Diffusion Databases for Mg-ICME

Project ID: LM036/ORNL

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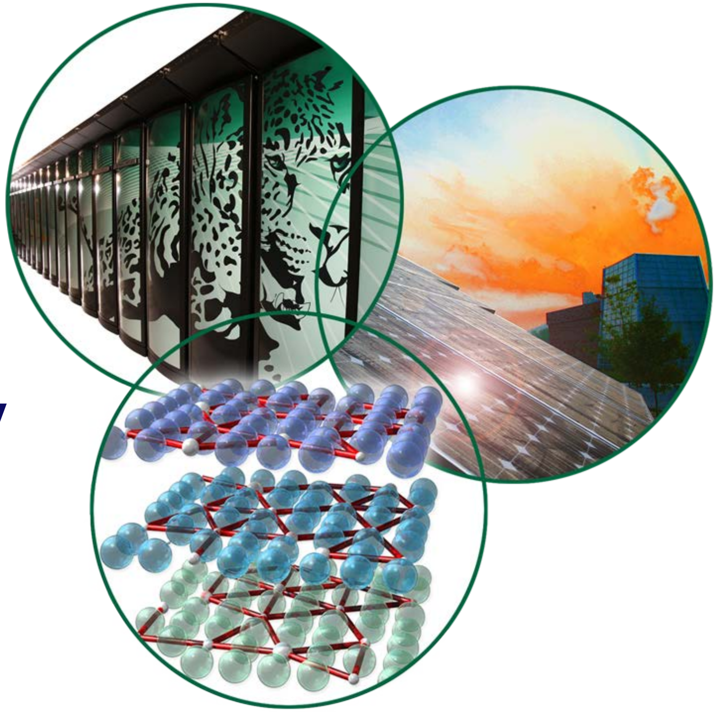

2012 DOE Annual Merit Review & Peer Evaluation Meeting – Vehicle Technologies Program

Washington, D.C.

May 14-18, 2012

OAK RIDGE NATIONAL LABORATORY
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Overview

Timeline

- Project start date: May 2008
- Project end date: Sep 2012
- Percent complete: 75%

Barriers

1. Predictive modeling tools - e.g., ICME
2. Performance – higher performance through predictive modeling
3. Cost – Reducing cost of Mg alloys by modeling for rare earth replacements

Budget

- **Total project funding**
  - DOE share: $2,350K
  - Contractor share: None
- **Funding received in FY11**
  - $600K
- **Funding for FY12**
  - $600K

Partners

- **Universities:**
  - University of Central Florida
  - Virginia Tech
  - University of Newcastle, Australia
- **Industrial Partners (no cost):**
  - U.S. AMP ICME Team
  - Magnesium Elektron
- **Project lead:** ORNL

Objectives

- To develop a Mg tracer diffusion database using primarily secondary ion mass spectrometry (SIMS) for diffusion depth profile measurements of stable isotopes (e.g., ^{25}Mg) in Mg-rich alloys
  - Provide diffusion data for various tasks in the Mg-Integrated Computational Engineering (ICME) project
    - FY11 alloy system investigated: Mg-Al-Zn
    - Included Mg, Zn tracer & diffusion couple studies in hcp Mg-Al, Mg-Zn and Mg-Al-Zn alloys
  - Develop scientific procedures & techniques including:
    - Precision annealing technique for Mg alloys without oxidation, i.e., Shewmon-Rhines capsule design in FY11
    - Analysis of tracer diffusion data using non-linear fitting techniques & integration of various types of diffusion data
    - ORNL website (ornl.gov/sci/diffusion) in FY11 that provides latest experimental data & analysis, and facilitates communication between local and international partners

Relevance to Vehicle Technologies: Materials

- Mg-ICME Objectives:
  - Initiate and coordinate international effort for developing integrated suite of validated computational materials modeling tools for Mg alloy development
  - Tools are linked to analysis systems used in:
    - Manufacturing & engineering design (extrusion, sheet forming and high pressure die casting).
    - Microstructure engineering
    - Future alloy development to meet performance/cost requirements, e.g., Rare earth replacements
  - Education of high-caliber materials-science & engineering students and facilitation of strong local and international collaborations

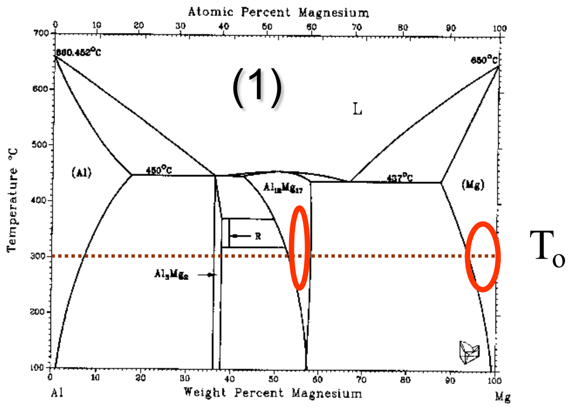
Milestones

Subtasks	FY 2011				FY 2012			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Self-diffusion studies in pure Mg								
Tracer diffusion studies of Mg and Zn in Mg-Al-Zn-Mn alloys								
Tracer diffusion studies of Mg, Nd, Ce in Mg-Al-Nd,Ce alloys								
Interdiffusion studies in Mg-Al-Zn-Mn alloys using diffusion couples								
Diffusion website for data repository, analysis and theory								
Relating interdiffusion and tracer diffusion coefficients using diffusion theory to extract Al, Mn tracer coefficients								
Molecular dynamics simulations of grain boundary diffusion in Mg & effective diffusion simulation								

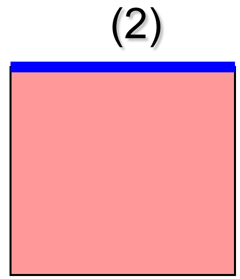
Approach/Strategy

- **Measure tracer diffusion coefficients of Mg, Zn in Mg-rich phases in the Mg-Al-Zn-Mn system using secondary ion mass spectrometry (SIMS) within single grains**
  - Approach primarily based on tracer diffusion in homogeneous alloys is robust, accurate, assumption-free, easier to comprehend and utilize.
  - In case of a monoisotopic element such as Al, interdiffusion experiments involving diffusion couples will be combined with measured tracer diffusivities for Mg, Zn along with thermodynamics to extract tracer coefficients using diffusion theory (e.g., Darken-Manning theories).
- **Unique aspects developed in FY11 include:**
  - Development of Shewmon-Rhines diffusion capsule: (a) to prevent oxidation of Mg-alloys during annealing, (b) to monitor temperature-time profiles of actual samples to correct for heat-up and cool-down times, and conduct accurate analysis.
  - Molecular dynamics simulations of grain boundary diffusion for select grain boundaries in pure Mg.
  - Diffusion website for diffusion data and analysis repository, and improve collaborative efforts between partners.
  - Development of new SIMS technique on angled polish sections in case of deep diffusion depths.

