Interdiffusion and Phase Growth Kinetics in the Magnesium-Aluminum Binary System

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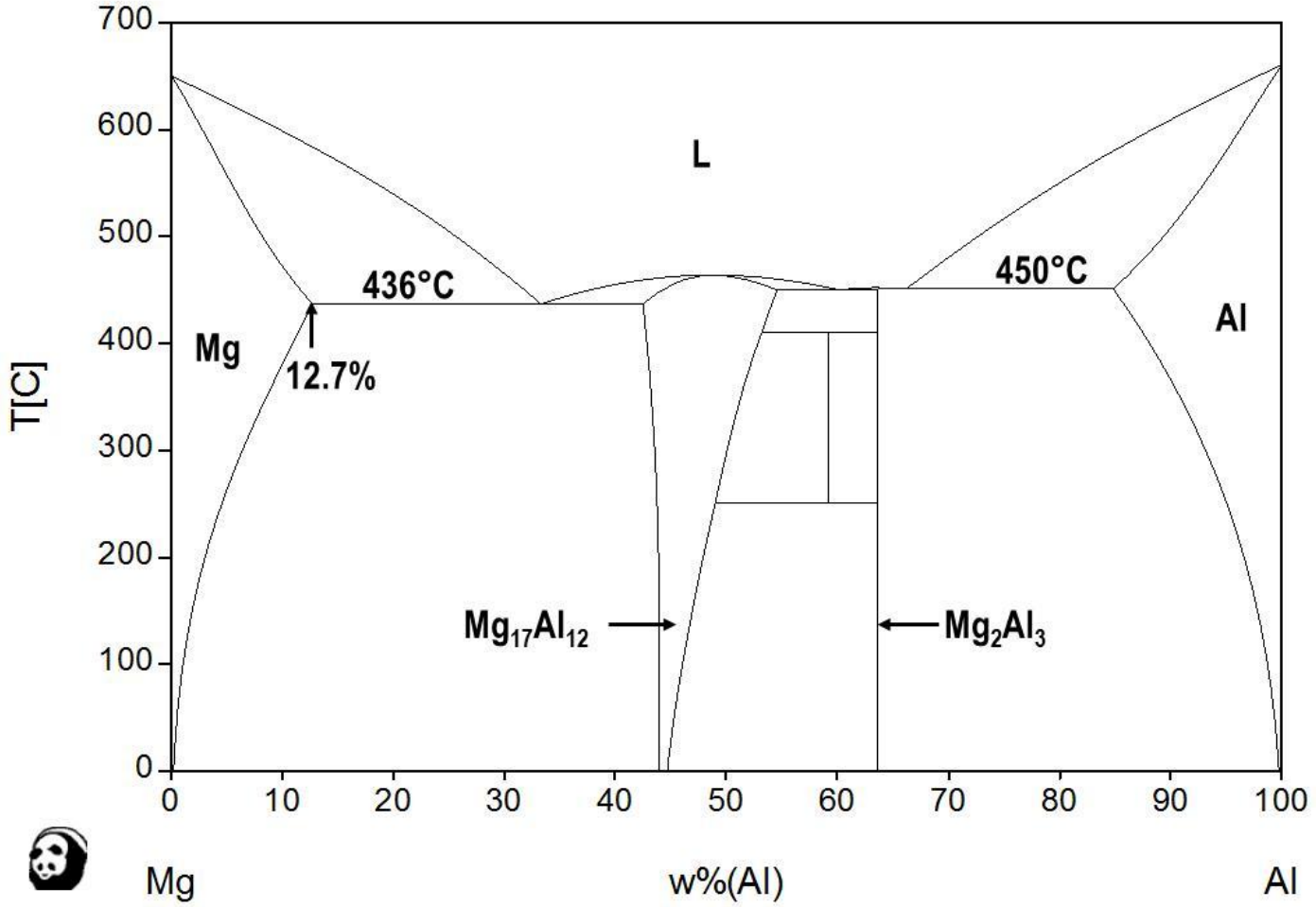
Kaustubh N. Kulkarni and Alan A. Luo; J. Phase Equilib. Diff.; 34; 2013; p. 104

Outline

- Use of CALPHAD in Mg alloy development
- Why interdiffusion data needed in Mg-Al alloys
- Experimental methodology
- Analysis of interdiffusion coefficients as functions of composition
- Analysis of impurity diffusion coefficients
- Growth kinetics of $Mg_{17}Al_{12}$ (γ) and Al_3Mg_2 (β) phases
- Conclusions

