Diffusion Databases for ICME

Project ID: LM036

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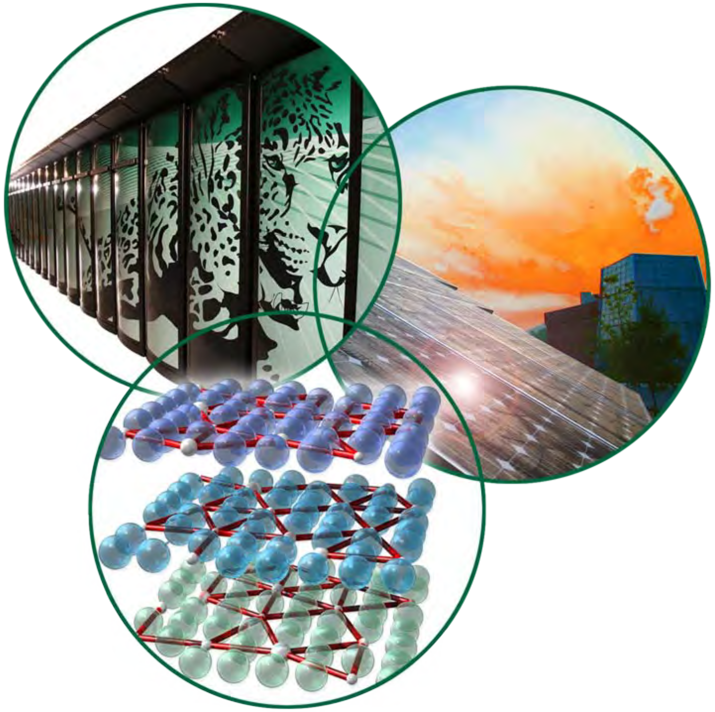


2011 DOE Vehicle Technologies Program Review

Washington, D.C.

May 12, 2011

Overview

Timeline

- Project start date: May 2008
- Project end date: Sep 2011
- Percent complete: 50%

Barriers

- Barriers addressed
  1. Design data and modeling tools
  2. Manufacturability
  3. Performance

Budget

- **Total project funding**
  - DOE share: $1750K
  - Contractor share: None
- **Funding received in FY10**
  - $600K
- **Funding for FY11**
  - $600K

Partners

- **Universities:**
  - University of Central Florida
  - Virginia Tech (Sep 2010)
  - University of Newcastle, Australia (Feb 2011)
- **Industrial Partners (no cost):**
  - U.S. AMP ICME Team
  - Magnesium Elektron (Jan 2011)
- **Project lead:** ORNL

Objectives

- To develop a Mg tracer diffusion database using secondary ion mass spectrometry (SIMS) for diffusion depth profile measurements of stable isotopes (e.g., ^{25}Mg) in Mg-rich alloys used in automotive materials
  - Provide diffusion data for various tasks in the Mg-Integrated Computational Engineering (ICME) project
    - Mg Alloy system being investigated: Mg-Al-Zn-Mn
  - Develop scientific methods & analysis including:
    - Techniques/procedures for secondary ion mass spectrometry (SIMS) used for isotopic (tracer) diffusion studies in Mg polycrystalline alloys
    - Ultra-high vacuum (UHV) deposition system for thin film isotopic deposition of reactive elements such as Mg
    - Integration of various types of diffusion data, e.g., interdiffusion/intrinsic diffusion, to extract tracer diffusion data for monoisotopic elements (e.g., Al)
    - Effective diffusivity model that incorporates diffusion contributions due to variations in microstructure, e.g., grain size distribution, grain boundaries.

Relevance to Vehicle Technologies: Materials

- Mg-ICME Objectives:
  - Initiate and co-ordinate 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
  - Education of high-caliber materials science & engineering students and facilitate strong collaborative efforts
  - Address scientific & technical gaps in fundamental knowledge base

Milestones & Metrics

Go/No-Go

Subtasks	Year 1: 2008				Year 2: 2009				Year 3: 2010				Year 4: 2011			
			Q 3	Q 4	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2	Q 3	Q 4
Synthesis of ^{25}Mg, ^{68}Zn isotope foils; **SIMS techniques** & procedures in ims7f-Geo												✓				
UHV sputter deposition system for high-purity, thin films of enriched isotopes											✓					
Tracer diffusion studies of ^{25}Mg**,** ^{68}Zn **in Mg-Al-Zn**												✓*			✓	
Tracer diffusion studies of ^{25}Mg in **Mg-Al-Mn**																
Tracer diffusion of **radioactive** Al, Mn in Mg-Al-Zn, Mg-Al-Mn #																
Interdiffusion studies in binaries/ternaries using diffusion couples												✓*			✓	
Relating interdiffusion and tracer diffusion coefficients using diffusion theory																

Contingent upon availability of radioisotope ^{26}Al and Time of Flight (TOF) SIMS system at ORNL to handle radioactive samples

✓* **Partially completed (binary alloys)**

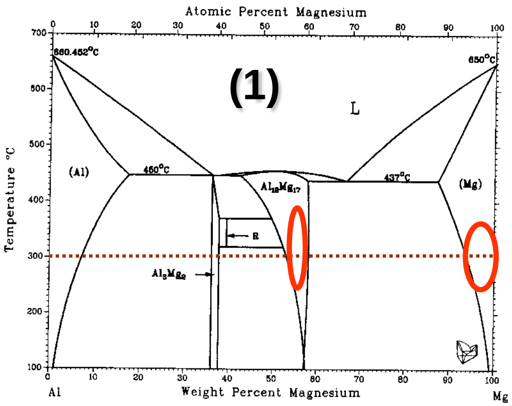
✓ **Completed (including ternary alloys)**

Approach/Strategy

- Measure tracer diffusion coefficients for Mg-rich phases in the Mg-Al-Zn-Mn system by analysis of diffusion depth profiles of isotopes in Mg alloys that are measured using secondary ion mass spectrometry (SIMS)
  - Approach based on tracer diffusion in homogeneous alloys is robust, accurate, assumption-free, independent of thermodynamic databases, and easier to comprehend and utilize.
    - Hence approach is superior to "mobility" diffusion databases developed by diffusion software "DICTRA" (Sweden).
  - Details of the technical approach for tracer diffusion measurements/analysis called the "thin film approach" are illustrated in the next slide.

- *Unique aspects include:*
  - Use of stable isotopes (^{25}Mg, ^{68}Zn) rather than radioactive isotopes as tracers thus utilizing vast DOE stable isotopic repository and reducing R&D costs associated with handling and processing radioactive isotopes
  - Utilization of latest SIMS system (Cameca ims7f-Geo) for routine diffusion depth profile measurements of stable isotopes diffused in polycrystalline Mg alloys at various temperatures and times
  - Development of new SIMS techniques, e.g., SIMS measurements on angled polish (<2 degrees taper) sections to solve technical barriers
  - Design & development of a ultra-high vacuum (UHV) system to minimize isotopic losses and provide high-purity isotopic thin films on alloys
  - Use of interdiffusion/intrinsic diffusion experiments (involving traditional diffusion couples) along with thermodynamics to extract tracer diffusivities of monoisotopic elements such as Al and Mn
    - For radioactive isotopes such as Al (^{26}Al), a cheaper Time of Flight (TOF) SIMS system has been proposed at ORNL.
  - Experimental analysis and 3D modeling of volume and grain boundary diffusion in polycrystalline Mg alloys to incorporate microstructure effects

