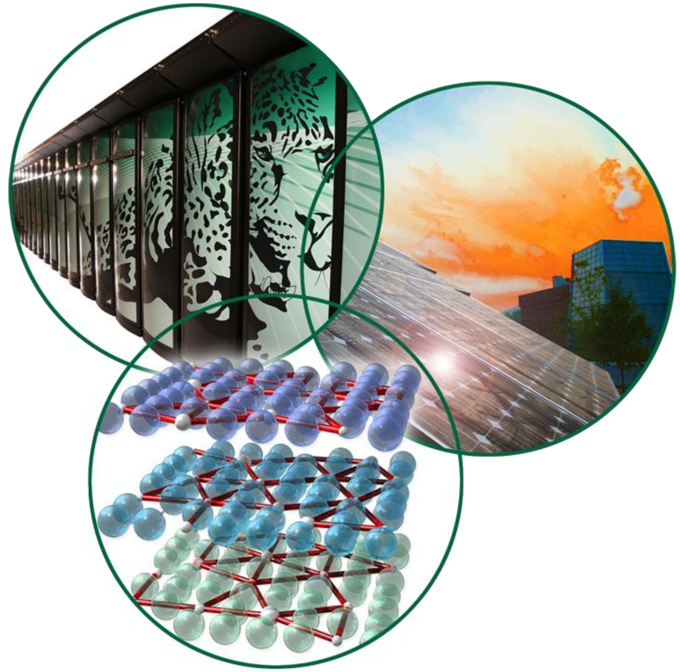
Design and Modeling of Grain Boundary Diffusion Experiments in Magnesium Thin Films using SIMS



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DOE-EERE Vehicle Technologies Program

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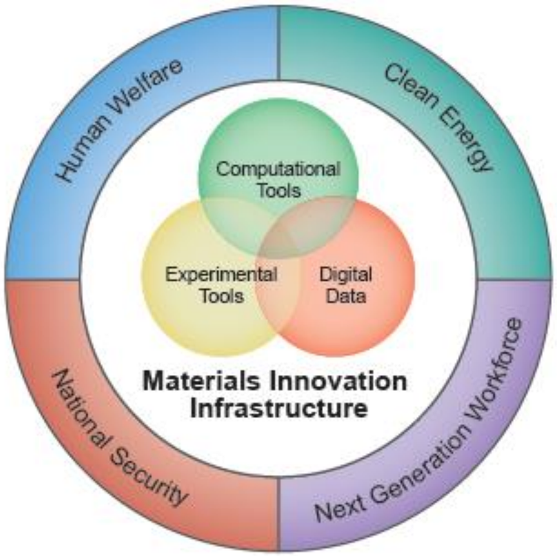
Outline

- Importance of grain boundary (gb) diffusion
- Motivation
- Harrison's classification scheme
  - Regime A
  - Regime B
  - Regime C
- B-kinetics: Experimental conditions for Mg self-diffusion
  - Notable obstacles and gb diffusion modeling to optimize experimental conditions
- GB diffusion modeling using Mathcad (ver 15)
  - Whipple solution (infinite source)
  - Suzuoka solution (finite/thin film source)
  - Averaged Suzuoka solution (measured with SIMS)
  - Computing SIMS intensity in tail region under various experimental conditions
- Conclusions: SIMS potential for gb diffusion studies