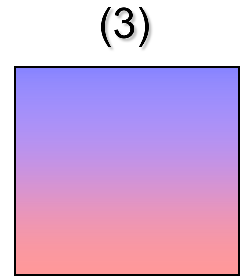
Tracer Diffusion: SIMS-based thin-film stable-isotope technique



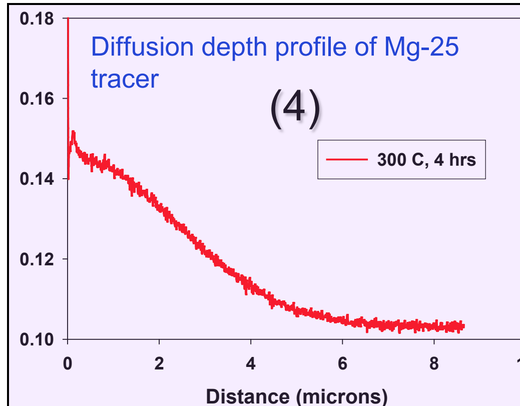
(1) Prepare single phase alloy sample (e.g., Mg-5%Al) at T_o



(2) Deposit thin film (100 nm) of stable isotope of an alloy element (e.g., Mg^{26}) on annealed sample



(3) Anneal at T_o for desired times (mins to hrs) to cause isotope to diffuse inwards

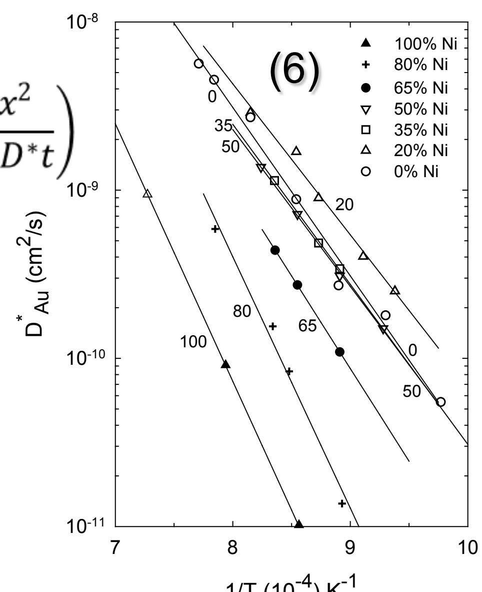


(4) Measure depth profile of isotope or isotope ratio with SIMS

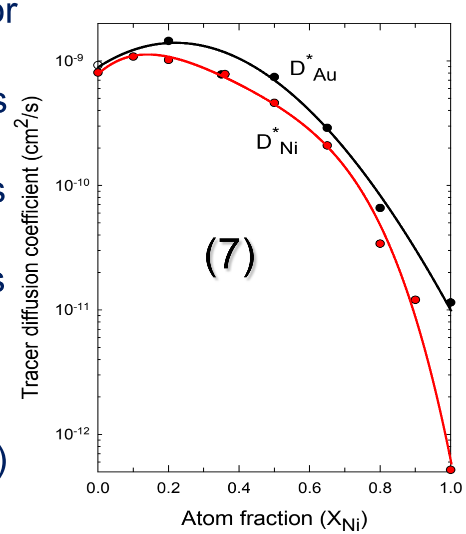
(5)

$$C^*(x,t) \approx \frac{h}{\sqrt{\pi D^* t}} \exp\left(-\frac{x^2}{4D^* t}\right)$$

(5) Fit depth profile data for isotope in (4) with above thin-film solution to extract tracer diffusivity D^*.



(6) Repeat for different temperatures and compositions to check for Arrhenius fits (e.g. Au in Au-Ni alloys, *Kurtz et al., Acta Met.'55*)



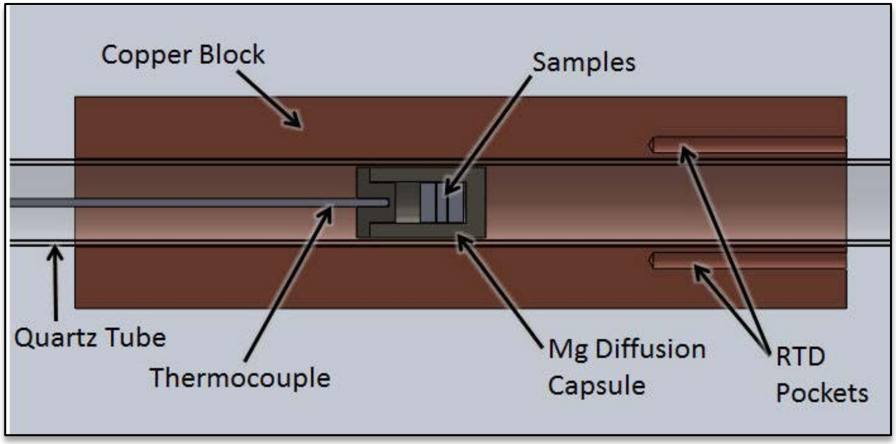
(7) Fit using suitable polynomials for functional form of isotopic diffusivity $D_k^*(X_1, X_2, \ldots, T)$ (e.g. Au-Ni tracer diffusion at 900°C, *Reynolds et al. Acta Met.'57*)

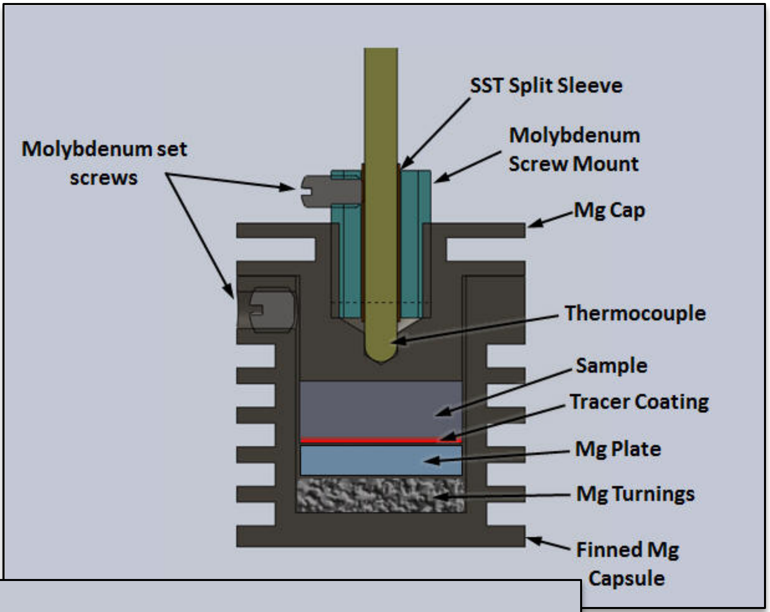
Technical Accomplishments and Progress

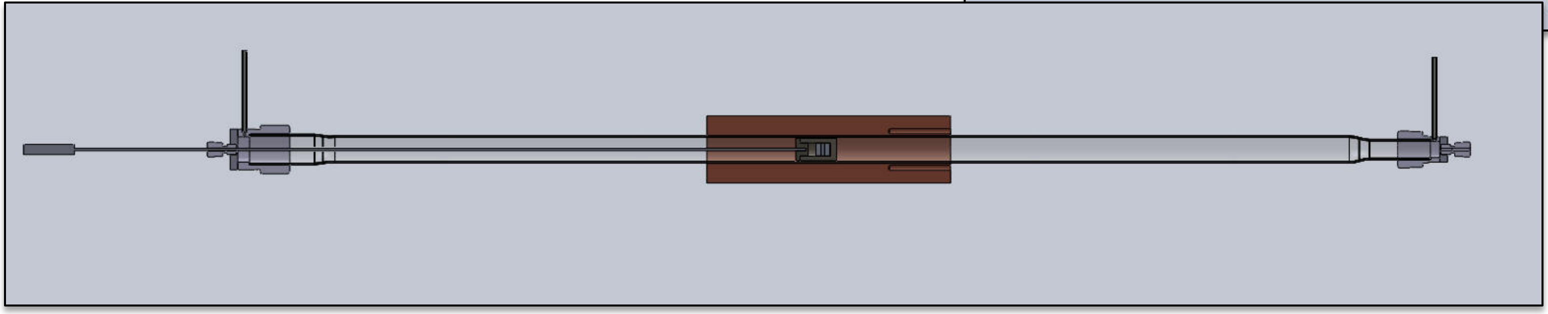
Key Areas of accomplishments/progress:

