Ca(s)
  - $K=1/(a(Mg)^2+a(Ca)^1)$
  - a -- Activity of elements – from Factsage
- Mean atomic volume of precipitates
  - $v^P_{at} = V/((x+y)*1000*6.02*!0^{23})$
  - V—Mole volume--from FactSage
- Solute concentration at the interface of precipitates and matrix
  - —from FactSage

Kinetics

—Calculation input parameters from FactSage

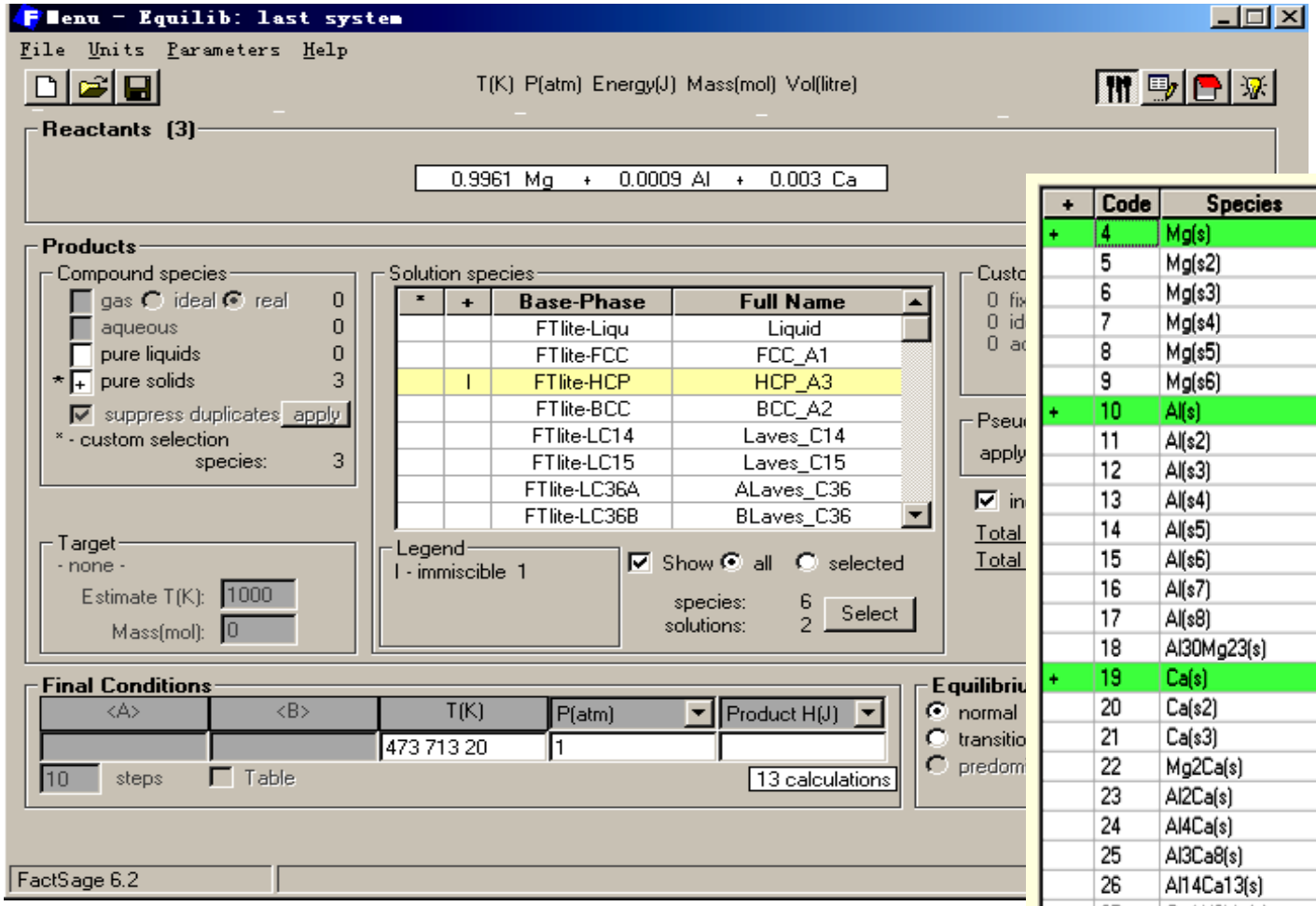
- Activity of solute element



Kinetics

—Calculation input parameters from FactSage

- Activity of solute element



+	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

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

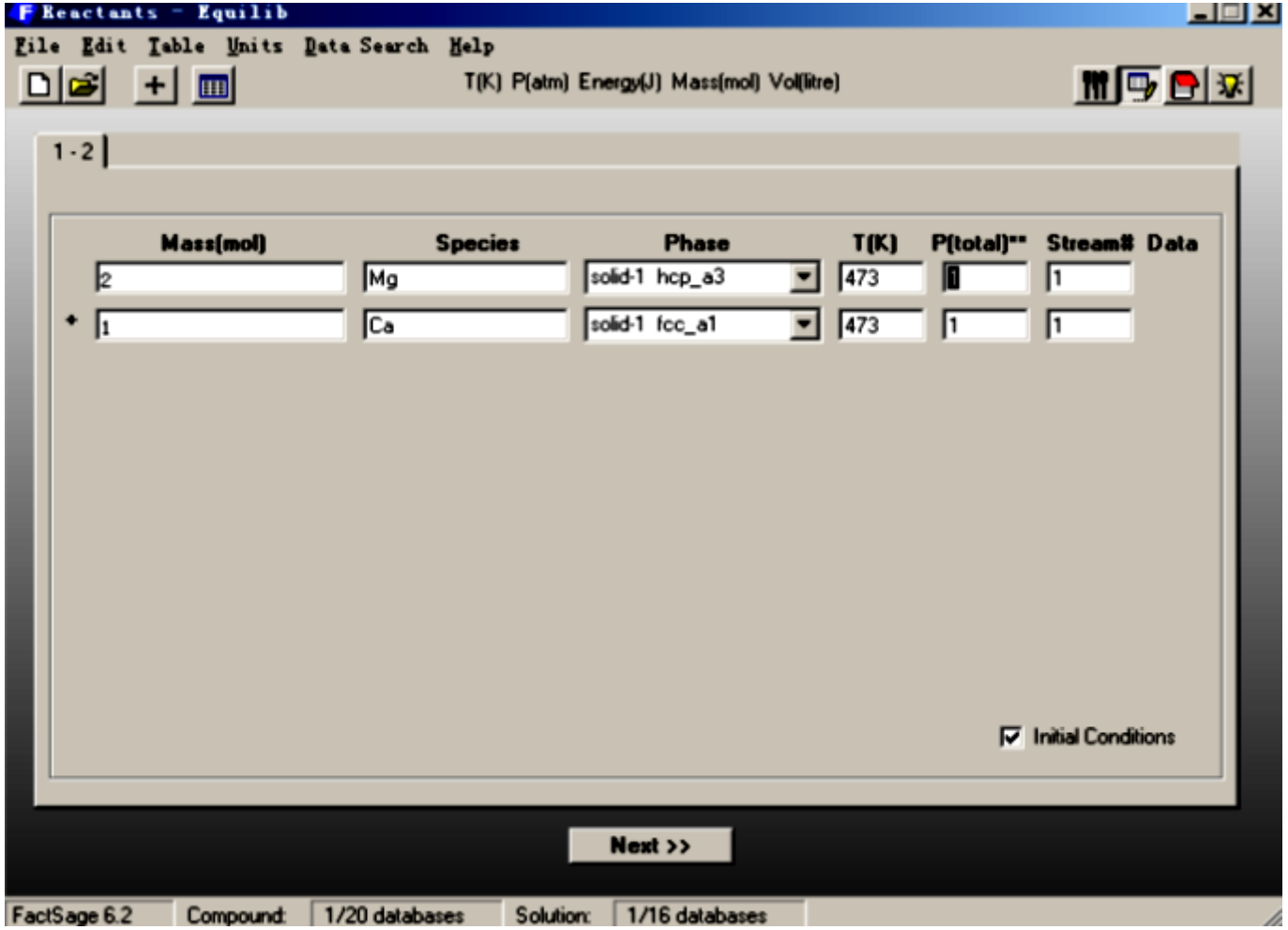
STREAM CONSTITUENTS	AMOUNT/mol		
Mg	9.9610E-01		
Al	9.0000E-04		
Ca	3.0000E-03		
	EQUIL AMOUNT	MOLE FRACTION	ACTIVITY
PHASE: HCP_A3#1	mol		
Al	9.0000E-04	9.0000E-04	1.7002E-03
Ca	3.0000E-03	3.0000E-03	2.2426E-03
Mg	9.9610E-01	9.9610E-01	9.9610E-01
TOTAL:	1.0000E+00	1.0000E+00	1.0000E+00
PHASE: HCP_A3#2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