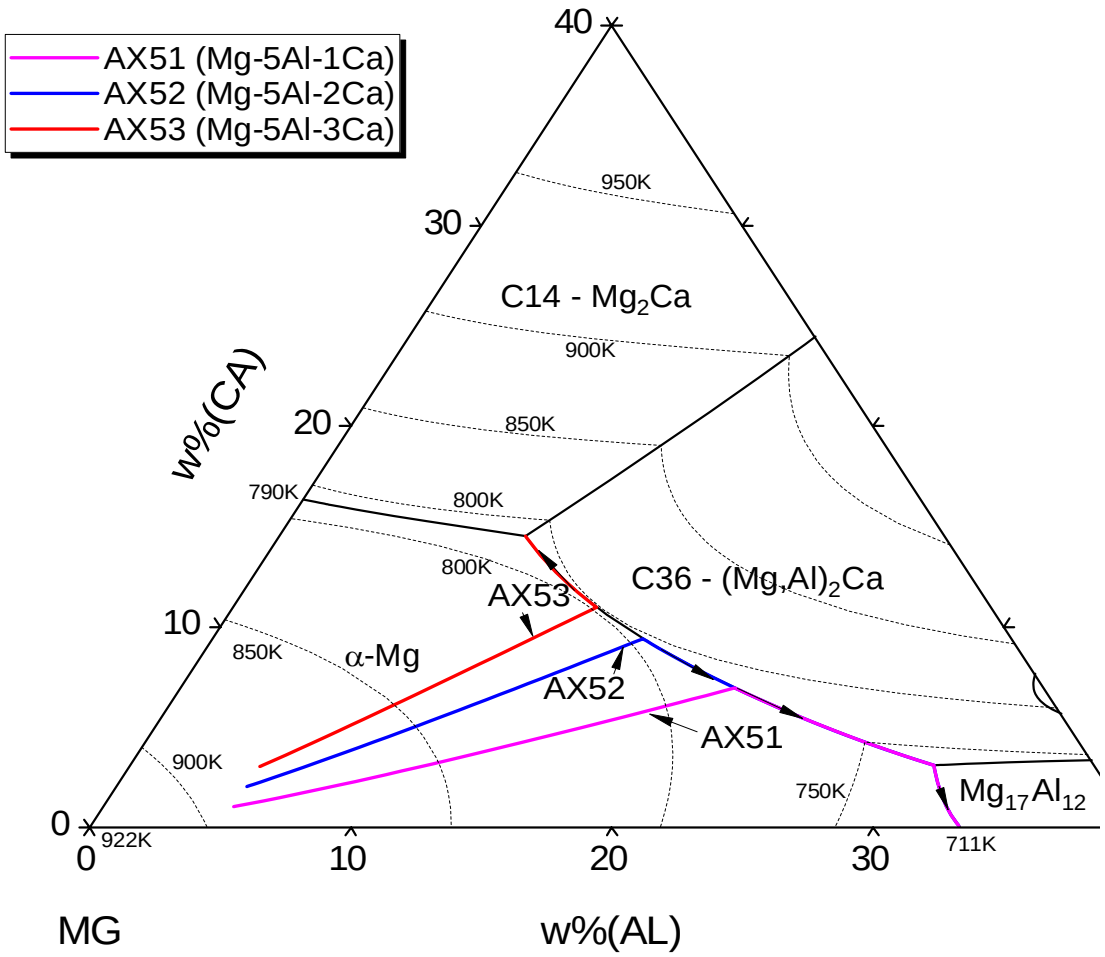
Mg-Al Binary System

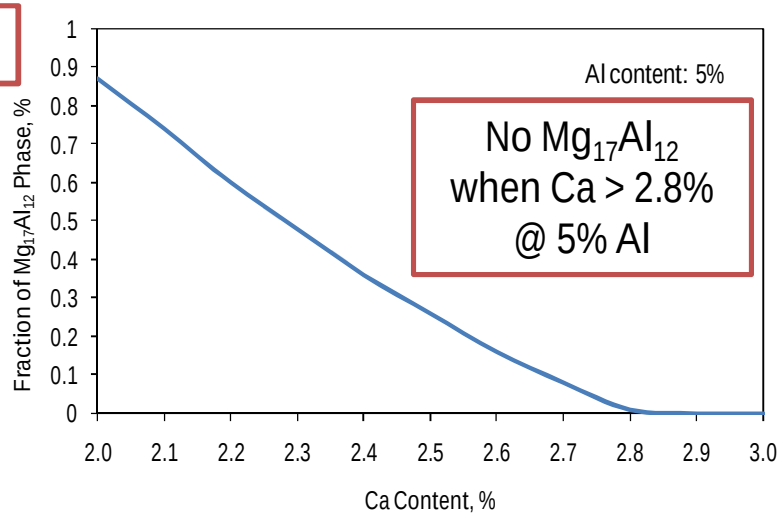
- $Mg_{17}Al_{12}$ (γ phase) - low eutectic temperature 436°C
- Limited strengthening - no metastable phases and large precipitates

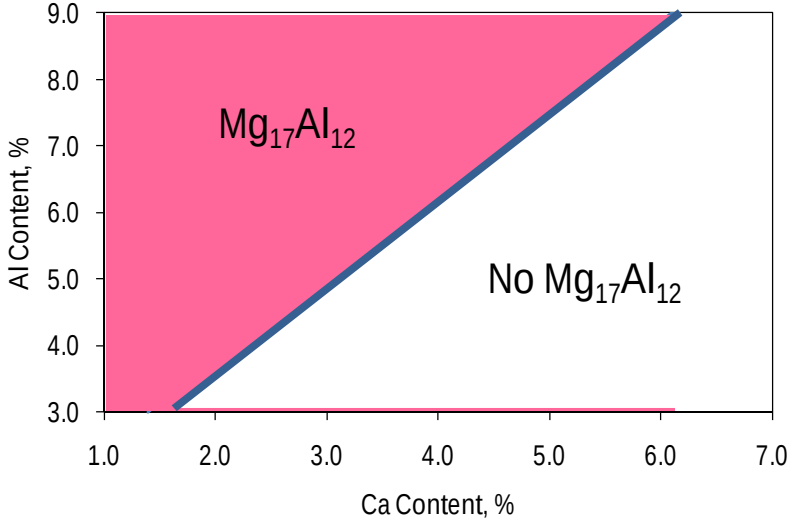


Mg-Al-Ca System: Creep-Resistant Alloys

Calculated liquidus projection & alloy solidification paths







A.A. Luo, B.R. Powell, A.K. Sachdev, Intermetallics, 2012, 24, 22-29

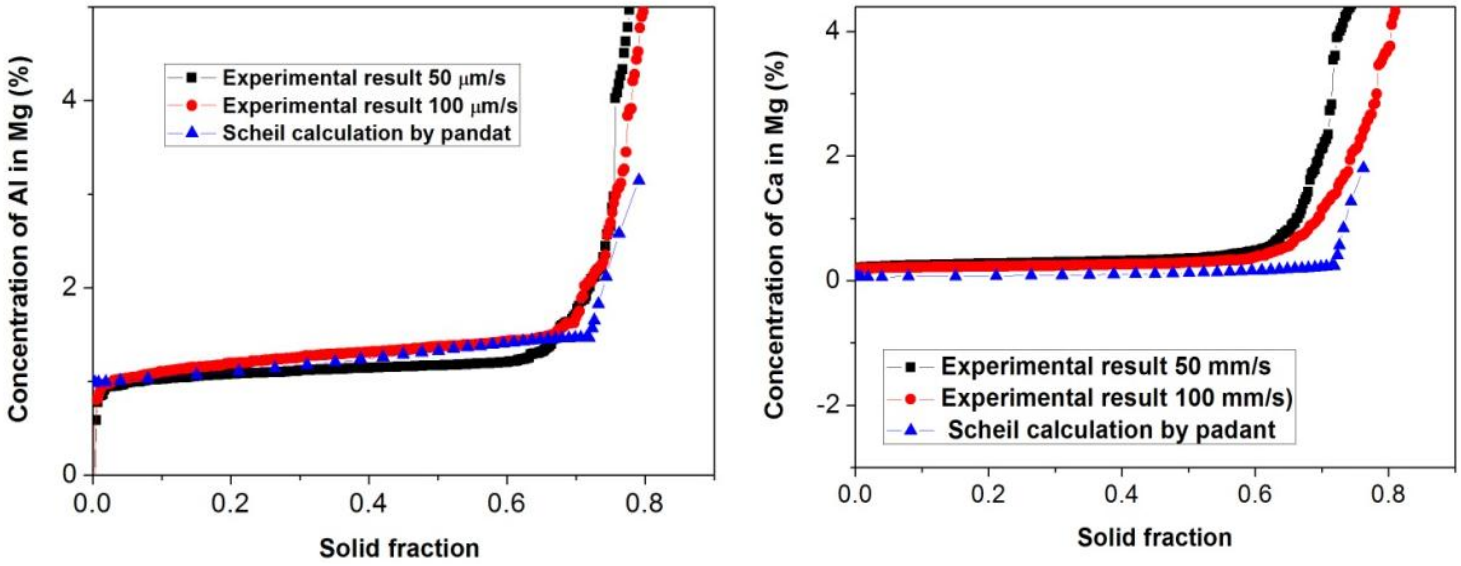
Solidification Microstructure:

Scheil Simulation vs. Experimental Results

❑ Gap: back diffusion of alloying elements is related to solidification rates

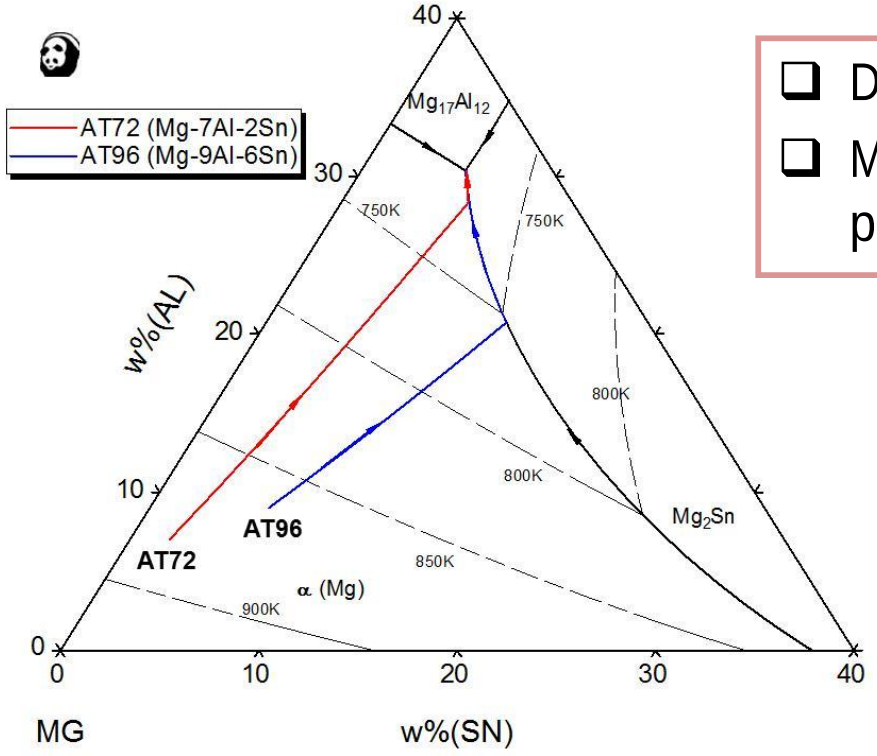
Alloy	Scheil Simulation, vol.%				Measurement, vol.%
	$(Mg,Al)_2Ca$	Mg_2Ca	$Mg_{17}Al_{12}$	Total Fraction	Total Fraction
AM50	-	-	4.3	4.3	4.8
AX51	2.0	0	2.7	4.7	5.5
AX52	4.1	0	0.9	5.0	5.8
AX53	5.8	0.1	0	5.9	6.2

A.A. Luo, B.R. Powell, A.K. Sachdev, Intermetallics, 2012, 24, 22-29

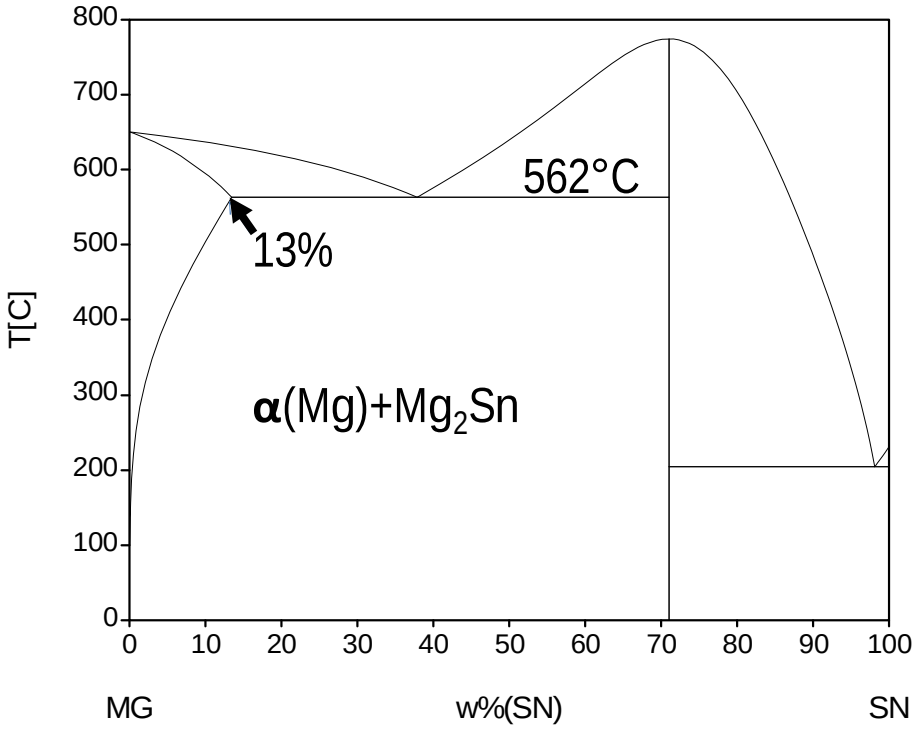


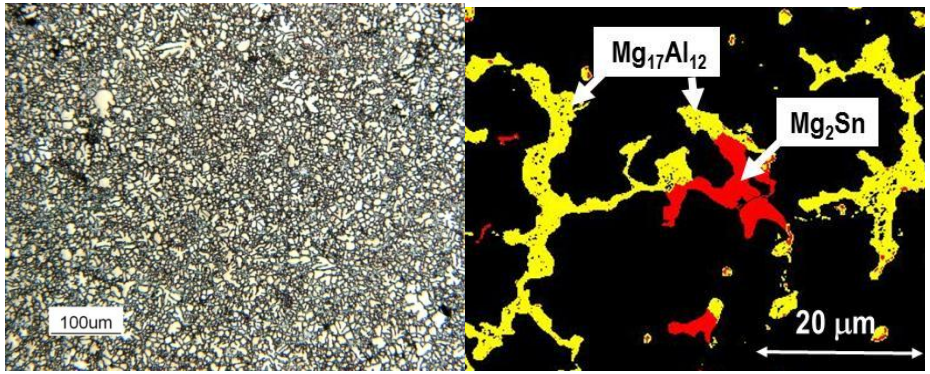
X. Zheng, A.A. Luo, C. Zhang, J. Dong, R.A. Waldo, Metallurgical and Materials Transactions A, 2012, 43A, 3239-3248.

Mg-Al-Sn System: Precipitation Hardening



- Dual phase strengthening: $Mg_{17}Al_{12}$ and Mg_2Sn
- Mg_2Sn: decreasing solubility with T -potential precipitation hardening





A.A. Luo, P. Fu, X. Zeng, L. Peng, B. Hu, A.K. Sachdev, in Magnesium Technology 2013, TMS, 341-345.