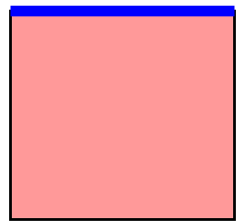
Thin Film Approach for Tracer Diffusion Measurements/Analysis



T_o

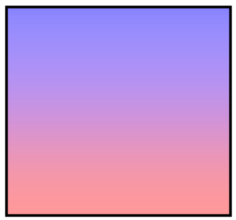
(1) Prepare single phase alloy sample (e.g., Mg-5%Al) at T_o

(2)

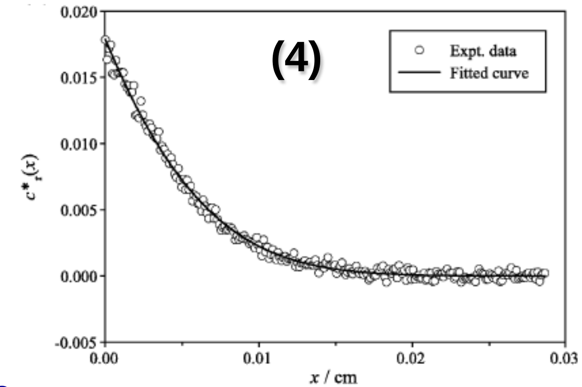


(2) Deposit thin film (100 nm) of enriched isotope of an alloy element (e.g., Mg^{25}) on sample surface

(3)



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

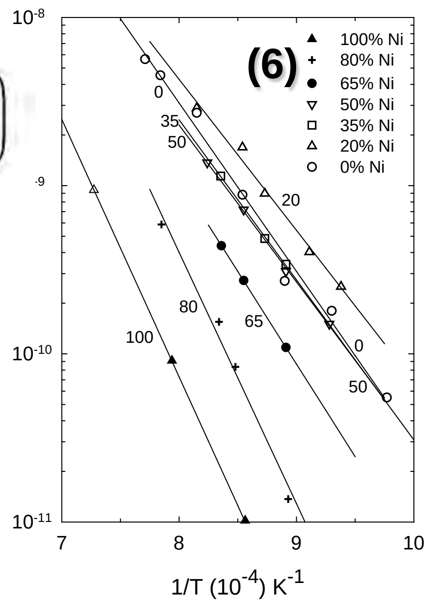


(4) Measure depth profile of isotope or isotope ratio with SIMS (e.g., O^{18} with Time of Flight technique, *De Souza et al., Sol. State Ionics '05)*

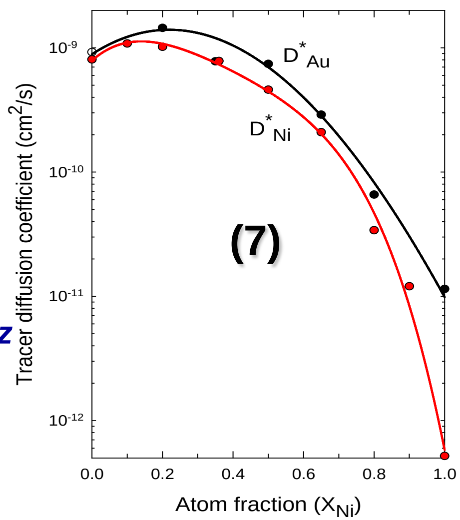
(5)

$$c^*(x,t) = \frac{S}{2\sqrt{\pi D^* t}} \exp\left(-\frac{x^2}{4D^* t}\right)$$

(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

Five Key Areas of accomplishments/progress:

A. Sample Preparation and Control of Instrument Parameters in the Cameca ims7f-Geo SIMS System for Depth Profile Measurements in Mg alloys

B. Ultra-High Vacuum (UHV) Thin Film Deposition System/Validation

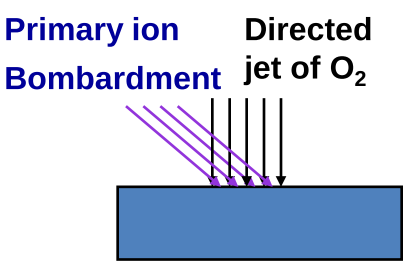
C. Mg tracer diffusion in polycrystalline Mg samples
   - Mg-Al-Zn alloy measurements planned in Spring 2011

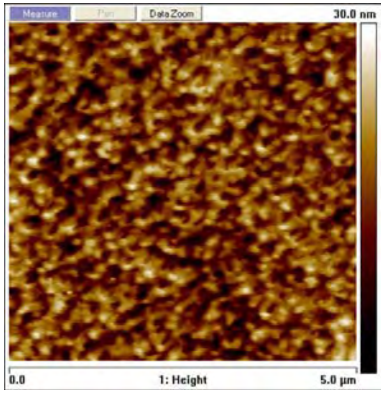
D. Interdiffusion Studies in Mg-Al, Mg-Zn

E. Volume and grain boundary diffusion modeling in polycrystalline microstructures

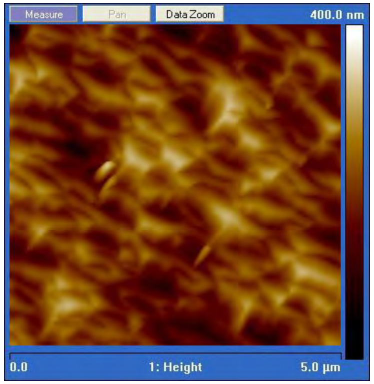
A. Control of Instrument Parameters in Cameca ims7f-Geo SIMS System

- Metallic layers that are polycrystalline will form sputtered topography under most primary bombardment conditions
  - For certain metals this topography can be minimized or eliminated by careful selection of primary bombardment conditions (species, energy, angle, etc.) in the imsf7f-Geo SIMS system.
  - E.g., for Al and Mg that from highly reactive and form amorphous oxides readily, a controlled O leak during analysis is beneficial (available with ims7f-Geo)
    - Amorphous oxide is relatively insensitive to orientation-dependent differential sputtering
  - A eucentric substrate rotation stage ($150K) may also be utilized (not available currently).
- Minimization of the sputter topography is critical for the accurate measurement of diffusion data
  - Otherwise leads to broadening of depth profile, incorrect slopes and hence inaccurate data

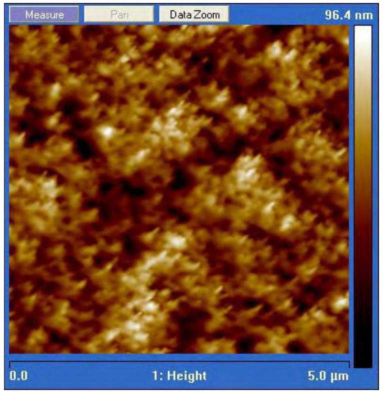




As-deposited 2 µm Mg film:
Atomic Force Microscopy (AFM) average roughness - R_a ~7 nm