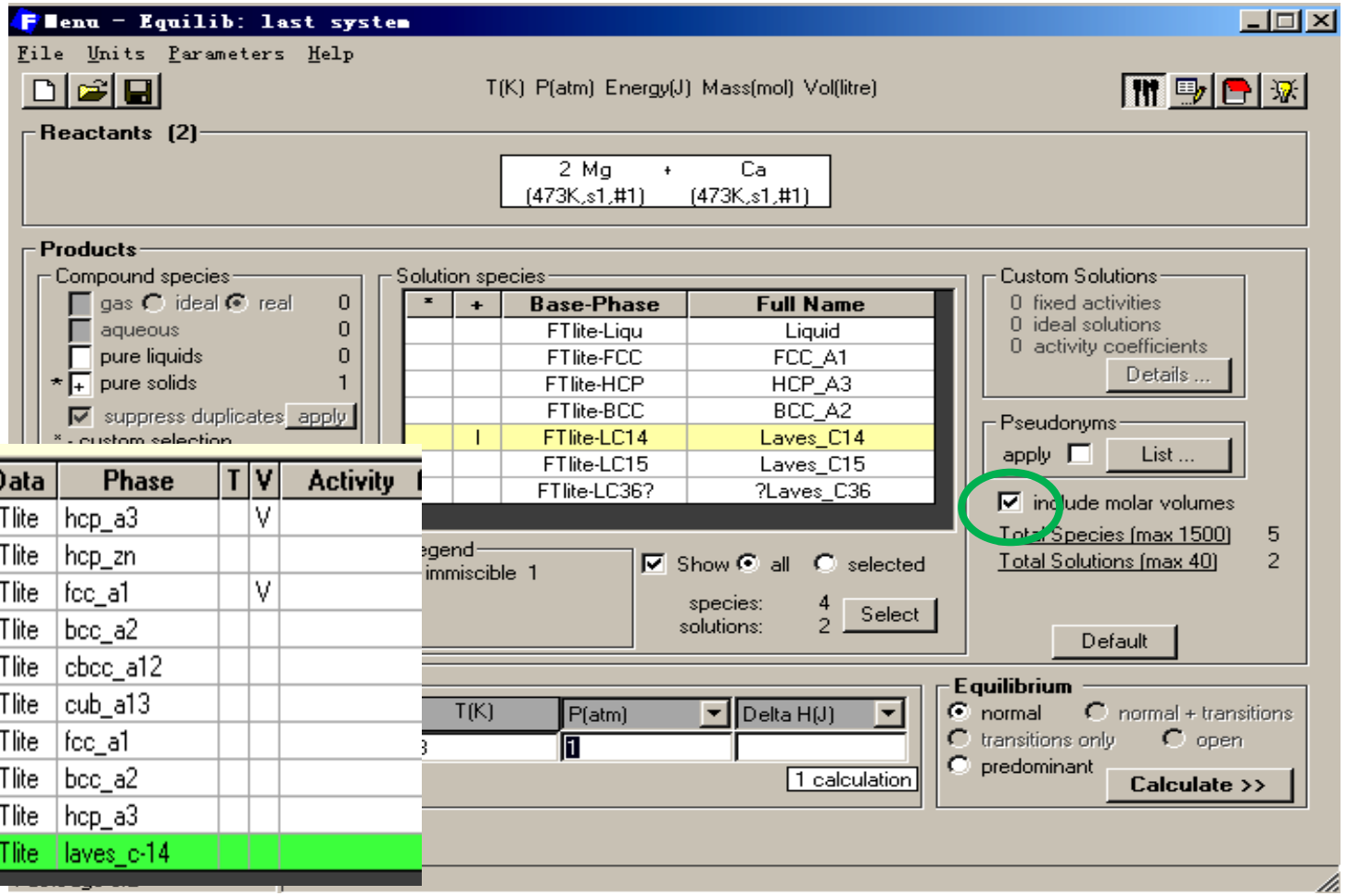
- Standard formation energy



Kinetics

—Calculation input parameters from FactSage

- Standard formation energy

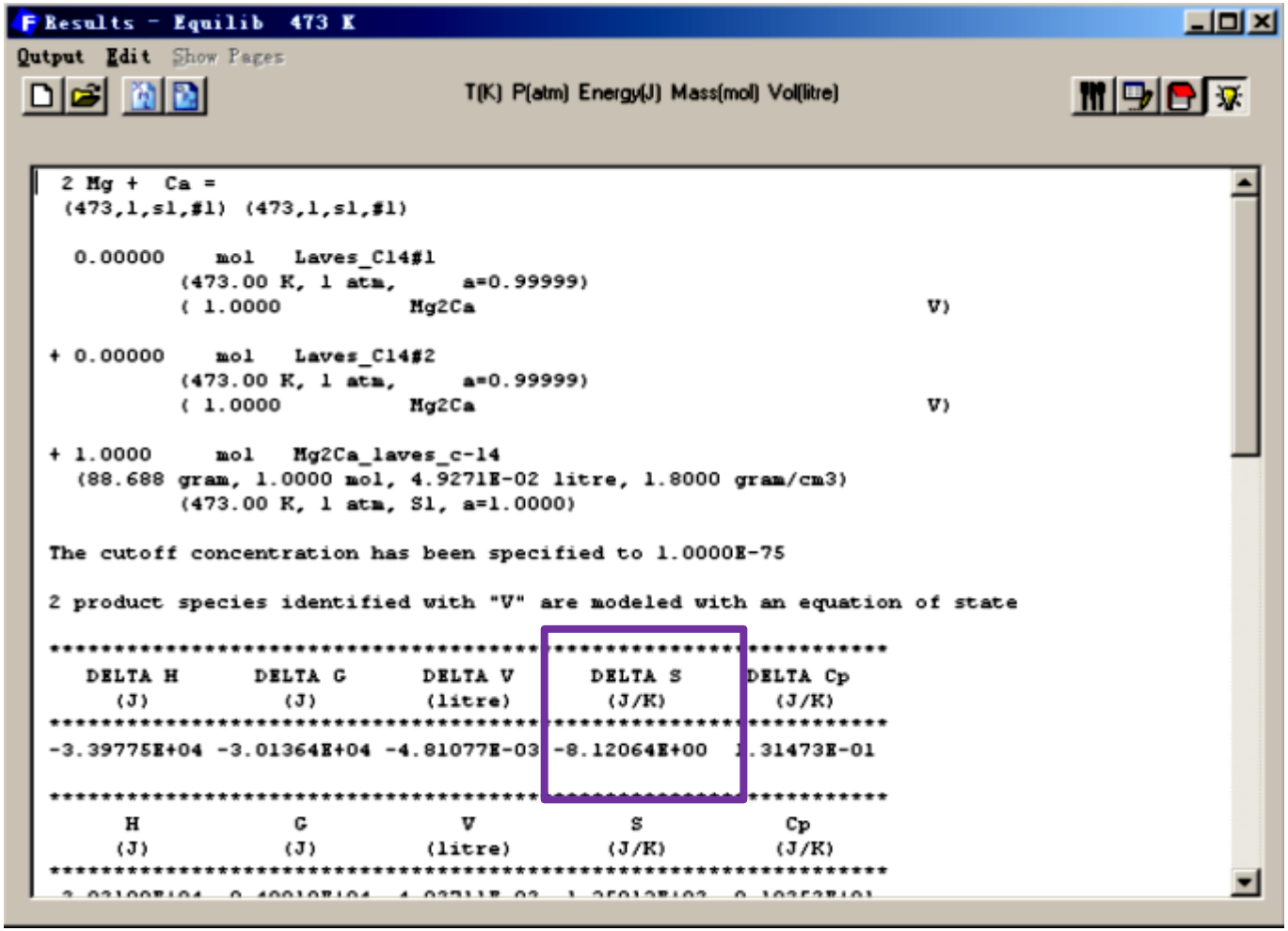


+	Code	Species	Data	Phase	T	V	Activity
	3	Mg(s)	FTlite	hcp_a3		V	
	4	Mg(s2)	FTlite	hcp_zn			
	5	Mg(s3)	FTlite	fcc_a1		V	
	6	Mg(s4)	FTlite	bcc_a2			
	7	Mg(s5)	FTlite	cbcc_a12			
	8	Mg(s6)	FTlite	cub_a13			
	9	Ca(s)	FTlite	fcc_a1			
	10	Ca(s2)	FTlite	bcc_a2			
	11	Ca(s3)	FTlite	hcp_a3			
+	12	Mg2Ca(s)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

