High-Throughput Study of Diffusion and Phase Transformation Kinetics of Magnesium-Based Systems For Automotive Cast Magnesium Alloys

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Project ID: LM093

Timeline

Start date: Oct. 1, 2013
End date: Sept. 30, 2016
Percent complete: 60%

Budget

- Total project funding
  - $600,000
  - $196,073
- Funding received in FY14: $186,182.66
- Funding for FY15: $203,200

Barriers

Barriers addressed

- Insufficient diffusion/mobility databases for Mg alloys
- Phase transformation kinetics not well understood in cast Mg alloys

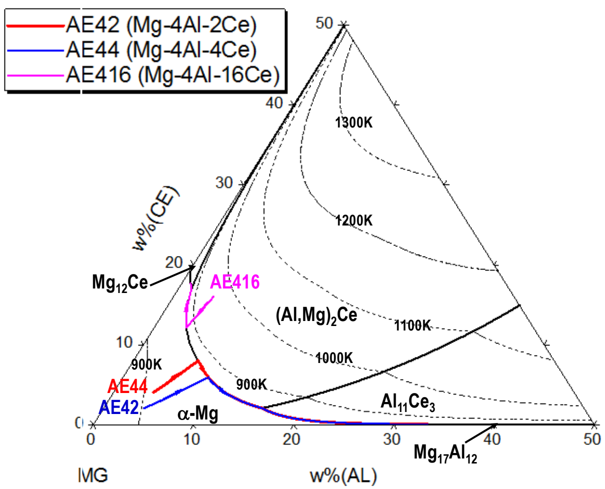
Partners

- Lead: The Ohio State University (PI: Alan Luo; co-PI: J.-C. Zhao)
- Subcontractor: CompuTherm LLC, Madison, WI
- Industry Partner: General Motors, Warren, MI

Relevance and Overall Goal

Establish a diffusion database and scientific foundation for kinetic modeling of phase transformations in Mg alloys for automotive lightweighting.

- Thermodynamic database and CALPHAD (CALculation of PHAse Diagrams) tools are relatively complete
- Focus on Mg-Al-Zn/Mn (conventional alloys), low-cost Mg-Al-Ca/Sr (creep-resistant alloys) Mg-Al-Sn (high-strength alloys)
- Integrated computational materials engineering (ICME) development for lightweight automotive castings



Diffusion, kinetics and ICME models

Detailed Objectives

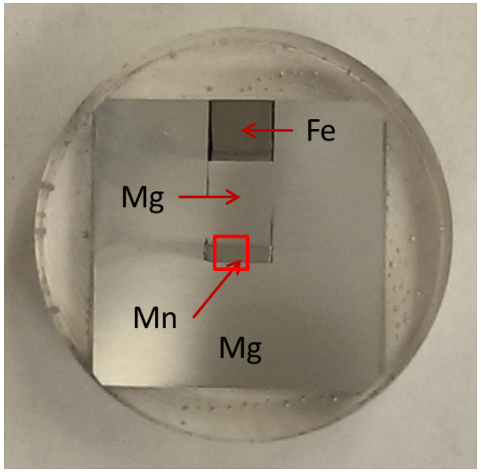
- Diffusivity & mobility databases for the Mg-Al-Zn-Sn-Ca-Sr-Mn system
- Effective experimental study of precipitation kinetics to model validation
- Modified KWN models to handle plate & needle shaped precipitates in Mg alloys
- Extraction of interfacial energy of model Mg alloy systems
- Modified micromodel to handle back-diffusion during casting
- Data and models to NIST and industry

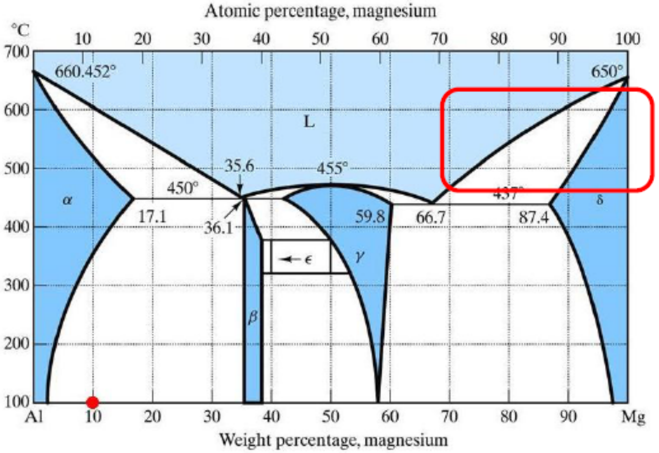
Milestones

- Milestone 1 (12 months): Preliminary mobility database for Mg alloy systems - complete
- Milestone 2 (18 months): Precipitation model based on modified KWN model - complete
- Milestone 3 (30 months): Modified solidification micromodel including back-diffusion during casting – on track
- Milestone 4 (36 months): Complete databases and models to NIST and industry – on track

Technical Approach

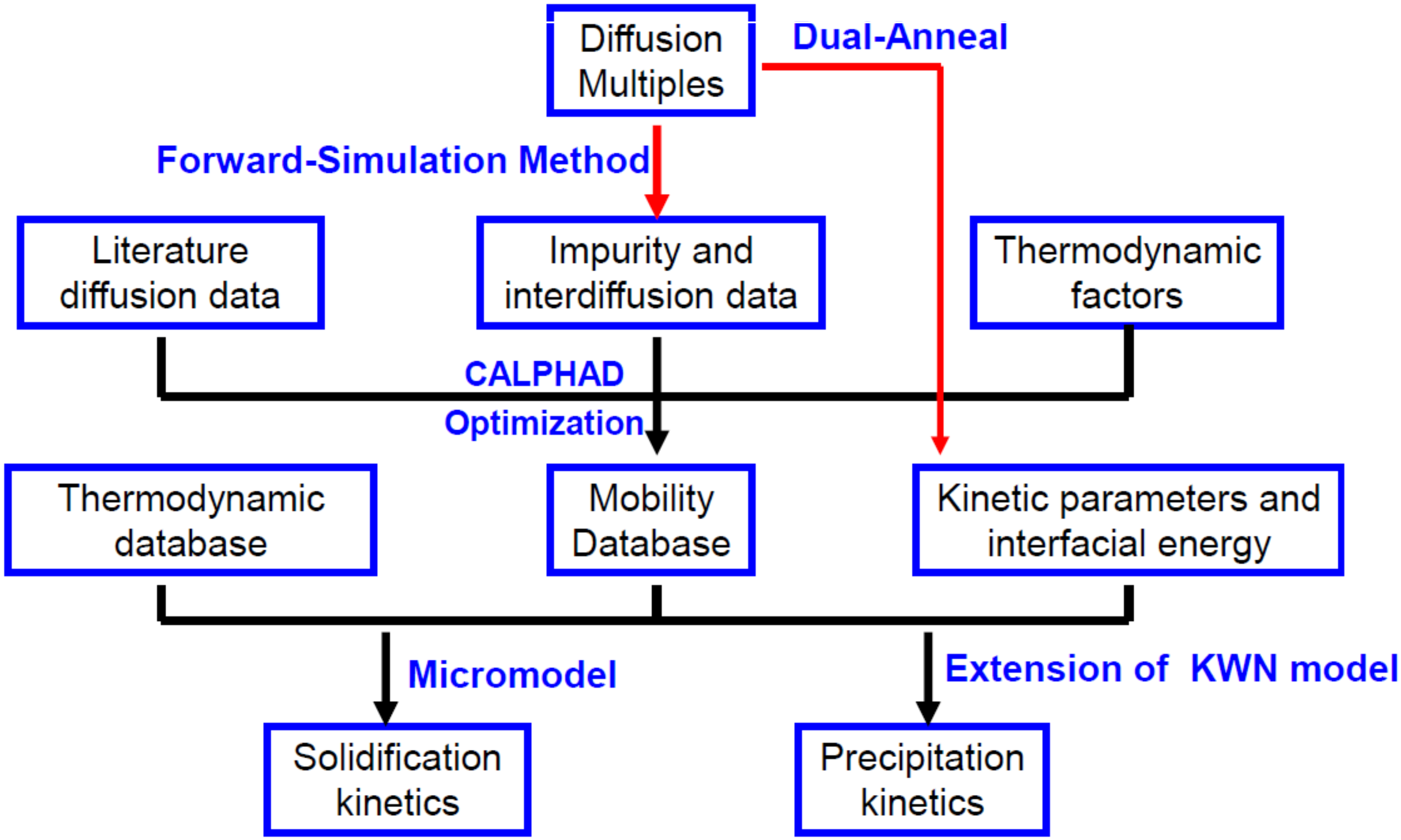
- ❑ Diffusion multiples:
  - high-throughput collection of diffusion profiles
  - liquid-solid diffusion multiples for high-temperature diffusivity evaluation
- ❑ Forward-simulation method: efficient extraction of diffusivity data
- ❑ Micromodel for casting: back diffusion integrated into solidification modeling
- ❑ Precipitation model in cast alloys: Extension of Kampmann-Wagner numerical (KWN) model to non-spherical and non-cuboidal precipitates in Mg alloys





Al–Mg phase diagram

Technical Approach Summary



Technical Accomplishments and Progress: Task 2. Diffusion

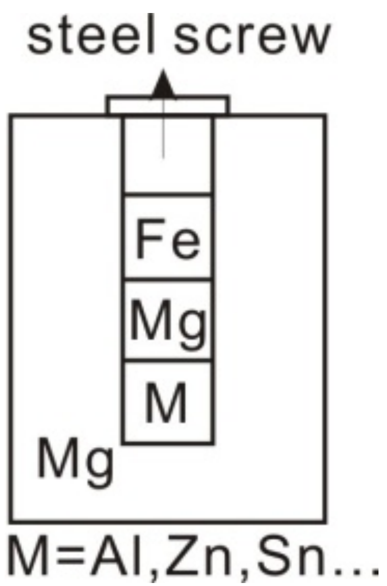
- Established a preliminary atomic mobility database of Mg-Al-Zn-Sn-Ca-Sr-Mn system.
- Made diffusion multiples and carried out characterization.
- The forward simulation method was used to generate the inter-diffusion coefficients from the diffusion profiles of two Mg-Zn and Mg-Mn samples measured by EPMA (Electron Probe Micro-Analysis).