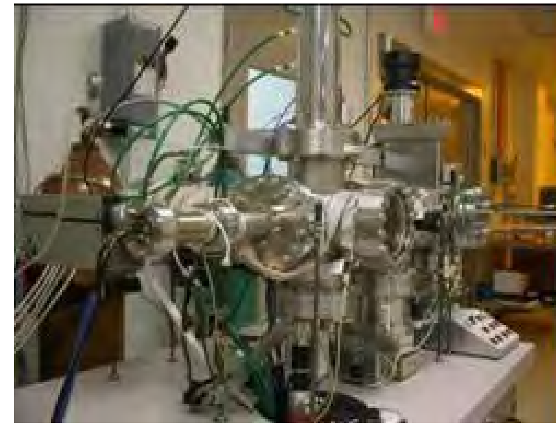
"Typical" SIMS conditions: R_a ~40nm



Improved SIMS conditions: R_a ~10nm

B. New UHV System for high purity Mg isotopic thin film deposition

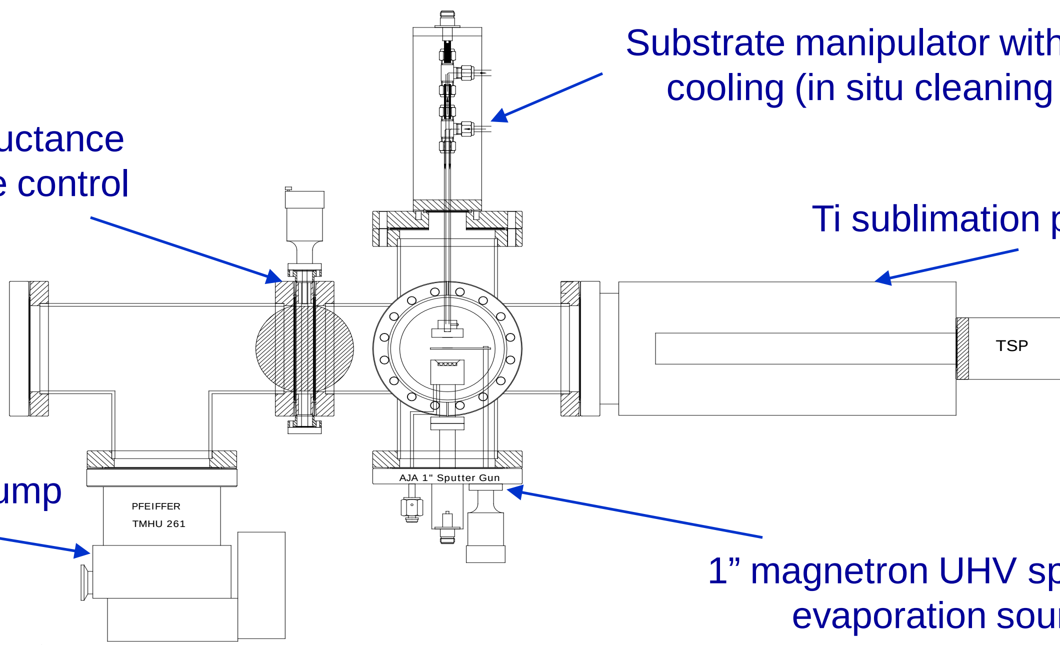
- Application-specific UHV sputter system design.
  - Short target-substrate spacing for high deposition rates (~ 10 x increase).
  - UHV bake-able vacuum components and pumping (~10^4 x improvement)
  - Hot metal getter purification of Ar process gas at point-of-use.
  - All metal-sealed Ar process gas handling components.
  - Shielding in chamber to provide “getter sputtering” for further increased purity



Substrate manipulator with RF power and water cooling (in situ cleaning of sample surface)

Variable conductance for Ar pressure control

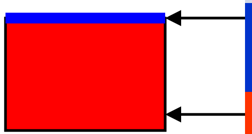
Ti sublimation pump for water vapor



Turbomolecular pump for Ar

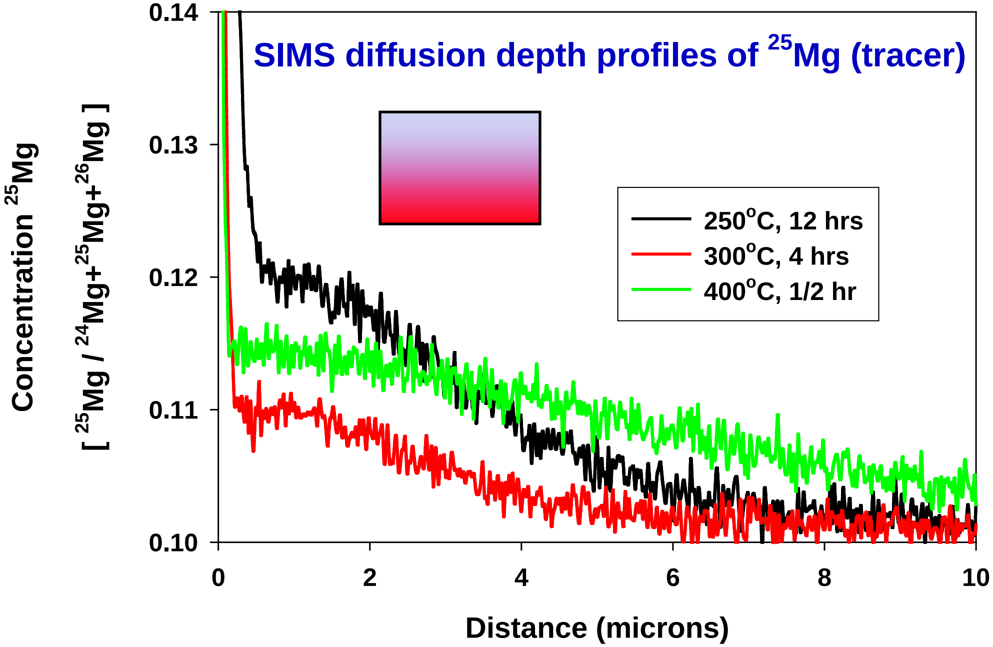
1” magnetron UHV sputter deposition (or evaporation source) w/ shutter

C. Mg tracer diffusion in polycrystalline Mg samples

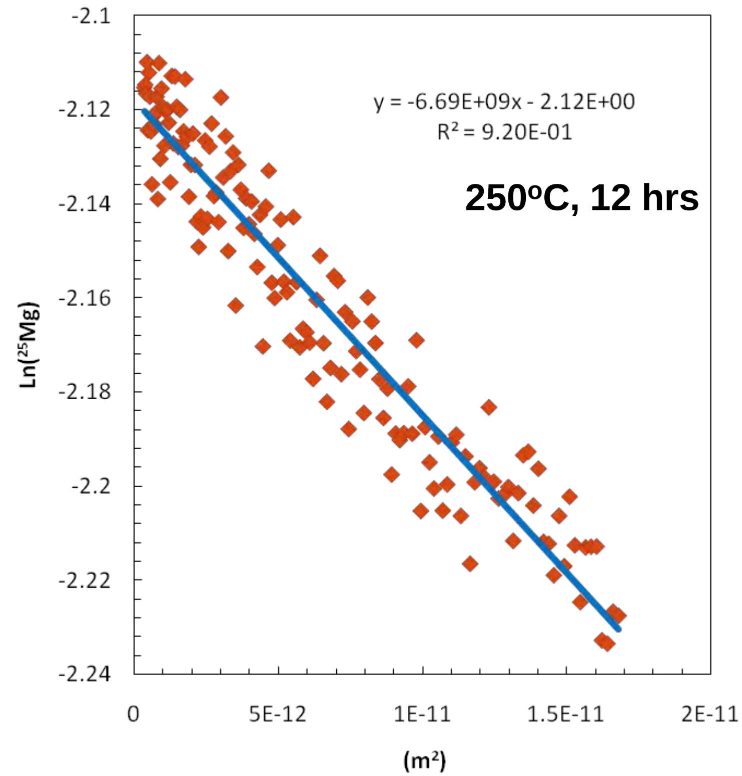


Initial Isotope Concentrations

	^{24}Mg	^{25}Mg	^{26}Mg
Enriched Tracer Film	0.018	0.979	0.003
Mg sample	0.790	0.100	0.110