Modeling Precipitation Kinetics

Importance of diffusion coefficients

Nucleation

$$J = N_v Z \beta^* \exp\left[\frac{-4\pi\gamma R^{*2}}{3kT}\right] \exp\left[-\frac{t}{\tau}\right]$$

$$\beta^* = \frac{16\pi\gamma^2 cD}{\Delta G_V^{\,2} a^4} \qquad \tau = \frac{V_\alpha^{\,2} \Delta G_V^{\,2} Dc}{8kT\gamma a^4}$$

Growth

$$\frac{dR}{dt} = \frac{D}{R}\frac{c_i - c_r^\alpha}{c^\beta - c_r^\alpha}$$

Coarsening

$$\overline{R}^3 - \overline{R}_0^{\,3} = \frac{8V_m D\gamma c_\infty^\alpha}{9R_g T(c^\beta - c_\infty^\alpha)}(t - t_1)$$

- Precipitation kinetics depends strongly on the diffusivities of alloying elements in the matrix
- Lack of experimental data on diffusivities as functions of compositions in Al and Mg alloys

Ref: J. D. Robson, "Modeling the evolution of particle size distribution during nucleation, growth and coarsening"; Materials Science and Technology; Vo. 20; pp 441-448

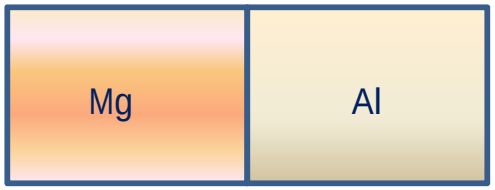
Interdiffusion in Multicomponent Systems

Interdiffusion flux of component i

$$\tilde{J}_i = -\sum_{j=1}^{n-1} \tilde{D}_{ij}^{n} \frac{\partial C_j}{\partial x} \quad (i = 1,2,...,n-1)$$

- n-component system = $(n-1)^2$ interdiffusion coefficients
- More complications: Dependence on composition
- Experimental data on interdiffusion, tracer diffusion and self diffusion coefficients used to evaluate Atomic Mobilities, which are more fundamentally related to individual elements

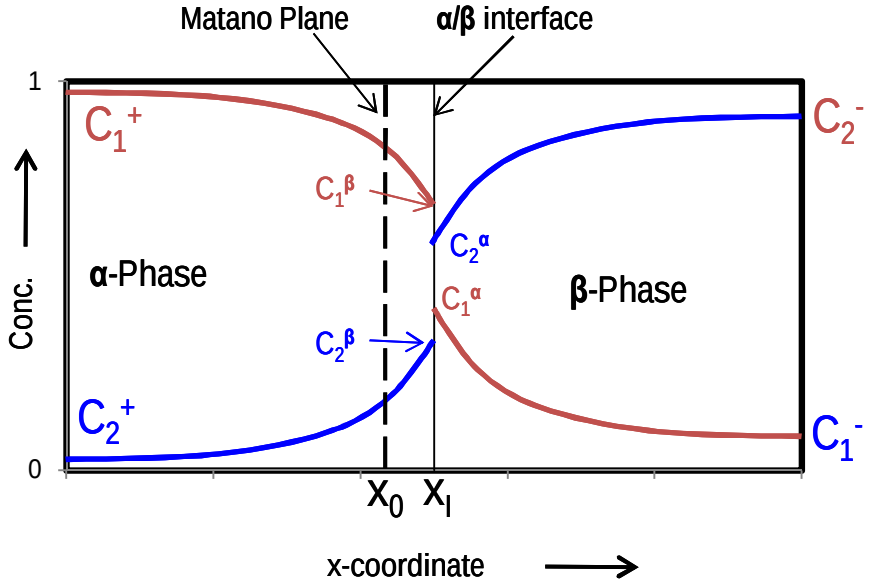
Experimental Work



Pure Mg and Al discs polished to 0.05μm finish; placed in contact with each other and clamped in a stainless steel jig

Diffusion annealing carried out in tube furnace with couple sealed in evacuated quartz capsule

Representative Photo



Typical concentration profiles for binary multiphase diffusion couple

- ❑ SEM and Optical for Diffusion Structures
- ❑ EPMA point-by-point for concentration profiles
  - ❑ Al-intensity measured
  - ❑ Balance Mg

Experimental Work

TIME (Hours)	Temperature (°C)		
	380	400	420
	24	24	24
	50	50	50
	91	94	94

- Diffusion annealing done at three different temperatures each for three different times
- All couples used for studying phase growth kinetics
- Three couples (indicated by Squares) selected for EPMA analysis

Determination of Binary Interdiffusion Coefficients

Fick's Law:

$$\tilde{J}_i = -\tilde{D}\frac{\partial C_i}{\partial x}$$

$\tilde{J}_i$ = Interdiffusion Flux

$\tilde{D}$ = Interdiffusion Coefficient

$\frac{\partial C_i}{\partial x}$ = Concentration gradient

- $\tilde{D}$ is a function of composition
- Need to determine interdiffusion fluxes and concentration gradients from experimental profiles

Determination of Interdiffusion Fluxes [1]

$$\tilde{J}_i\left(x^*\right) = \frac{C_i^- - C_i^+}{2t}\left[Y_i^* \int_{-\infty}^{x_i^*} \frac{\left(1-Y_i\right)}{V_m} dx + \left(1-Y_i^*\right) \int_{x_i^*}^{\infty} \frac{Y_i}{V_m} dx \right]$$

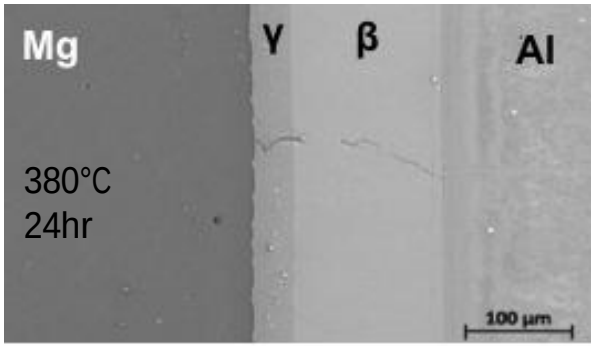
$$Y_i = \frac{C_i - C_i^+}{C_i^- - C_i^+}$$

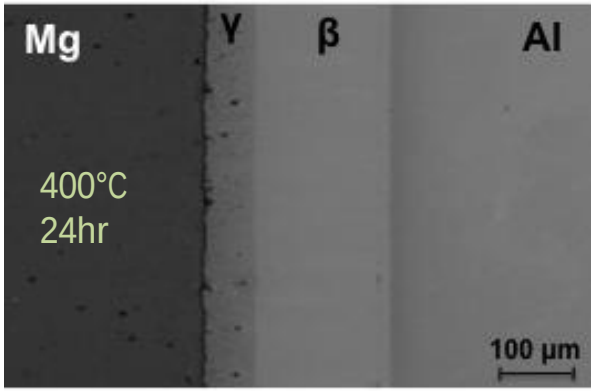
V_m = Molar Volume (Assumed constant for this work)