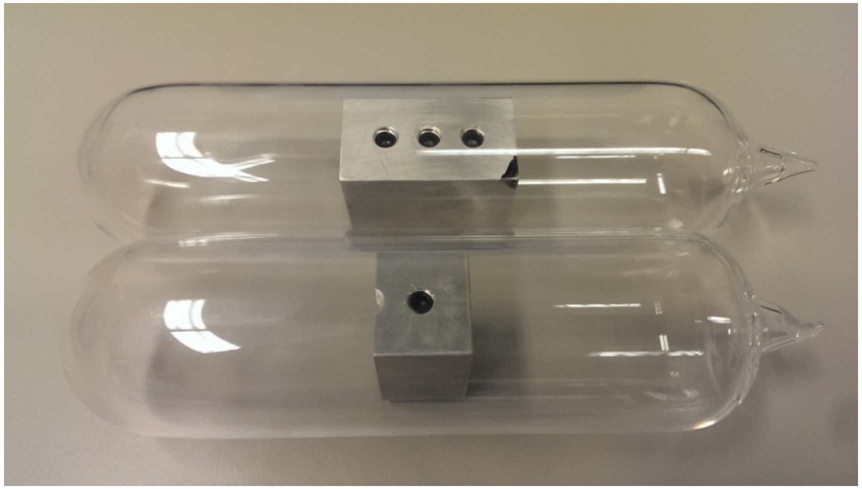
	System	No.	Heat treatment	SEM	EPMA
liquid-solid diffusion multiples for high temperature measurements	Mg-Al	3	450°C(2), 550°C 8hours	√	
	Mg-Mn	1	600°C, 48hours	√	600°C 48hours
	Mg-Sn	4	450°C(2), 500°C, 550°C 8hours	√	
	Mg-Zn	3	450°C(2), 500°C, 8hours	√	450°C 8hours
solid diffusion multiples for low temperature measurements	Multiple 1	4	315°C,790 hours 275°C, 1760 hours	√	
	Multiple 2	6			

Technical Accomplishments and Progress: Task 2. Diffusion

Diffusion multiples for high temperature measurements

- Design and preparation of liquid-solid diffusion multiples





Design

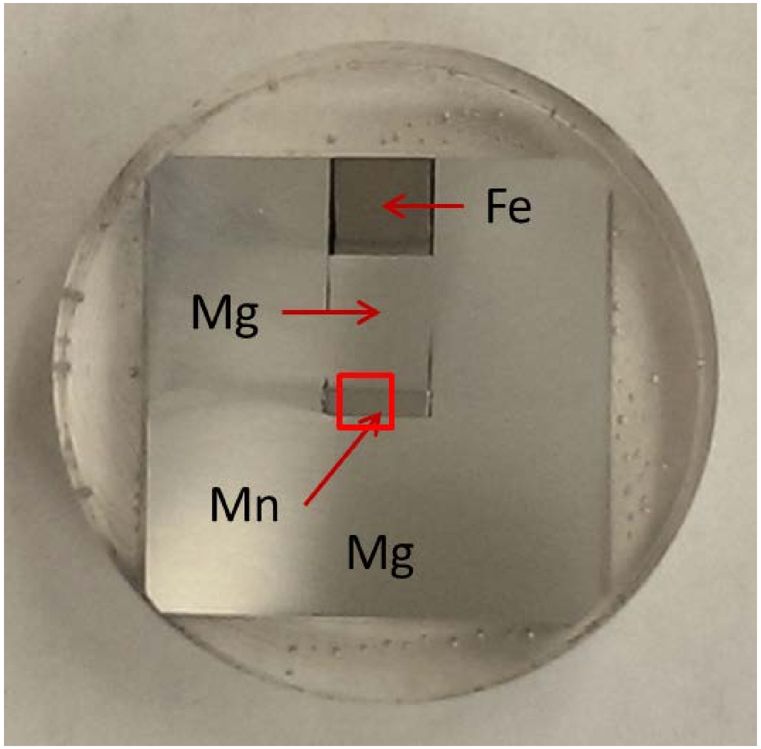
Assembly

Encapsulated in quartz tube

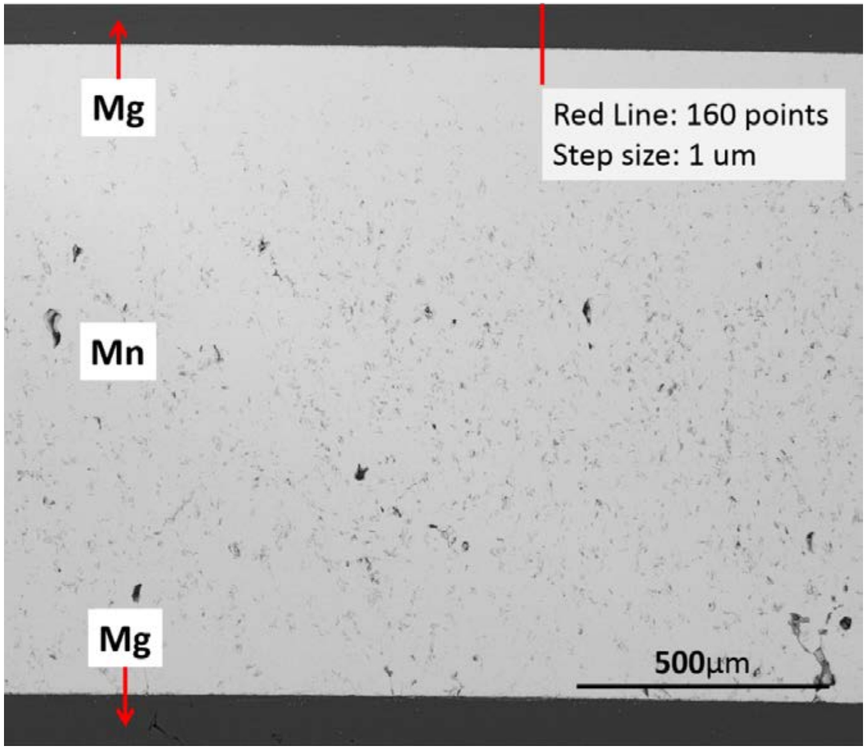
Technical Accomplishments and Progress: Task 2. Diffusion

Diffusion multiples for high temperature measurements

- ❑ Characterization of Mg-Mn sample heated at 600°C for 48 hours



A polished section of Mg-Mn diffusion multiple heated at 600°C for 48 hours

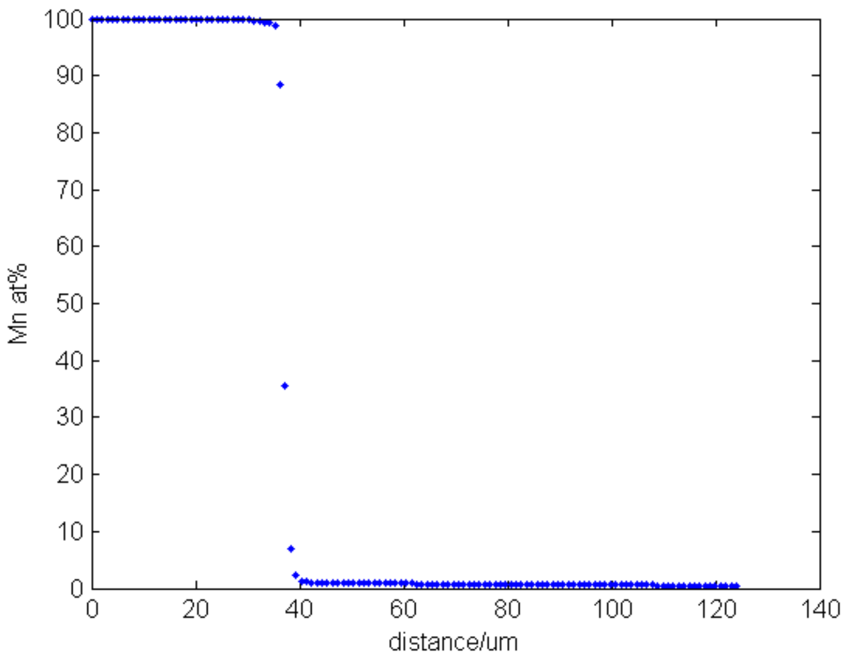


BSE image showing a red line for EPMA scan analysis

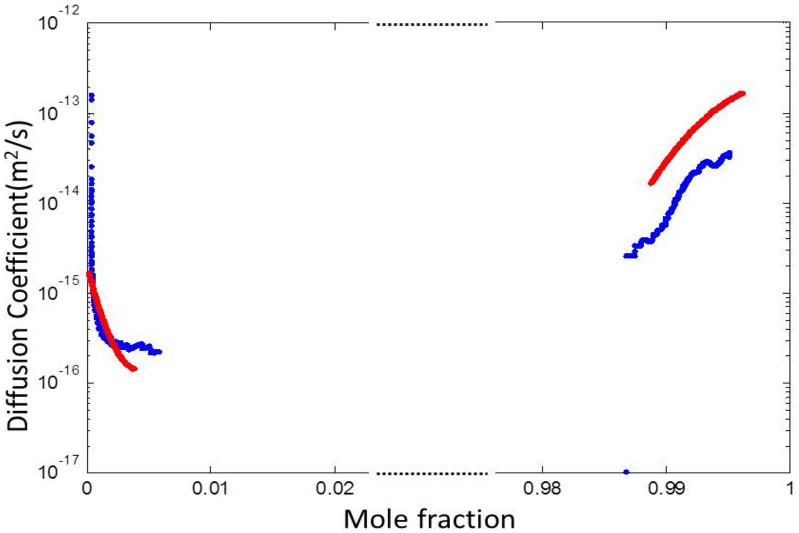
Technical Accomplishments and Progress: Task 2. Diffusion

Diffusion multiples for high temperature measurements

- Characterization of Mg-Mn sample heated at 600°C for 48 hours
- The forward simulation method is used to extract the inter-diffusion coefficients from the concentration profiles measured by EPMA.