Kinetics

—Calculation input parameters from FactSage

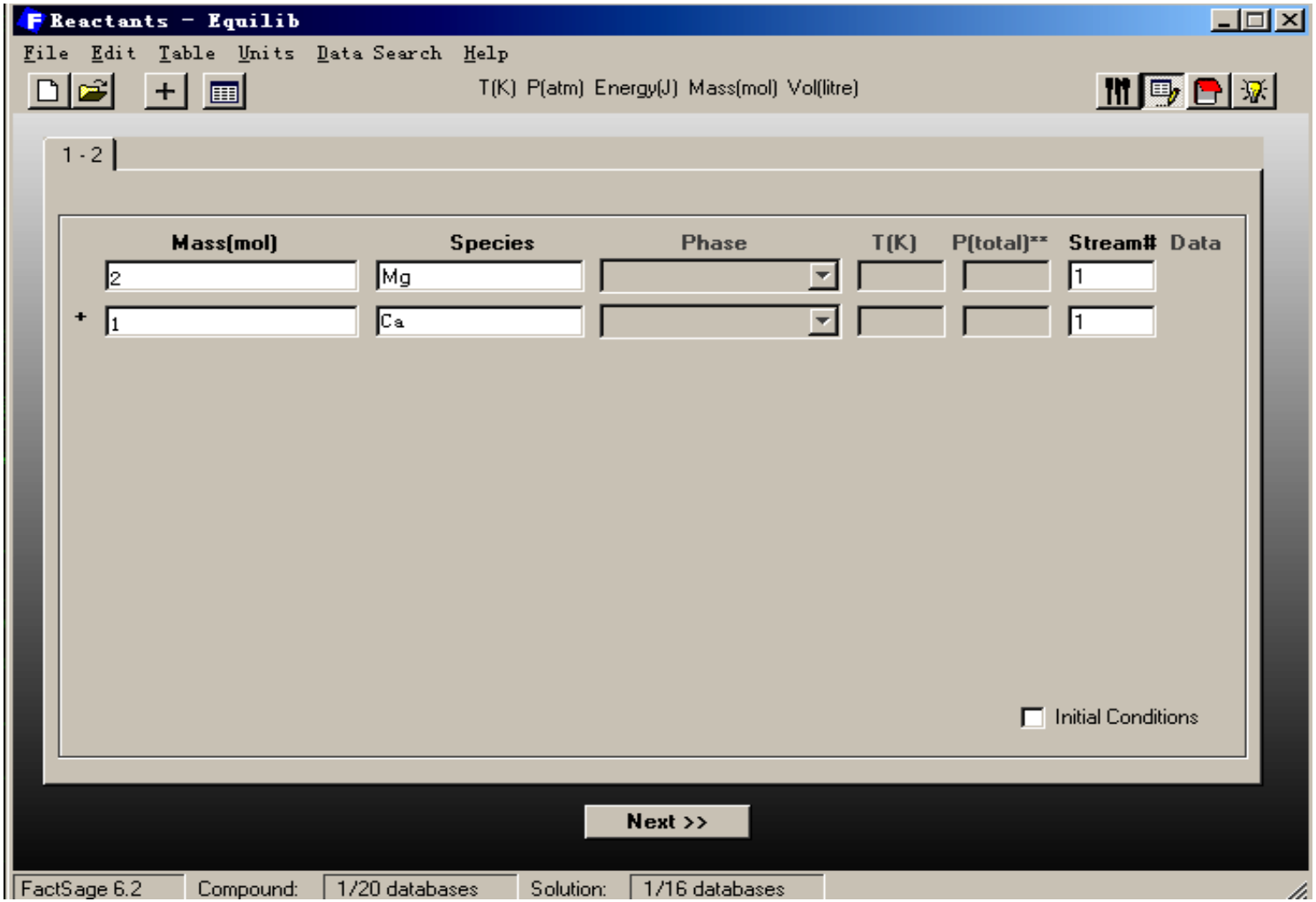
- Standard formation energy



Kinetics

—Calculation input parameters from FactSage

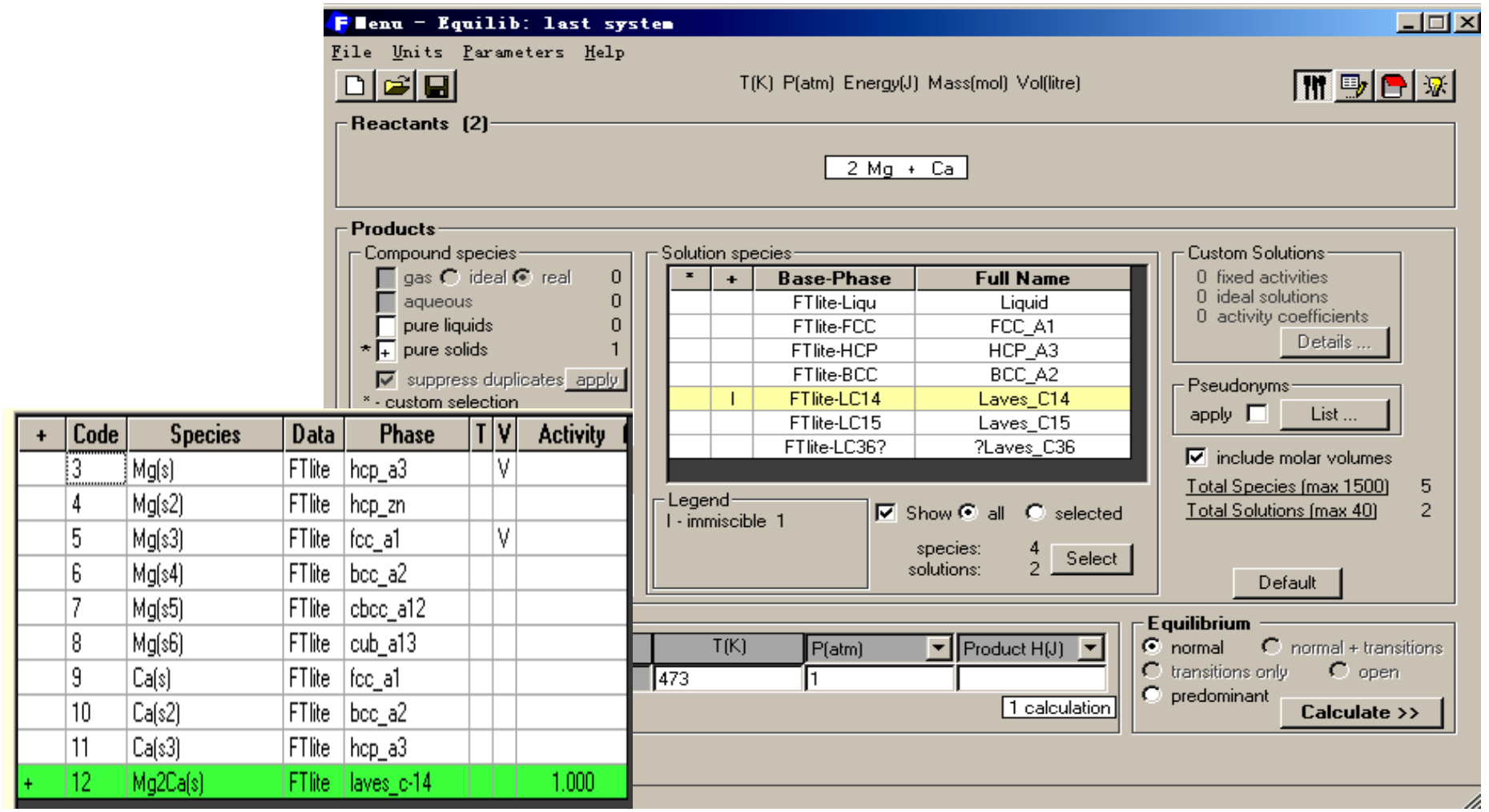
- Mean atomic volume of precipitates



Kinetics