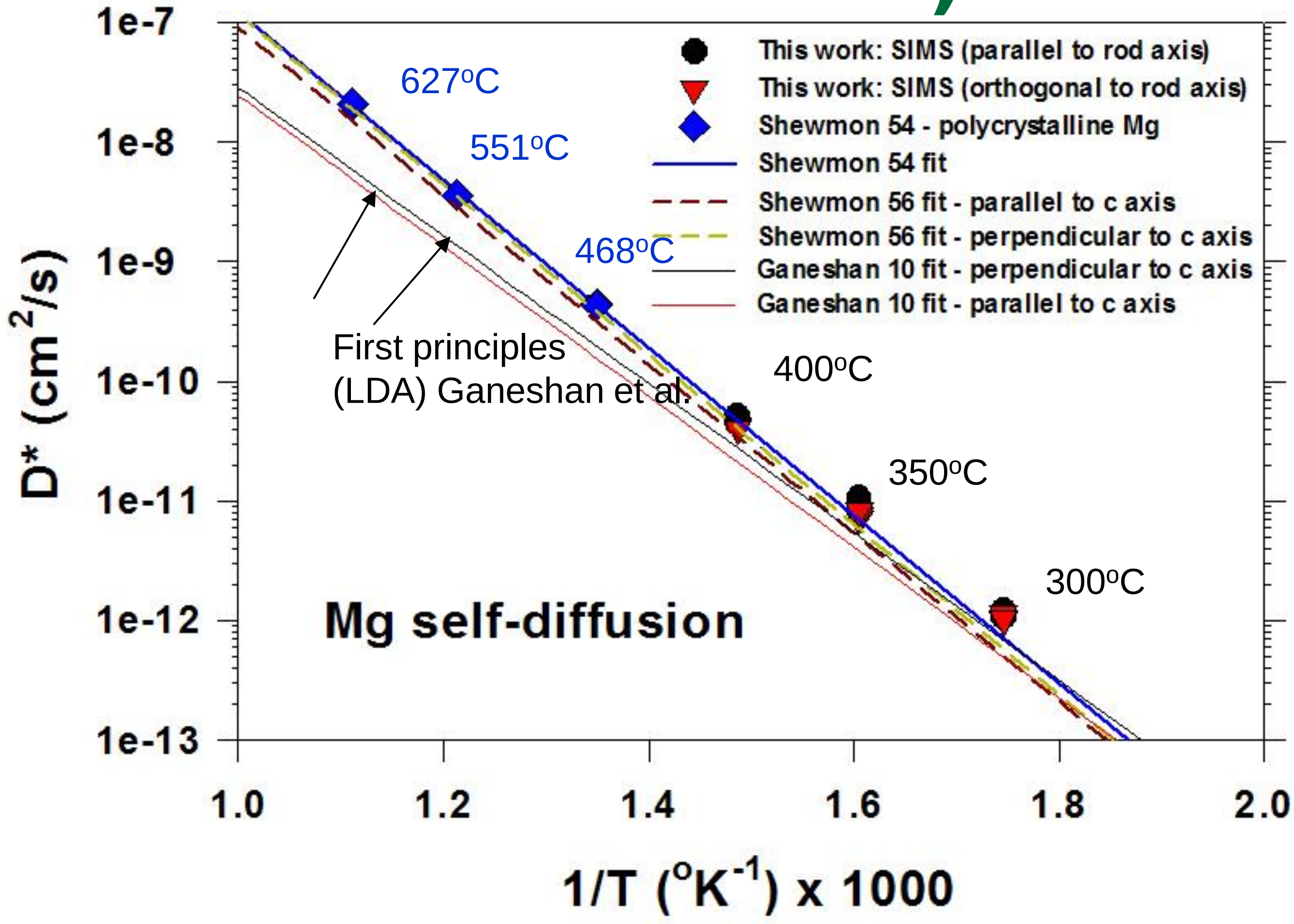
Motivation

- **Mg grain boundary (GB) diffusion data not available**
- **Importance:**
  - **Fine grained Mg for higher strength**
    - ***GB diffusion effects enhanced with smaller grains***
  - **Preferential nucleation of precipitates at GBs**
  - **GB diffusion controls grain growth and creep processes**
  - **Impurity diffusion along GBs (e.g., Dy in NEO magnets)***
  - **Electromigration in microelectronic devices**
- **Integral part of "diffusion genome" required for MGI efforts**



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

Mg Self-Diffusion Data (Previous Work)



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

➤ ***No grain boundary diffusion data in Mg***

Effective Diffusion in a Polycrystalline Microstructure

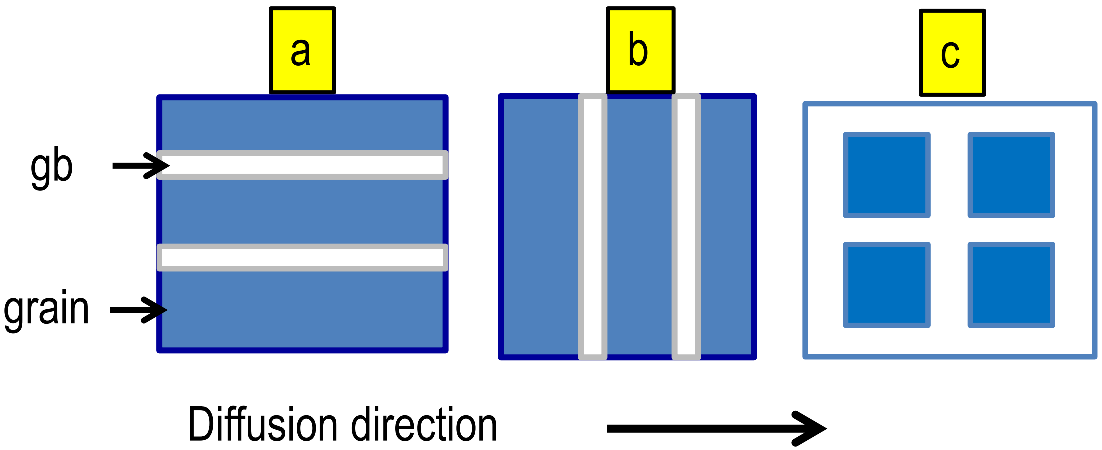
Tracer Diffusion Coefficients
(Bulk, Surface & Grain Boundary)