A. Improved diffusion annealing based on Shewmon-Rhines technique with precision temperature monitoring
B. Mg-self diffusivities using SIMS-based thin-film stable-isotope technique that validated and extended historic radiotracer data
C. Mg & Zn tracer diffusion in polycrystalline Mg-Al-Zn alloys
D. Interdiffusion Studies in Mg-Al-Zn
E. Molecular Dynamics simulations of grain boundary diffusion in Mg
F. Collaborative diffusion website for data, results and theory

A: Diffusion annealing technique





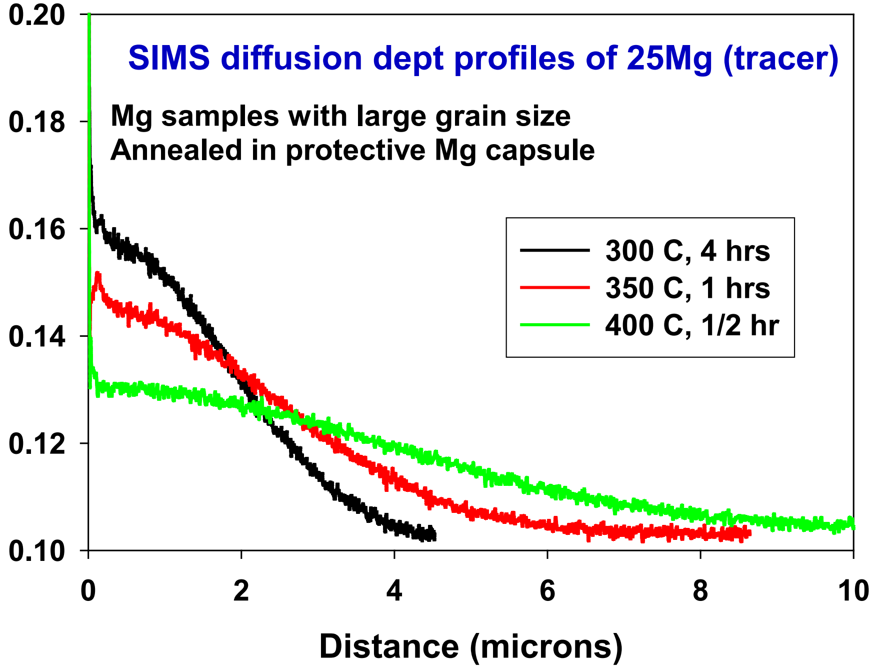


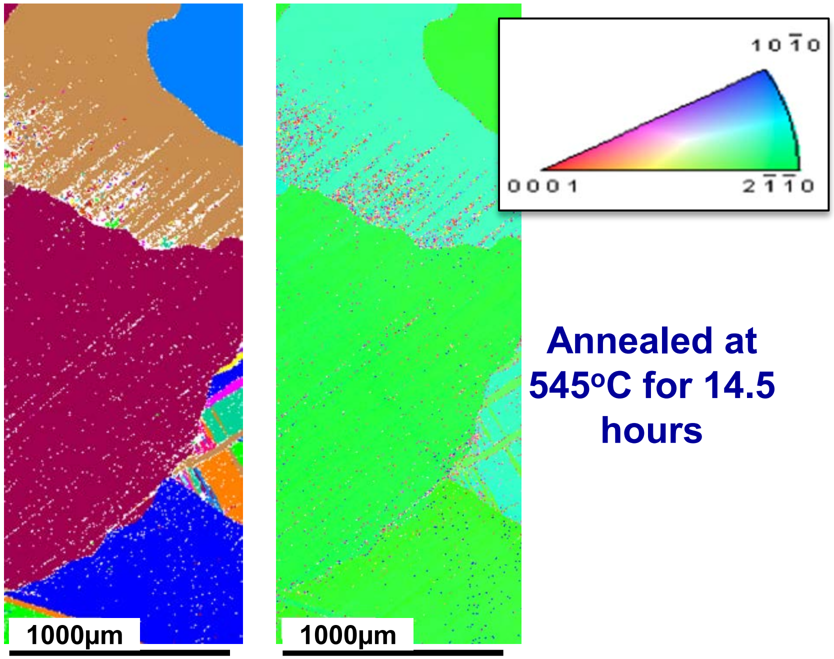
- Design allows rapid heating (Cu block, fin design) and cooling (liquid nitrogen)
- Mg capsule & turnings act as natural getter to prevent oxidation
- Thermocouple in capsule allows full correction and more accurate analysis especially for short anneal times (10 minutes)

B. Mg self-diffusion validation with published radiotracer data

FY11 data

Large-grained Mg samples using diffusion capsule for annealing





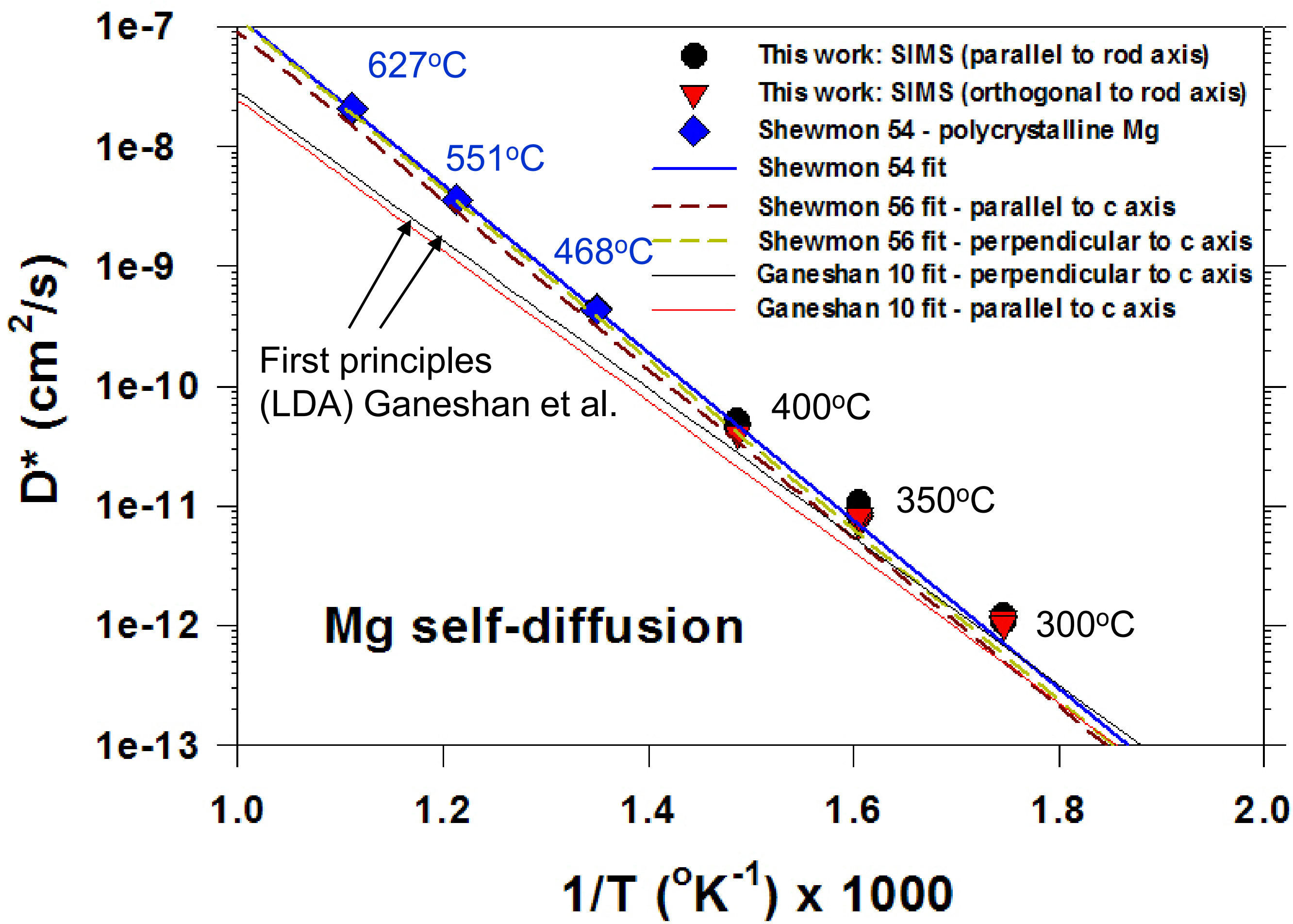
Annealed at 545°C for 14.5 hours

SIMS concentration depth profiles of ^{25}Mg as a function of depth in Mg polycrystalline samples with very large grain sizes (hundreds of µm)