—Calculation input parameters from FactSage

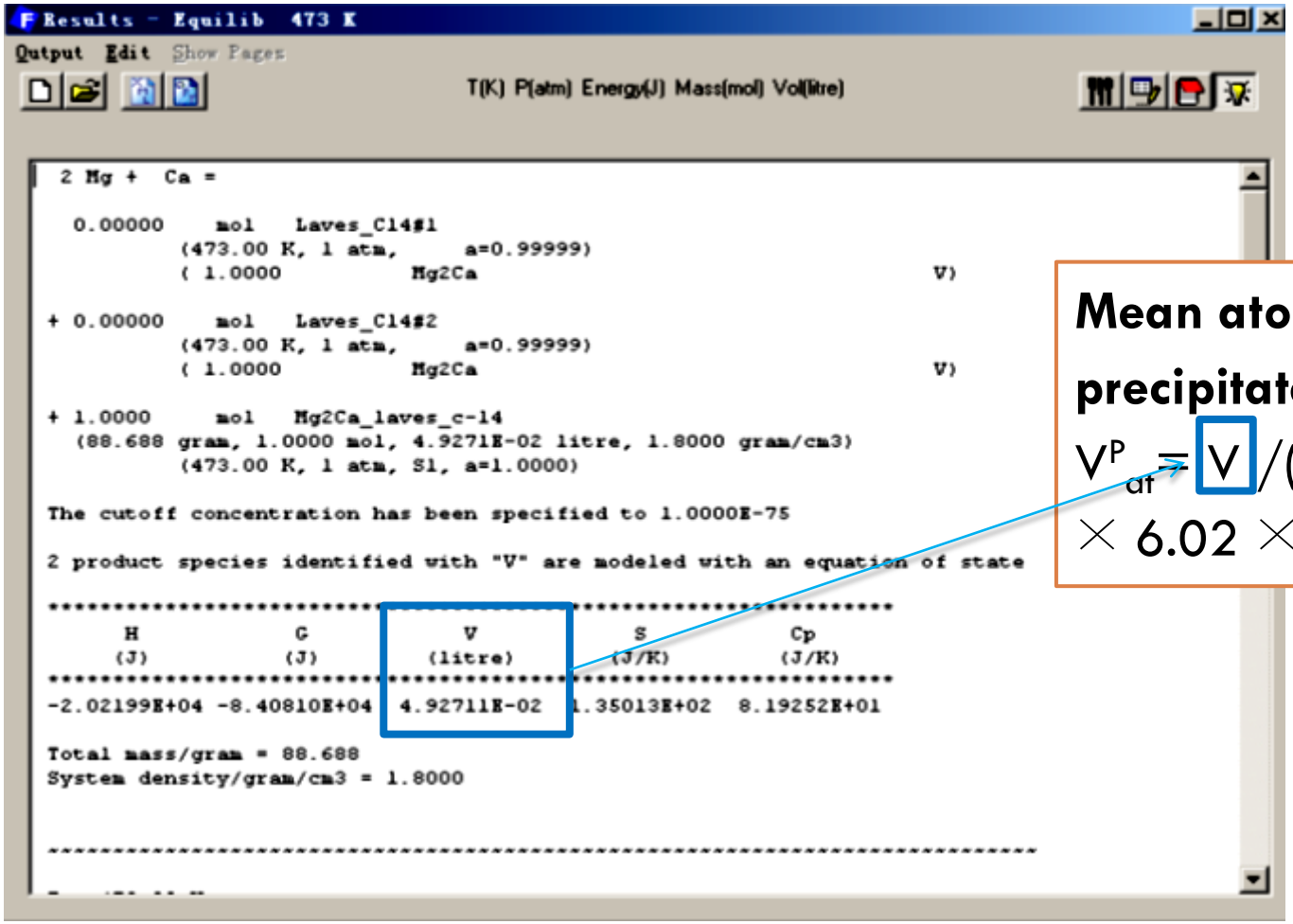
- Mean atomic volume of precipitates



Kinetics

—Calculation input parameters from FactSage

- Mean atomic volume of precipitates



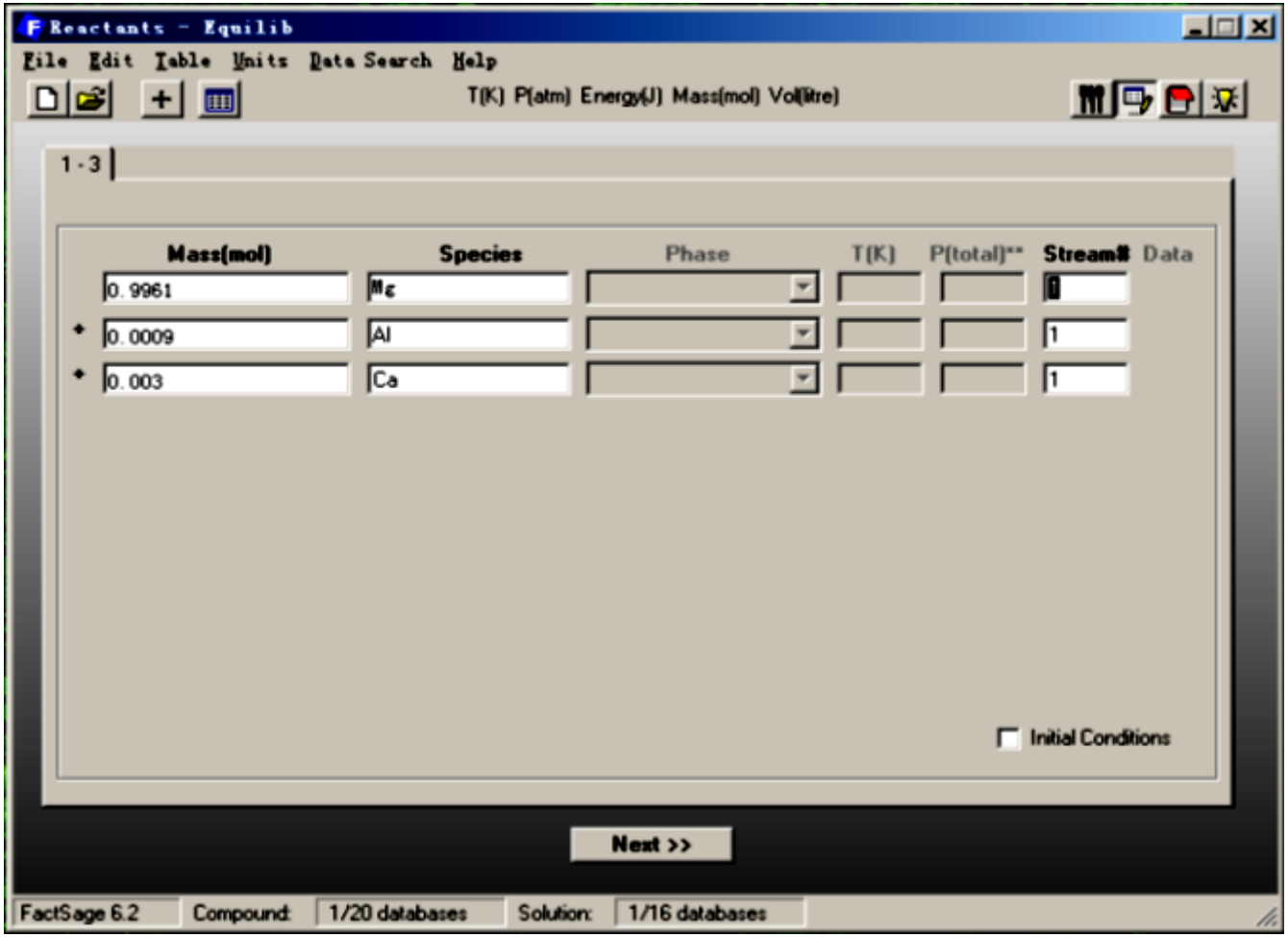
Mean atomic volume of precipitates(AxBy):