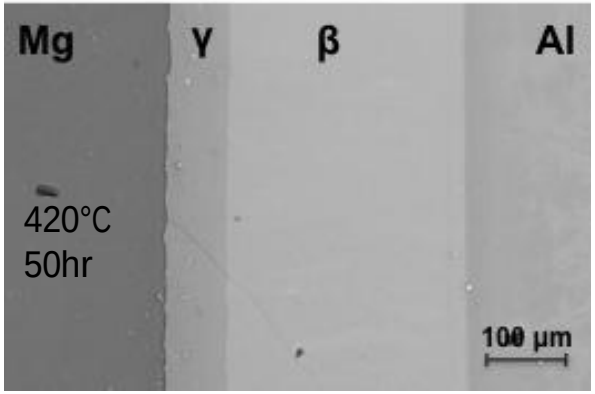
- Fluxes determined directly from concentration profiles
- Avoids errors related to positioning of Matano plane
- *Multi*Diflux program:
  - Fitting of concentration profiles
  - Determination of gradients and fluxes

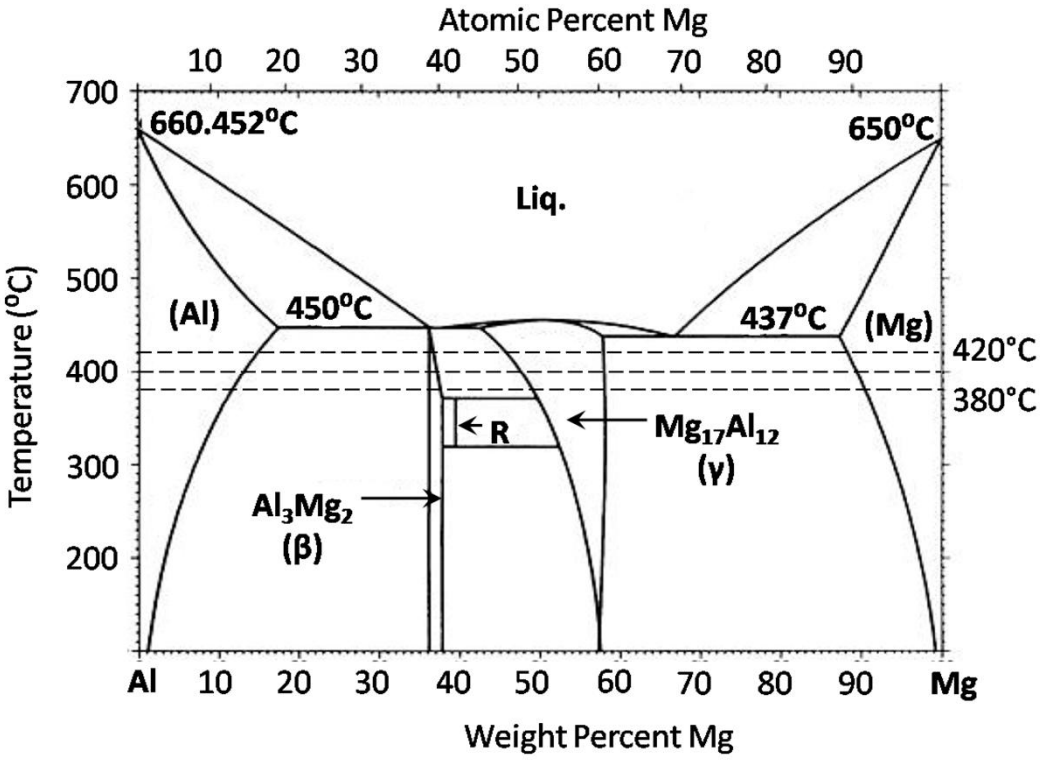
1. M. A. Dayananda, *Metall. Trans. A*, 1983, 14A (9), pp. 1851-1858

Diffusion Structures Developed in Mg/Al Couples[1]







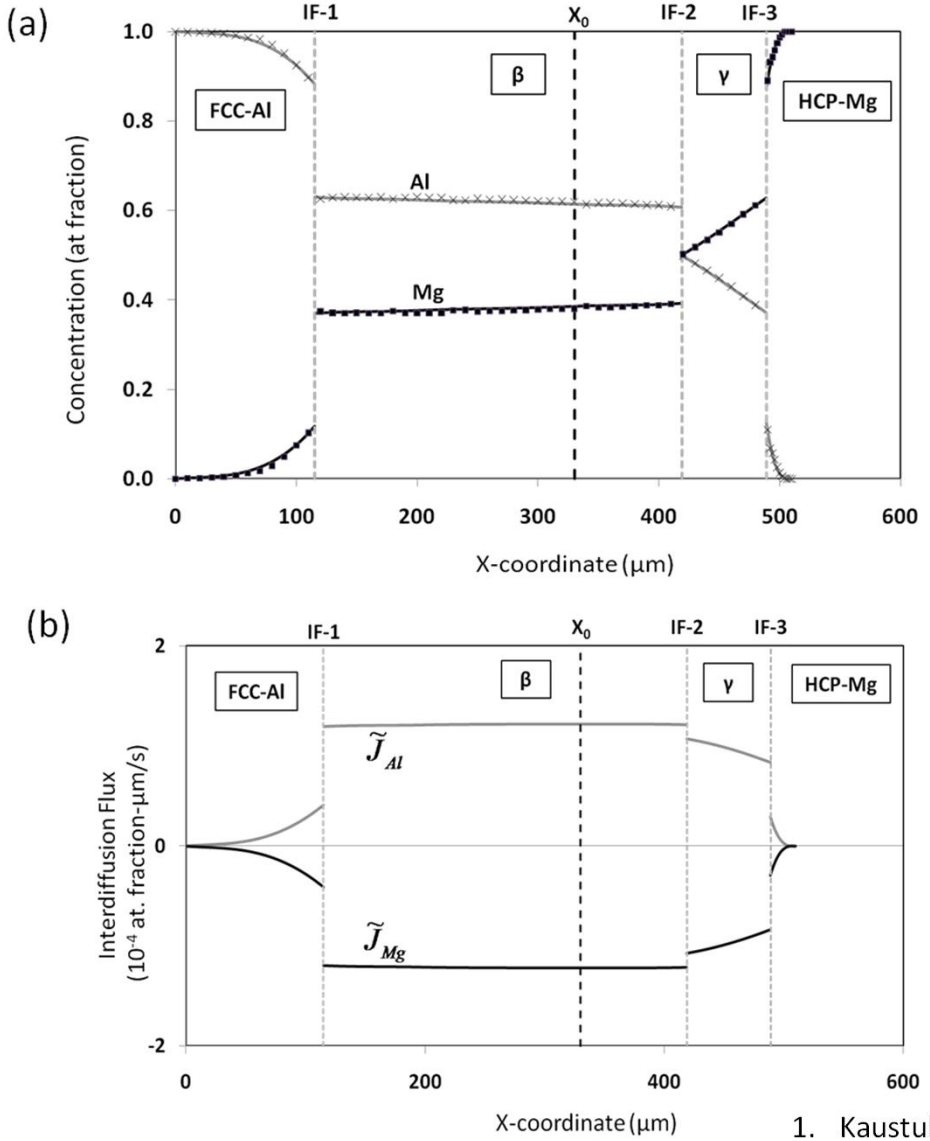


- ❑ Two intermediate phases developed in accordance with Phase Diagram by Muray [2]
- ❑ Planar Interfaces Developed