Electron Backscatter Diffraction (EBSD) map (inverse pole figure – top right) of grain orientations in a pure polycrystalline Mg rod after annealing treatment. *left*: Identical grain structure map with enhanced contrast.

- ***Optimized SIMS profiles within single grains yield more accurate bulk diffusivities***

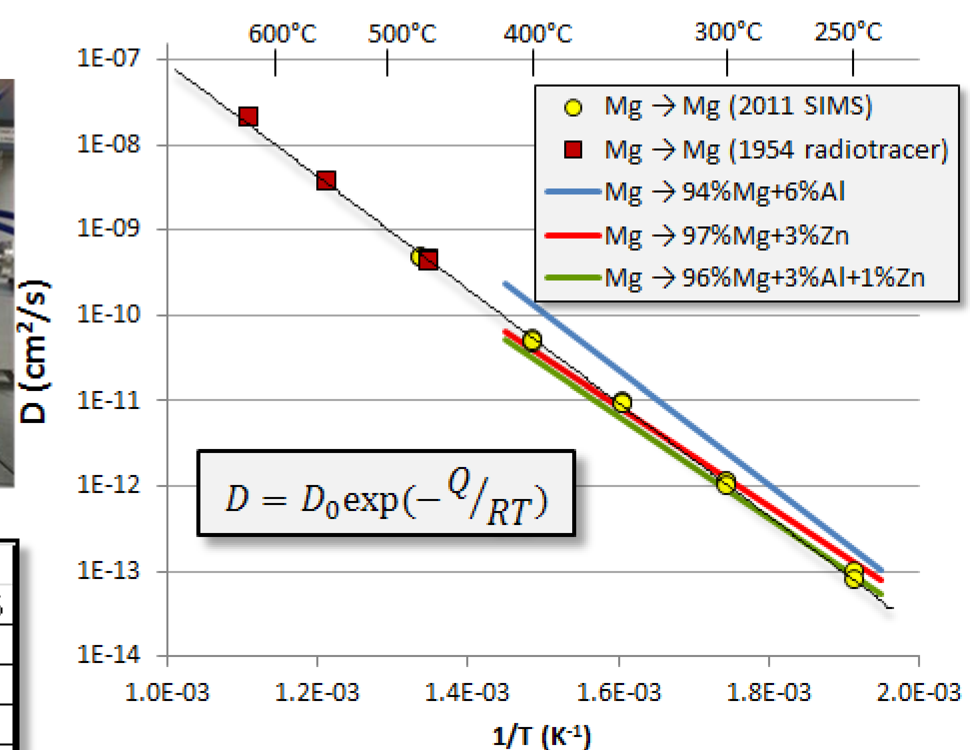
Mg self-diffusion validation contd.



- *Experimental results consistent with polycrystalline radiotracer measurements*
- *Tracer diffusivities in directions parallel to rod axis are higher (by 5-24%) compared to diffusivities normal to rod axis (orthogonal)*

C. Mg & Zn tracer diffusion in polycrystalline Mg-Al-Zn alloys

Setup for thin film sputter deposition on Mg alloy samples.

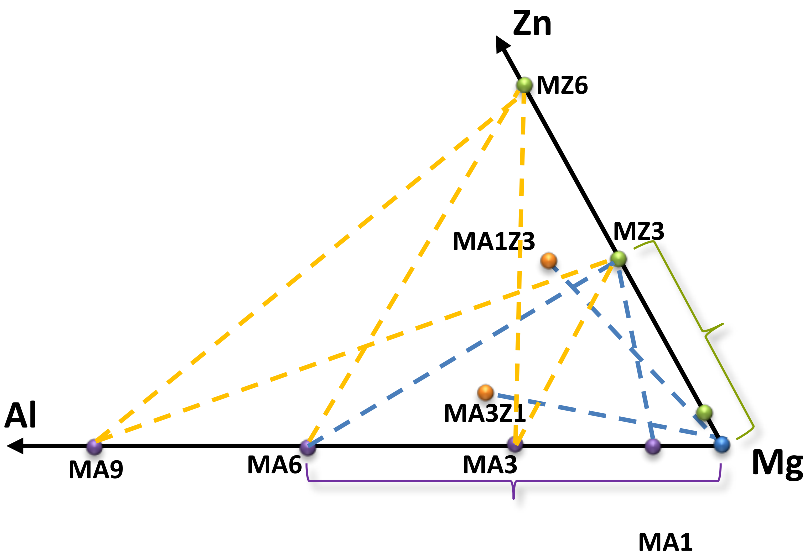


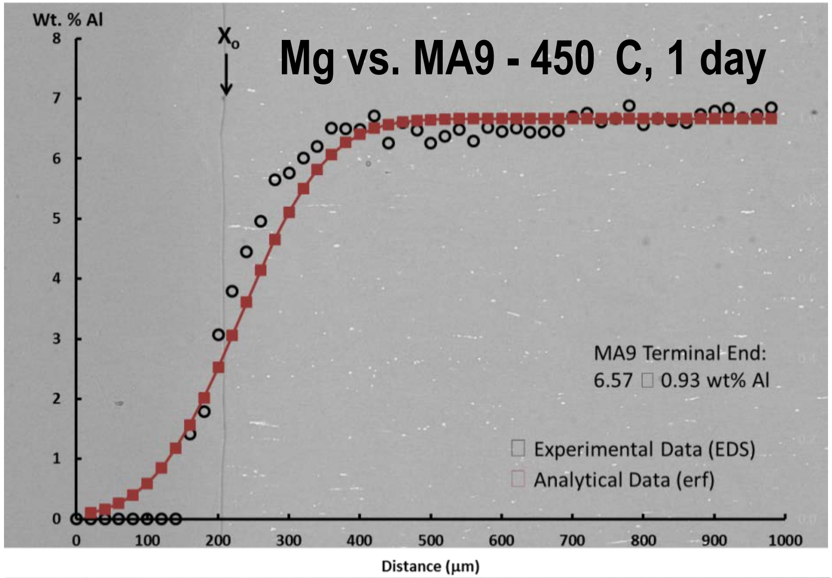
	Mg		MA6		MZ3		MA3Z1	
	Wt %	At %	Wt %	At %	Wt %	At %	Wt %	At %
Mg	100	100	93.3	93.9	97.4	99	96	96.9
Al	-	-	6.7	6.1	-	-	2.9	2.7
Zn	-	-	-	-	2.6	1	1	0.4
D_0 (cm^2/s)	0.42		1.15		0.017		0.022	
Q (kJ/mol)	127		128		111		114	

Mg tracer diffusivities as a function of reciprocal temperature for pure Mg and three Mg alloys (Wt %)