$V^{P}_{at} = V/((x+y) \times 1000 \times 6.02 \times 10^{-23})$

Kinetics

—Calculation input parameters from FactSage

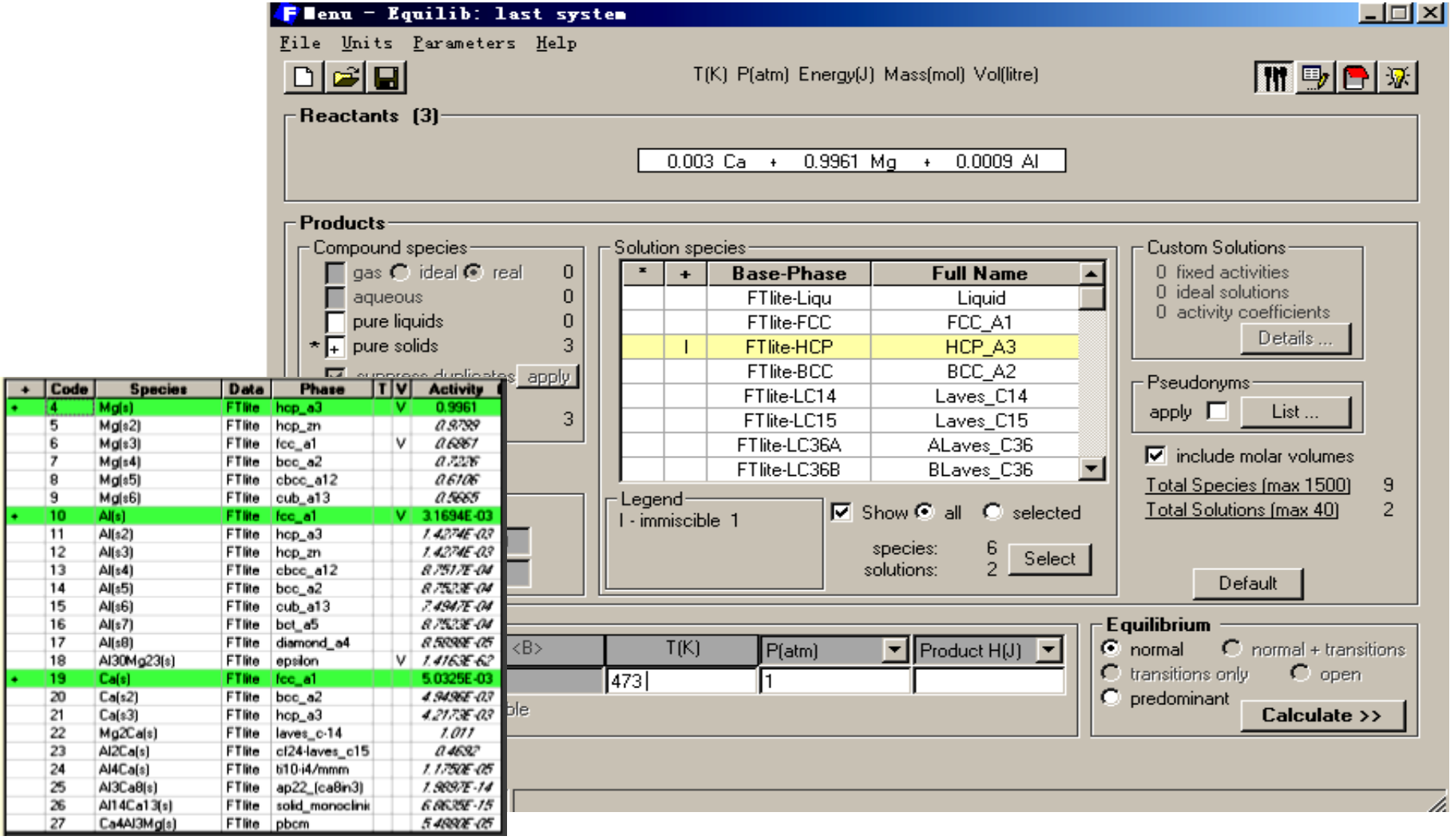
- Mean atomic volume of matrix



Kinetics

—Calculation input parameters from FactSage

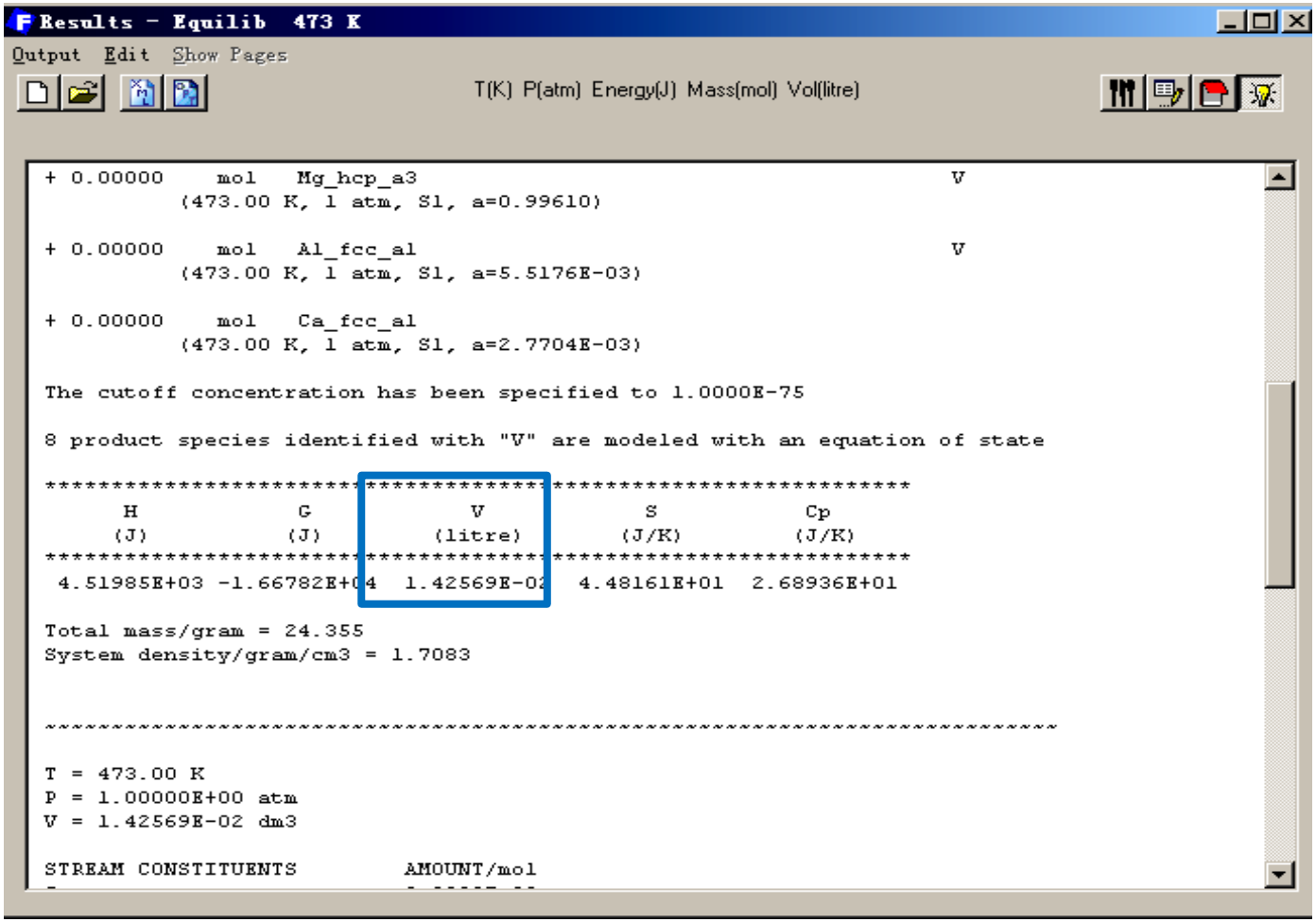
- Mean atomic volume of matrix