1. Kaustubh N. Kulkarni and Alan A. Luo; J. Phase Equilib. Diff.; 34; 2013; p. 104
2. T. B. Massalski ed.; Binary Alloy Phase Diagram; ASM International

Concentration and Flux Profiles [1]

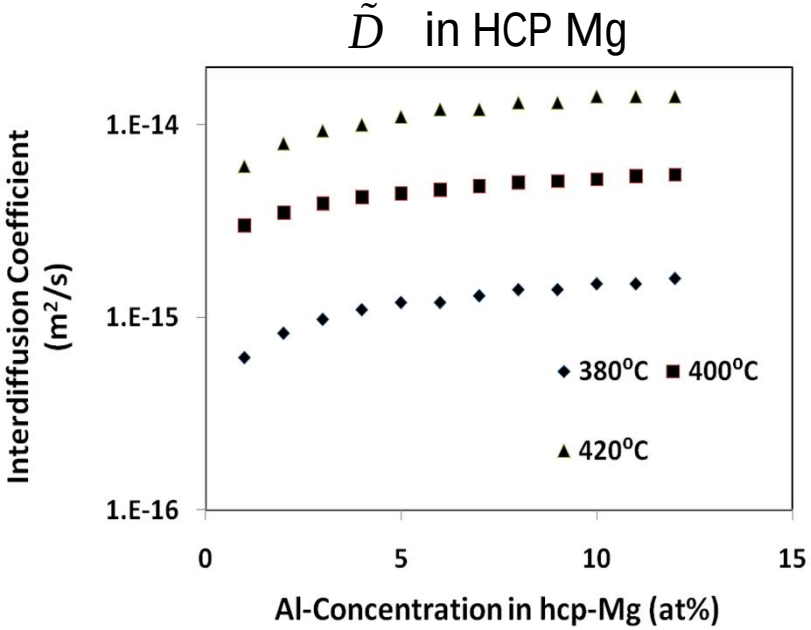
380°C 24 hr

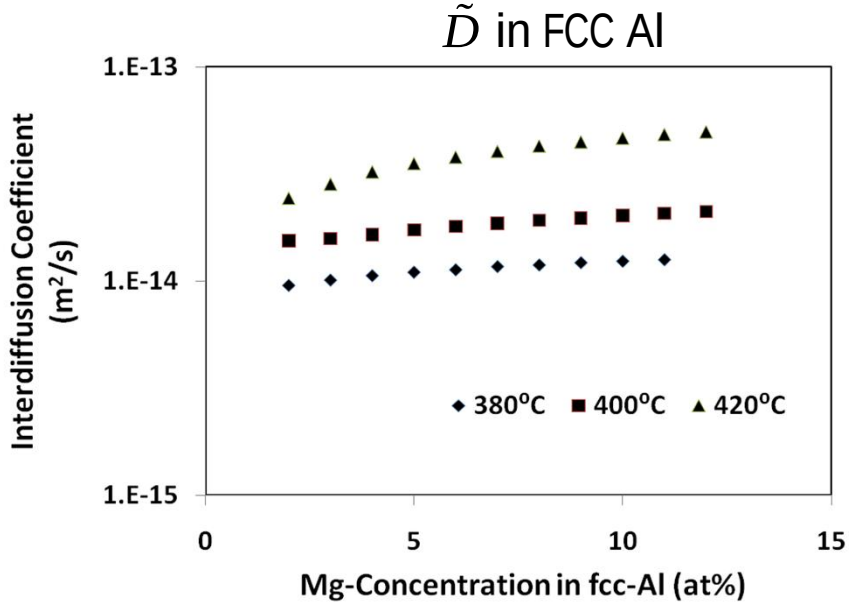


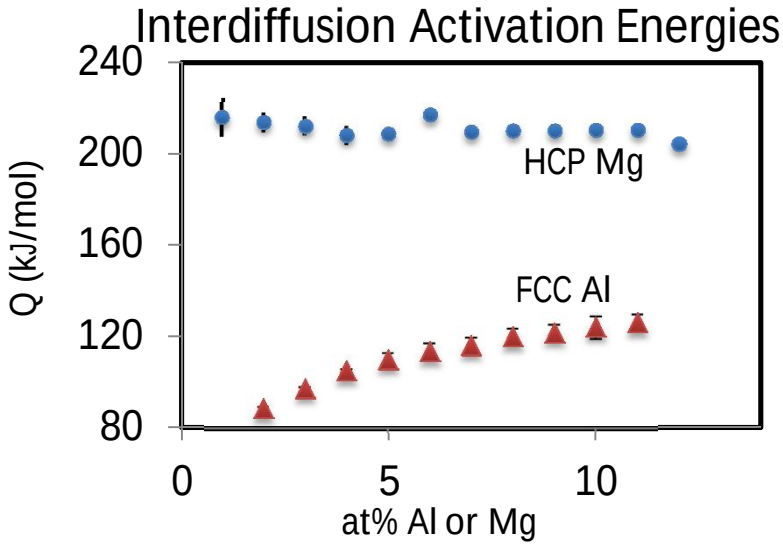
- *Multi*Diflux[2] program used for interdiffusion analysis
- Concentration profiles fitted with cubic hermite polynomials in each phase
- Concentration profiles in **β** phase assumed linear due to small gradient
- Interdiffusion fluxes evaluated directly from fitted concentration profiles
- Interdiffusion coefficients were then evaluated as functions of composition

1. Kaustubh N. Kulkarni and Alan A. Luo; J. Phase Equilib. Diff.; 34; 2013; p. 104
2. M. A. Dayananda and L. R. Ram-Mohan; *Multi*Diflux; Purdue University

Interdiffusion Coefficients in Al and Mg [1]



