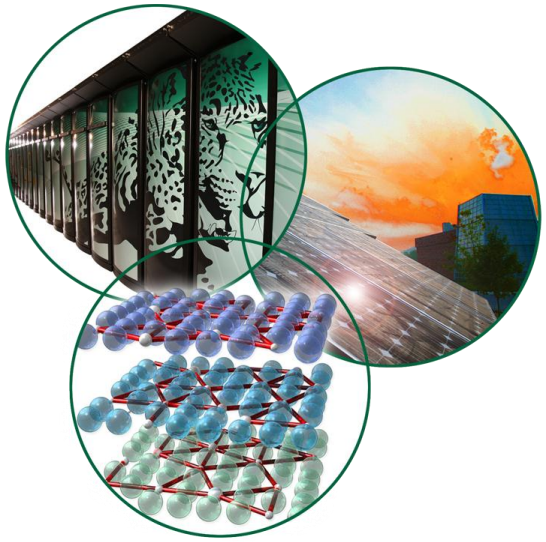
Tracer Diffusion Databases – Benefits and Techniques

Nagraj Kulkarni[1], Bruce Warmack[1], B. Radhakrishnan[1], Yongho Sohn[2], Kevin Coffey[2], Jerry Hunter[3], Graeme Murch[4] & Irina Belova[4]

[1]Oak Ridge National Laboratory, [2]University of Central Florida

[3]Virginia Tech, [4]University of Newcastle (Australia)



2012 TMS Annual Meeting & Exhibition

Symposium: Computational Thermodynamics and Kinetics

March 13, 2012

U.S. DEPARTMENT OF ENERGY

Virginia Tech.

UNIVERSITY OF CENTRAL FLORIDA 1963

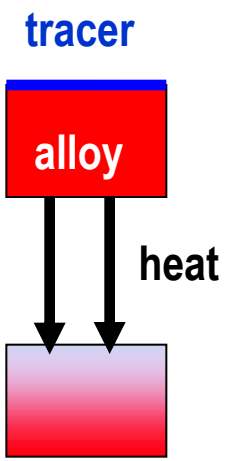
THE UNIVERSITY OF NEWCASTLE AUSTRALIA

OAK RIDGE NATIONAL LABORATORY

MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

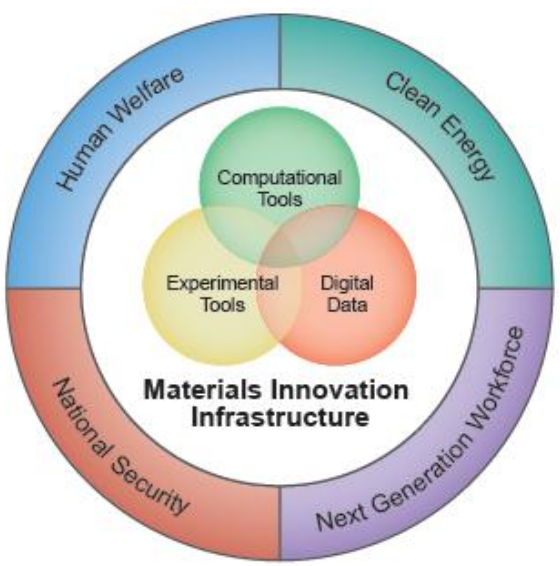
Outline

- Genomics for MGI or Cyber-Infrastructure for ICME
  - Thermo G, Diffusion G, Interfacial G, Property G's, ...
- Tracer Diffusion for the Diffusion Genome
  - Key Benefits
- Radioactive vs Stable Isotopes as Tracers
  - Compare and contrast
- Mg-alloy tracer diffusion update
  - Mg-Al-Zn tracer diffusion studies



Genomics for MGI

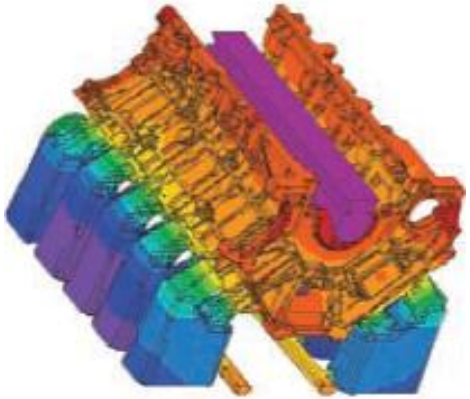
- **Materials Genome Initiative for Global Competitiveness**
  - **A new national infrastructure for data sharing and analysis that will provide a greatly enhanced knowledge-base for design and discovery of new materials.**
  - **Effort will foster enhanced computational capabilities, data management, and an integrated engineering approach for materials deployment to better leverage and complement existing Federal investments.**

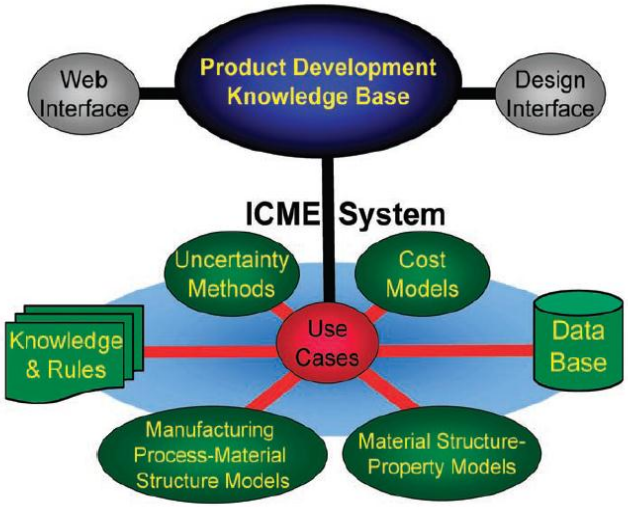


❖ ***Fundamental databases and tools that will enable reduction of the 10-20 year materials creation and deployment cycle by 50% or more.***

Cyber-Infrastructure for ICME

- Integrated Computational Materials Engineering (ICME): A Transformational Discipline for Improved Competitiveness and National Security
  - Integrate computational materials science tools into a holistic system that can accelerate materials development, transform the engineering design optimization process, and unify design and manufacturing.
  - Mg-ICME Cyber Infrastructure (CI) for exchanging data and models between collaborators (web-based).





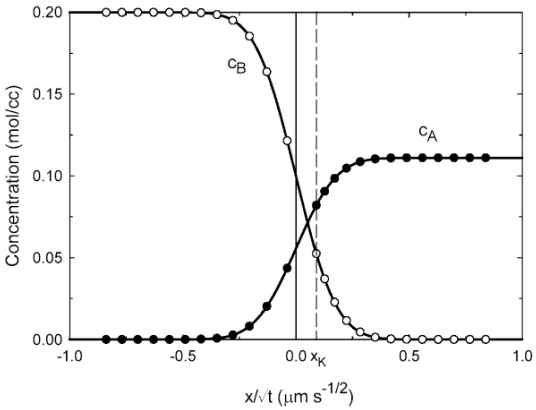
❖ *Fundamental databases and tools that will enable reduction of the 10-20 year materials creation and deployment cycle by 50% or more.*

Diffusion Database vs Genome

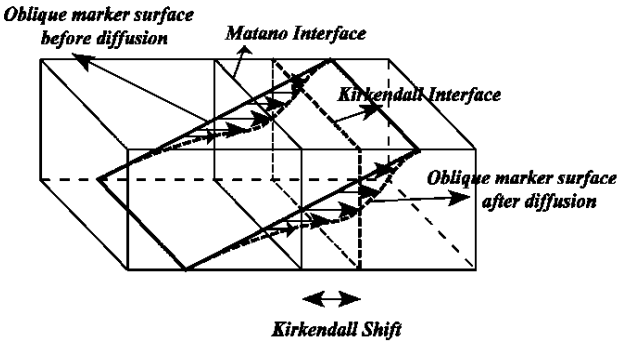
- A diffusion database typically provides the bulk diffusion coefficient of a component as a function of composition and temperature
- A diffusion genome is a science and knowledge-base system of diffusion information that includes databases:
  - May include diffusion mechanisms at various temperatures
  - May provide specific information (data or text) on volume, orientation-dependent, grain boundary diffusion, etc., and effective (microstructure-dependent) data
  - Provides raw/fundamental data or "protodata" and details on methods and techniques used
  - Can be constantly-improved over time, and adapted by the user for desired application without too much effort

Why Tracer Diffusion for Genome?

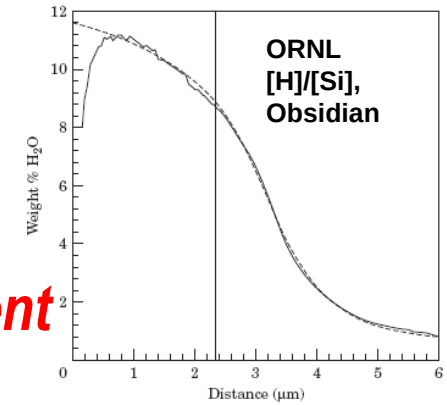
- Interdiffusion data (matrix) from diffusion couples
  - Steep gradients, molar volume changes, grain boundary effects, long times at low temperatures
  - Very difficult in compounds with limited stoichiometry



- Intrinsic diffusion data (matrix) from couples
  - Require suitable "inert" markers

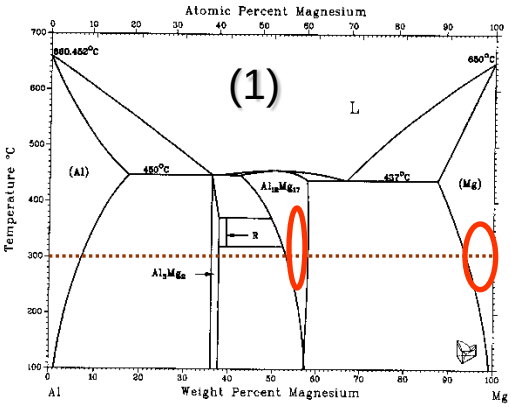


- Tracer diffusion data (unique)
  - Most reliable but use of radioactive isotopes as tracers is time-consuming and expensive
  - SIMS-based technique with stable isotopes as tracers looks promising

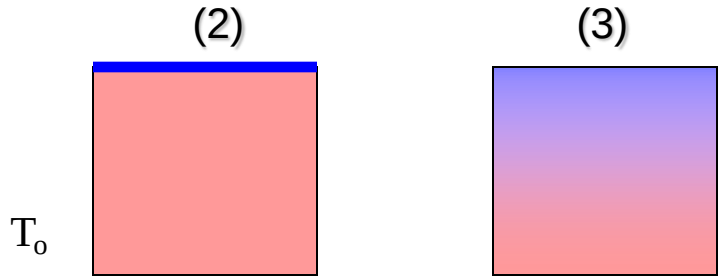


➢ *Need a unique kinetic coefficient for each component*

Tracer Diffusion: Thin-film Technique

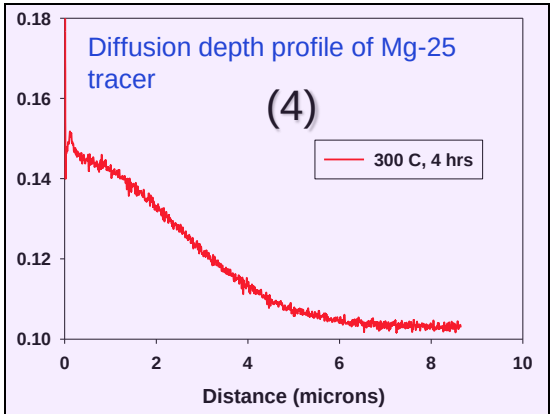


(1) Prepare single phase alloy sample (e.g., Mg-5%Al) at T_o



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

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

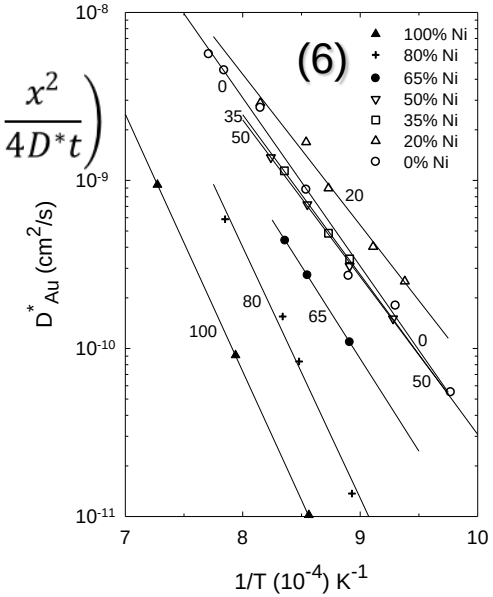


(4) Measure depth profile of isotope or isotope ratio with SIMS

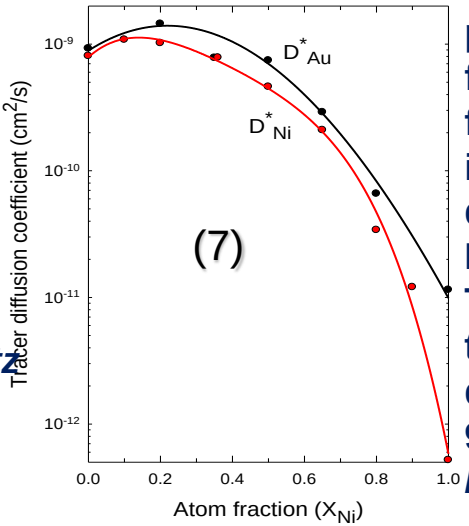
(5)