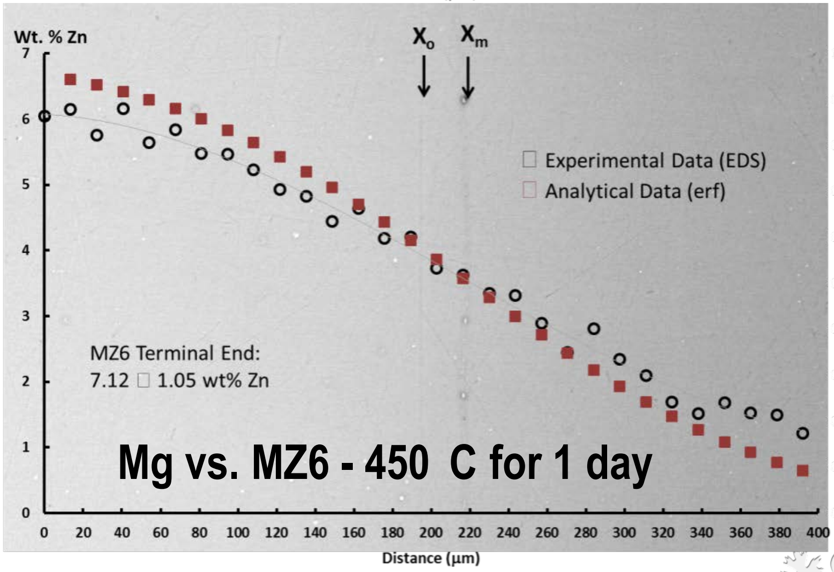
➢ ***Mg and Zn tracer data in a number of Mg-Al-Zn alloys is being collected (8-10 alloy compositions in ternary by summer 2012)***

D. Interdiffusion Studies in Mg-Al-Zn





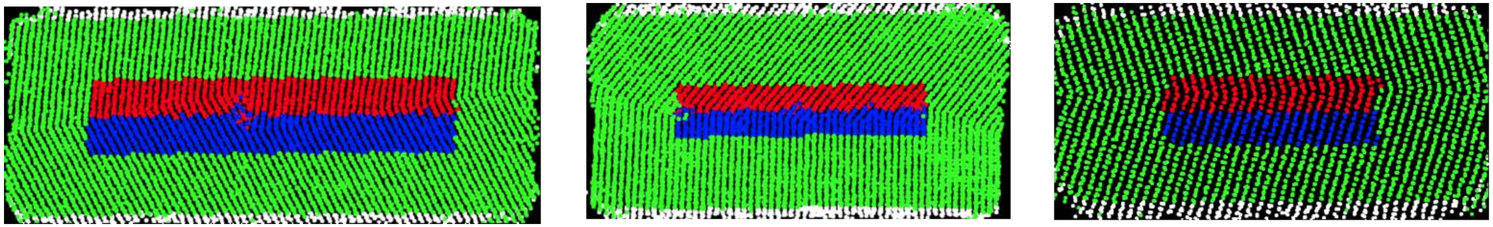
Selected diffusion couples in hcp Mg-Al-Zn for interdiffusion studies



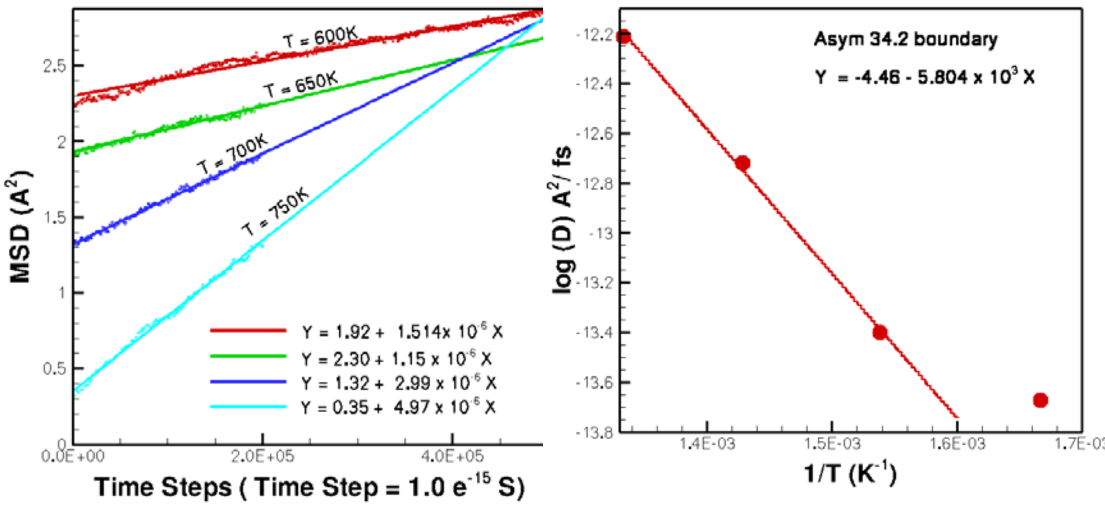
- ***Interdiffusion data combined with measured Mg tracer (this work) and thermodynamic data (Φ) is used to compute unknown Al tracer diffusivity using diffusion theory (Darken-Manning relations)***

D_{inter} (Mg s.s.) = [$X_{Mg} D^*_{Al} + X_{Al} D^*_{Mg}$] Φ Darken relation in binary Mg-Al

E. Molecular Dynamics Simulation of Grain Boundary Diffusion in Mg



Atomic structures of the 34.2°asymmetric tilt (left), 40.3°general (center) and 34.2° symmetric (right) boundaries after expansion and equilibration at 750K. The red and blue atoms correspond to the ones used for measuring MSD. The white atoms at the free surface are constrained to move parallel to grain boundary.



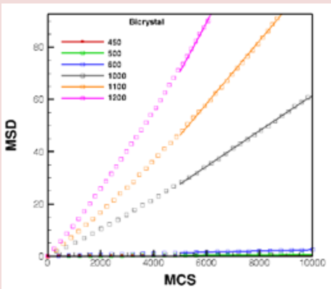
Mean square displacement measurements for the asymmetric tilt boundary as a function of temperature (top left) and the Arrhenius plot (top right) for calculating the activation energy.

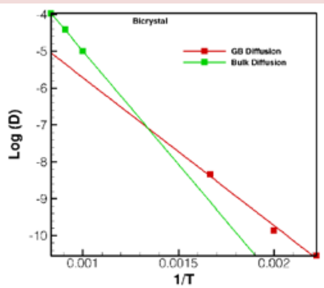
Grain Boundary Type	Activation Energy (Cal/mole)	D at 750K (cm^2/s)
34.2 asymmetric	11,680	4.97×10^{-7}
40.3 general	13,480	5.0×10^{-7}
34.2 symmetric	----	-----

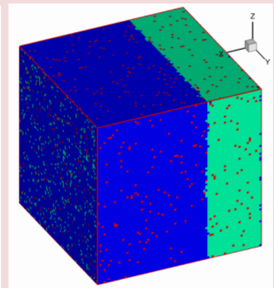
Calculated diffusion coefficients and activation energies for the selected boundaries. The symmetric tilt boundary did not show any measurable mean square displacement at the highest temperature (750K).