Kinetics

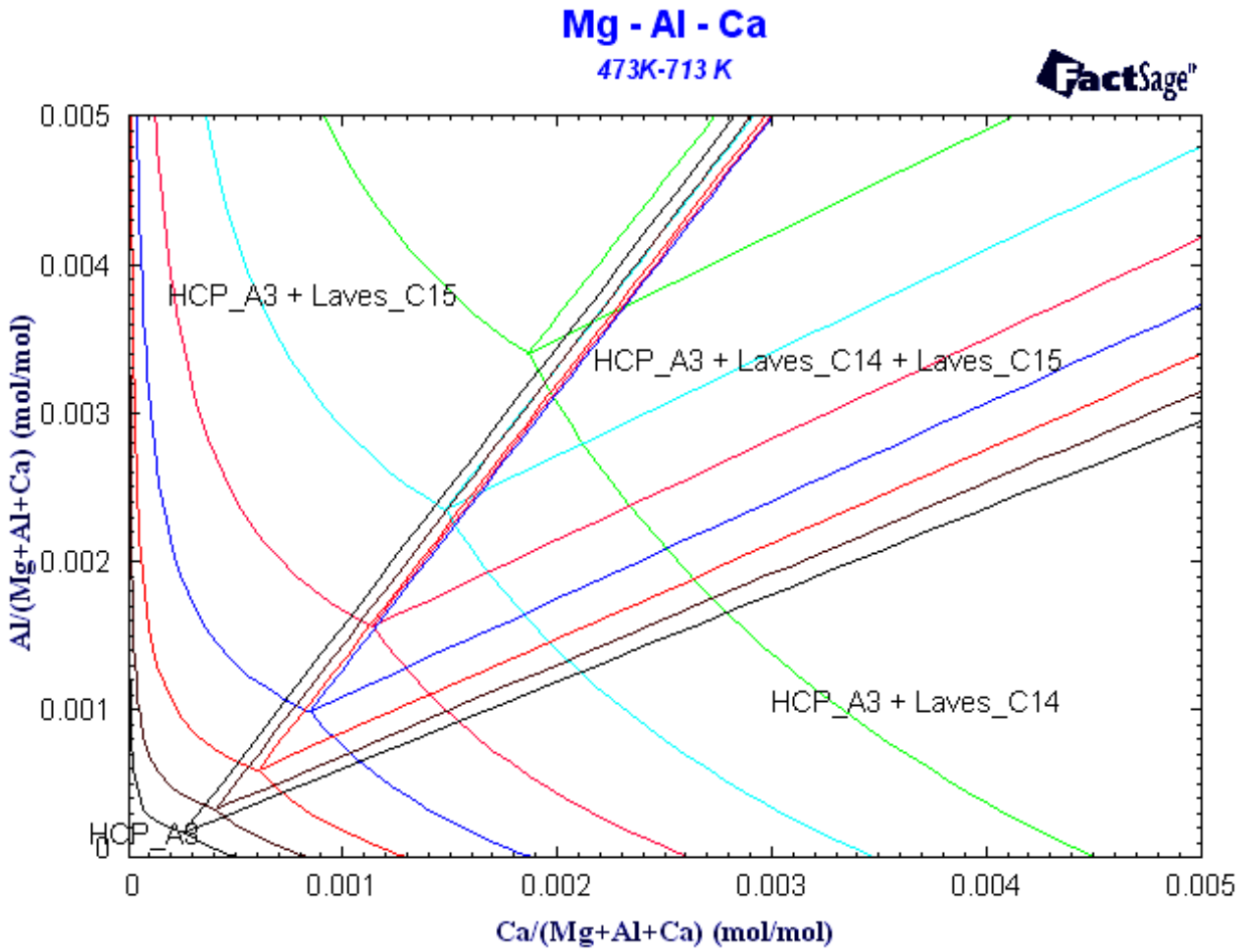
—Calculation input parameters from FactSage

- Mean atomic volume of matrix



Kinetics
—Calculation input parameters from FactSage

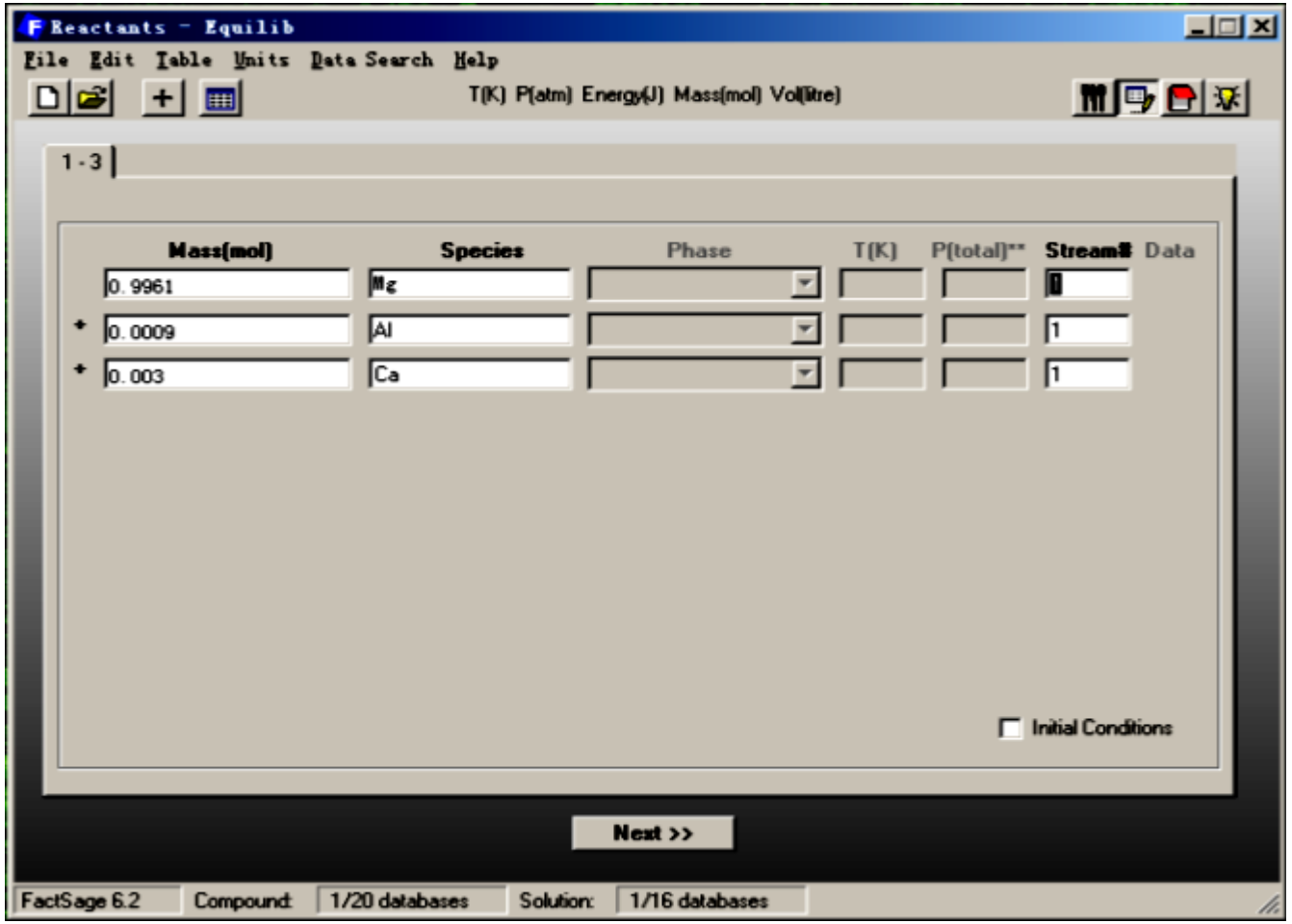
- Equilibrium concentration at the matrix/precipitates interface