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

(5) Fit tracer depth profile in (4) with above thin-film solution to extract D*

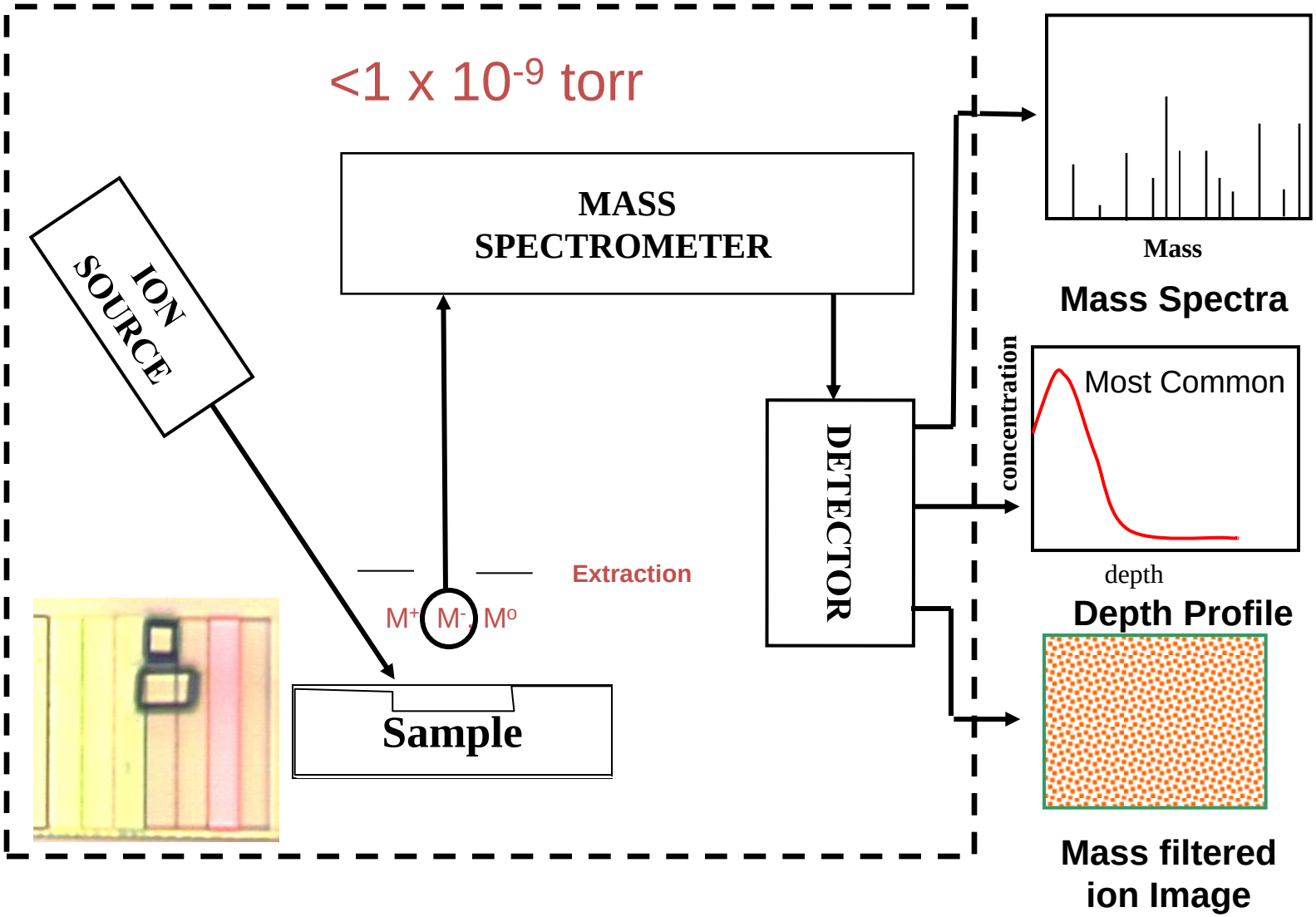


(6) Repeat for different temperatures and compositions to check for Arrhenius fits (e.g. Au in Au-Ni alloys, *Kurtz et al., Acta Met.'55*)

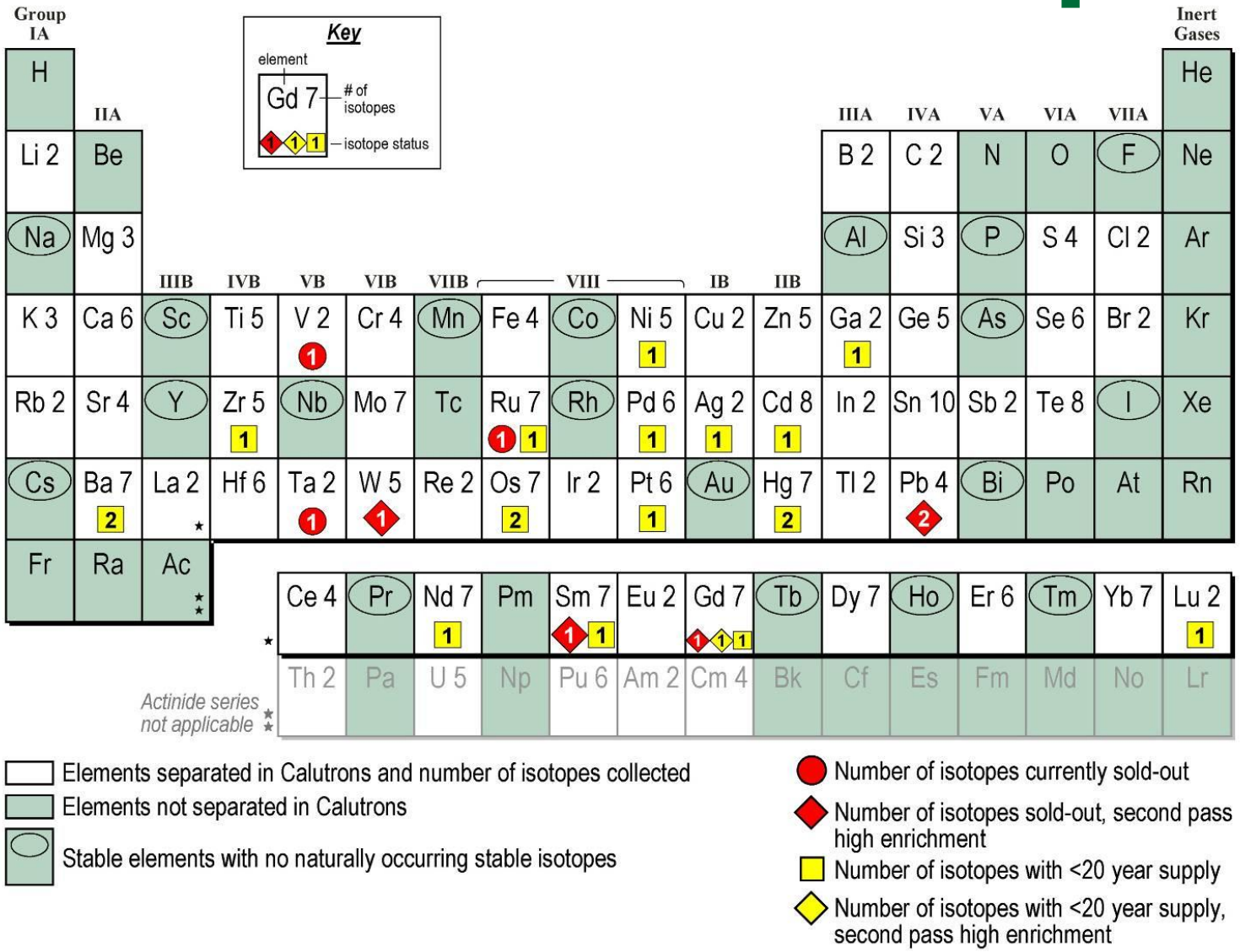


(7) Fit using suitable polynomials for functional form of isotopic diffusivity $D_k^*(X_1, X_2, \ldots, T)$ (e.g. Au-Ni tracer diffusion at 900°C, *Reynolds et al. Acta Met. '57*)

Tracer Diffusion: SIMS technique



DOE – ORNL Isotopes



➢ ***Cannot avoid working with radioactive isotopes in some cases, e.g., Al, Nb, Mn, etc. since elements are monoisotopic***

Tracer Diffusion: Key Benefits

Rigorous application of diffusion formalism

- Intrinsic fluxes where driving forces are chemical potential gradients (Onsager):

$$J_k = -\sum_{i=1}^{n-1} L_{ki}^{n}\, grad\, \mu_i \qquad (k = 1, 2, \ldots, n) \qquad \sum_{k=1}^{n} J_k = -J_v$$

- L_{ki}'s obtained from tracer diffusion data using Manning relations:

$$L_{11} = \frac{X_1}{V} \cdot \frac{Dt_1}{R \cdot T} \cdot \left[1 + \frac{2 \cdot X_1 \cdot Dt_1}{M_o \cdot (X_1 \cdot Dt_1 + X_2 \cdot Dt_2 + X_3 \cdot Dt_3)} \right]$$