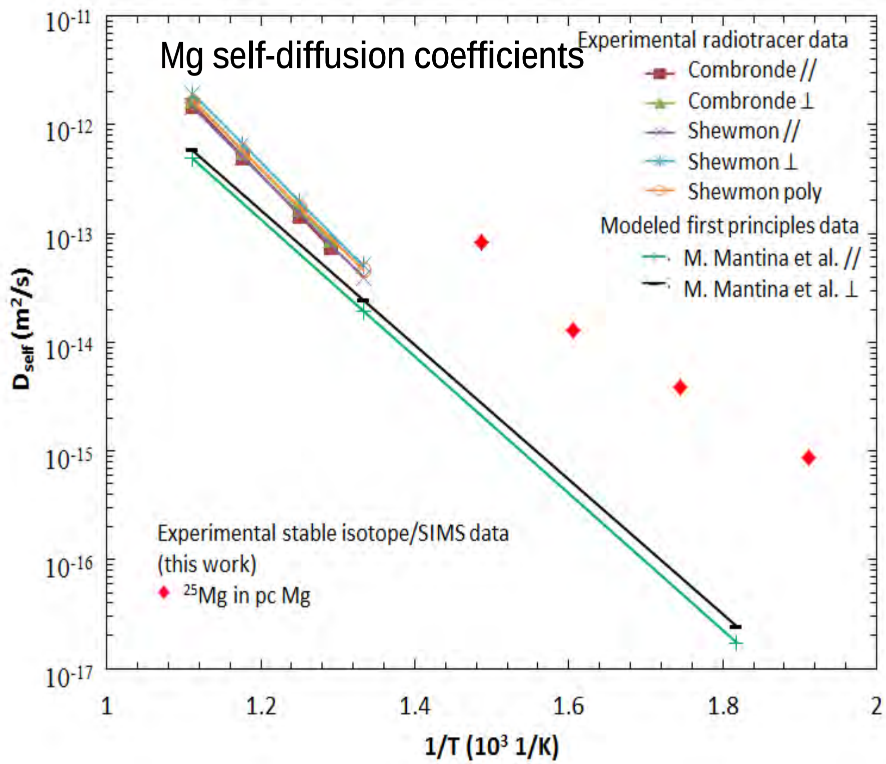
SIMS concentration depth profiles of ^{25}Mg as a function of depth in Mg polycrystalline samples annealed at various temperatures and times. In each case, the initial condition was a 100 nm thick film of enriched ^{25}Mg (98%) isotope deposited on a polycrystalline Mg sample.

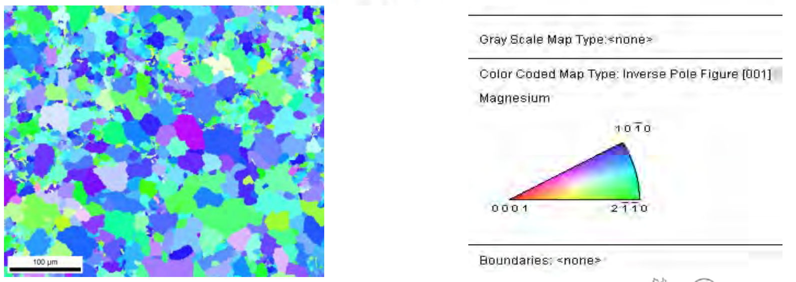


Ln(^{25}Mg) concentration as a function of the square of the penetration distance for the tracer diffusion experiment at 250°C, 12 hrs. From the slope of this plot, the tracer diffusion coefficient was calculated: Slope = -1/4*Dt, where D* is the tracer diffusion coefficient and t, the diffusion time.

C. Mg tracer diffusion in polycrystalline Mg (contd.)

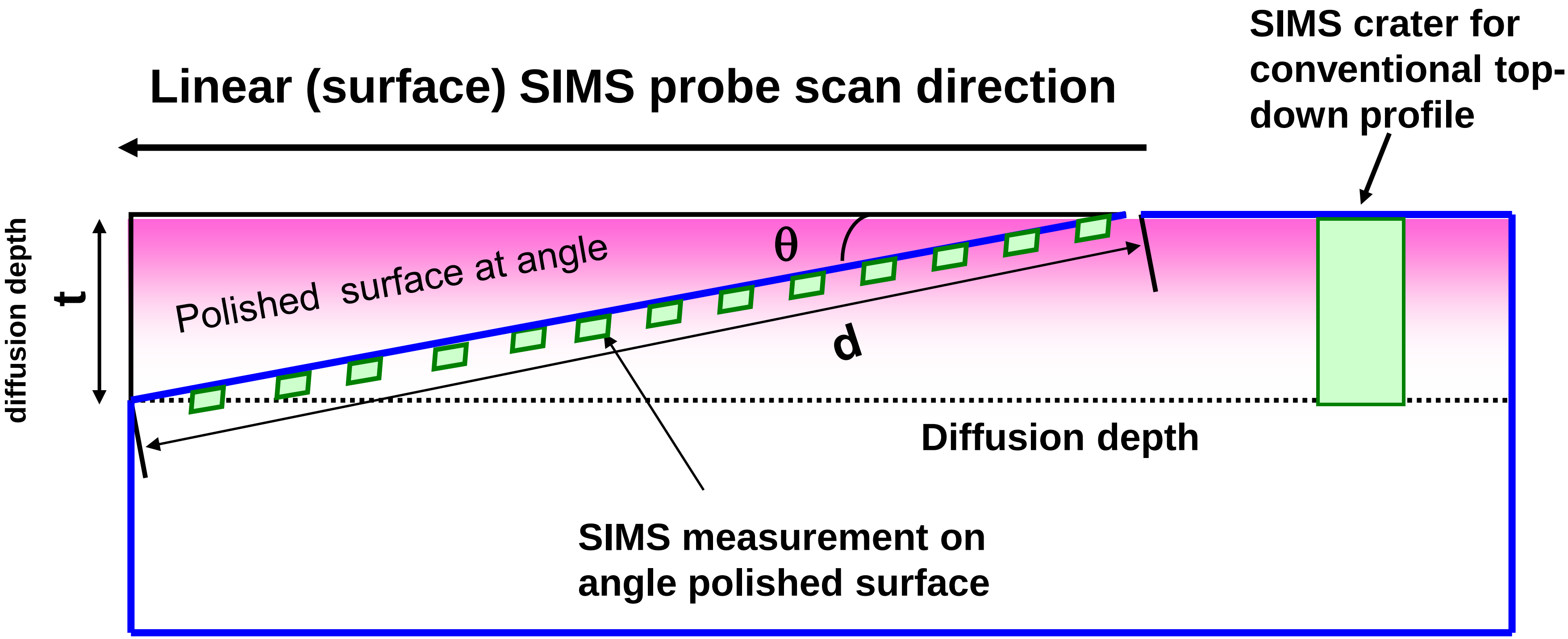
- Current Mg tracer diffusivities in pure Mg (self-diffusion) polycrystalline specimens appear to be higher in comparison with literature (radioactive tracer data).
- Potential causes include:
  - Microstructure / grain boundary diffusion effects
  - Higher purity samples (ppm impurities) compared to literature samples (hundreds of ppm impurities)
  - Sputter roughening due to broad grain size distribution (average 10 μm) causing incorrect depth measurements. Optimization of SIMS sputter conditions difficult for large-grain sizes (tens of μm).
  - Recrystallization/grain growth due to some remaining stored internal energy after processing (extruded rods)
- Ongoing work
  - Experiments are being repeated in larger grain size specimens (hundreds of μm) with high temperature annealing so that volume diffusion dominates.
  - Discrete SIMS measurements on angle polish sections (<2 degree) are being conducted on samples with various diffusion depths.
  - Both short diffusion anneals (for top-down SIMS depth profiles) and long diffusion anneals (for angle polish SIMS measurements) are being conducted.
  - Corrections for more accurate sputter depth measurements as a function of grain orientation using SIMS image processing software are being explored
  - Tracer studies in Mg single crystals and in Mg-Al-Zn alloys are being conducted