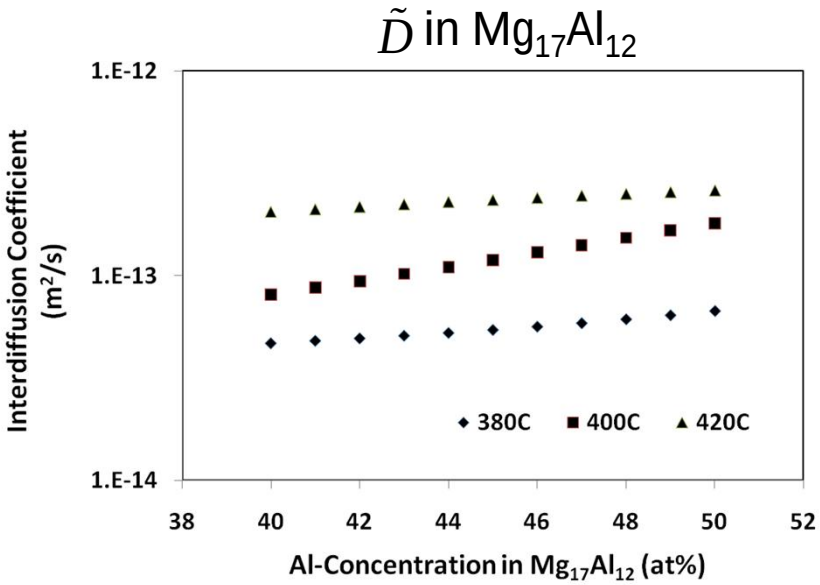


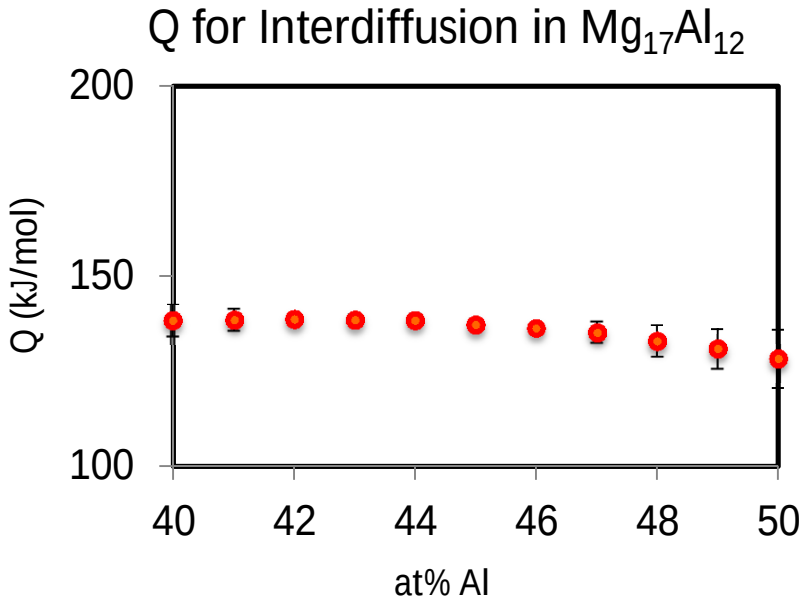


- The activation energy for interdiffusion in Mg does not change much with composition but that in Al increases with increasing Mg
- Atomic radius of Mg (0.16nm) is 12% larger than that of Al (0.143nm)
  - Al matrix maybe strained with increasing Mg-content increasing the activation energy for migration

1. Kaustubh N. Kulkarni and Alan A. Luo; J. Phase Equilib. Diff.; 34; 2013; p. 104

Interdiffusion Coefficients in Intermetallics[1]





- Activation energy for interdiffusion in $Mg_{17}Al_{12}$ does not vary much with composition

- Average value of activation energy for interdiffusion in Al_3Mg_2 phase is 44±1.8 kJ/mol

1. Kaustubh N. Kulkarni and Alan A. Luo; J. Phase Equilib. Diff.; 34; 2013; p. 104

Interdiffusion Coefficients: Comparison with Literature

Interdiffusion coefficients in β and γ phases at 425ºC reported in various studies.				
Phase	Interdiffusion coefficient (m^2/s)			
	Reported by Heumann [1]	Reported by Funamizu by Heumann's method [2]	Reported by Funamizu by Kidson's method [2]	Estimated from present work at average composition of the phase
β	1.7×10^{-12}	1.4×10^{-12}	1.1×10^{-12}	3×10^{-12}
γ	2.1×10^{-13}	1.5×10^{-13}	1.2×10^{-13}	3×10^{-13}

$$\tilde{D}_i = -\frac{W_i}{2t \cdot \Delta C_i} \int_0^{C_i^{1/2}} x\, dc_i = \frac{-\tilde{J}_i}{\left(\Delta C_i / W_i\right)}$$

- This is the FIRST report on Interdiffusion Coefficients and Activation Energies as functions of compositions in Mg-Al Binary System
- The interdiffusion coefficients evaluated assuming constant values over given phase regions as reported in literature match closely with the ones evaluated at average composition in the present study

1. Th. Heumann and A. Kottmann; Z. Metallk.; Vol. 44; 1953; p. 139
2. Y. Funamizu and K. Watanabe; Trans. Jap. Inst. Met.; Vol. 13; 1972; p. 278

Impurity Diffusion Coefficients in Al
Hall's Method[1]

Variable *u* is assumed to be a linear function of Boltzmann Parameter $\lambda = x/\sqrt{t}$

$$u = h\lambda + \phi$$

u is evaluated from relative concentration variable *C'*

$$\frac{C_i - C_i^{-\infty}}{C_i^{+\infty} - C_i^{-\infty}} = C' = \frac{1}{2}(1 + erf(u))$$

Values of *h* and $\boldsymbol{\Phi}$ are evaluated from plot of *u* versus $\boldsymbol{\lambda}$; which are then used for evaluating interdiffusion coefficients

$$\tilde{D} = \frac{1}{4h^2} + \frac{\phi\sqrt{\pi}}{2h^2}\exp\left(u^2\right)C'$$

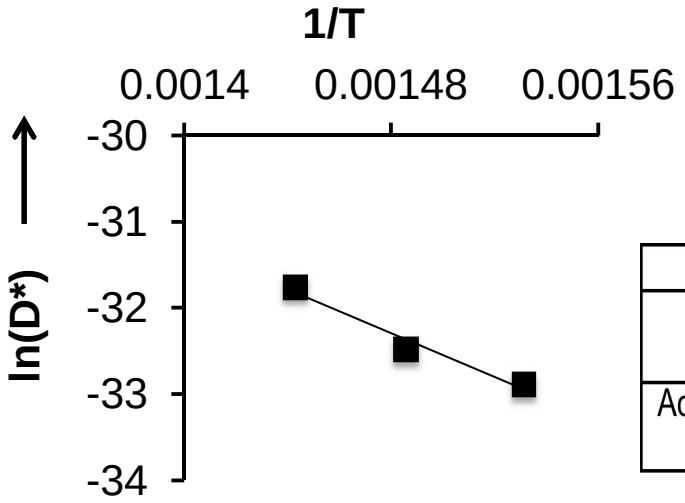
Impurity Diffusion Coefficient

$$D_i^* = \lim_{C_i \to 0} \tilde{D} = 1/4h^2$$

This method is suitable for estimating impurity diffusion coefficient in the terminal alloys where the concentration profile shows a long tail