$$L_{ij} = L_{ji}$$

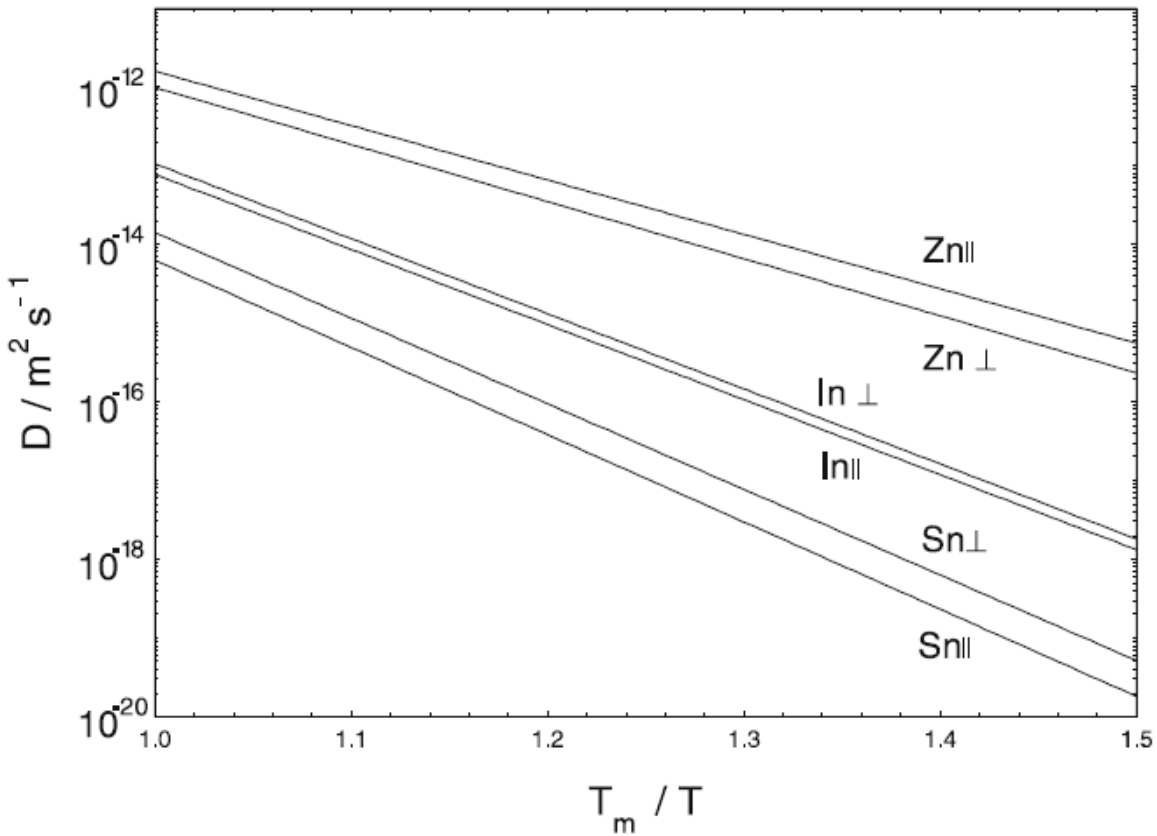
$$L_{12} = \frac{2 \cdot X_1 \cdot Dt_1 \cdot X_2 \cdot Dt_2}{V \cdot R \cdot T \cdot M_o \cdot (X_1 \cdot Dt_1 + X_2 \cdot Dt_2 + X_3 \cdot Dt_3)}$$

$$L_{13} = \frac{2 \cdot X_1 \cdot Dt_1 \cdot X_3 \cdot Dt_3}{V \cdot R \cdot T \cdot M_o \cdot (X_1 \cdot Dt_1 + X_2 \cdot Dt_2 + X_3 \cdot Dt_3)}$$

- Chemical potentials from thermodynamic database
  - ➢ *Cross-terms cannot be ignored as in Darken (correlation effects influence cross-terms)*
  - ➢ *Tracer diffusion data is independent of thermodynamic database (with exceptions, e.g., Al since Al tracer is not available currently)*

Tracer Diffusion Benefits - contd.

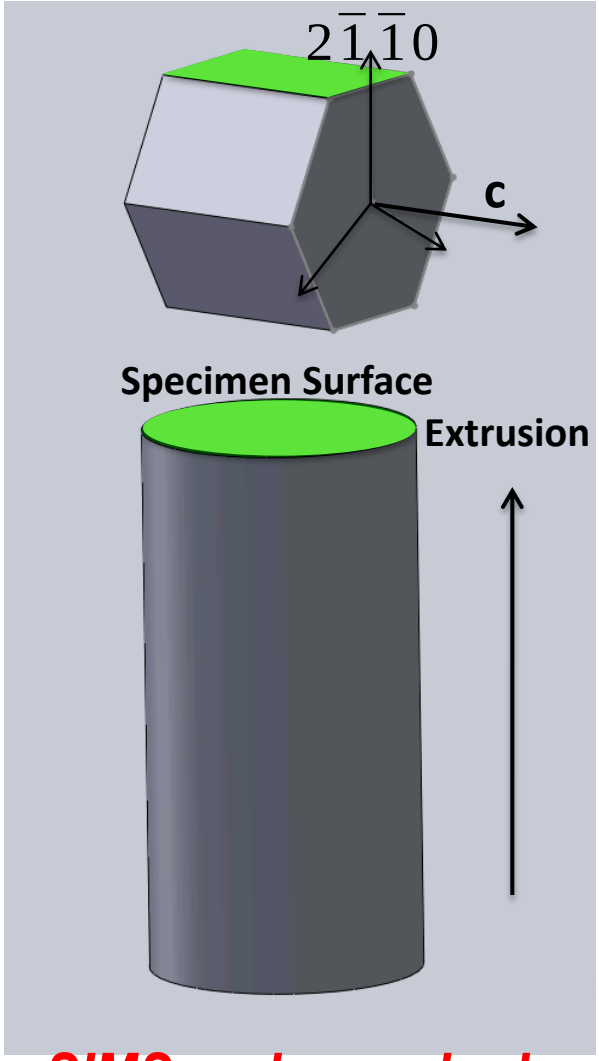
Anisotropy in diffusion coefficients

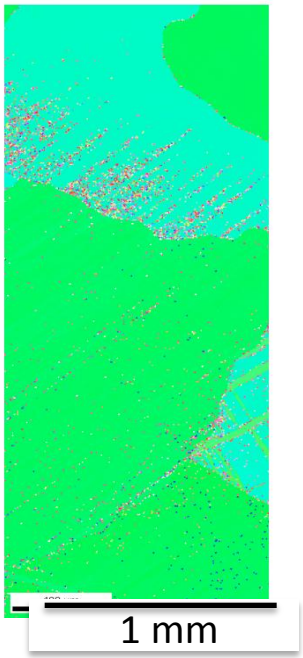


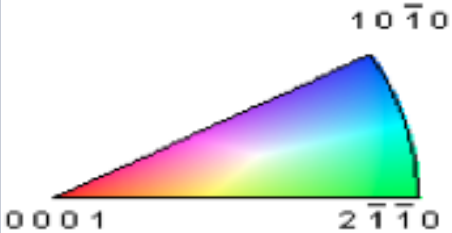
Self-diffusion in single crystals of Zn (hex.), In and Sn (tetrag.) parallel and perpendicular to their unique axis (Mehrer, Diffusion in Solids)

- ***In some systems, e.g., YBCO, anisotropy can be 100X***
- ***In Mg, self-diffusion perpendicular is slightly higher than parallel***

SIMS Measurements capture anisotropy in Mg self-diffusion







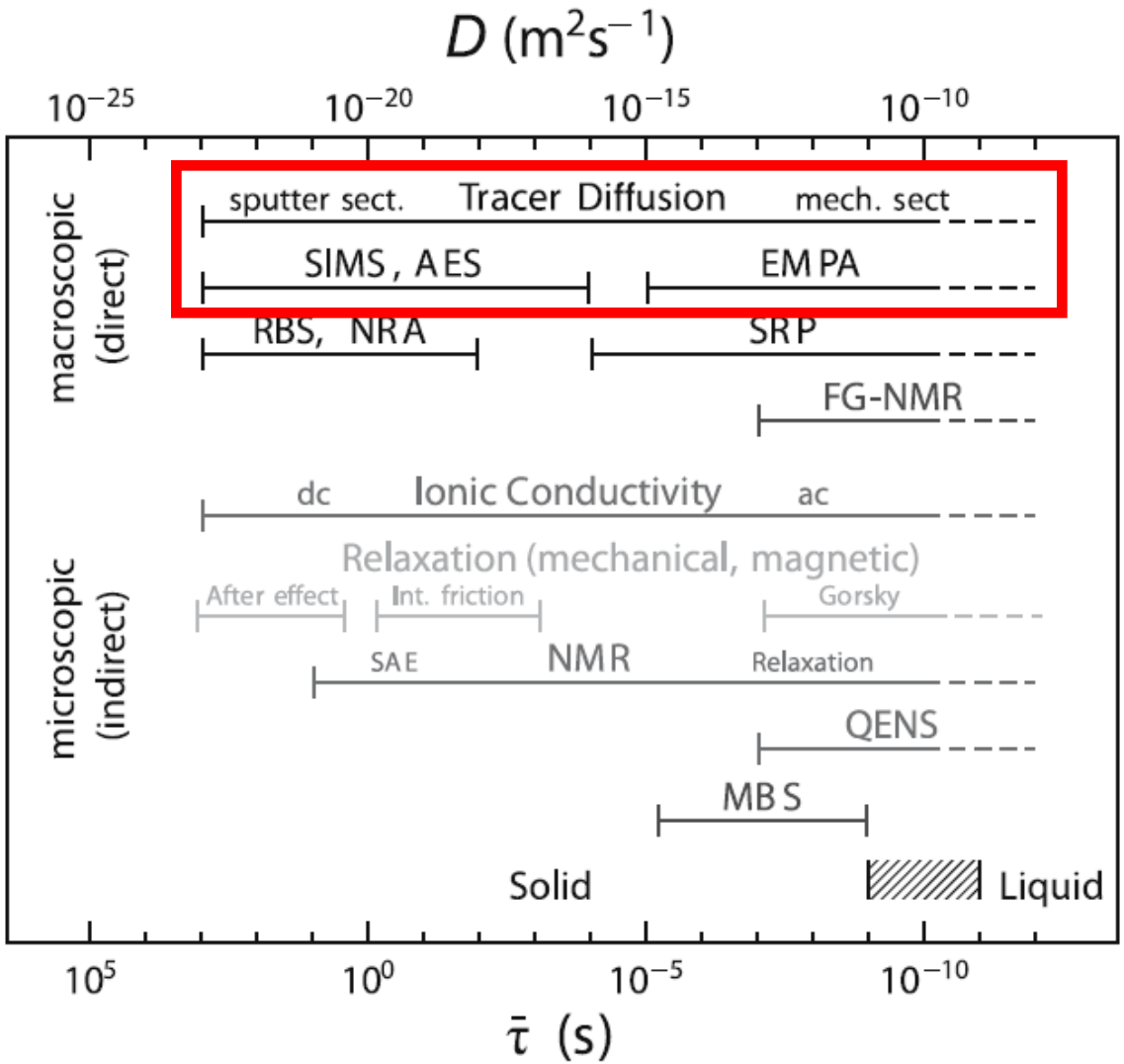
- Large green grain has $2\bar{1}\bar{1}0$ direction normal to specimen surface
- Measured diffusion coefficient is normal to c-axis; shows slightly higher value than that measured parallel to c-axis (section surface parallel to rod axis)
- Consistent with known anisotropy in diffusion in magnesium single crystals (*Shewmon 56*)

Extruded rod annealed at 545°C for 14.5 hrs

➢ ***SIMS on large single crystal grains in extruded & annealed Mg rods instead of single crystals used by Shewmon***

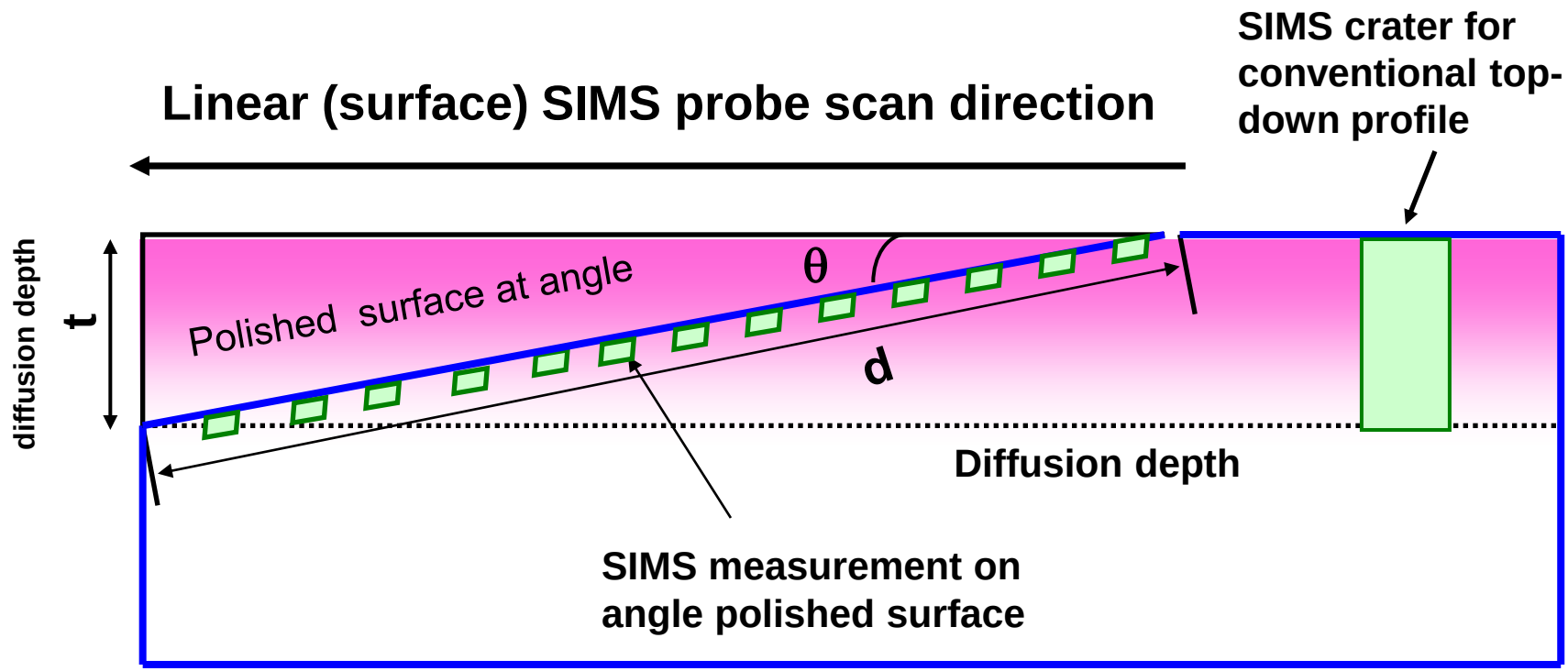
Tracer Diffusion Benefits - contd.