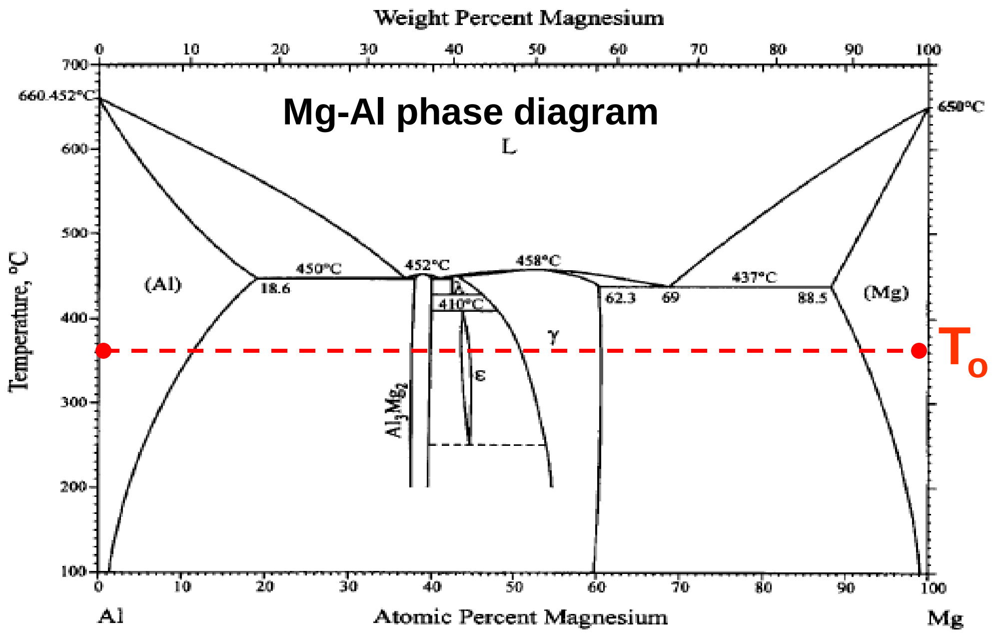
Microstructure orientation (inverse pole figure) map using electron backscatter diffraction (EBSD). Average grain size is 10 μm.

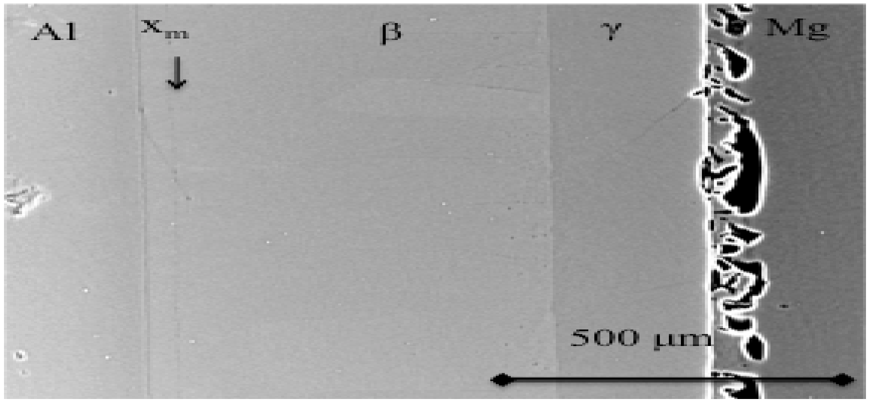
C. Mg tracer diffusion (contd.): SIMS measurements on angle polished sections for deep diffusion depths



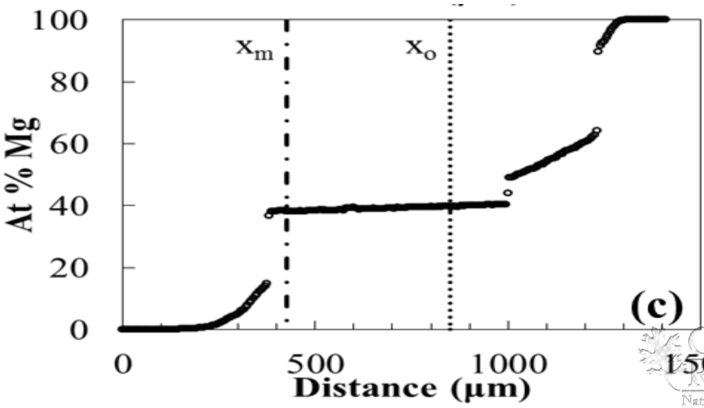
d = t / sin(θ) : angle polish surface used for SIMS discrete/depth profile measurements
t = 100 μm: tracer diffusion depth
θ = 1 deg; d = 5730 μm; Magnification = 5730 /100 ~ 57
Hence, 5730/20 ~ 286 discrete SIMS measurements every 20 μm along d

D. Interdiffusion in Mg-Al

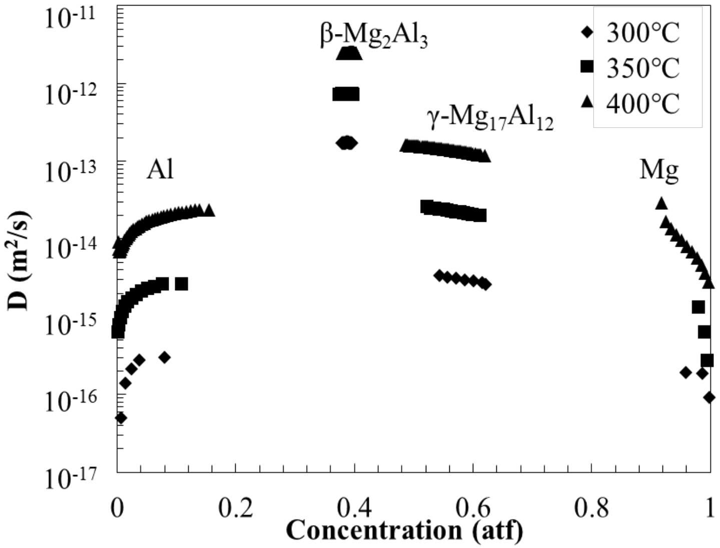


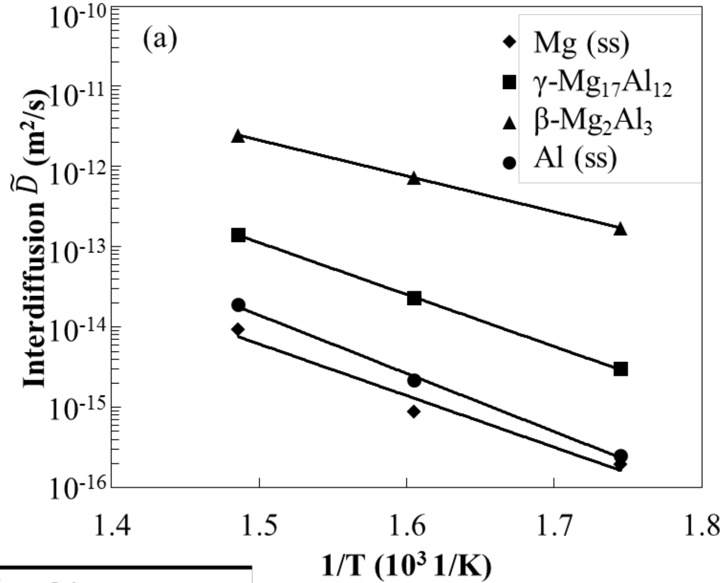


- Diffusion couples were formed by bonding pure Mg with pure Al samples and annealing them at various temperatures, e.g., T_o, to cause interdiffusion of both Mg and Al.
- Most phases given by the phase diagram at the diffusion temperature are observed in the diffusion region; however some are not, e.g., the ε phase was not observed at any temperature investigated.
- From the concentrations measured in the diffusion zone as a function of distance (below) using an electron microprobe (EPMA), the so-called "interdiffusion" coefficients can be calculated for all compositions with the observed phases using an analytical treatment (Boltzman-Matano) of Fick's law of diffusion.