1. L. D. Hall; J. Chem. Phys.; 1953; VO. 21 (1); p. 87

Impurity Diffusion Coefficients in Al



Activation energy and frequency factor for the impurity diffusion of Mg in FCC-Al			
Parameter	Reported by Rothman et al. [1]	Reported by Hirano et al. [2]	**Observed in Present Work**
Activation Energy (kJ/mol)	130	114.7 ± 1	**105.4 ± 4.2**

Al Single Crystal
394-655°C

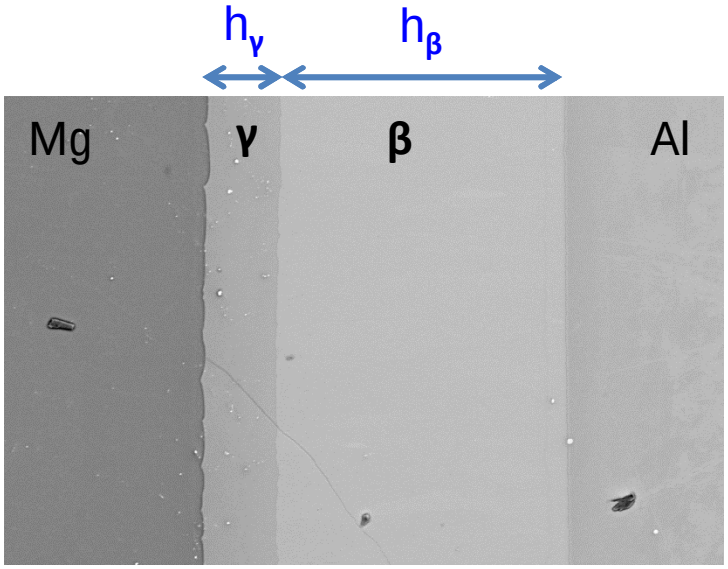
Al Poly- Crystal
325-650°C

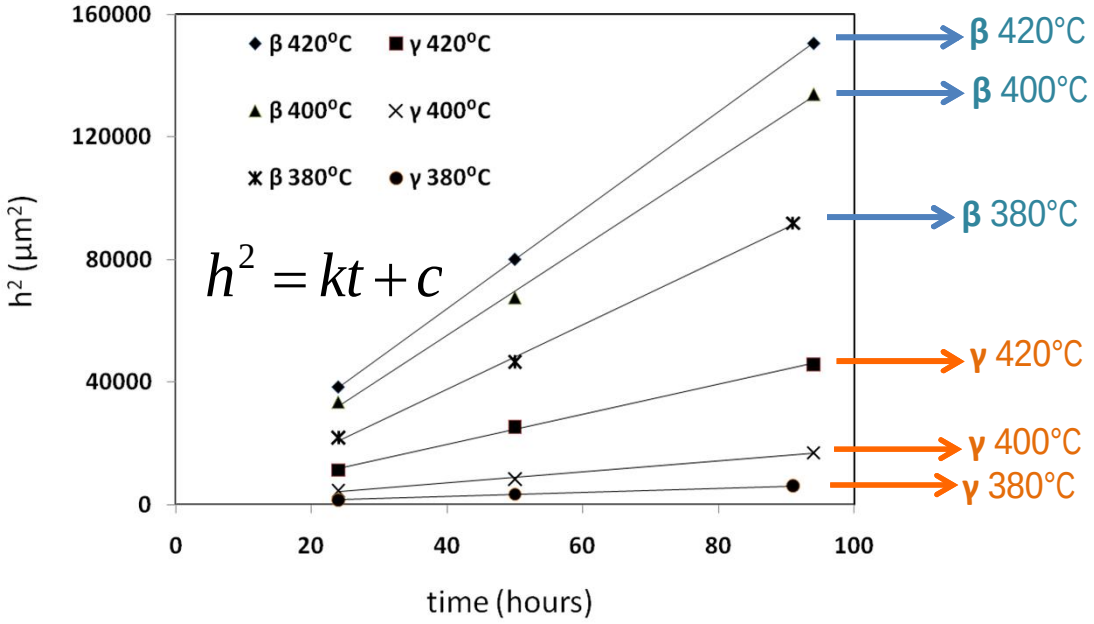
Al Poly- Crystal
380-420°C

Activation energy for impurity diffusion of Mg in Al agrees well with that estimated by Hirano and Fujikawa by Tracer technique

1. S. J. Rothman et al.; Phys. Stat. Solidi B; Vol. 63; 1974; p. K29
2. K. Hirano and S. Fujikawa; J. Nucl. Mater.; Vol. 69/70; 1978; p. 564

Phase Growth Kinetics





Incubation time in minutes

	380°C	400°C	420°C
β-Al_3Mg_2	241	95	1
γ-$Mg_{17}Al_{12}$	71	51	6

- Parabolic growth indicates diffusion controlled growth of both intermetallic phases
- Growth of **β** phase is faster than **γ**. However, incubation times for **β** are also higher at all temperatures

1. Kaustubh N. Kulkarni and Alan A. Luo; J. Phase Equilib. Diff.; 34; 2013; p. 104

Activation Energies for Growth

Phase	Activation Energy for Growth (kJ/mol)		
	Funamizu et al. [1]	Brubaker et al. [2]	Present Work
β-Al_3Mg_2	62.8 ± 2.1	83.2 ± 10.8	37.3 ± 4.1
γ-$Mg_{17}Al_{12}$	143.7 ± 1.7	185.9 ± 7.4	187.7 ± 1.9

Weld treatment for 15 min at 400°C and most experiments then done below 400°C

$$h^2 = kt$$

i.e. Incubation time not considered

$$h^2 = kt + c$$

& No weld treatment at higher temperature

- The differences on account of
  - Pre-weld treatment in case of Funamizu et al. (phase may have nucleated)
  - not accounting for incubation time by Brubaker et al.

- Agreement with Brubaker et al. for **γ**-phase having lower Incubation time

1. Y. Funamizu and K. Watanabe; Trans. Jap. Inst. Met.; Vol. 13; 1972; p. 278
2. C. Brubaker and Z. K. Liu; Magnesium Technology 2004; ed. Alan Luo; TMS, 2004; p. 229

Conclusions

- Multiphase diffusion couples assembled at 380, 400 and 420°C showed presence of two intermediate layers viz. Al_3Mg_2 **(β)** and $Mg_{17}Al_{12}$ **(γ)**
- FIRST report on interdiffusion coefficients and activation energies as functions of compositions in binary Mg-Al system
  - Activation energy for interdiffusion increased with Mg-content in FCC Al possibly due to larger atomic size of Mg
  - Activation energy does not change with composition in HCP Mg and in$Mg_{17}Al_{12}$ intermetallic
- Activation energy for impurity diffusion of Mg in Al measured by Hall's method was found to be 105.4±4.2 kJ/mol
- Parabolic growth of both **β** and **γ** phases suggest diffusion controlled growth
- Activation energy for the growth of Al_3Mg_2 **(β)** was found to be much lower than that of $Mg_{17}Al_{12}$ **(γ)** however, the incubation time for the former was higher