Data over large temperature range



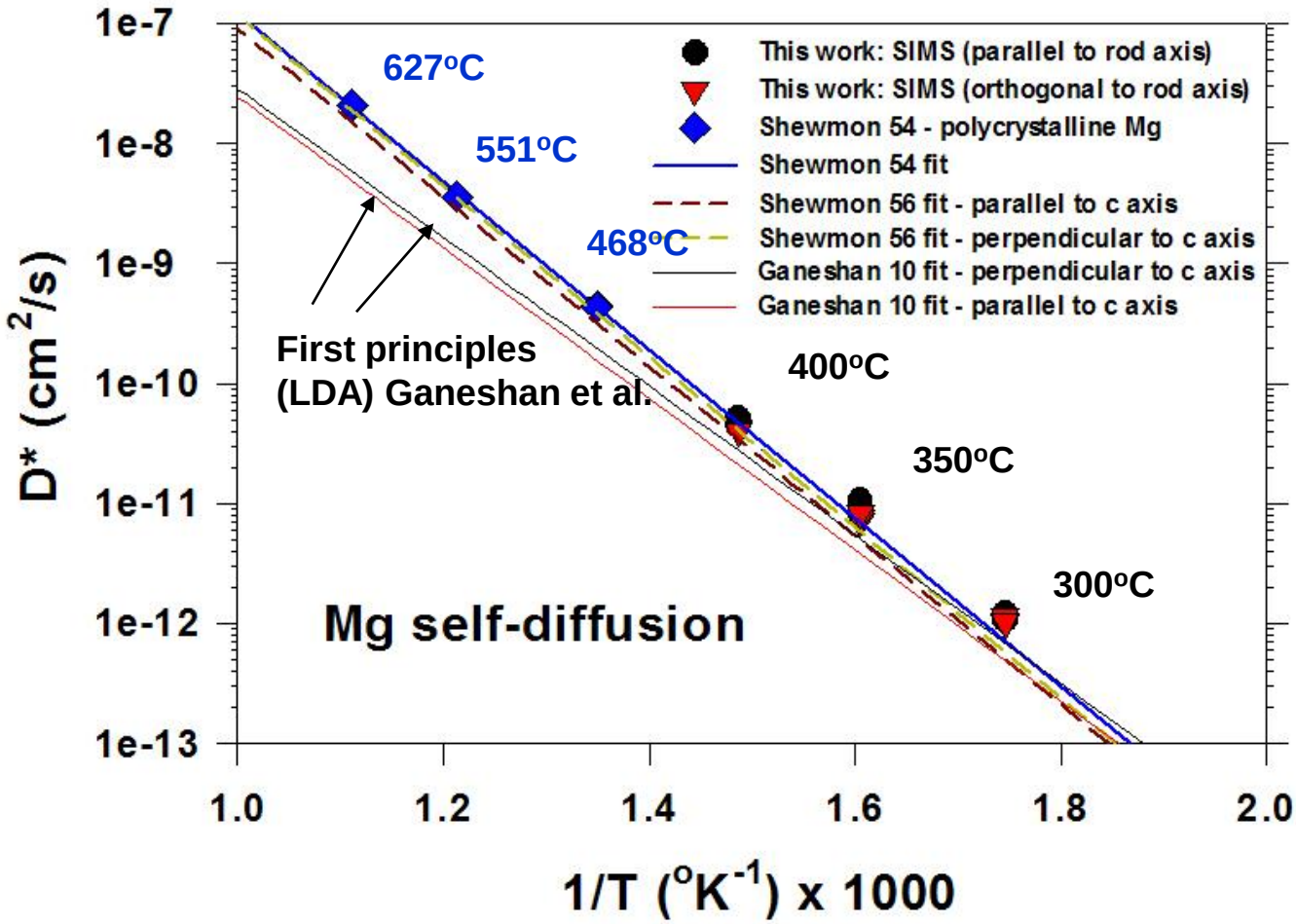
Typical ranges of diffusivity (Mehrer, Diffusion in Solids)

Angle polish SIMS for shallow or 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

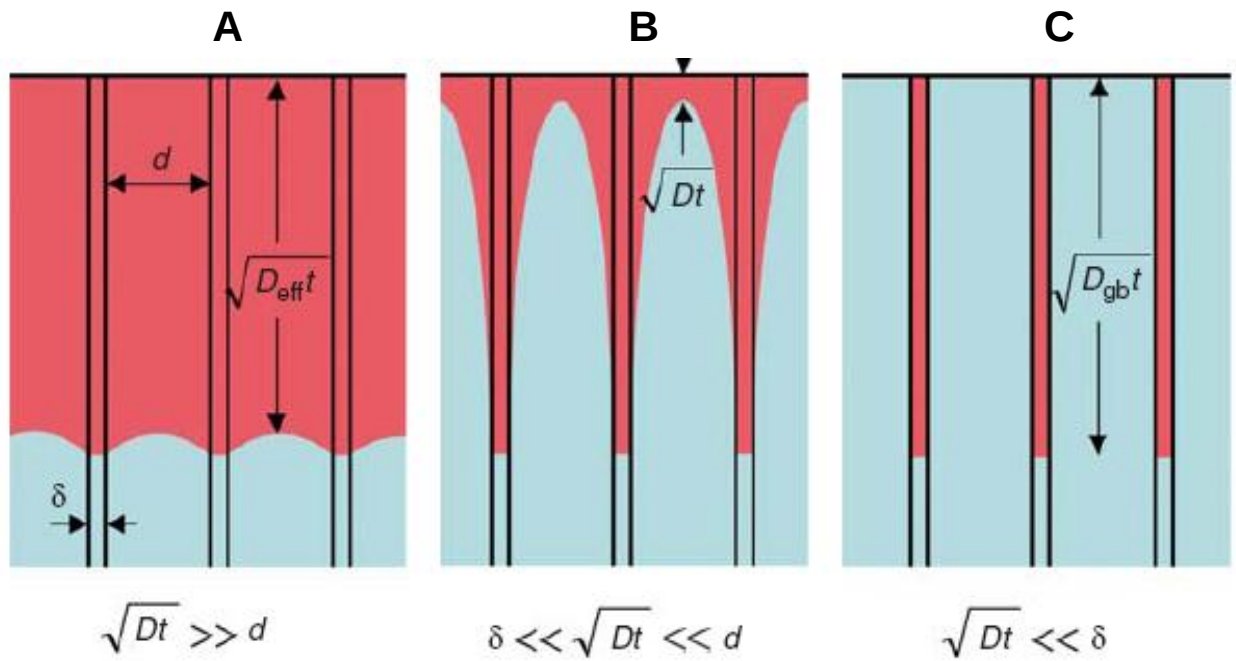
Mg Self-Diffusion



- ***SIMS + radiotracer data for large temperature range***
- ***Both radiotracer with single crystals and SIMS with large-grained textured polycrystal show anisotropy in self-diffusivities***

Tracer Diffusion Benefits - contd.

Volume and grain boundary diffusion coefficients

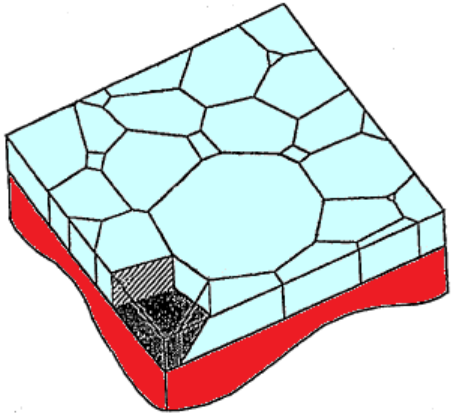


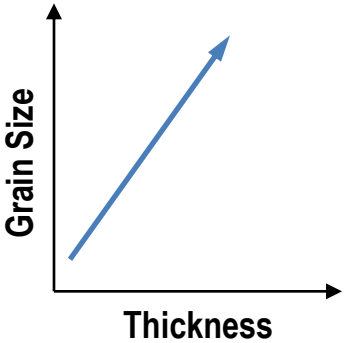
Schematic illustration of diffusion regimes in a polycrystalline material according to Harrison's classification scheme. D is the bulk (volume) diffusion coefficient, D_{gb} is the grain boundary diffusion coefficient, d is the grain size, δ is the grain boundary width, and t is the diffusion time. [De Souza, Martin et al., MRS Bulletin, vol. 34, Dec 2009].

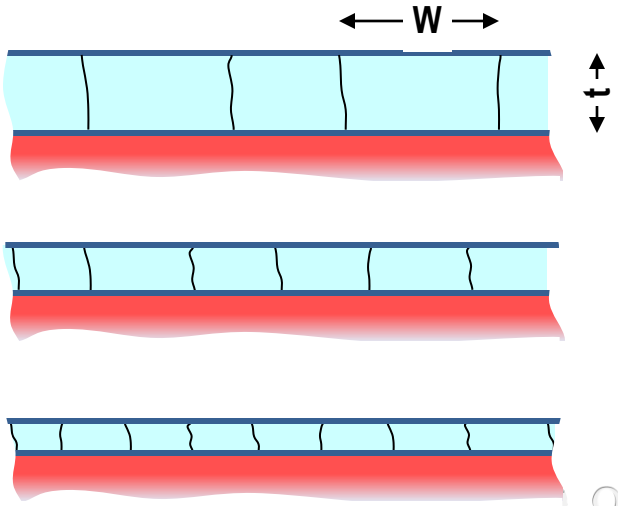
Tracer Diffusion Benefits - contd.