D. Interdiffusion in Mg-Al (contd.)





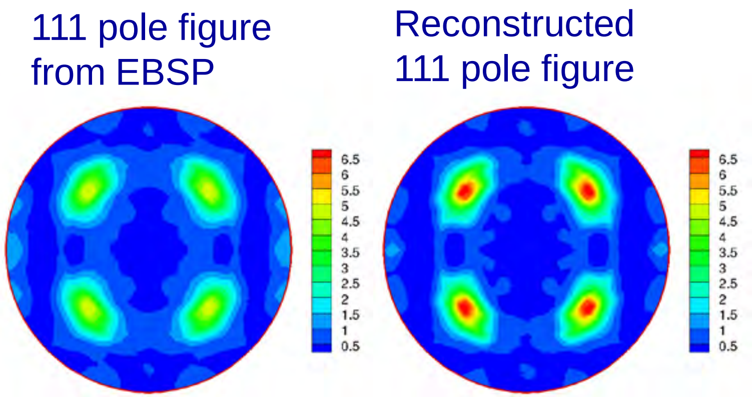
Interdiffusion Coefficients, $\widetilde{D}$ (m²/s)				
Temperature	Mg s.s.	γ-$Al_{12}Mg_{17}$	β-Al_3Mg_2	Al s.s.
400°C	9.3×10^{-15}	1.4×10^{-13}	2.5×10^{-12}	1.9×10^{-14}
350°C	8.8×10^{-16}	2.3×10^{-14}	7.3×10^{-13}	2.2×10^{-15}
300°C	1.9×10^{-16}	2.9×10^{-15}	1.7×10^{-13}	2.5×10^{-16}

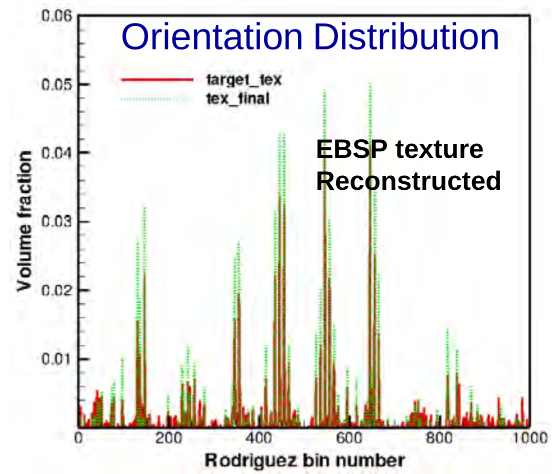
D_{inter} (Mg s.s.) = $[\, X_{Mg} D^*_{Al} + X_{Al} D^*_{Mg} \,]\, \Phi$ Darken relation

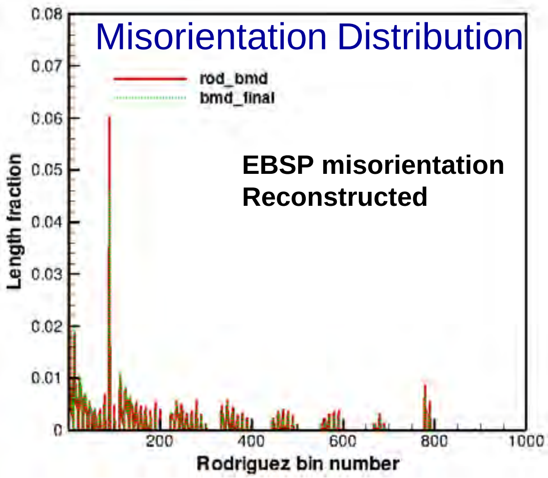
- **The above relation derived by Darken connects the interdiffusion coefficient D_{inter} (Mg s.s.), the tracer diffusivities (D^*_{Mg} and D^*_{Al}), the concentrations (X_{Mg} and X_{Al}), and the thermodynamic factor (Φ), which can be obtained from a thermodynamic database.**

- **Only D^*_{Al} is unknown (since the Al tracer diffusion coefficient cannot be currently measured), while all the other diffusion coefficients can be obtained from tracer and interdiffusion experiments. Hence the Al tracer diffusion coefficient, D^*_{Al}, can be determined.**

E. Volume and grain boundary diffusion modeling in polycrystalline microstructures







Three-dimensional reconstruction of grain structure based on EBSP data so that both the texture and the boundary misorientation distribution are captured accurately in the model

- Diffusion data obtained from Molecular Dynamics (MD) will be used as input to the microstructural length scale simulation
- Characteristic input microstructure will be obtained using
  - Microstructural mapping of EBSP scans to a three-dimensional grain structure
- Diffusion equation will be solved numerically for a given microstructure using location dependent diffusion coefficients

Collaborations

- University collaborators
  - University of Central Florida (key subcontract): UHV system for isotopic thin film deposition and annealing, interdiffusion and intrinsic diffusion studies, graduate student research
  - Virginia Tech (key subcontract): SIMS measurements & techniques, some microscopy in their center
  - University of Newcastle, Australia (recent subcontract): Consultation on tracer diffusion studies and analysis of microstructure effects
- Industry collaborators
  - Mg-ICME team (no-cost): Meetings & discussions
  - Mg-Elektron: Provided Mg-alloy samples prepared by casting and processing, consultations
  - Princeton Scientific: Provided single crystal Mg in different orientations
- ORNL (prime contract)
  - Project lead/strategy & co-ordination, HTML and SHaRE microscopy facilities, supply and processing of isotopes, diffusion simulations, etc.

Proposed Future Work

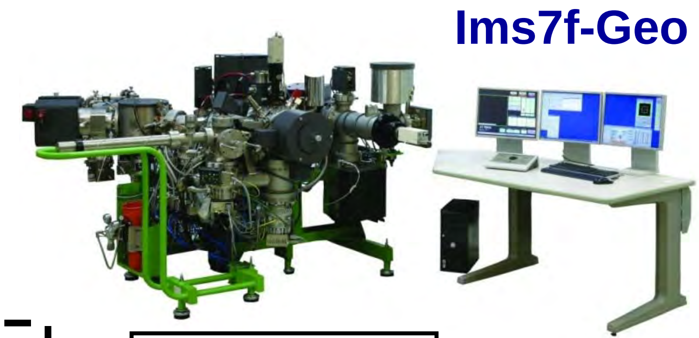
- Future work in remainder of FY11:
  - Develop technique for SIMS tracer diffusion measurements on angled polish sections (<2 degrees) that are likely to be needed for deep diffusion penetration depths, e.g., high temperature diffusion
  - Mg single crystal self-diffusion measurements to compare with published single crystal radiotracer data
  - Mg, Zn tracer diffusion experiments and analysis in Mg-Al-Zn alloys (8-10 select alloys)
  - Interdiffusion/intrinsic diffusion measurements in incremental Mg-Al-Zn alloys to extract Al tracer diffusivity
  - MD simulations of volume and grain boundary diffusion in Mg-Al; Effective diffusion modeling in polycrystalline Mg-Al