Concentration profile measured by EPMA

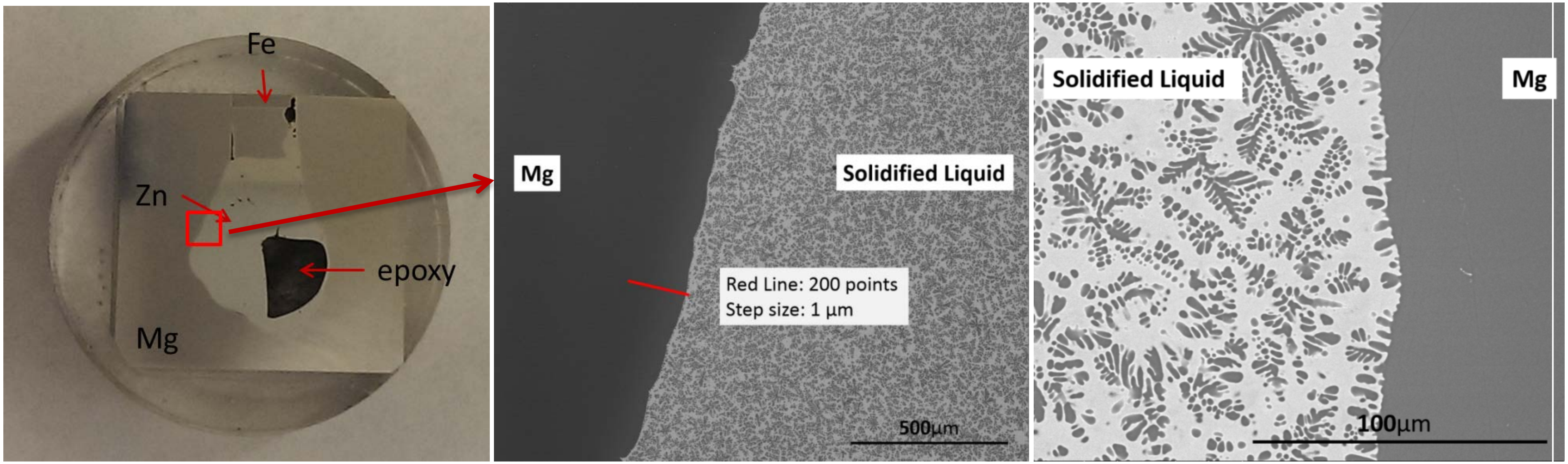


Comparison of the inter-diffusion coefficients obtained from forward simulation (red lines) with those obtained by the Sauer-Freise method (blue lines)

Technical Accomplishments and Progress: Task 2. Diffusion

Diffusion multiples for high temperature measurements

- Characterization of Mg-Zn sample heated at 450°C for 8 hours



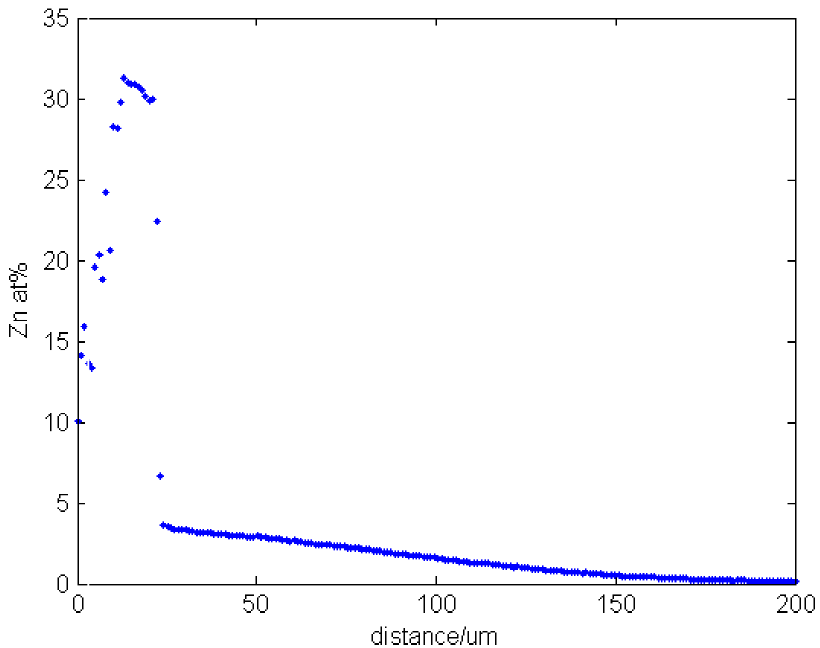
A polished section of Mg-Zn diffusion multiple heated at 450°C for 8 hours

BSE image of Mg-Zn interface with the red line for EPMA scanning.

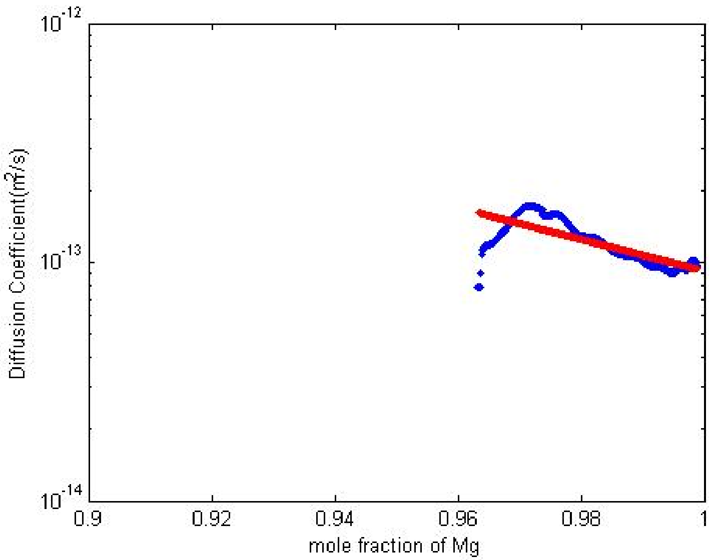
Technical Accomplishments and Progress: Task 2. Diffusion

Diffusion multiples for high temperature measurements

- Characterization of Mg-Zn sample heated at 450°C for 8 hours
- The forward simulation method is used to extract the inter-diffusion coefficients from the concentration profiles measured by EPMA.



Concentration profile measured by EPMA

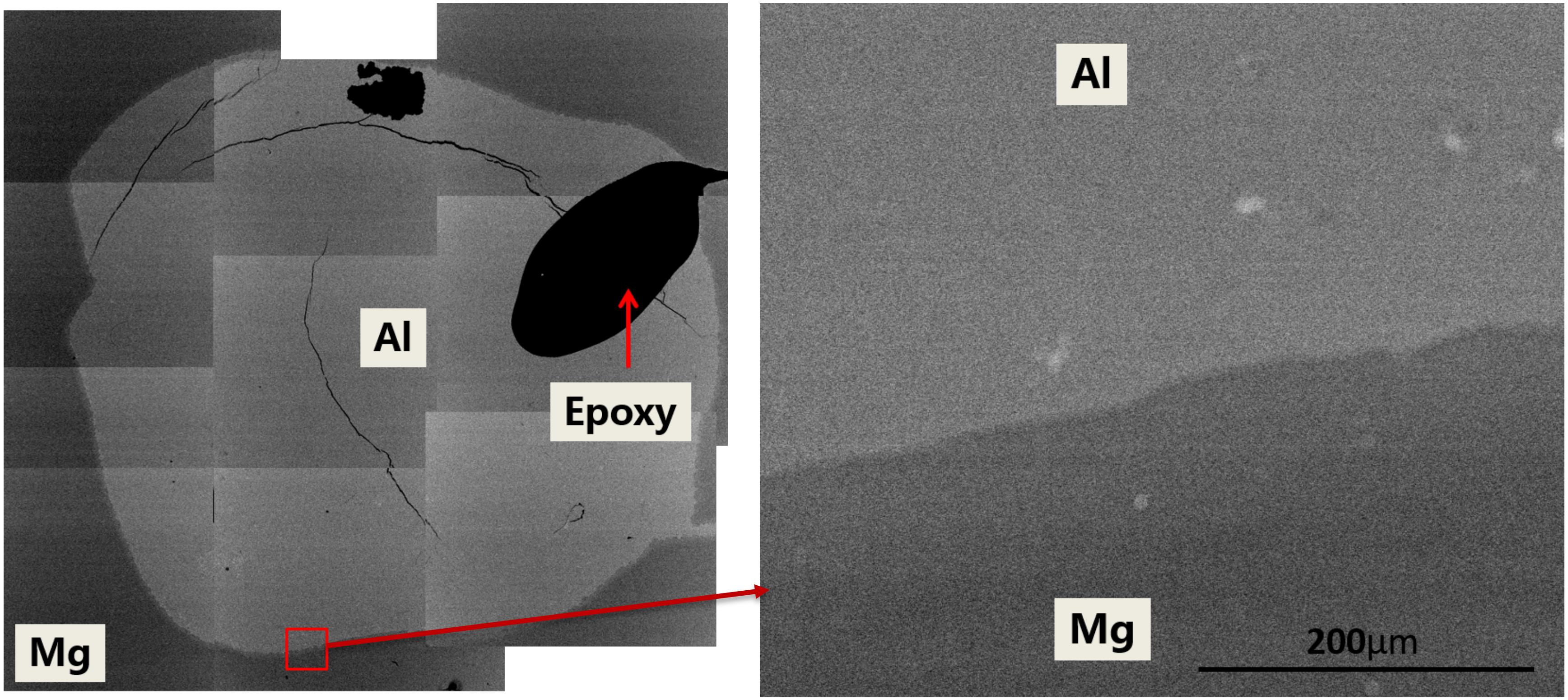


Comparison of the inter-diffusion coefficients obtained from forward simulation (red lines) with those obtained by the Sauer-Freise method (blue lines)