Kinetics

—Calculation input parameters from FactSage

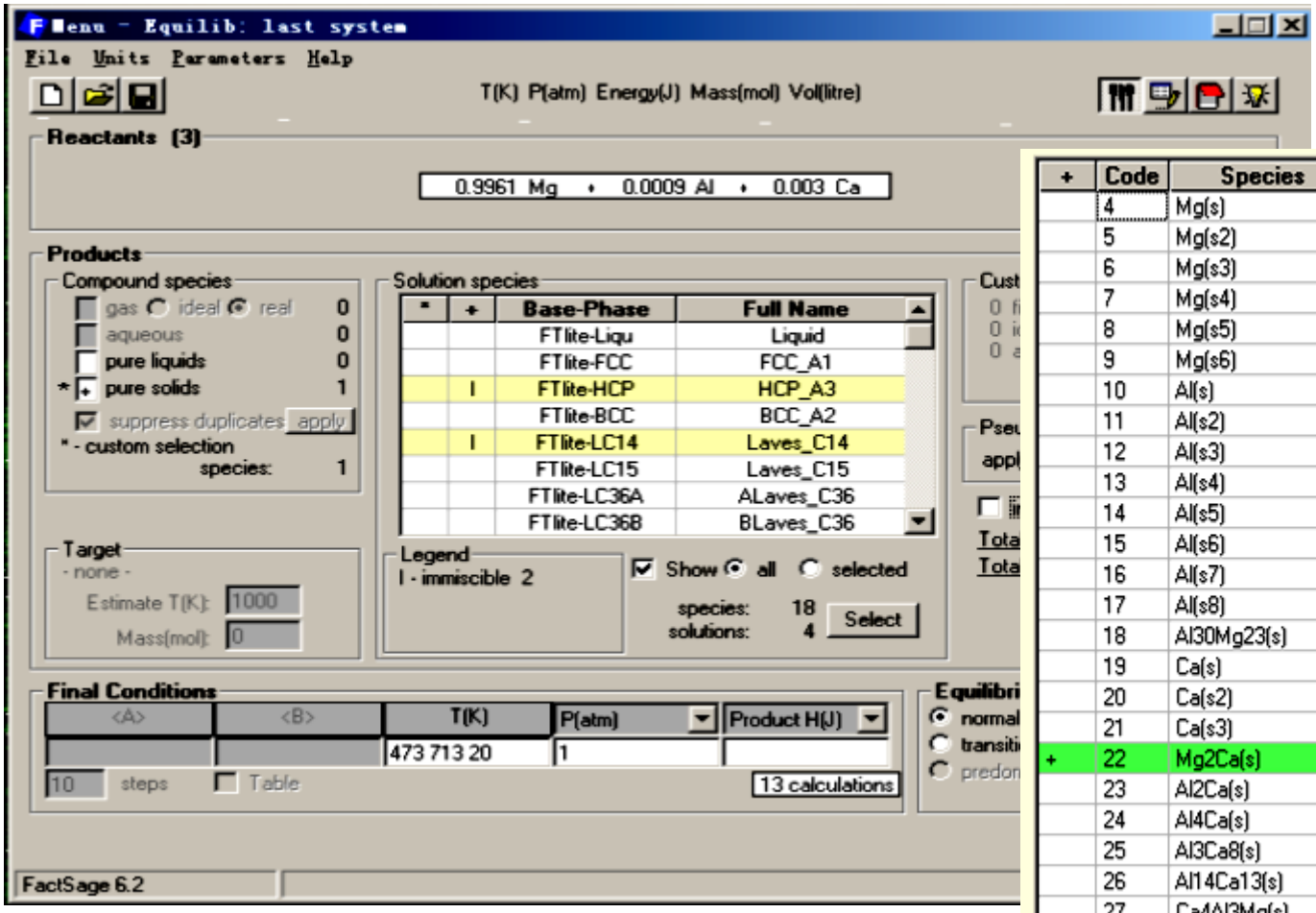
- Equilibrium concentration at the matrix/precipitates interface



Kinetics

—Calculation input parameters from FactSage

- Equilibrium concentration at the matrix/precipitates interface

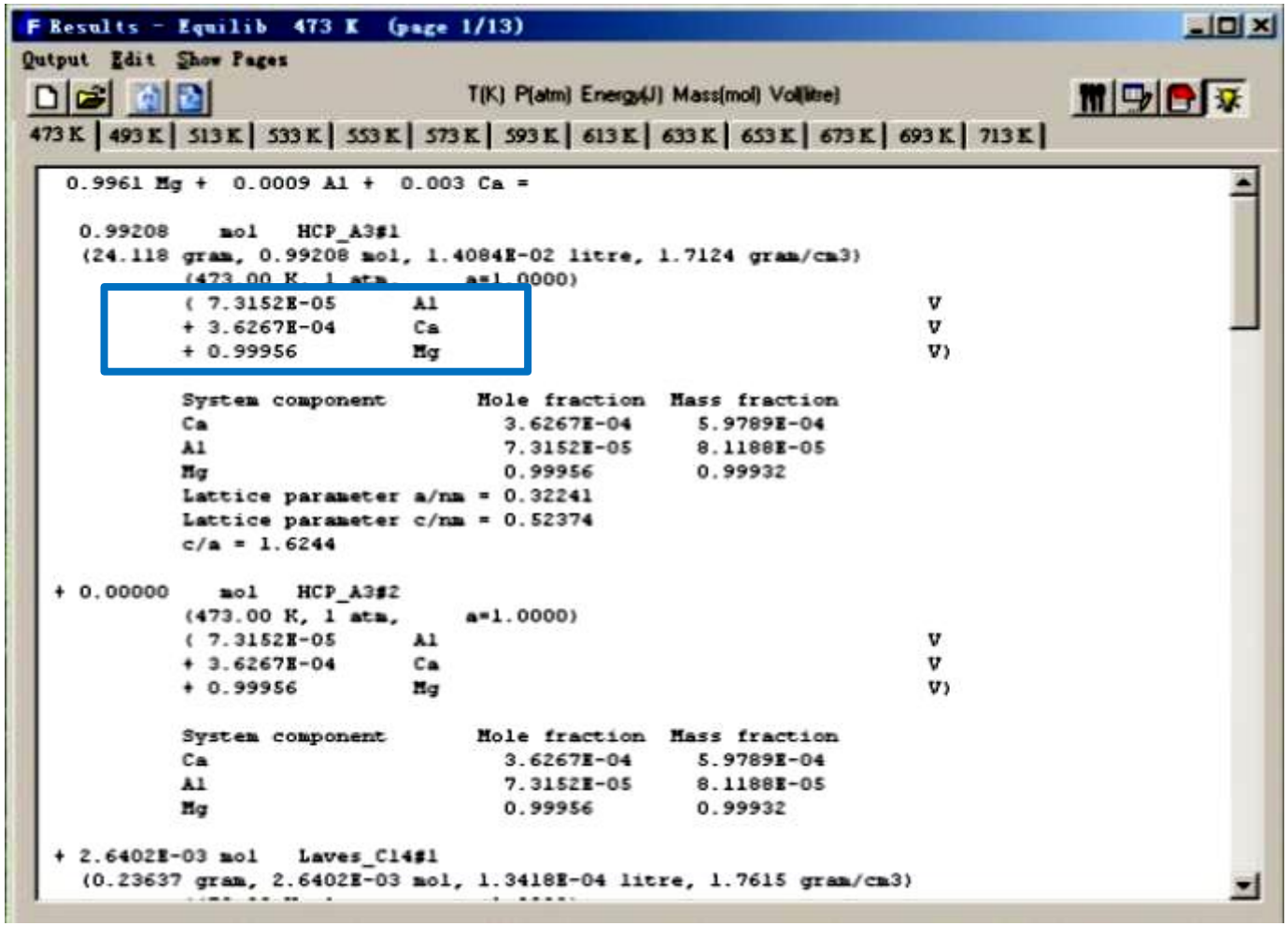


+	Code	Species	Data	Phase	T	V	Activity
	4	Mg(s)	FTlite	hcp_a3		V	0.9996
	5	Mg(s2)	FTlite	hcp_zn			0.9760
	6	Mg(s3)	FTlite	fcc_a1		V	0.5750
	7	Mg(s4)	FTlite	bcc_a2			0.5850
	8	Mg(s5)	FTlite	cbcc_a12			0.4455
	9	Mg(s6)	FTlite	cub_a13			0.4021
	10	Al(s)	FTlite	fcc_a1		V	4.4935E-04
	11	Al(s2)	FTlite	hcp_a3			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	pbcm			1.3691E-07