- Future work in FY12 (proposed):
  - Continue tracer diffusion and interdiffusion experiments and analysis in Mg-Al-Mn and Mg-Al-Zn-Mn alloys
  - Tracer diffusion measurements with radioactive isotopes of Al (if available) and Mn assuming TOF SIMS system will be available or use other arrangements for SIMS analysis of hot samples
  - Extend grain boundary and effective diffusion modeling to polycrystalline Mg-Zn and Mg-Al-Zn
  - Tracer diffusion studies in select rare-earth and rare-earth replacement alloys
  - Exploratory work on combinatorial deposition of Mg alloys on heated substrate (< 800^{o}C) using a newly installed magnetron co-sputtering deposition system
    - *In situ* isotopic thin film sputter deposition in the same system on co-sputtered alloy films using a direct line-of-sight sputter gun (to be purchased/installed)

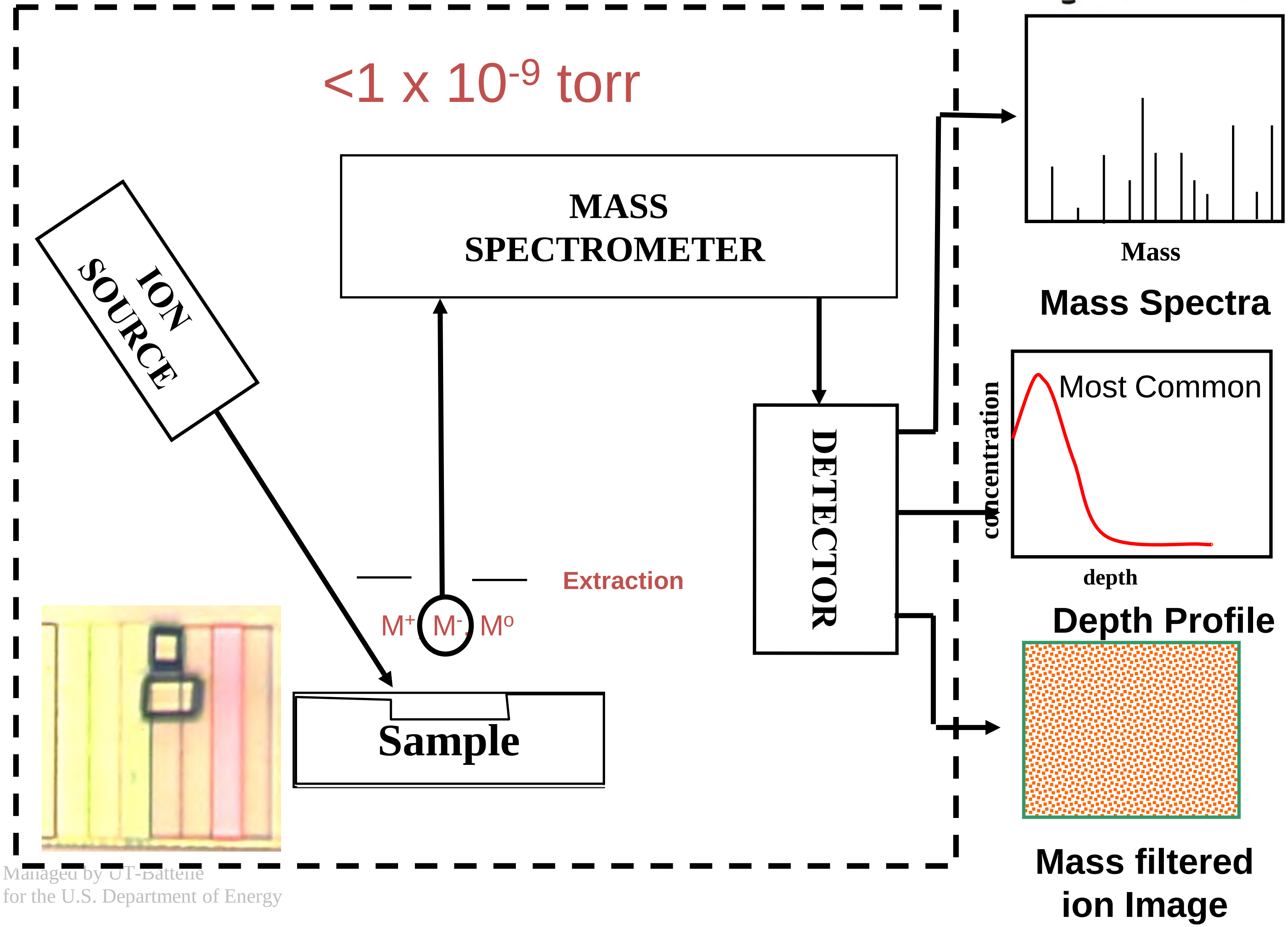
Summary

- Relevance: A tracer diffusion database in Mg alloys is of fundamental importance to the ICME and other materials design efforts in establishing design and modeling tools, optimizing manufacturing processes, and predicting performance requirements.
- Approach: While the current thin film approach for tracer diffusion appears adequate, complementary interdiffusion experiments and modeling approaches are being utilized to obtain tracer diffusivities of monoisotopic elements and address diffusion in polycrystalline alloys respectively.
- Key accomplishments/progress
  - Special UHV deposition system was designed/constructed for reactive element (Mg) deposition and to minimize isotopic losses.
  - Techniques and procedures for diffusion depth profile measurements in the SIMS system (ims7f-Geo) were improved, e.g., optimizing conditions to minimize sputter roughness in polycrystalline samples, use of SIMS on angled polish sections.
    - More advanced Cameca ims7f-Geo SIMS system used instead of ims3f for improved measurements
  - New approaches were initiated to understand microstructure effects and extract tracer diffusivities of monoisotopic elements (e.g., Al):
    - Grain boundary/volume diffusivity using MD simulations in Mg-Al, and 3D effective diffusion modeling to incorporate microstructure features
    - Interdiffusion/Intrinsic diffusion measurements in binary Mg-Al, Mg-Zn to extract tracer diffusivity of Al
    - Proposal to develop a Time-of-Flight SIMS system developed to handle radioactive samples such as ^{26}Al if DOE initiates production
- Collaborations between ORNL, university (UCF, Virginia Tech) and industry partners are essential.