Technical Accomplishments and Progress: Task 2. Diffusion

Diffusion multiples for high temperature measurements

- ❑ Characterization of Mg-Al sample heated at 450°C for 8 hours

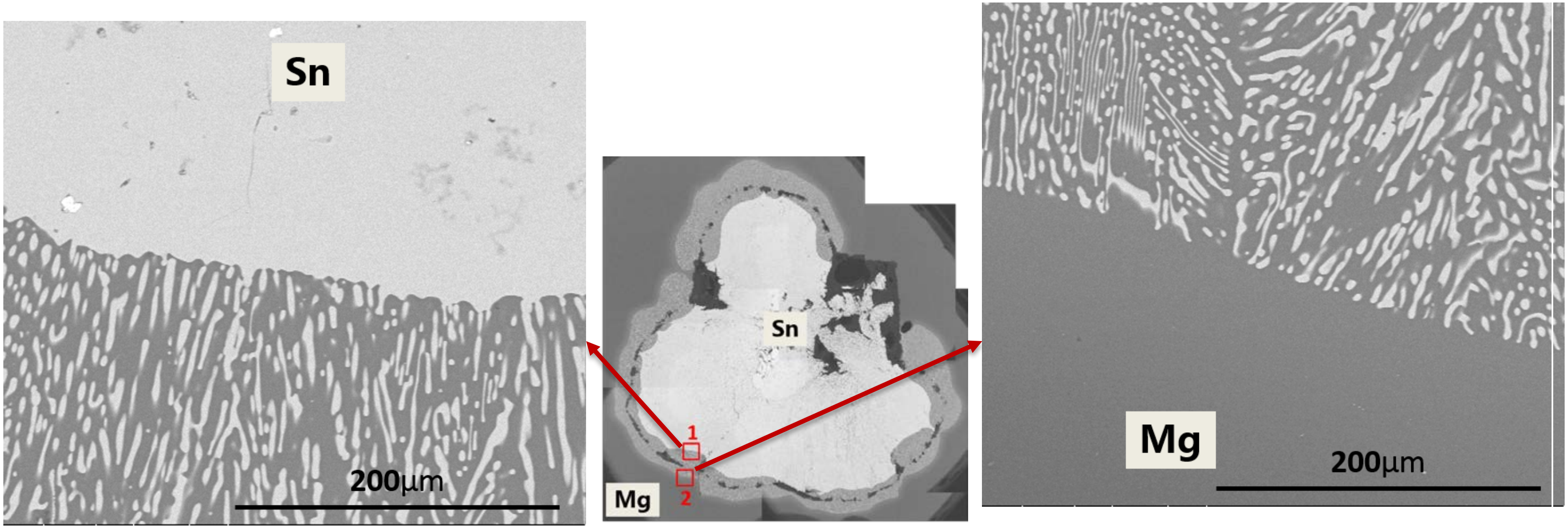


BSE images of the Mg-Al diffusion multiple heated at 450°C for 8 hours

Technical Accomplishments and Progress: Task 2. Diffusion

Diffusion multiples for high temperature measurements

- Characterization of Mg-Sn sample heated at 550°C for 8 hours

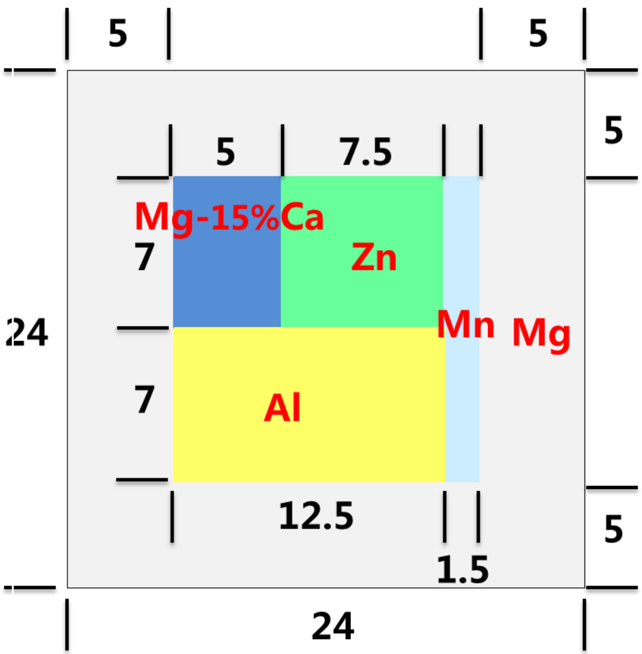


BSE images of the Mg-Al diffusion multiple heated at 450°C for 8 hours

Technical Accomplishments and Progress: Task 2. Diffusion

Diffusion multiples for low temperature measurements

❑ Sample design

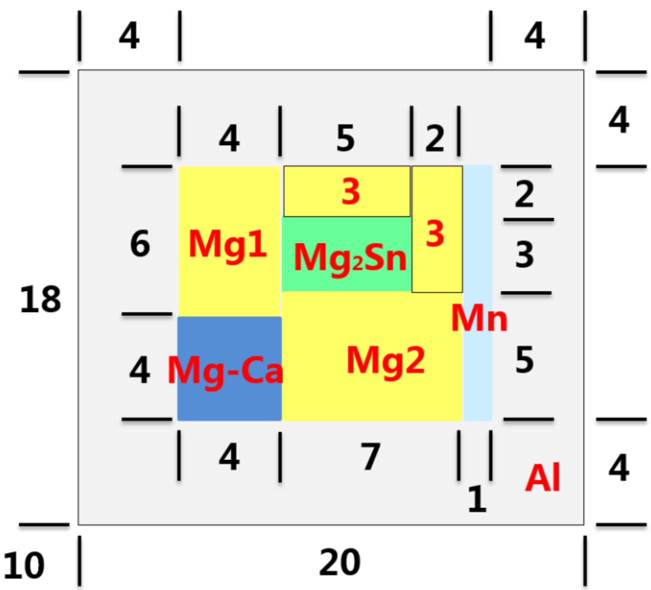


Unit: mm; Thickness: 14

- Mg_2Sn: 3X5X6;
- Mg 1: 4X6X10;
- Mg 2: 5X7X10;
- Mg 3: 2X5X6;
- Mg cap: 2X5X7.
- Diffusion system:

  Mg-Sn; Mg-Al;
  Mg-Mn; Mg-Ca
  Al-Mn

Unit: mm
Thickness: 10

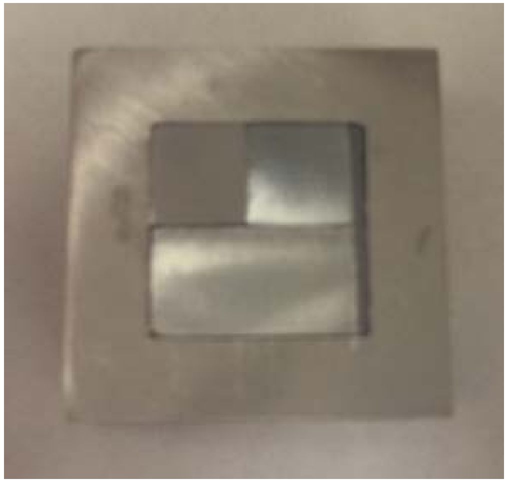


The original design using Mg cartridge

The updated design using Al cartridge

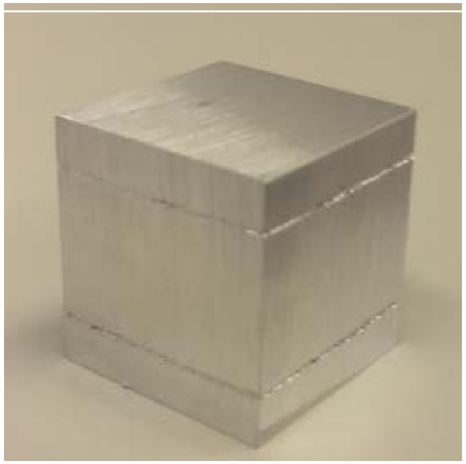
Technical Accomplishments and Progress: Task 2. Diffusion

Diffusion multiples for low temperature measurements

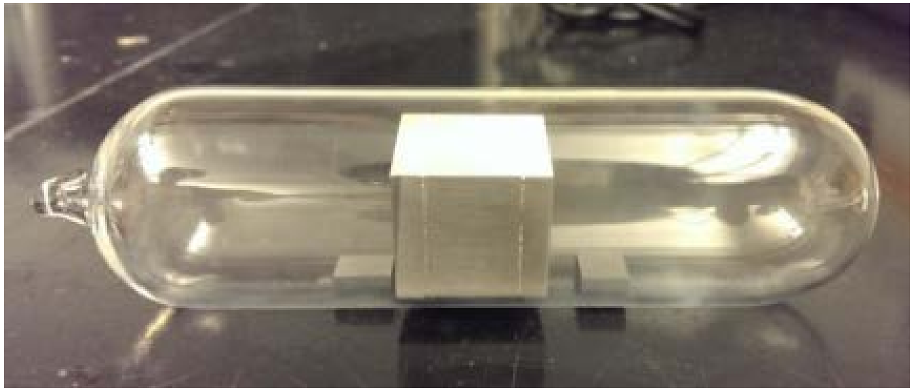


Assembly

Welded



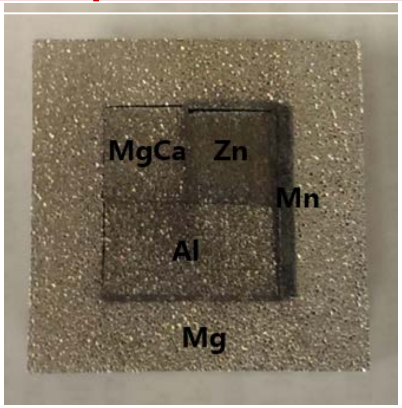
Hot isostatic pressed



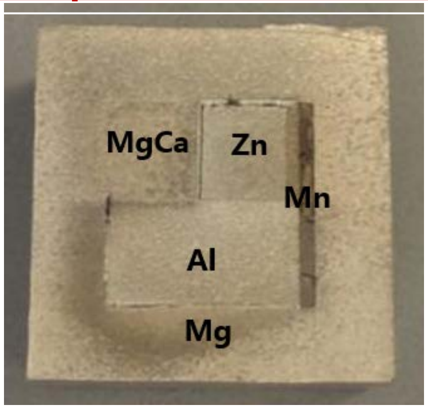
Encapsulated in quartz tube

Technical Accomplishments and Progress: Task 2. Diffusion

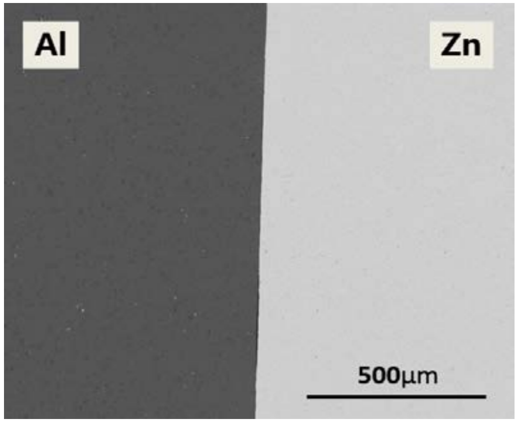
Diffusion multiples for low temperature measurements