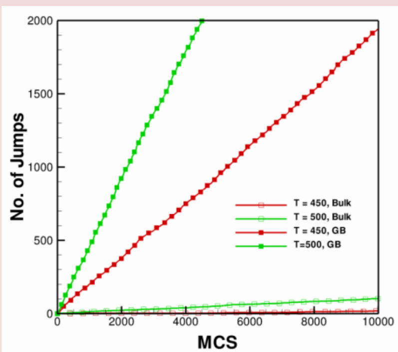
- ***The simulated diffusion coefficients for the two tilt boundaries at 750 K were at least three orders of magnitude higher than the value for volume diffusion in polycrystalline magnesium at 741 K experimentally measured by Shewmon and Rhines (1954).***

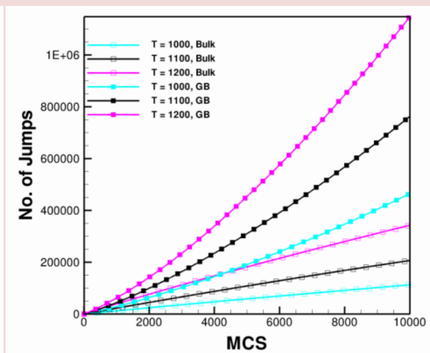
Effective diffusion coefficient for a bicrystal & polycrystal using random walkers





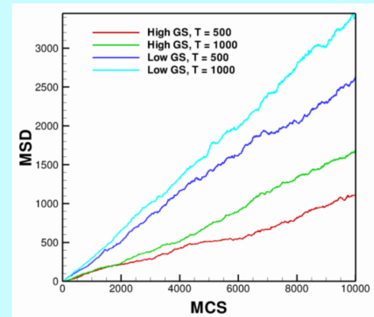


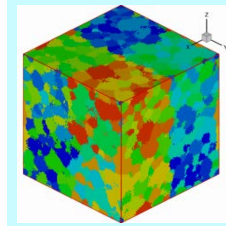


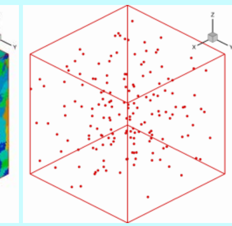


- MSD curves are non-linear
- Effective diffusion coefficients obtained from long-time slope of MSD-time curves
- Simulations show the transition from GB dominated diffusion at low T to bulk dominated diffusion at high T

Bicrystal Simulations







3-D grain structure and the random walkers

- Effective diffusivity increases with decreasing grain size
- Effective diffusivity increases with temperature at a give grain size

Polycrystal Simulations

Future Work

- ***Validate mesoscale model for tracer diffusion in polycrystalline magnesium***
- ***Extend the model for chemical diffusion in two component Mg alloy (Mg-Al)***
- ***Investigate the effect of simultaneous evolution of microstructure during diffusivity measurements***

F: ORNL Diffusion website

- http://www.ornl.gov/sci/diffusion (private)

Note: The contents of this website are confidential and are restricted to the collaborators listed below and to their in-house associates. The contents are for their personal use and may not be distributed without permission of the PI.

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Isotopic Diffusion Databases for Magnesium Integrated Computational Materials Engineering (Mg-ICME)

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- Diffusion
- Interdiffusion
- Theory
- Communications
- Literature

Principal Investigator: Nagraj Kulkarni, Oak Ridge National Laboratory (865) 576-0592; e-mail: kulkarnins@ornl.gov

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VirginiaTech Invent the Future

UNIVERSITY OF CENTRAL FLORIDA

THE UNIVERSITY OF NEWCASTLE AUSTRALIA

Industrial Partner: U.S. Automotive Materials Partnership Integrated Computational Materials Engineering (ICME) Team, Magnesium Electron North America

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Resources

- Team Personnel
- UCF Facilities
- SIMS-XPS VaTech

http://www.ornl.gov/sci/diffusion/index.html 2/29/2012

Home | Diffusion | Interdiffusion | Theory | Communications | Literature

Experimental Progress in Diffusion Studies

- 20120201 Mg-25 tracer diffusion into alloys - new
- Zn Tracer
- 20110915-20120120 Mg MAZ alloy samples - grain growth and conditioning anneals (xlsx catalog)
- 20110823-1109 Mg-25 Deposition and Diffusion of Mg-25 into Mg: Mg Self-Diffusion Summary
- 20110826-0903 Temperature Equilibration
- 20110815 Mg MAZ alloys - elemental analysis of Mg MAZ alloys
- 20110809 Annealing 99.9% Mg, 595°C, 9hr
- 20110801 Temperature equilibration of a dummy sample.html
- 20110728 Anneal 99.9% Mg, 597°C, 9hr
- 20110719 Encapsulation and annealing
- 20110614 Annealing attempt with bare Mg pellet

Alloy Catalog (xlsx)
ASM phase diagrams

Apparatus

- Annealing encapsulation
- Annealing Furnace
- Thermometry
- Abrasive grit sizes (xls)
- Diamond Sawing
- Sputter Coating

Mg Abundances			
Isotope	^{24}Mg	^{25}Mg	^{26}Mg
Natural	0.7899	0.1001	0.1100
Tracer1	0.0180	0.9787	0.0033
Tracer2	0.0183	0.9786	0.0031

Al Abundances		
Isotope	^{26}Al	^{27}Al
Natural	trace	1.000
Tracer		

Zn Abundances					
Isotope	^{64}Zn	^{66}Zn	^{67}Zn	^{68}Zn	^{70}Zn
Natural	0.4889	0.2781	0.0411	0.1857	0.0062
Tracer	0.0012	0.0011	0.0005	.9971	0.0001
Tracer2 (NA)	0.0099	0.0081	0.0038	0.978	0.0002

Mn Abundances		
Isotope	^{53}Mn	^{55}Mn
Natural	trace	1.000
Tracer		

- NIST SRM980 Specs
- Galy 2003 - Magnesium isotope heterogeneity of the isotopic standard SRM980
- Coplen 2002 - Isotope Abundance Var of Selected Elements.pdf
- Rosman 1997 - Isotopic compositions of the elements.pdf

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Collaborations and Coordination

OAK RIDGE NATIONAL LABORATORY
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- Annealing
- Analysis
- Modeling

THE UNIVERSITY OF NEWCASTLE AUSTRALIA

Theory

$$\delta C = C_0 \frac{\delta\xi}{2\sqrt{\pi D t}} \exp\left(-\frac{\xi^2}{4Dt}\right)$$