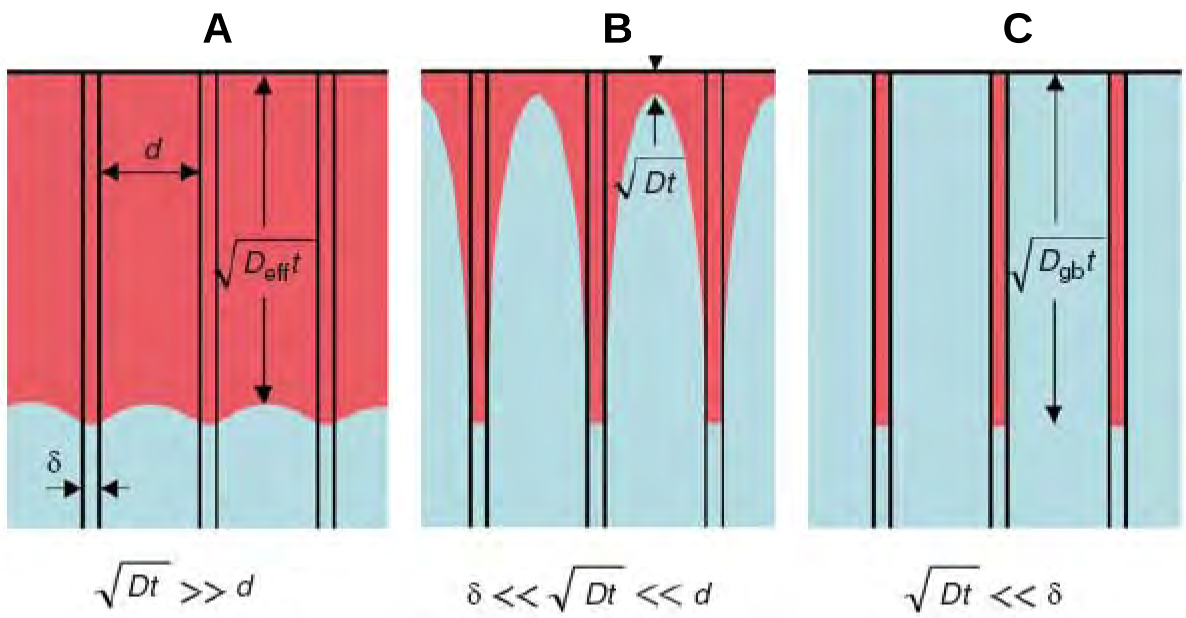
Technical Back-Up Slides



A. SIMS Technique (backup):



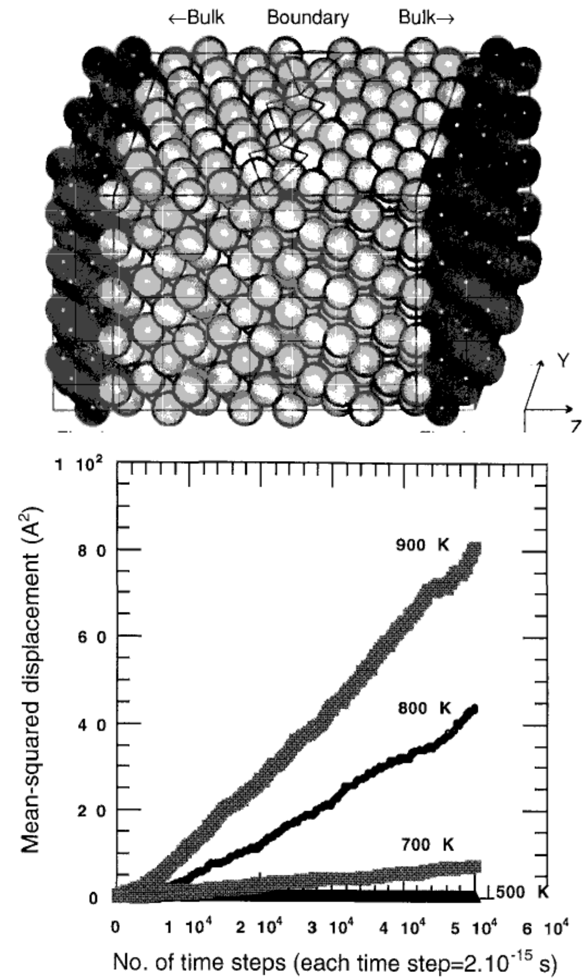
C. Mg tracer diffusion in polycrystalline Mg (backup): Diffusion regimes



Schematic illustration of diffusion regimes in a polycrystalline material according to Harrison's classification scheme. D is the bulk (volume) diffusion coefficient, D_{gb} is the grain boundary diffusion coefficient, d is the grain size, δ is the grain boundary width, and t is the diffusion time. In regime (A), an effective diffusion coefficient, D_{eff}, that is a weighted average of the bulk and grain boundary diffusion coefficients can be determined by analysis of the SIMS tracer diffusion depth profile. In the (B) regime, both the bulk and the grain boundary diffusion coefficient can be determined while in the (C) regime, only the grain boundary diffusion coefficient can be determined [Martin et al., MRS Bulletin, vol. 34, Dec 2009].

E. Volume & grain boundary diffusion modeling (backup): Molecular Dynamics (MD) simulations

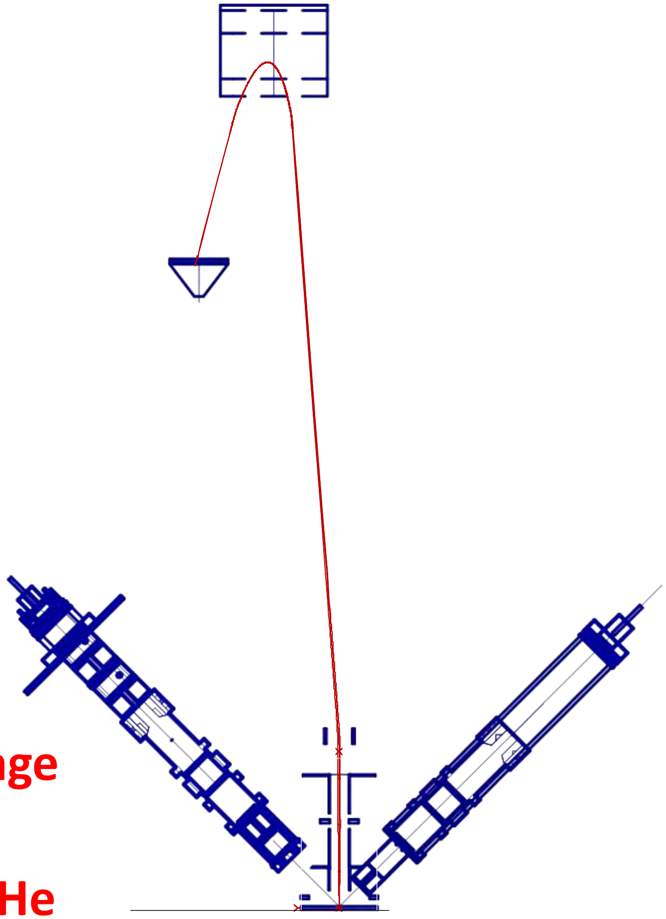
- Perform MD simulations for Mg-Al binary alloy
  - Single crystals (volume/bulk diffusion)
  - Bi-crystals containing desired grain boundary types (grain boundary diffusion
  - Tri-crystal containing the desired triple line (diffusion along triple lines)
- Use available EAM or MEAM potentials for the alloy
- Calculate bulk / grain boundary / triple line diffusion coefficients from mean square displacement data obtained using MD (Liu and Plimpton, 1995)



MD simulation domain of Al bicrystal (top) and mean square displacement data (bottom) from Liu and Plimpton, 1995

Proposed Future Work (backup): Liquid Metal Ion (LMI) / Molecular Ion Gun Time of Flight (TOF) Mass Spectrometer

1. Molecular Ion Beam Sputtering
   - <10 nm Depth Resolution
   - High Sputter Rate
2. Liquid Metal Ion Beam Analysis
   - <100 nm Spatial Resolution
3. Reflectron Time of Flight Mass Analysis
   - Mass Resolution M/DM>2000
   - Radioactive (e.g. ^{26}Al) Isotope Analysis



- **Multi-User Facility – Spread Costs, Optimize Usage**
- **Support from DOE, NNSA, 3 ORNL Directorates**
- **Integrated with NanoSIMS 50 and Zeiss Orion® He Imaging System Proposal**