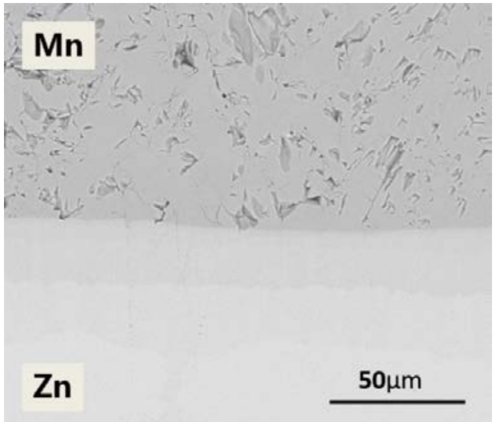


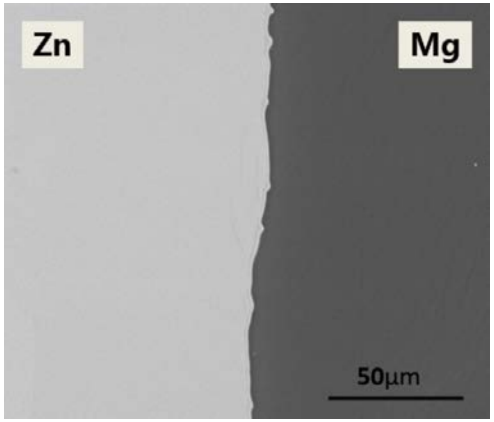
315°C for 790 hours



275°C for 1760 hours







BSE images of three diffusion systems in the diffusion multiple heated at 315°C for 790 hours.

Technical Accomplishments and Progress: Task 2. Diffusion

A preliminary atomic mobility database for Mg alloys

- CALPHAD (CALculation of Phase Diagrams) approach using literature data

$$\boldsymbol{M_B} = M_B^0 \exp\left(\frac{-Q_B}{RT}\right)\frac{1}{RT} = \exp\left(\frac{RT\ln M_B^0}{RT}\right)\exp\left(\frac{-Q_B}{RT}\right)\frac{1}{RT}$$

The composition dependency of $RT\ln M_B^0$ and Q_B can be expressed by:

$$\Phi_B = \sum_i x_i\,\Phi_B^i + \sum_i\sum_{j>i} x_i x_j\left[\sum_{r=0}^{m} {}^r\Phi_B^{i,j}(x_i - x_j)^r\right] + \sum_i\sum_{j>i}\sum_{k>j} x_i x_j x_k\left[\sum_s v_{ijk}^s\ {}^s\Phi_B^{i,j,k}\right]\ (s = i, j, k)$$

Assuming the monovacancy atomic exchange as the main diffusion mechanism, the tracer diffusivity D_i^* is related to the atomic mobility M_i by the Einstein's relation:

$$D_i^* = RTM_i$$

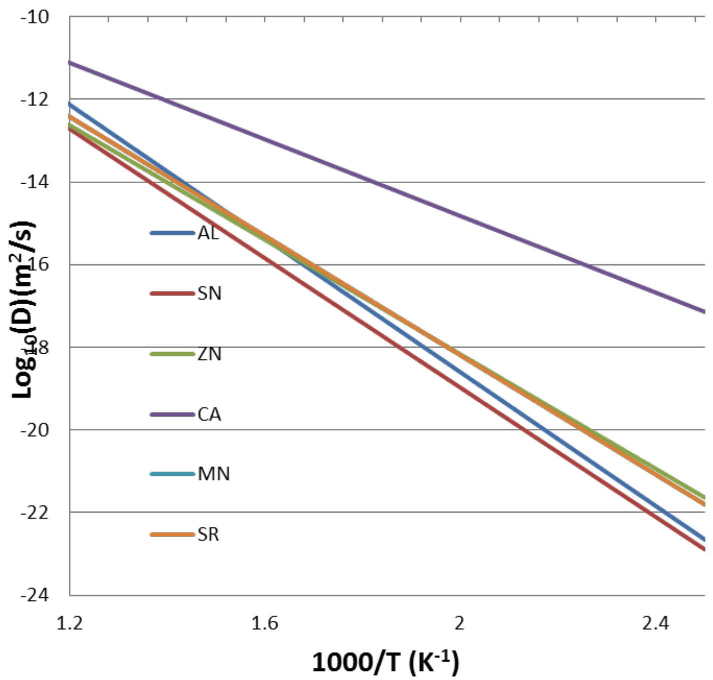
For a substitutional solution phase, the interdiffusion coefficient in terms of the volume fixed reference frame can be given by the following expression:

$$\tilde{D}_{kj}^n = \sum_i (\delta_{ik} - x_k)\cdot x_i \cdot M_i \cdot \left(\frac{\partial\mu_i}{\partial x_j} - \frac{\partial\mu_i}{\partial x_n}\right)$$

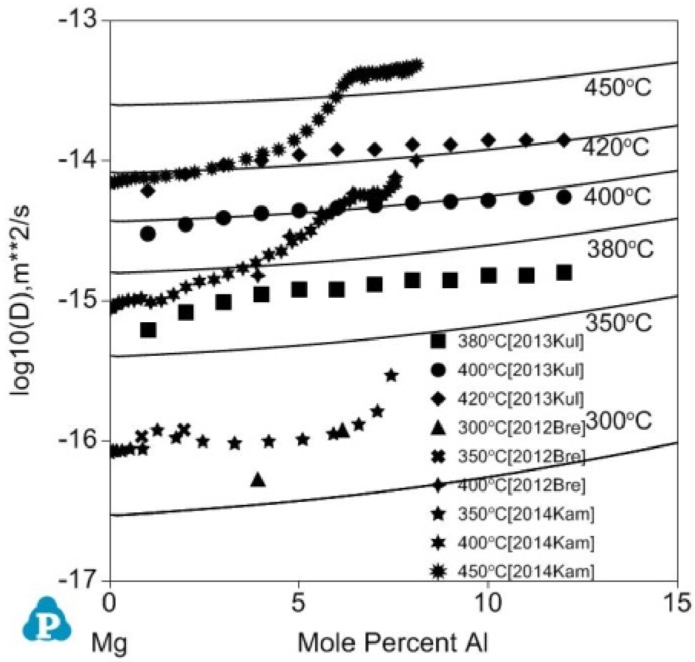
Technical Accomplishments and Progress: Task 2. Diffusion

A preliminary atomic mobility database for Mg alloys

- This preliminary atomic mobility database will be improved by the data from our diffusion multiple experiments.



Impurity diffusion coefficients of the elements in Mg calculated from the database based on literature data and empirical methods

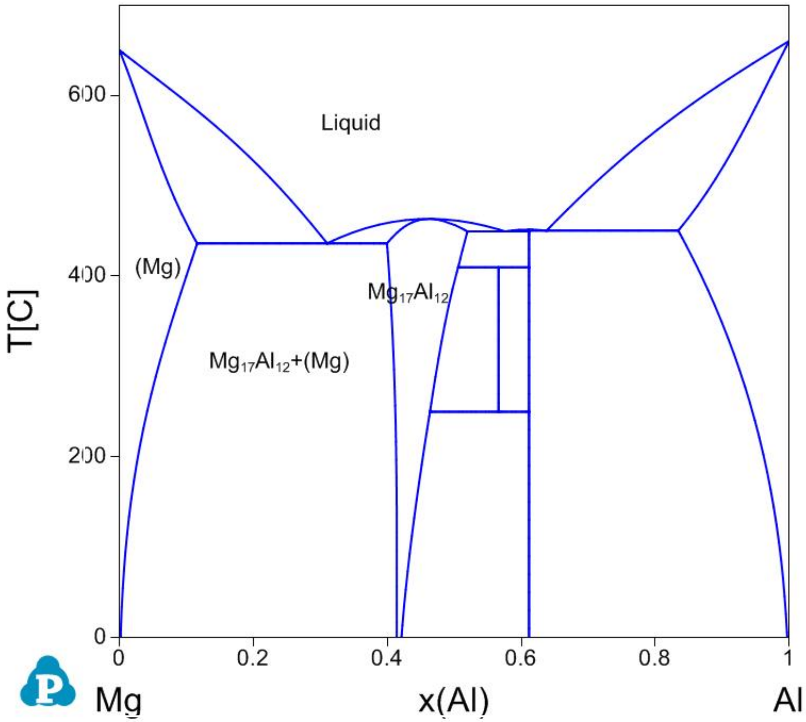


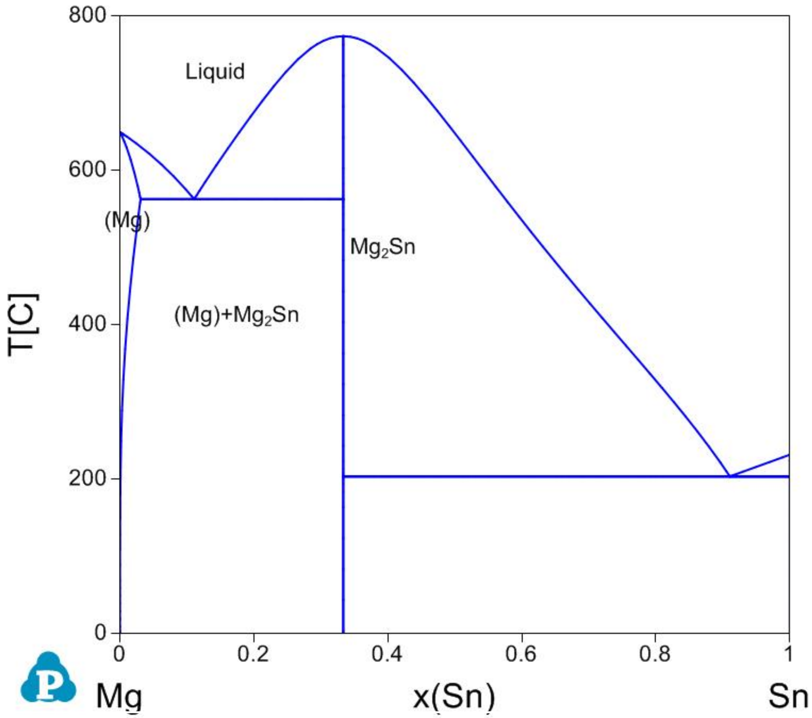
Calculated interdiffusion coefficients in the Mg rich region of Mg-Al system along with the experimental data