Grain boundary diffusion using films: Harrison A (planned)

- 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 elements produces variety of multicomponent films for diffusion studies



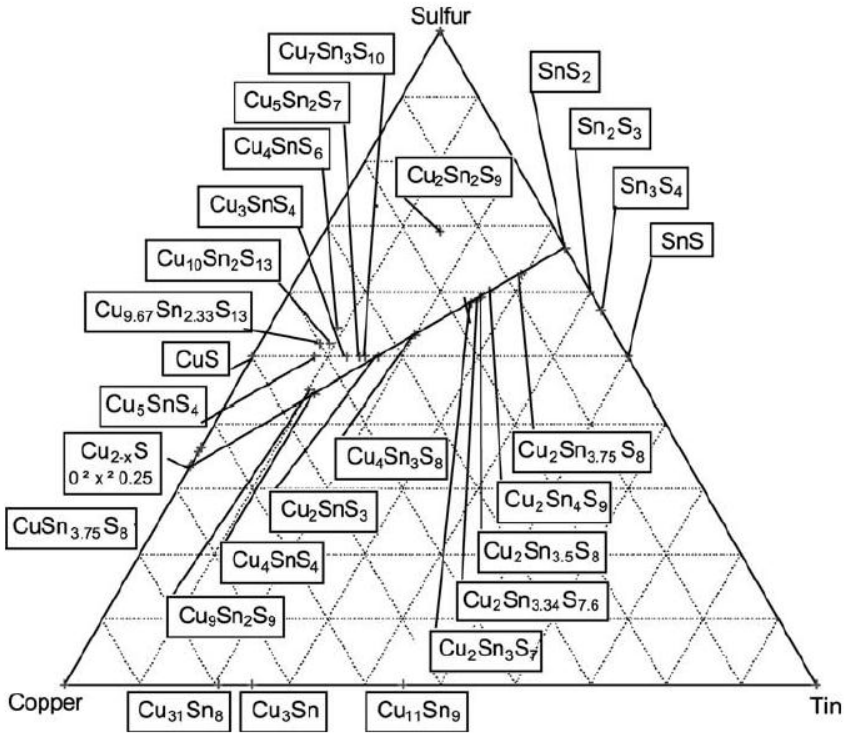




Oak Ridge National Laboratory

Tracer Diffusion Benefits - contd.

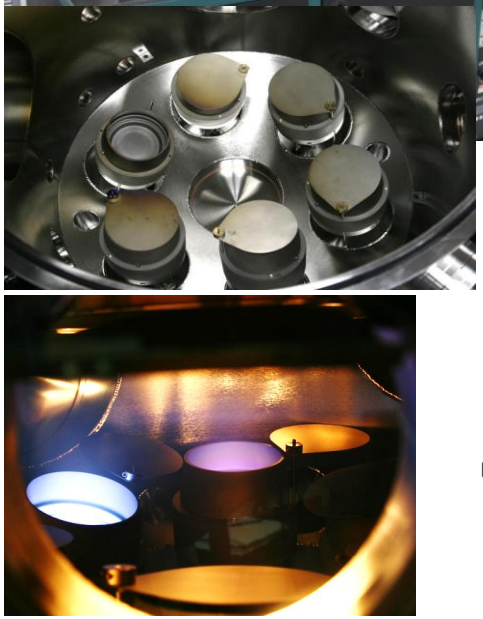
Data for stoichiometric compounds

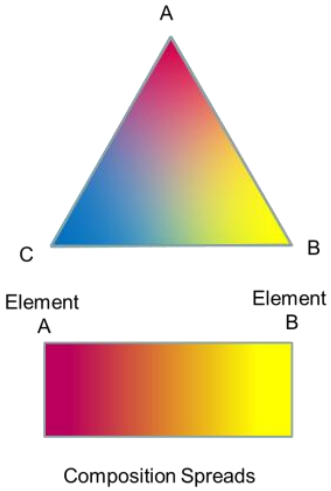


Ternary Cu-Sn-S (PV system) phase diagram

S. Fiechter et al. / Journal of Physics and Chemistry of Solids 64 (2003)

- ***May be easier to prepare "thin-film" compounds to measure tracer diffusivities***





Magnetron Co-sputtering System

Tracer Measurements: Radiotracer vs SIMS technique

Attribute	Radiotracer	SIMS-stable isotope
Technique	Serial sectioning, residual activity – established technique	SIMS complexity, sputter roughening, calibration, ion mixing, etc.
Thin film solution – depth profile	Orders of magnitude	1-2 orders at most
Temperature	High temperature for larger depth sectioning	Low to moderate temperature to reduce sputter time (2-4 hrs for 5-10 μm)
Diffusion measurements in polycrystalline sample	Average diffusivity	Single crystal or average diffusivity
Diffusion regimes	Harrison A, B and C	Harrison A (effective)
Cost	Safety for each experiment, isotope cost	SIMS capital cost ($3-4M, isotope cost

SIMS Technique Complexity: Sputter roughness at ~2 μm depth

Impact Energy, kV	O-leak	Angle	Avg. Roughness, nm
Unsputtered			7.2
3	yes	37	10.7
2	yes	40.6	10.7
3	yes	40.6	12.2
3	yes	46	17.4
2	no	40.6	22.1
2.5	no	56.5	25.4
2.5	yes	56.5	26.2
3	no	37	27.9
3	no	54.5	28.3
3	no	40.6	28.5
3	yes	54.5	29.5
3	no	46	30.7
8	no	39	33.6
5	yes	44	36.5
5	no	44	37.7
3	yes	50	42.8
8	yes	39	48.2

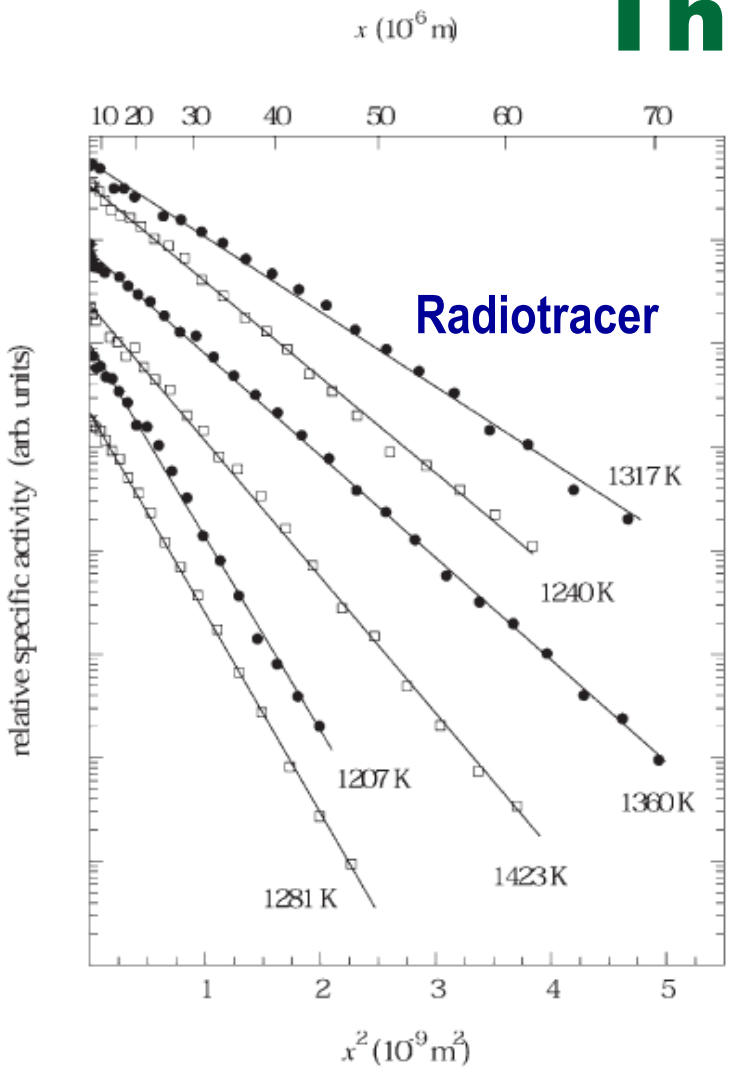
- Lower energy and closer to normal incidence give higher steady state oxygen concentrations
- Oxygen leak gives higher steady state oxygen concentration
- High steady state oxygen concentration leads to better oxidation
- Sputtering from an amorphous oxide gives less roughness than sputtering from a polycrystalline or crystalline material

Typical conditions

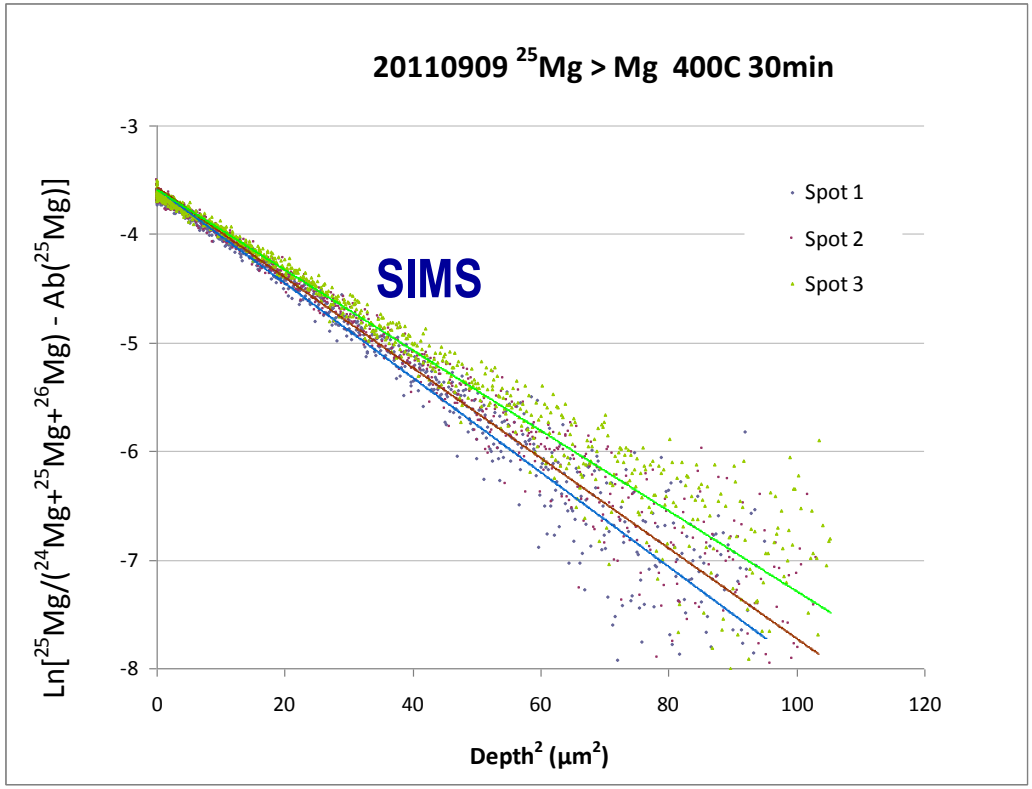
O-leak pressure in main chamber = 2 x 10^{-6} torr

➢ ***Variety of SIMS parameters affect sputter roughness which impacts data quality***

Thin Film Solution



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

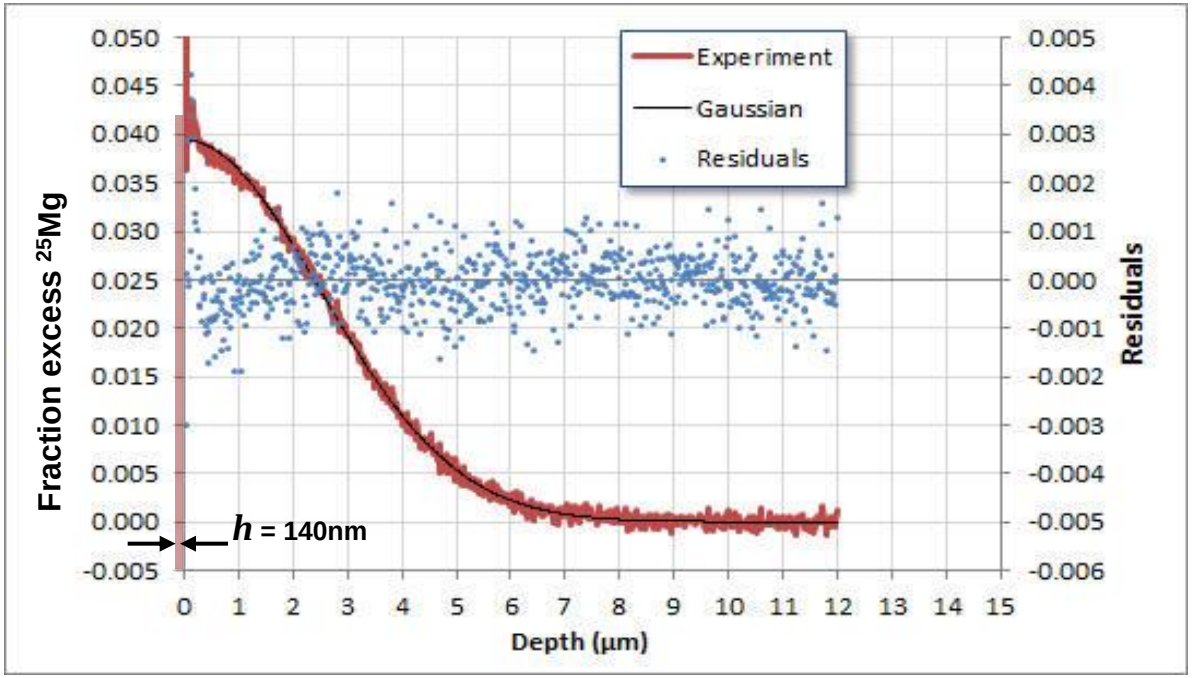


Gaussian plot of Ni-63* diffusion in NiAl using technique of serial sectioning of radiotracer (Frank et al., Acta Mater. 2001)

Gaussian plot of excess Mg-25 in pure Mg using SIMS depth profiling:

- Fit dominated by noise

Fitting of SIMS depth profiles

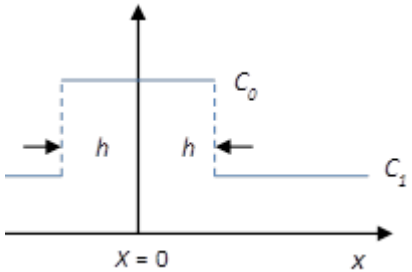


Example of SIMS measured excess abundance of tracer (Mg-25) as a function of depth for a magnesium sample diffused for ~1 hour at 350°C.