Kinetics

—Calculation input parameters from FactSage

- Equilibrium concentration at the matrix/precipitates interface

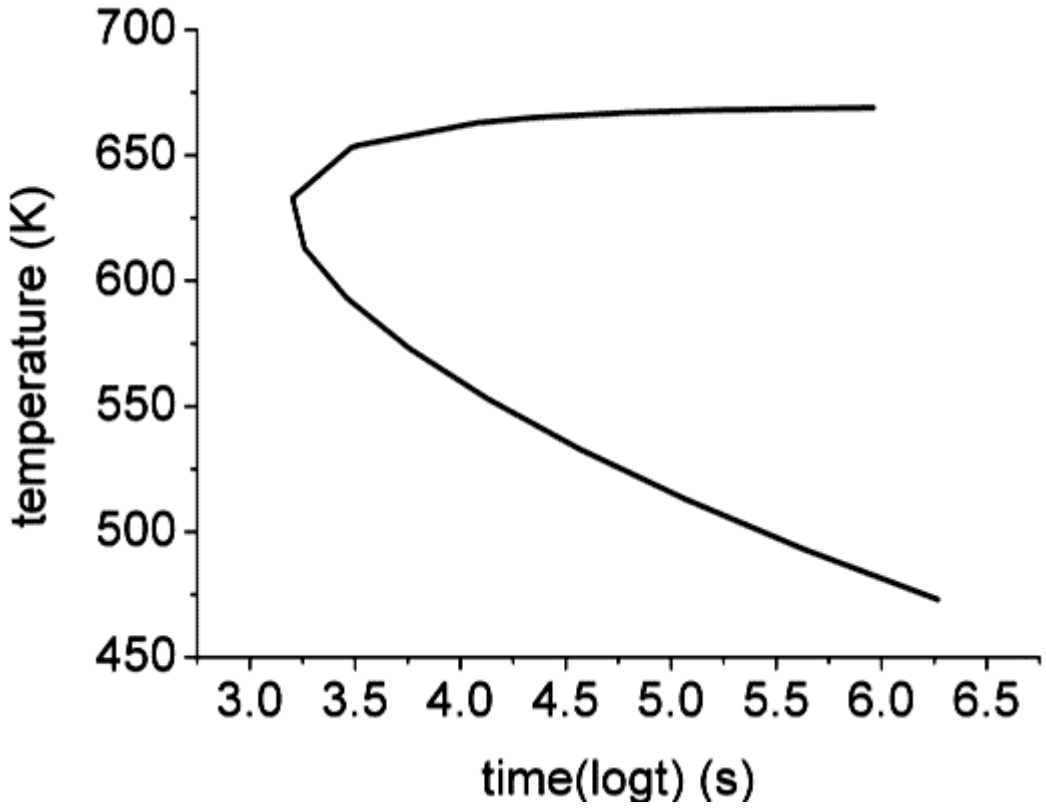


Kinetics

–Results (TTT diagram)

Alloy 1: Mg-0.0027Al-0.0012Ca---Al2Ca 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



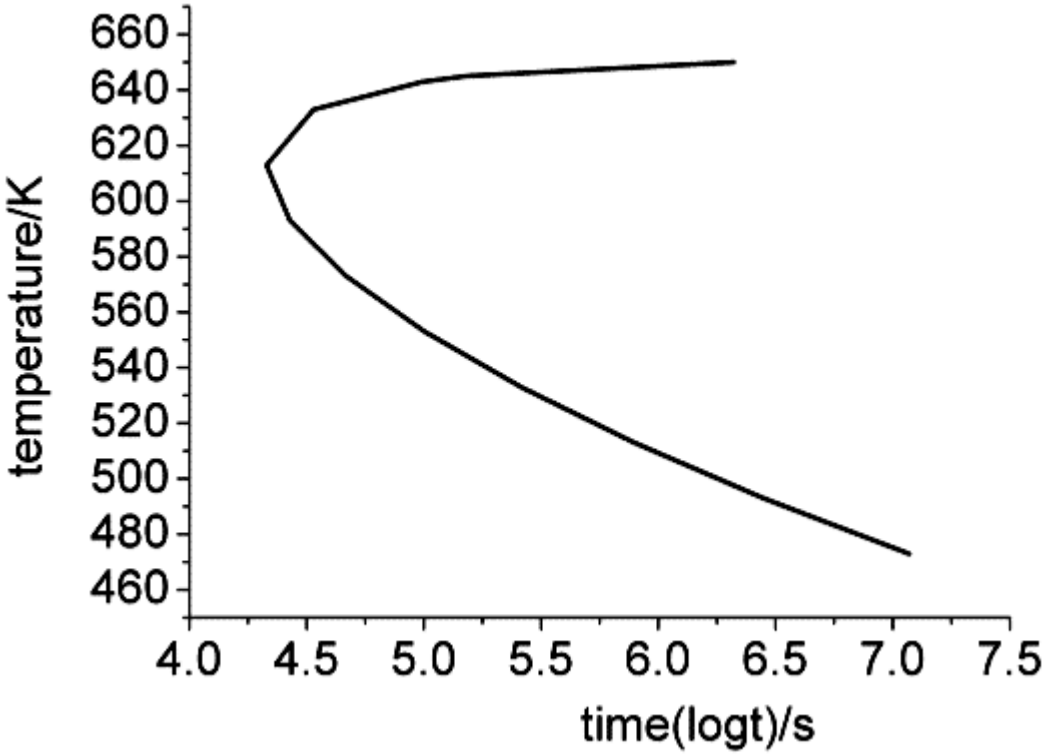
The incubation time of alloy 1 is 1590 seconds (26.5minutes) at 633K (360oC).

Kinetics

–Results (TTT diagram)

Alloy 2: Mg-0.0009Al-0.003Ca---Mg2Ca 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 26.5minutes at 633K (360oC). However, the incubation time of alloy 2 is 5.9 hours at 613K (340oC).
- Effects on the incubation time

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

  - Incubation time has an inverse relationship with Z factor and β*.
- Effect of diffusivity and interfacial energy on β* and Z factor

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

  - $\beta^* \propto DX\gamma^2/\Delta g^2$ and $Z \propto -\Delta g/\gamma^{3/2}$ ⇒ $\beta^* Z^2 \propto DX/\gamma^{1/2}$
  - Increasing of γ decreases Z, while increasing of γ increases β*. Increasing of D increases β*.
- 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 50mJ/m^2 to 10mJ/m^2, the Z factor will increase almost10^1 and β* 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 Zeldvich 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 Mg2Ca is either 50mJ/m2 or 10mJ/m2, the Z factor will be from 10^{-2} to10^{-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 a-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) .

Reference

[1]C.R. HUTCHINSON, J.F. NIE, and S. GORSSE. "Modeling the Precipitation Processes and Strengthening Mechanisms in a Mg-Al-(Zn) Az91 Alloy." *METALLURGICAL AND MATERIALS TRANSACTIONS A* 36A (2005): 2093-105. Print.
[2]Robert W.Balluffi, Samuel M.Allen, W. Craig Carter. *Kinetics of Materials*. Massachusetts: A John wiley&sons.inc, 2005. Print.
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[4]Vehkamäki, Hanna. "Classical Nucleation Theory in Multicomponent Systems." Department of Physical Sciences University of Helsinki, 2006. 96. Print.
[5]Věra Rothová, Jiří Čermák. "Interdiffusion in Mg / Mg17al12 System." *Hradec nad Moravicí* 23.-25.5 (2006): 1-8. Print.
[6]Wuu-Liang Huang, Teh-Ching Liu, Pouyan Shen, Allen Hsu. "Ca-Mg Inter-Diffusion in Synthetic Polycrystalline Dolomite-Calcite Aggregate at Elevated Temperatures and Pressure." *Miner Petrol* 95 (2009): 327-40. Print.
[7]Xiaoyu Zhang, Jibamitra Ganguly, Motoo Ito. "Ca–Mg Diffusion in Diopside: Tracer and Chemical Inter-Diffusion Coefficients." *Contrib Mineral Petrol* 159 (2010): 175-86. Print.
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Thank You !

Questions & Comments