Technical Accomplishments and Progress: Task 3. Precipitation

Simulation of precipitation hardening in Mg Alloys

- Simulated systems: Precipitation of $Mg_{17}Al_{12}$ in Mg-Al-Zn alloy
  Precipitation of Mg_2Sn in Mg-Sn alloy
  Precipitation of $Mg_{17}Al_{12}$ and Mg_2Sn in Mg-Al-Sn alloy

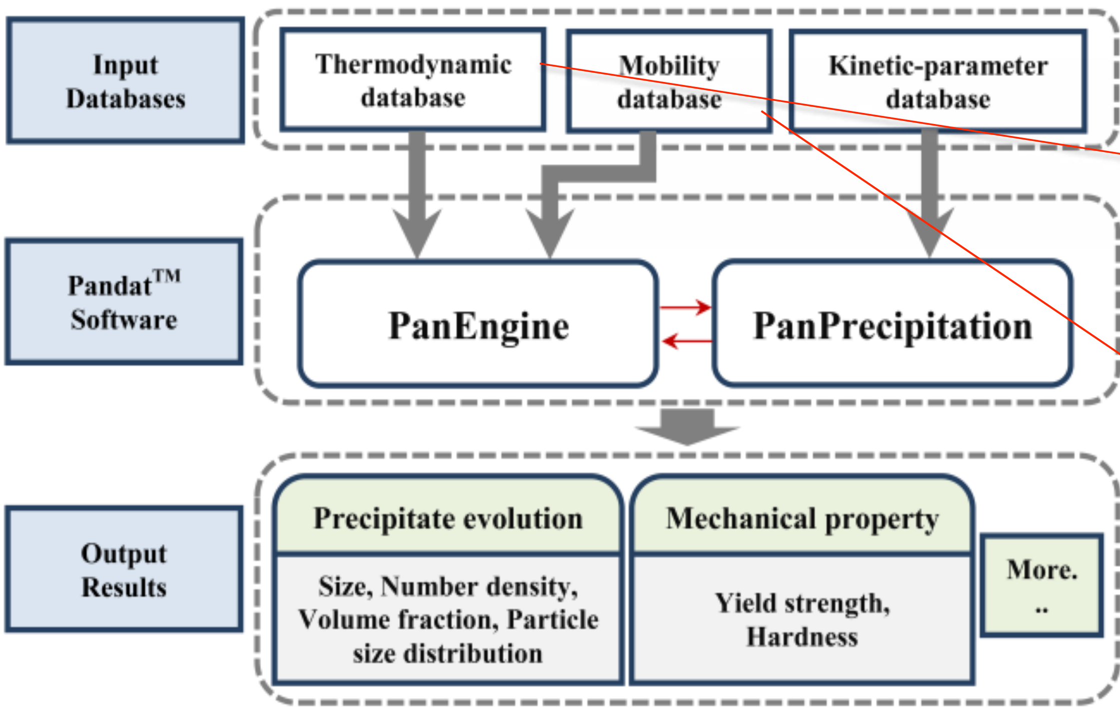




Technical Accomplishments and Progress: Task 3. Precipitation

Simulation of precipitation hardening in Mg Alloys

- Approach: KWN model implemented in PanPrecipitation module of Pandat software and couple to Mg thermodynamic and atomic mobility databases



The architecture of PanPrecipitation

KWN model (Kampmann-Wagner-numerical)

- ***Nucleation***

$$J = N_0 Z\beta \exp\left(-\frac{\Delta G^*}{kT}\right)\exp\left(-\frac{\tau}{t}\right)$$

- ***Growth***

$$\frac{dR}{dt} = \frac{K}{R}\left(\frac{1}{R^*} - \frac{1}{R}\right)$$

$$K = \frac{2\alpha V_m}{(C^{\alpha\beta}][M]^{-1}[C^{\alpha\beta})}$$

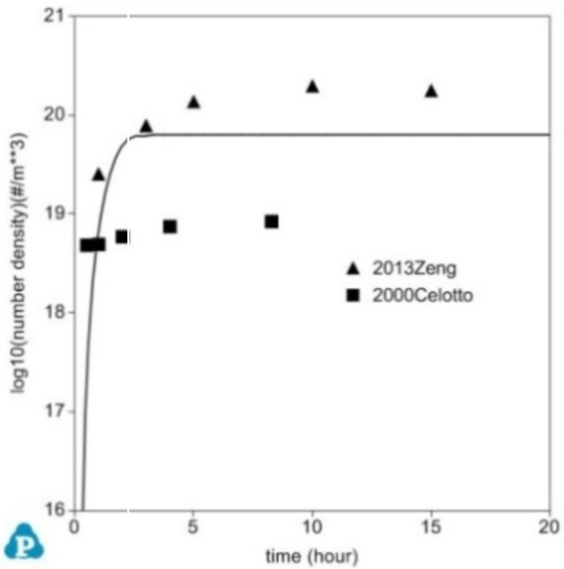
- ***Continuity equation***

$$\frac{\partial N(r,t)}{\partial t} = -\frac{\partial (N(r,t)v(r,t))}{\partial r} + \delta(r - r_{cr}(t))j(t)$$

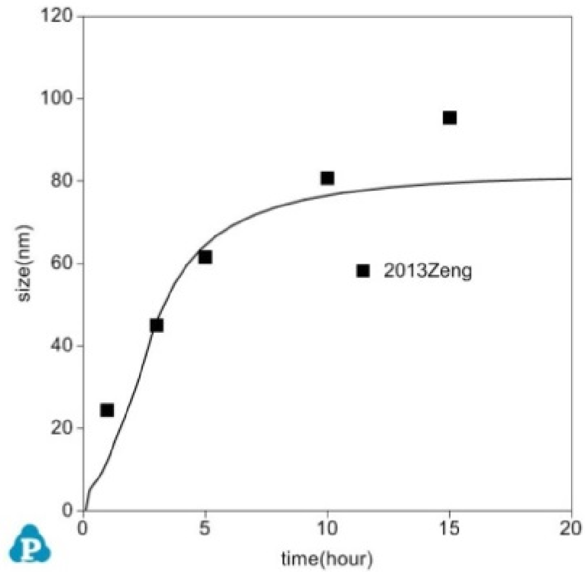
Technical Accomplishments and Progress: Task 3. Precipitation

Simulation of precipitation hardening in Mg Alloys

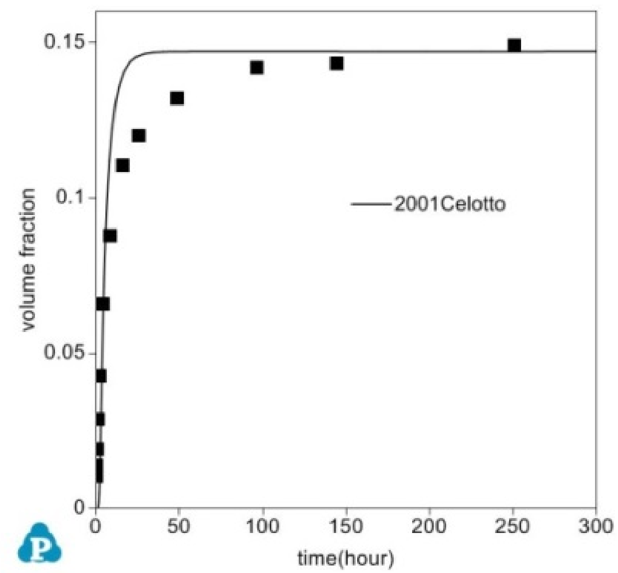
- Precipitation simulation for AZ91 (Mg-9Al-1Zn) alloy aged at 200°C