Thin-film error function solution

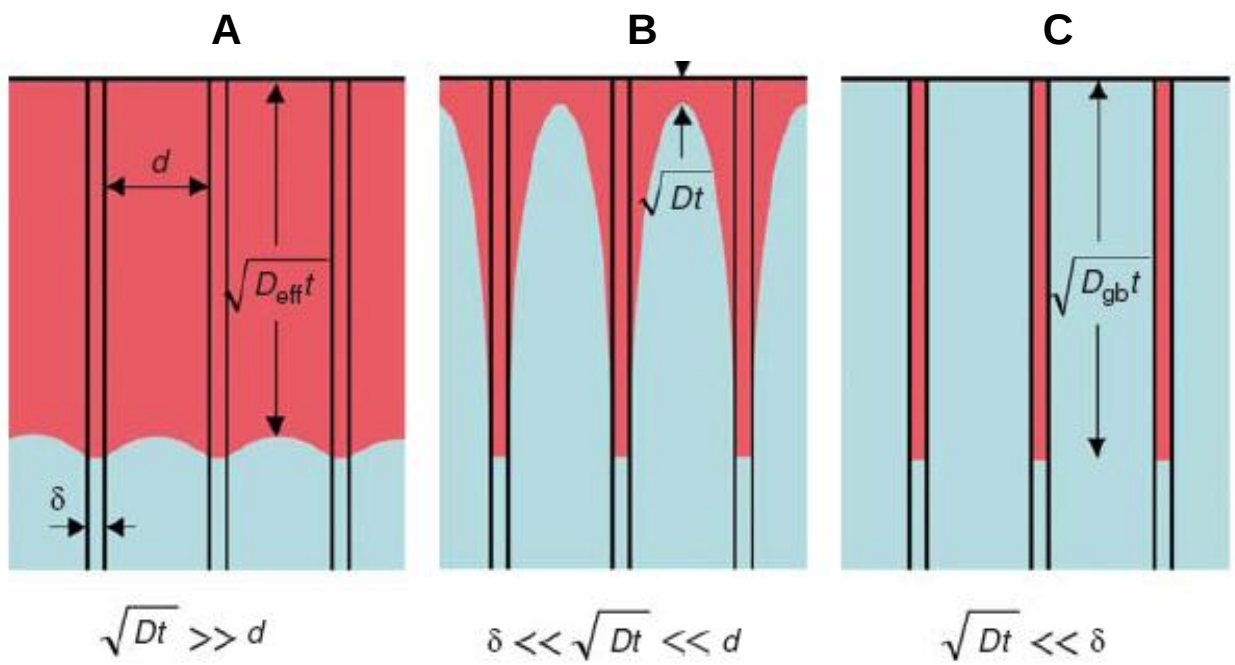
$$f(x) = \frac{C(x) - C_B}{C_0 - C_B} = \frac{1}{2}\left[\mathrm{erf}\left(\frac{x+h}{2\sqrt{Dt}}\right) - \mathrm{erf}\left(\frac{x-h}{2\sqrt{Dt}}\right)\right]$$

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



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

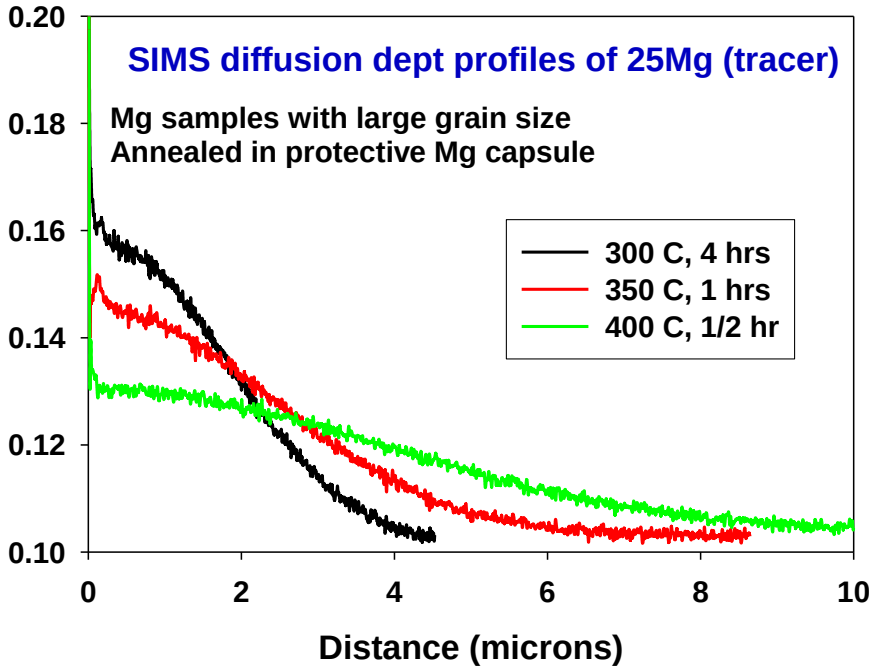
Diffusion regimes in polycrystalline samples



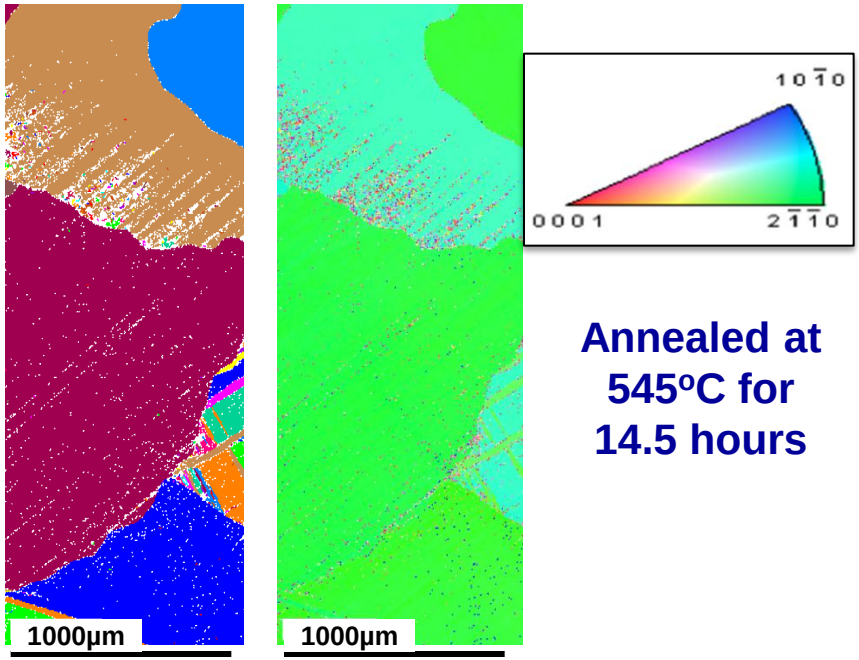
Harrison's classification scheme for diffusion in polycrystalline materials

- ***Radiotracer can be used for A, B and C***
- ***SIMS can be used for A and part B (volume diffusivity), C is not accessible.***

Diffusion measurements within single grains of polycrystalline sample



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



Annealed at 545°C for 14.5 hours

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.

➢ ***Depending upon spot size (1 – 50 μm) and grain size, either individual single crystal diffusivity or average diffusivity can be measured with SIMS***

Tracer Measurements in Mg-Al-Zn

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

- Annealing
- Analysis
- Modeling

UNIVERSITY OF CENTRAL FLORIDA

- Coating
- Interdiffusion
- Analysis

ORNL
project
coordination

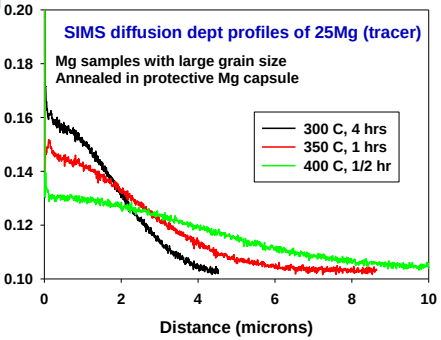
THE UNIVERSITY OF NEWCASTLE AUSTRALIA

Theory

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

VirginiaTech
Invent the Future

- SIMS
- XPS
- Characterization



Magnesium Elektron
SERVICE & INNOVATION IN MAGNESIUM

- Material casting
- Extrusion

ICME-CI

OAK RIDGE National Laboratory

ORNL Diffusion website

- http://www.ornl.gov/##.##

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.

Site hosted by Oak Ridge National Laboratory / Disclaimers / *Contact the webmaster*

c

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

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Diffusion
Interdiffusion
Theory
Communications
Literature

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

U.S. DEPARTMENT OF ENERGY

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

Resources

- Team Personnel
- UCF Facilities
- SIMS-XPS VaTech

Collaborators:

Oak Ridge National Laboratory
Bruce Warmack, (865) 574-6202; e-mail: warmackrj@ornl.gov
Balasubramaniam Radhakrishnan, (865) 241-3861; e-mail: radhakrishnb@ornl.gov
Peter Todd [retired]
Argonne National Laboratory
John Mundy [retired]
Virginia Tech
Jerry Hunter (540) 391-0366; e-mail: hunterje@vt.edu
Jay Tuggle, jaysmail@vt.edu
University of Central Florida
Yongho Sohn, (407) 882-1181, ysohn@mail.ucf.edu
Katrina Bermudez, kbermudez@knights.ucf.edu
Kevin Coffey, (407) 823-2175, krcoffey@mail.ucf.edu
Edward Dein, (407) 823-3584, Edward.Dein@ucf.edu
University of Newcastle, Australia
Graeme Murch, 61(2)49216191; e-mail: graeme.murch@newcastle.edu.au
Irina Belova, 61(2)49215717; e-mail: irina.belova@newcastle.edu.au