UNIVERSITY OF CENTRAL FLORIDA

- Coating
- Interdiffusion
- Analysis

ORNL project coordination

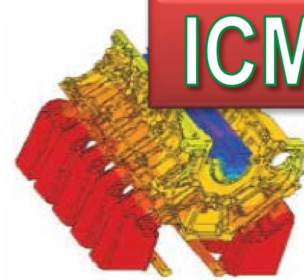
VirginiaTech Invent the Future

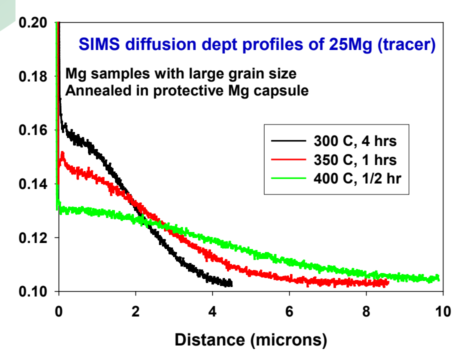
- SIMS
- XPS
- Characterization

Magnesium Elektron
SERVICE & INNOVATION IN MAGNESIUM

- Material casting
- Extrusion

ICME-CI



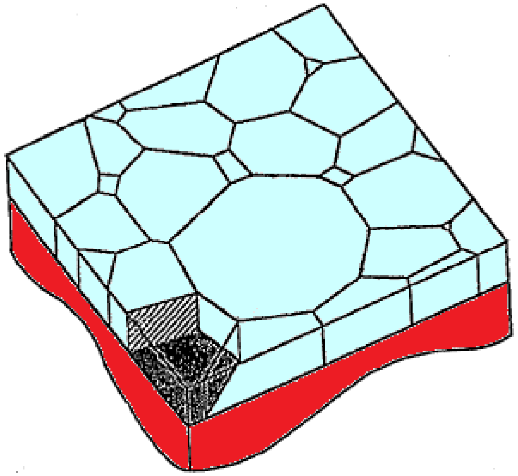


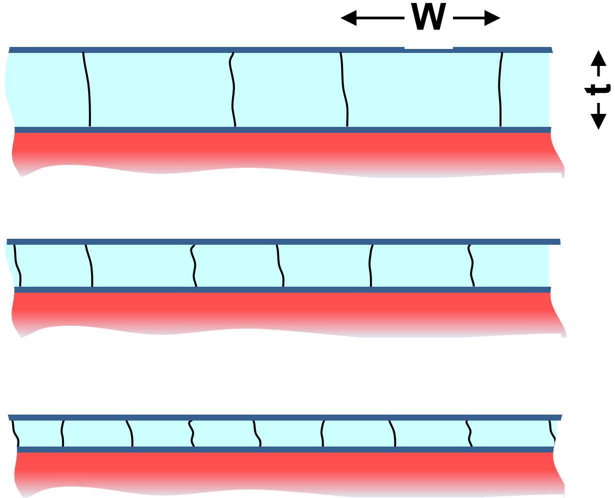
Proposed Future Work

- **Future work in remainder of FY12:**
  - Mg, Zn tracer diffusion experiments and analysis in Mg-Al-Zn-Mn alloys
  - Interdiffusion measurements using incremental diffusion couples in Mg-Al-Zn-Mn alloys to extract Al, Mn tracer diffusivities
  - Mg, Nd, Ce tracer diffusion studies in Mg-Al-Nd, Ce alloys (only preliminary data likely)
  - Initiate experimental work on continuously selectable alloys and grain-boundary diffusion
- **Future work in FY13 (proposed):**
  - Tracer diffusion and interdiffusion experiments and analysis in Mg-Al-Nd,Ce alloys
  - Tracer diffusion studies in rare-earth replacement alloys (e.g., Mg-Sn-X)
  - Experimental and theoretical grain-boundary studies
  - Thermodynamic measurements (enthalpy, phase stability & activity measurements) and optimization (with ICME team) in Mg-RE and Mg-RE replacement alloys

Grain boundary diffusion using thin films

- The proportion of diffusion due to bulk and boundary effects can be controlled through grain size
- Grain size is generally pinned by top and substrate boundaries to be ~2X the thickness of annealed thin films
- Co-deposition of Mg, Al and Zn produces variety of alloy films for diffusion studies





Summary

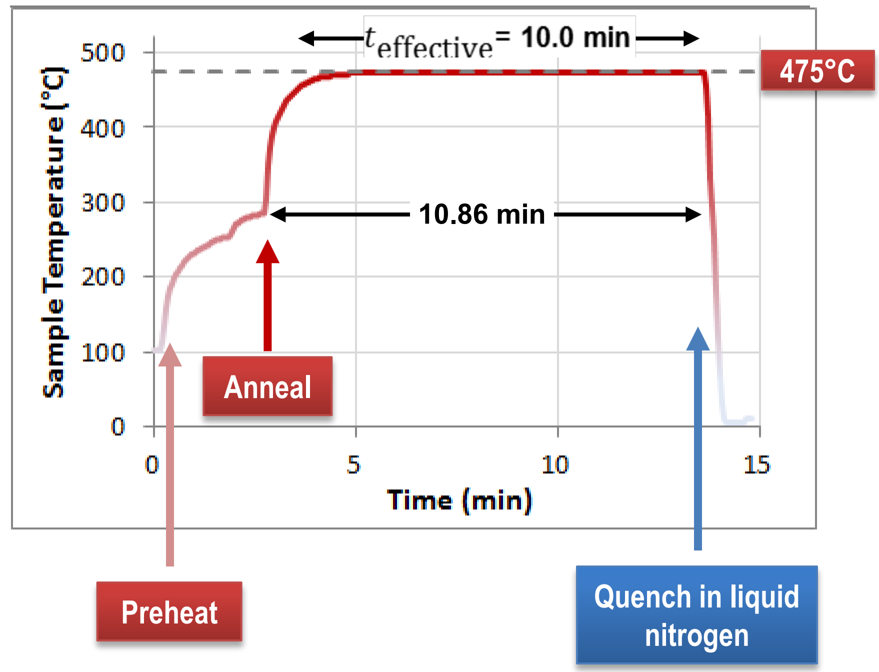
- **Relevance**
  - A tracer diffusion database in Mg alloys is of fundamental importance to the ICME and other integrated materials design efforts (e.g., Materials Genome Initiative) in establishing design and modeling tools, optimizing manufacturing processes, and predicting performance requirements.
- **Key accomplishments/progress**
  - Obtained Mg self-diffusivities in pure polycrystalline Mg samples using our SIMS-based thin-film stable-isotope technique, validating and extending historic radiotracer measurements to lower temperatures.
  - Obtained Mg & Zn tracer diffusivities in a number of alloys in the Mg-Al-Zn system.
  - Developed a superior annealing technique for Mg based on the Shewmon-Rhines approach.
  - MD simulations of select grain boundary diffusivities in polycrystalline Mg revealed that these were about three orders of magnitude larger the volume diffusivities.
  - Conducted interdiffusion studies in the Mg-Al-Zn system using solid-to-solid diffusion couples that were annealed at various temperatures and times.
  - Diffusion website that facilitated communication between local and international collaborators, and served as a repository for data, experiments, analysis, theory and relevant literature.

Technical Back-Up Slides

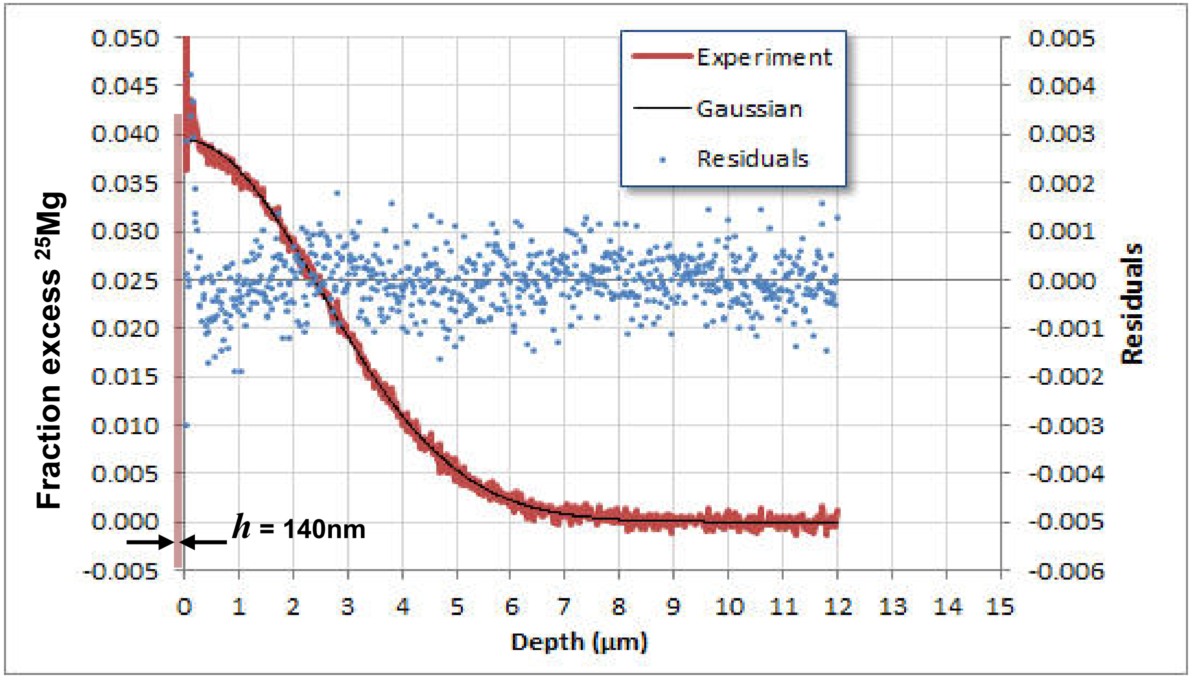
Mg self-diffusion validation contd. Temperature profile corrections