Number density



Size



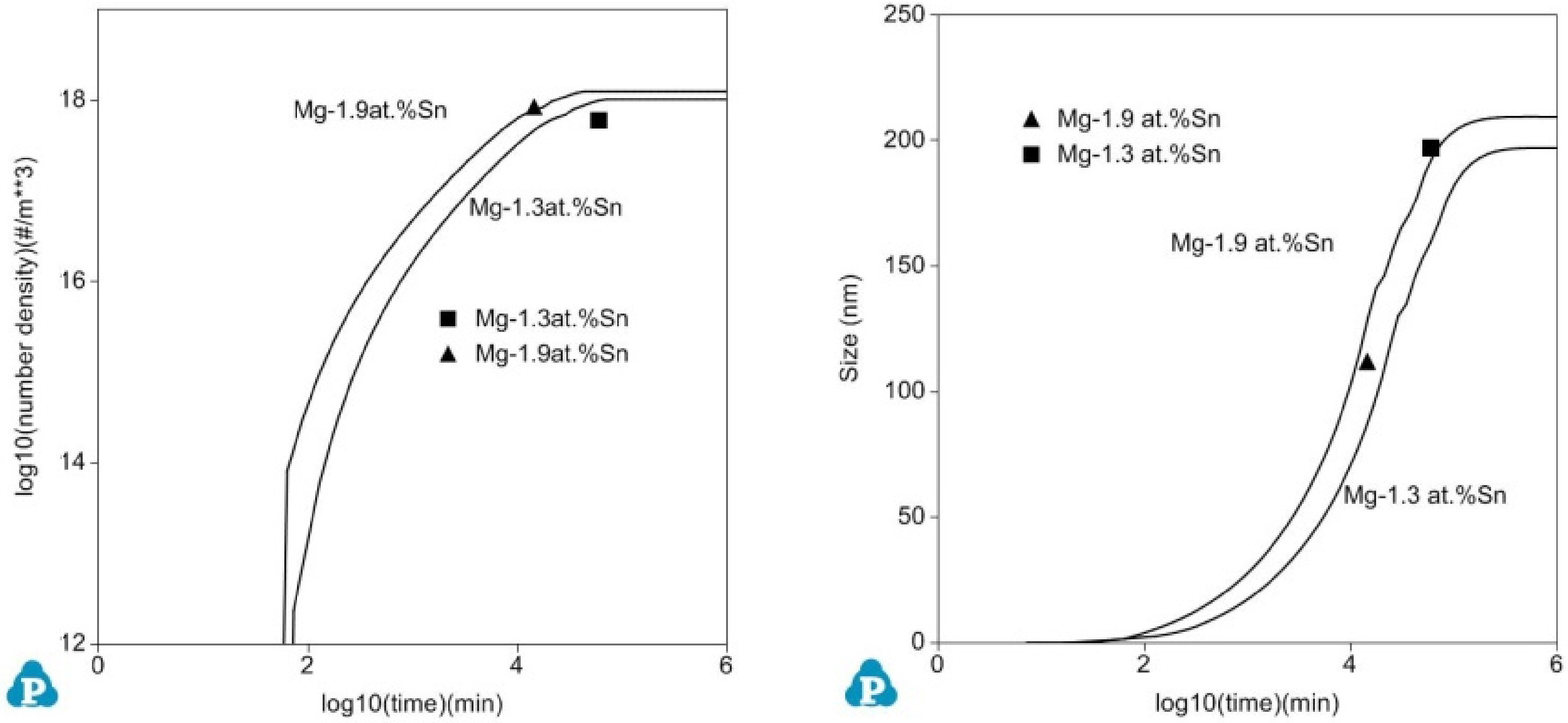
Volume fraction

$Mg_{17}Al_{12}$ precipitation in Mg-9Al-1Zn alloy: simulation and experimental data

Technical Accomplishments and Progress: Task 3. Precipitation

Simulation of precipitation hardening in Mg Alloys

- ❑ Precipitation simulation for Mg-Sn alloys aged at 200°C

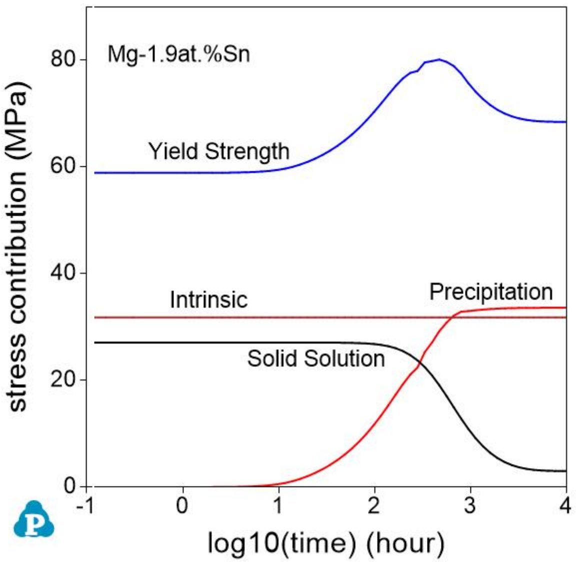


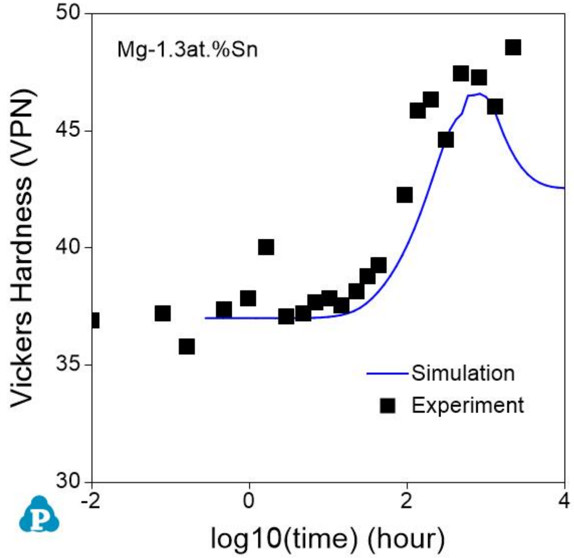
Mg_2Sn precipitation in two Mg-Sn alloys: simulation and experimental data

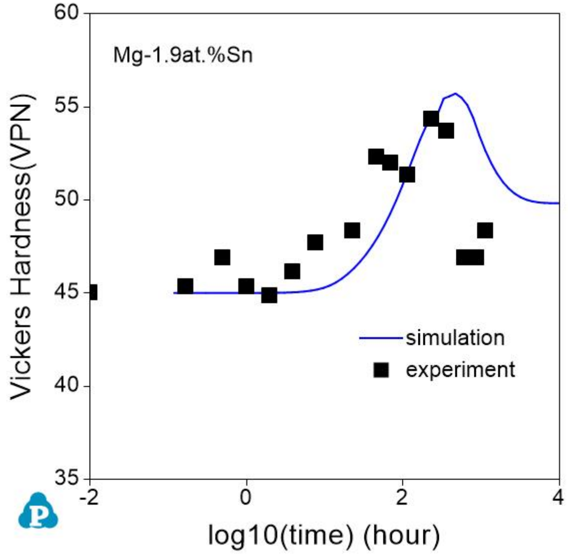
Technical Accomplishments and Progress: Task 3. Precipitation

Simulation of precipitation hardening in Mg Alloys

- Precipitation simulation for Mg-Sn alloys aged at 200°C







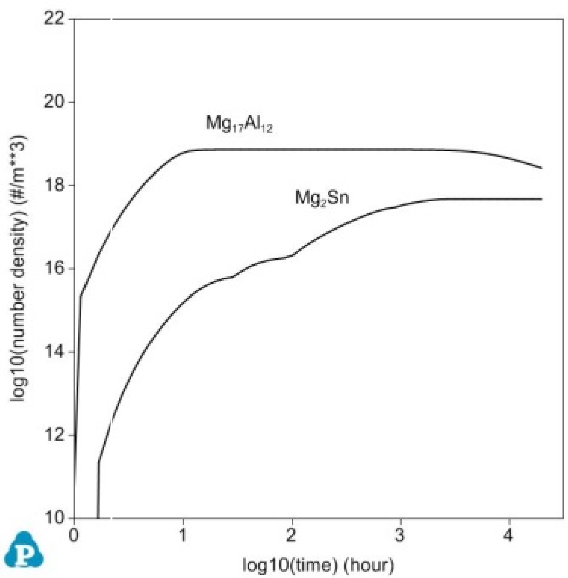
Yield strength in Mg-1.9 at.% Sn alloy

Age-hardening curves in two Mg-Sn alloys: simulation and experimental data

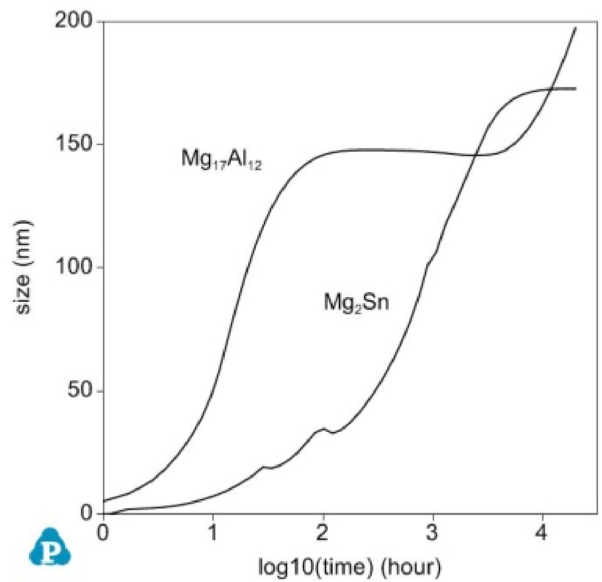
Technical Accomplishments and Progress: Task 3. Precipitation

Simulation of precipitation hardening in Mg Alloys

- Precipitation simulation for AT72 (Mg-7Al-2Sn) alloy aged at 200°C



Number density



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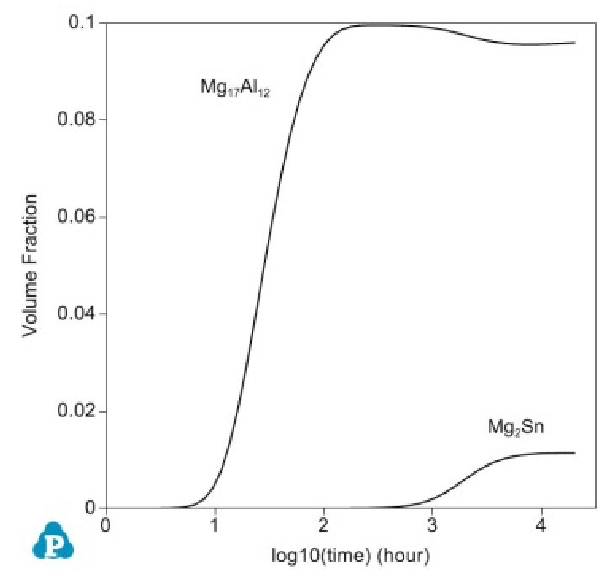


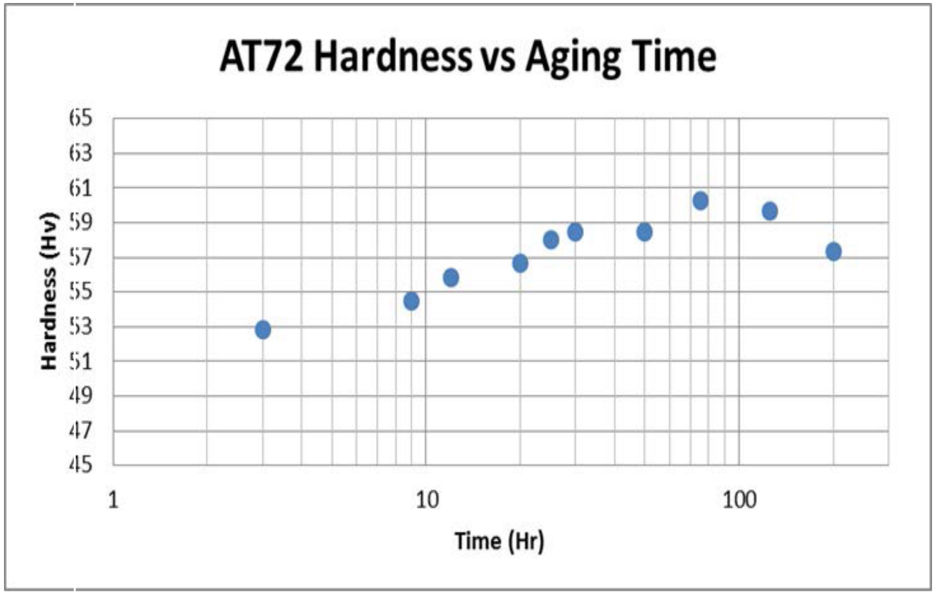
Volume fraction

$Mg_{17}Al_{12}$ and Mg_2Sn precipitation in in AT72 (Mg-7Al-2Sn) alloy:
simulation and experimental data