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

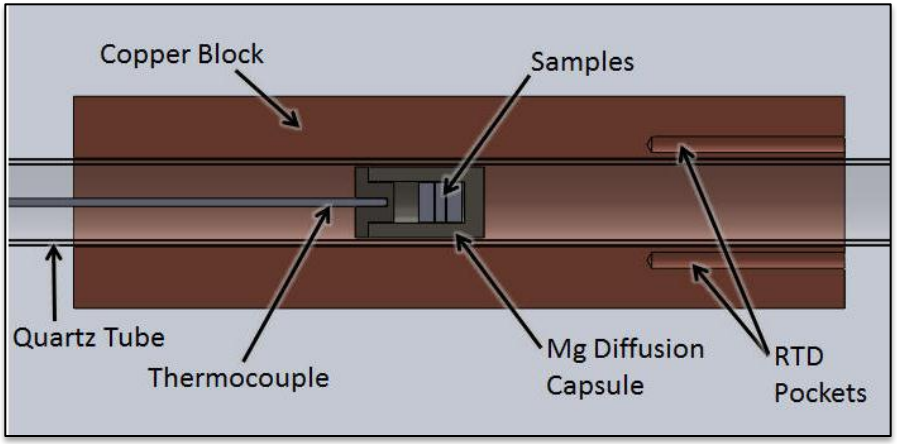
Isotope	^{53}Mn	^{55}Mn
Natural	trace	1.000
Tracer		

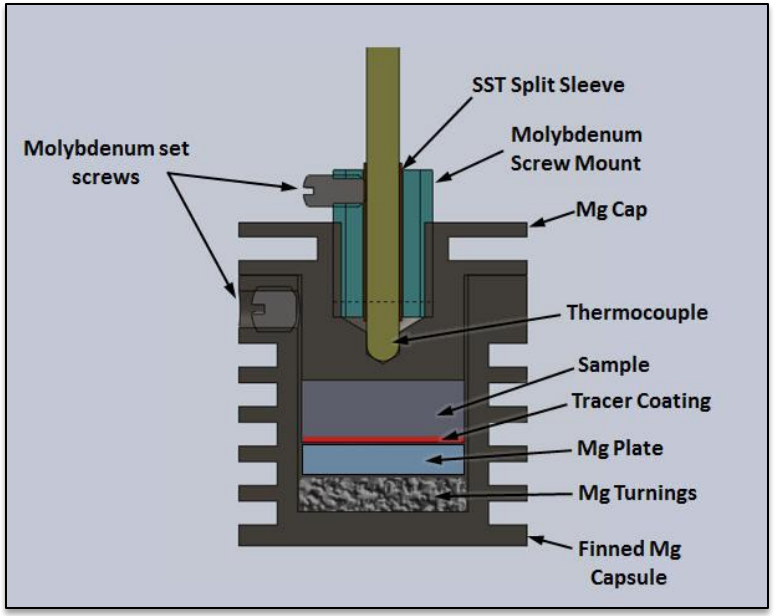
- NIST SRM980 Specs
- Galy 2003 - Magnesium isotope heterogeneity of the isotopic standard SRM980
- Coplen 2002 - Isotope Abundance Var of Selected Elements.pdf
- Rosman 1997 - Isotopic compositions of the elements.pdf

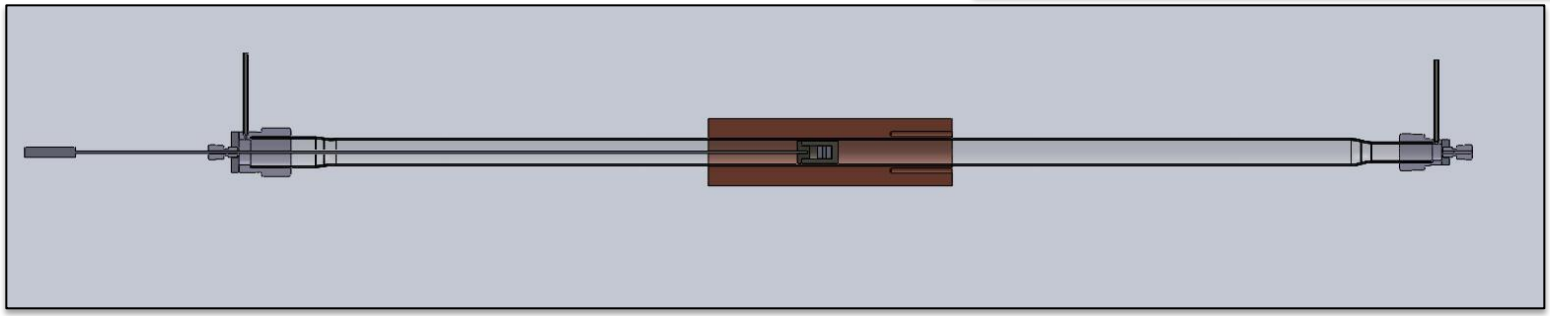
Site hosted by Oak Ridge National Laboratory / Disclaimers / Webmaster / Home

Mg Diffusion Annealing Technique

Shewmon-Rhines capsule upgrade





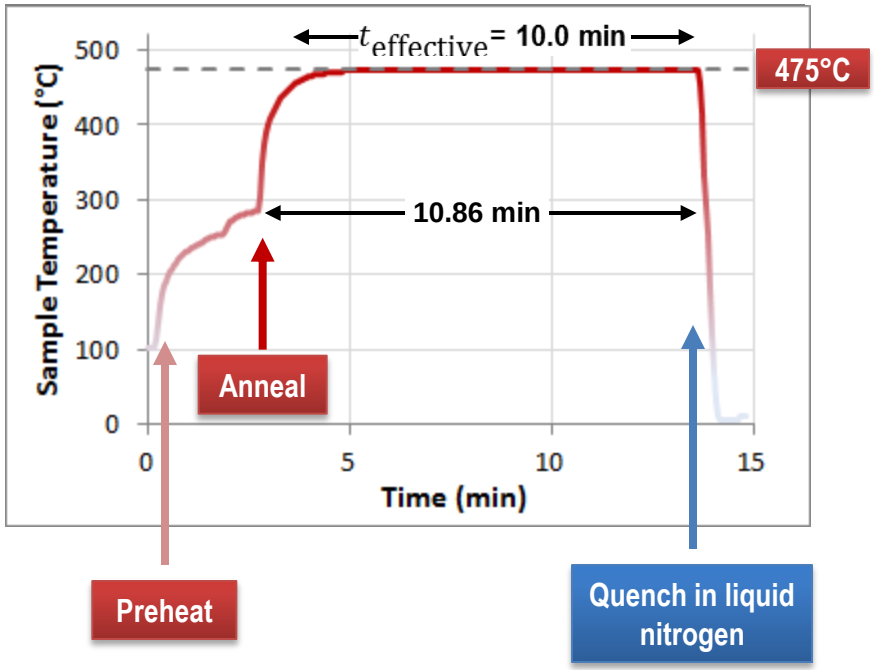


- Mg turnings act as natural getter to prevent oxidation
- Design allows rapid heating (Cu block, fin design) and cooling (liquid nitrogen)
- Thermocouple in capsule allows full correction and more accurate analysis especially for short anneal times (10 minutes)

Mg Self-diffusion Validation: 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