- Effective time at annealing temperature can be calculated using the actual profile and the activation energy (Rothman 1984)
- New capsule design allows rapid change *and* real-time temperature measurement for precise correction, even for times < 10 minutes
- Example shows 8.6% correction for Mg at 475°C for ~10 minutes

$$t_{\text{effective}} = \int \exp\left[-\frac{Q}{R}\left(\frac{1}{T(t)} - \frac{1}{T_{\text{anneal}}}\right)\right] dt$$



Mg self-diffusion validation contd.: Fitting of diffusion depth profiles



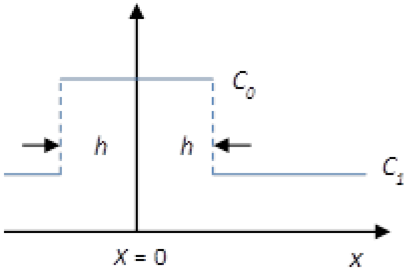
Example of SIMS measured excess abundance of tracer (Mg-25) as a function of depth for a magnesium sample diffused for ~1 hour at 350°C. The thin black curve shows the fit to obtain the diffusion coefficient and the blue dots are the residuals or differences between the experimental and fitted points. The fitted initial isotopic film thickness, h, is consistent with independent thickness measurements.

Thin-film error function solution

$$f(x) = \frac{C(x) - C_B}{C_0 - C_B} = \frac{1}{2}\left[\mathrm{erf}\left(\frac{x+h}{2\sqrt{Dt}}\right) - \mathrm{erf}\left(\frac{x-h}{2\sqrt{Dt}}\right)\right]$$

$$f(x) = \frac{C(x) - C_B}{C_0 - C_B} \approx \frac{h}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right)$$

If $h \ll 2\sqrt{Dt}$



- ➢ ***Thin-film error function solution fit (least-square) to obtain diffusivity, background abundance and initial tracer film thickness.***

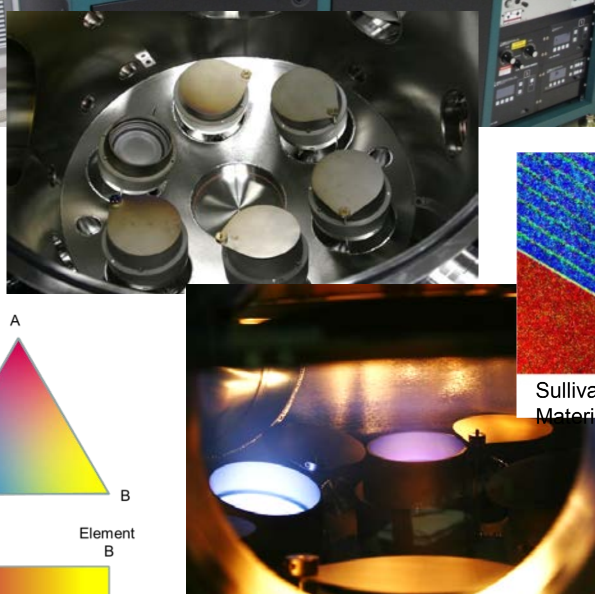
Mg-Al-Zn (MAZ) alloy synthesis & characterization

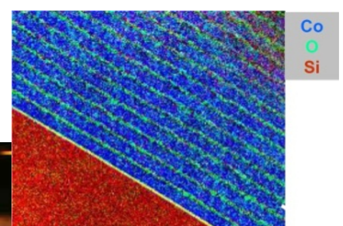
		Nominal composition (weight %)			Chemical analysis (weight %)						
Alloy	Phase	Mg	Al	Zn	Al	Zn	Mn	Ca	Pb	Si	Fe
MA1	α	99	1	0	0.97	0.0049	0.0054	0.0026	0.0021	0.0031	0.003
MA3	α	97	3	0	2.81	0.0035	0.0054	0.0036	0.0001	0.0043	0.0053
MA6	α	94	6	0	6.73	0.0056	0.0056	0.002	-	0.0029	0.0021
MA9	α	91	9	0	9.59	0.016	0.0054	0.0023	-	0.0025	0.0021
MA15*	α + γ	85	15	0	14.4	0.01	0.0049	0.002	-	0.0019	0.0023
MZ0.5	α	99.5	0	0.5	0.0065	0.49	0.0052	0.0022	0.0039	0.0037	0.0019
MZ1	α	99	0	1	-	0.84	0.0054	0.004	0.0038	0.0032	0.0022
MZ3	α	97	0	3	-	2.62	0.0052	0.0018	0.0033	0.0032	0.0029
MZ6	α	94	0	6	0.01	6.23	0.0052	0.0027	0.0029	0.0053	0.0021
MZ9*	α + δ	91	0	9	0.22	9.5	0.0053	0.0014	0.0026	0.0062	0.0021
MA3Z1	α	96	3	1	2.92	0.96	0.0055	0.0035	0.002	0.0047	0.0056
MA5Z2	α	93	5	2	5.12	1.96	0.0054	0.0027	-	0.0032	0.0022
MA1Z3	α	96	1	3	0.97	2.99	0.0052	0.0019	0.0021	0.0039	0.002
MA3Z3	α	94	3	3	2.95	2.96	0.0055	0.003	0.0002	0.0051	0.0057
MA1Z1	α	98	1	1	0.99	0.9	0.0054	0.0036	0.002	0.0035	0.0033

α: Hcp (hexagonal close packed); γ: $Mg_{17}Al_{12}$; δ: MgZn

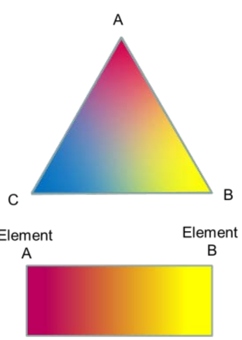
Other elements detected in trace amounts are Cu (<20 ppm), Sn (<20 ppm), Ni (<5 ppm), Zr (< 10 ppm) (ppm = parts per million).

Alloy film magnetron co-sputtering for Mg-alloys & compounds





Sullivan, CR. Laminated Materials Presentation



Composition Spreads

- Six by three-inch source magnetron sputtering system sponsored by ORNL to produce continuously variable alloys and films for grain-boundary studies
- Source tilt externally adjustable for producing either wedge or highly-uniform confocal coatings
- Substrate RF biasing for substrate plasma cleaning or ion-assisted deposition, 600 C substrate heating
- Load lock sample exchange for quick substrate changes with low chamber contamination.
- UHV base pressure of 10^{-9} Torr

Magnetron Co-sputtering System

Mesoscale simulation approach

- Input to the model is a realistic 3-d microstructure that matches experimental conditions
  - Either simulated or mapped from 2-d characterization data
- Random walkers are introduced and operate at the mesoscale
- Large 3D microstructures with periodic boundary condition
- The properties of the random walkers obtained from lower length scale models
  - Apparent activation energy for bulk, grain boundary or triple line diffusion
  - Flip attempt frequency is proportional to the activation energy
  - For each walker the local neighborhood defines the location type
- Diffusivity measured from simulation of mean square displacement (MSD) of walkers
- To introduce large number of non-interacting walkers large microstructure is required (need for parallel computing)