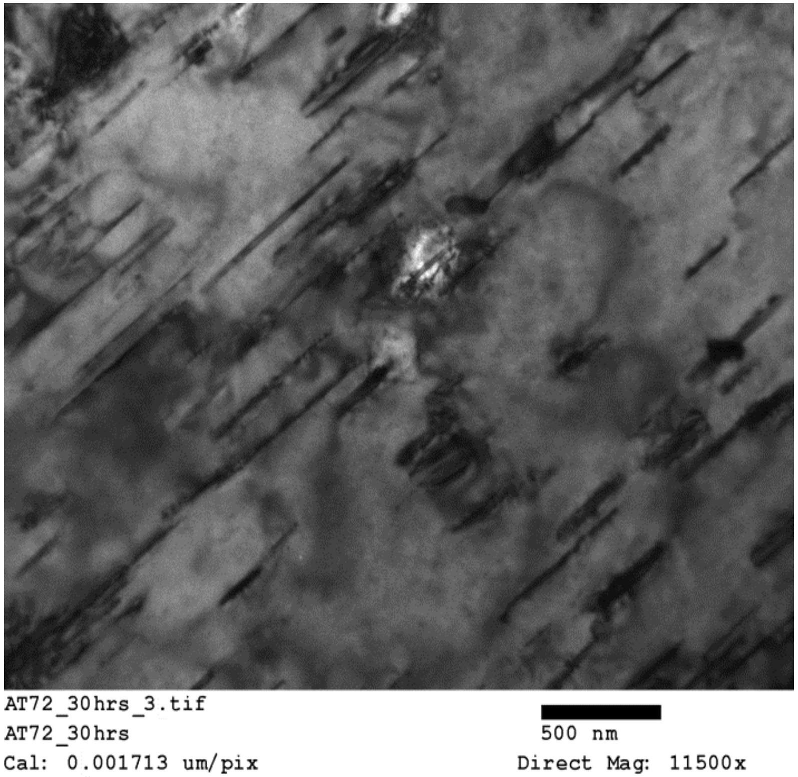
Technical Accomplishments and Progress: Task 3. Precipitation

Simulation of precipitation hardening in Mg Alloys

- ❑ Precipitation simulation for AT72 (Mg-7Al-2Sn) alloy aged at 200°C



Age-hardening curve for AT72 alloy at 200C



TEM bright field image showing precipitates in AT72 alloy aged 30 hours at 200C

Partners/Collaborators

- CompuTherm: partner in database implementation and kinetics modeling
- General Motors: collaborator in defining Mg alloy systems, casting processes, and applications.
- National Institute of Standards and Technology: data and model repository

CompuTherm FOR MATERIALS DESIGN

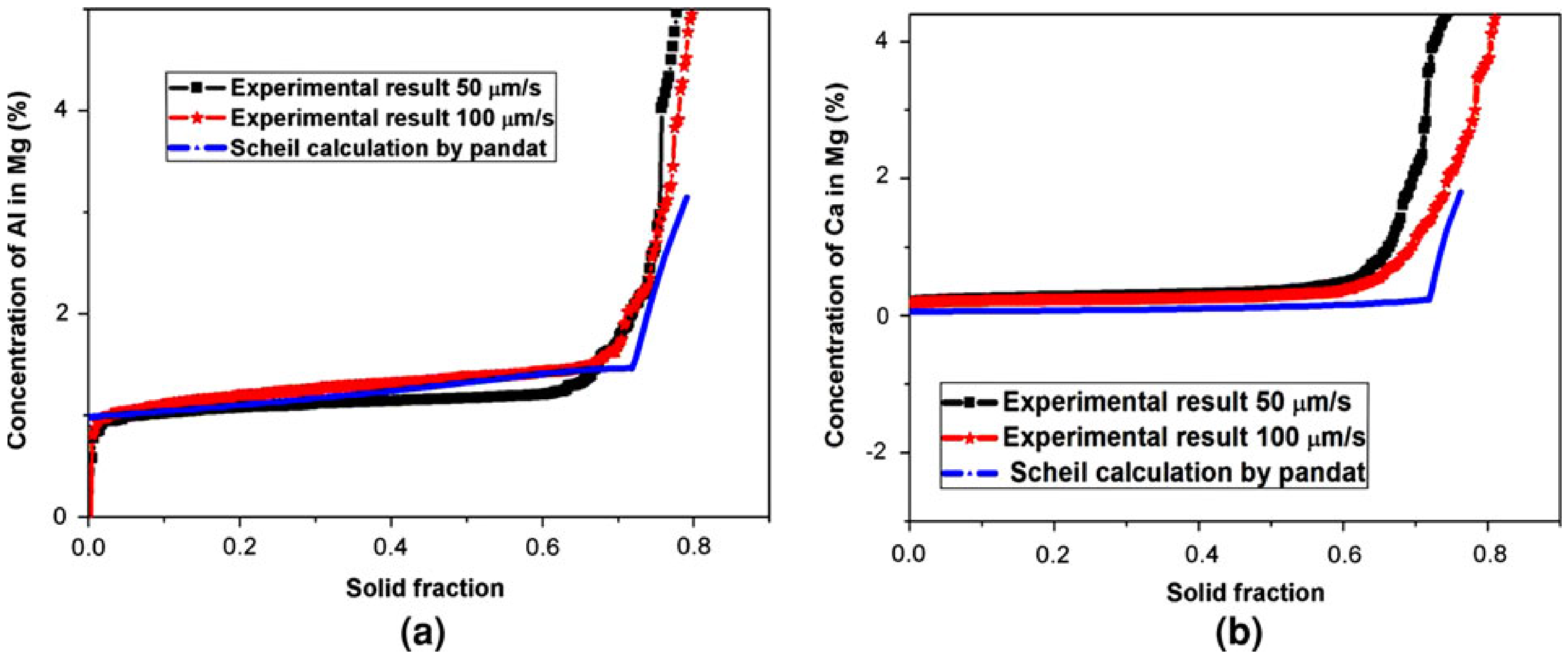
GM

The Ohio State University

NIST
National Institute of Standards and Technology
U.S. Department of Commerce

Remaining Challenges and Barriers

- Phase transformation kinetics not well understood in cast Mg alloys (example: Scheil model does not accurate prediction of microstructure in Mg die castings, need diffusion data and kinetic model)



Microsegregation of alloying elements in the AX44 (Mg-4Al-4Ca) alloy: (a) Al and (b) Ca

Zheng, Luo, Zhang, Dong, and Waldo, Metall. Mater. Trans. A, 2012, 43A, 3239-3248

Proposed Future Work

- Diffusion experiments:
  - More diffusion multiple samples for low-cost Mg alloy systems
  - More SEM and EPMA measurements of diffusion multiple samples
  - Improve the forward simulation code for high-throughput data generation.
- Mobility/diffusion database:
  - Improve the preliminary atomic mobility database from literature
  - Populate the database with our own experimental data.
- Precipitation simulation:
  - Carry out aging experiments on the Mg-Al-Sn samples and investigate the microstructure evolution of precipitation using TEM.
  - Calibrate and validate simulation model on Mg-Al-Sn alloys.
- Solidification simulation:
  - Develop a code to simulate the solidification of Mg alloys including back diffusion in castings.

Summary

- Using CALPHAD approach, an atomic mobility database for Mg alloy system has been established based on assessment of literature experimental data.
  - Will be provided to NIST diffusion database and MGI repository
  - Will be integrated to PANDAT mobility database
  - Open to other users/collaborators in industry/academia

- By coupling to thermodynamic and atomic mobility parameters, the microstructure evolution in the aging process of two Mg-Sn alloys and concurrent precipitation of $Mg_{17}Al_{12}$ and Mg_2Sn in Mg-7Al-Sn (wt.%) alloy are simulated. It is predicted that the precipitation of $Mg_{17}Al_{12}$ is much strong than that of Mg_2Sn.
  - Validated models for Mg alloys will be integrated to PANDAT PanPrecipitation module
  - Open to other users/collaborators in industry/academia

Publications and presentations

- Publications:
  - Zhang, C.; Cao, W.; Chen, S.L.; Zhu, J; Zhang, F.; Luo, A.A.; Schmid-Fetzer, R., “Precipitation Simulation of AZ91 Alloy”, ***JOM***, 2014, 66, (3), pp. 389-396.
  - Luo, A.A.; Sun, W.; Zhong, W.; Zhao, J.C., “Computational Thermodynamics and Kinetics for Magnesium Alloy Development”, ***Advanced Materials and Processes***, 2015, 173, (1), 26-30.

- Presentations :
  - Zhong, W.; Sun, W.; Zhao, J.C. 1; Luo, A.A., “Establishment of Mg Diffusivity Database Using Diffusion-Multiple and CALPHAD Approaches”, Computational Thermodynamics and Kinetics, ***TMS 2015 144th Annual Meeting & Exhibition***, March 15-19, 2015, Orlando, FL.

  - Sun, W.; Zhang, C; Klarner, A.D; Cao, W.; Luo, A.A., “Simulation of Concurrent Precipitation of Two Strengthening Phases in Magnesium Alloys”, Magnesium Technology 2015, ***TMS 2015 144th Annual Meeting & Exhibition***, March 15-19, 2015, Orlando, FL.