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



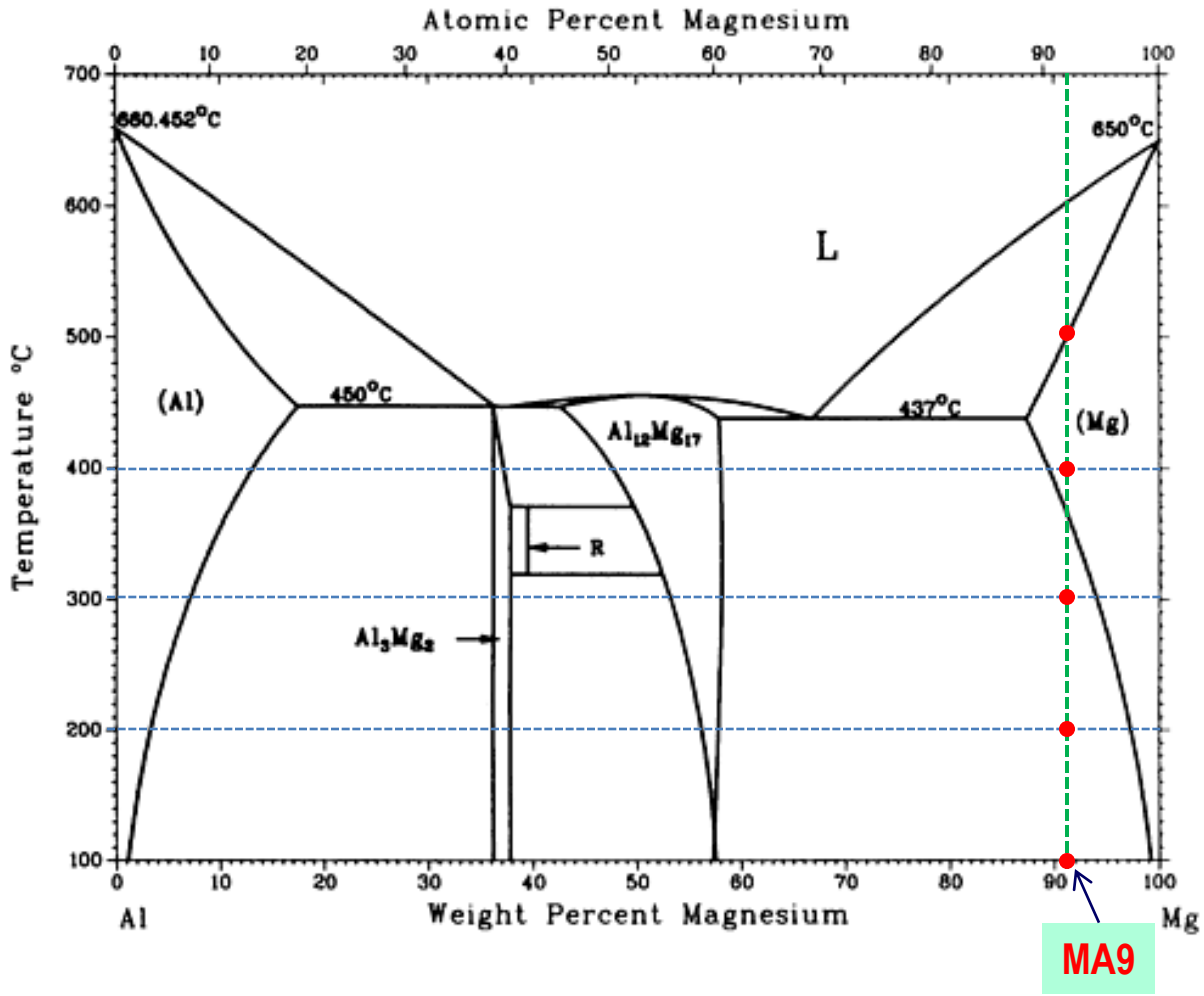
Mg-Al-Zn (MAZ) alloys

		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

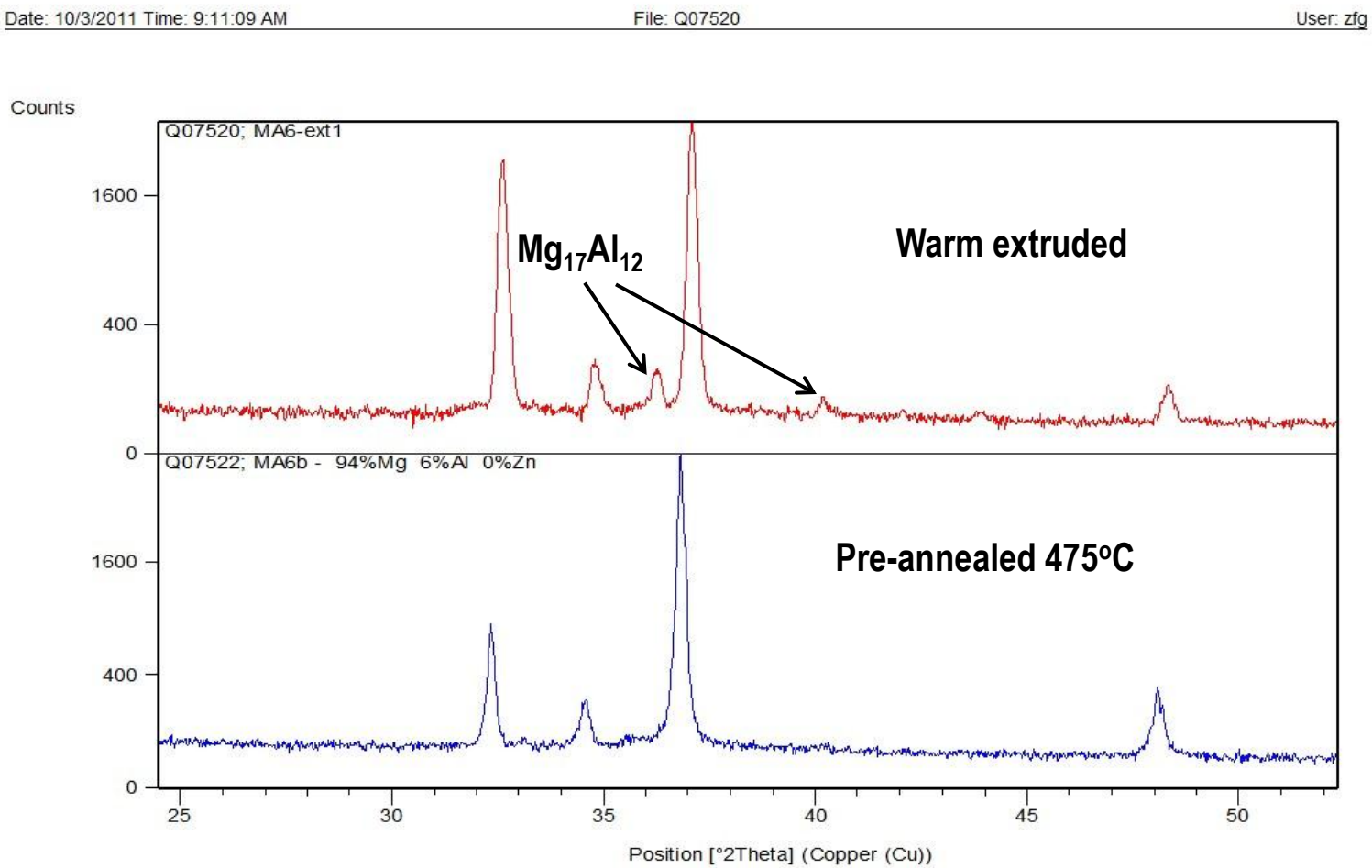
Other elements detected in trace amounts are Cu (<20 ppm), Sn (<20 ppm), Ni (<5 ppm), Zr (< 10 ppm) (ppm = parts per million).

Mg-Al Phase Diagram



➢ $Mg_{17}Al_{12}$ precipitates form during air cooling following warm extrusion

MA6 x-ray diffraction: as-extruded vs pre-annealed

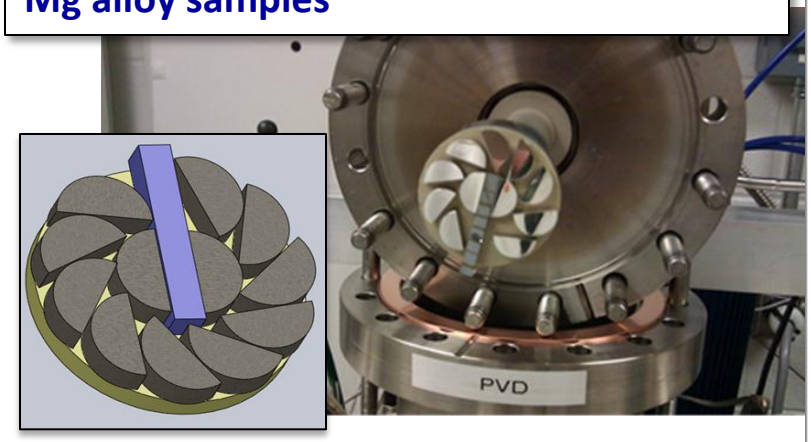


➢ ***Precipitate phase dissolved during pre-annealing at 475°C, 8 hrs***

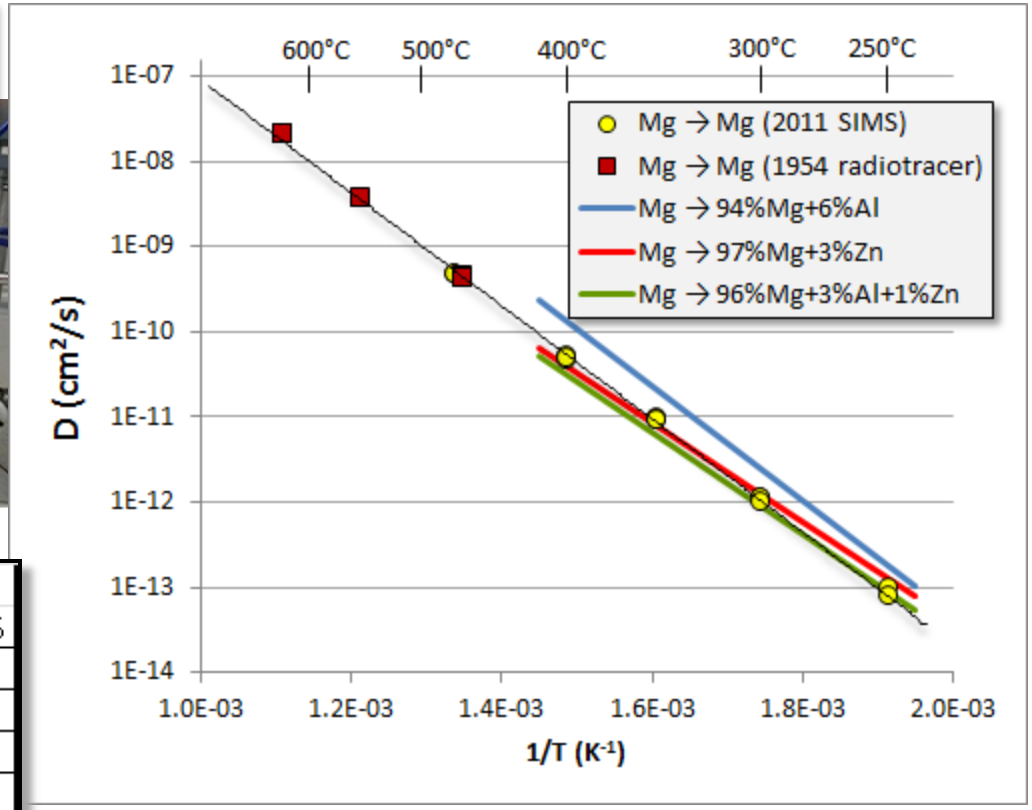
for the U.S. Department of Energy
National Laboratory

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)***

Summary

- Tracer diffusion provides a wealth of diffusion information that can be used to construct the diffusion genome for ICME or MGI
  - Volume, orientation dependent, grain boundary diffusion, effective diffusion, etc.
  - Tracer database permits use of complete Onsager phenomenological formalism for diffusion in the presence of chemical potential driving forces without assumptions
- Both radiotracer and SIMS-based stable isotope technique have some unique advantages that should be employed
- Mg and Zn tracer diffusion studies in several Mg-Al-Zn alloys are ongoing
  - Interdiffusion studies with diffusion couples are being conducted to extract Al tracer diffusivity using diffusion theory

OAK RIDGE National Laboratory

Acknowledgements

U.S. Department of Energy Assistant Secretary for Energy Efficiency and Renewable Energy Office of Vehicle Technologies as part of the Automotive Lightweight Materials Program under contract DE-AC05-00OR22725 with UT-Battelle, LLC

Special Thanks

John Allison and Bob McCune: Mg-ICME Program
Carol Schutte (Team Lead) and William Joost (Materials Engineer): Vehicle Technologies Program, DOE
Joe Carpenter: Former program manager, Automotive Lightweight Materials Program, DOE
Phil Sklad, Dave Warren: Automotive Lightweight Materials Program, ORNL

End

The phenomenological coefficients are dependent upon the collective correlation factors and the basic tracer jump frequencies

For example, for a binary alloy:

$$L_{AA} = \frac{a^2 w_A c_V c_A N f_{AA}}{kT}$$

$$L_{BB} = \frac{a^2 w_B c_V c_B N f_{BB}}{kT}$$

$$L_{AB} = L_{BA} = \frac{a^2 w_A c_V c_A N f_{AB}^{(A)}}{kT} = \frac{a^2 w_B c_V c_B N f_{AB}^{(B)}}{kT}$$

N: number of lattice sites per unit volume

$f_{ii},\ f_{ij}^{(i)}$ **: collective correlation factors (the correlated parts of the phenomenological coefficients)**

The Darken approximation

All off-diagonal phenomenological coefficients are put equal to zero.

$$L_{ij} = 0 \quad \text{for } i \neq j.$$

All atoms must follow uncorrelated random walks, i.e. the tracer and the diagonal collective correlation factors are simply given by:

$$f_i = 1 \qquad f_{ii} = 1$$

and the off-diagonal correlation factors are equal to zero:

$$f_{ij} = 0 \quad \text{for } i \neq j.$$

Very simple relations then exist between the diagonal phenomenological coefficients and the tracer diffusion coefficients:

$$L_{ii} = c_i \, Dt^*_i / kT$$

By enforcing this relation, the diagonal phenomenological coefficients are then corrupted in their meaning because they now 'carry' any off-diagonal information (Manning, Acta Met. 1967) .

Do the phenomenological coefficients have an atomistic meaning?

$$L_{ij} = \frac{< \mathfrak{R}_i \cdot \mathfrak{R}_j >}{6VkTt}$$

(Allnatt 1982)

$\mathfrak{R}_i$: **the 'collective displacement' or displacement of the '<u>center-of-mass</u>' of species i in time t.**

e.g.

$$L_{AA} = \frac{< \mathfrak{R}_A^2 >}{6VkTt} \qquad L_{AB} = \frac{< \mathfrak{R}_A \cdot \mathfrak{R}_B >}{6VkTt}$$

If the moving *A* species does not interfere with the moving *B* species

e.g. *A* and *B* do not compete for the same defects

or *A* and *B* do not interact (i.e. different sublattices)

$$\Rightarrow \quad < \mathfrak{R}_A \cdot \mathfrak{R}_B > = 0 \quad \text{and } L_{AB} = 0.$$

➢ ***In most cases of solid-state diffusion, the off-diagonal coefficients can be quite significant and should never be casually discarded.***

Murch et al. MST 2011

So. Are correlations important in diffusion ?

It depends.....

● At the very best, a tracer diffusion coefficient can be measured with a precision of 5%. A precision of 30% is still considered very good.
Thus for **self-diffusion in pure metals**, tracer correlations that typically produce a 30-50% reduction in the diffusion coefficient could be considered borderline in numerical importance.

● For typical **solute diffusion in metals**, the correlation factor can however make a sizable contribution (probably up to 10%) to the activation energy and, for a fast diffuser, perhaps reduce D_0 by an order of magnitude.

● For **self-diffusion in disordered alloys**, tracer correlation effects can reduce D_0 (of the fast diffuser) by roughly an order of magnitude in typical disordered alloys. Again there will be a contribution to the total activation energy of up to 10%.

● For **self-diffusion in intermetallics** <u>with antisite disorder</u>, tracer correlation effects are now greatly magnified because of jump reversals. D_0 can be reduced by up to 3 or 4 orders of magnitude and contributions to the activation energy may be as high as ~ 30%, perhaps more.

● **Collective** transport quantities such as interdiffusion and intrinsic diffusion coefficients are affected by collective correlation effects.
By and large, these effects will produce quite similar behaviour as for tracer correlation effects. For example, chemical diffusion in an intermetallic will be greatly affected.

● In quantities such as **Haven ratios and vacancy-wind factors**, most of the correlation effects that would lead to large changes in the individual diffusion coefficients, **now largely cancel out.**

-For typical **disordered alloys**, putting in the vacancy-wind factor would give a deviation of up to a factor of two (higher) than the Darken equation.
-For **intermetallics**, the deviation would be up to a factor of two (lower) than the Darken equation.
-For **ionic compounds**, the deviation would be less than 25% from the Nernst-Planck equation.