+

Microstructure

=

Effective Diffusion Coefficients
(Phase field, Monte Carlo; *Analytical*: Hart, series, Maxwell)



a

$$D_{eff}\,(Hart) = fDgb + (1-f)D$$

b

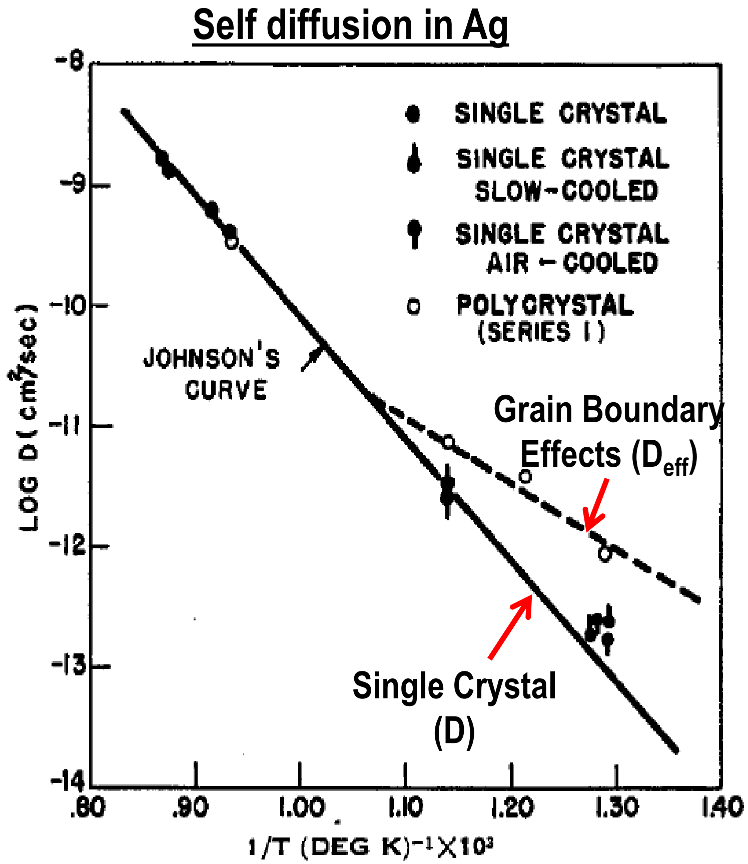
$$D_{eff}\,(series) = \frac{D_{gb}D}{fD_{gb} + (1-f)D}$$

c

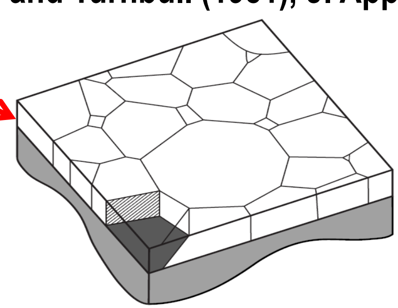
$$D_{eff}\,(Maxwell) = \frac{D_{gb}[(3-2f)D + 2fD_{gb}}{fD + (3-f)D_{gb}}$$

Grain Boundary Diffusion

- Bulk diffusion dominates at high temperature
- Grain boundary effects dominate at low temperature
- *Thin films:*
  - Better control of the necessary grain sizes due to dimensional constraints
  - Bamboo microstructure with controllable gb's (tilt)
  - Short diffusion distances (low T)
  - Ease of sample preparation and SIMS analysis



[Hoffman and Turnbull (1951), J. Appl. Phys., vol. 22]



Grain Boundary Diffusion Regimes

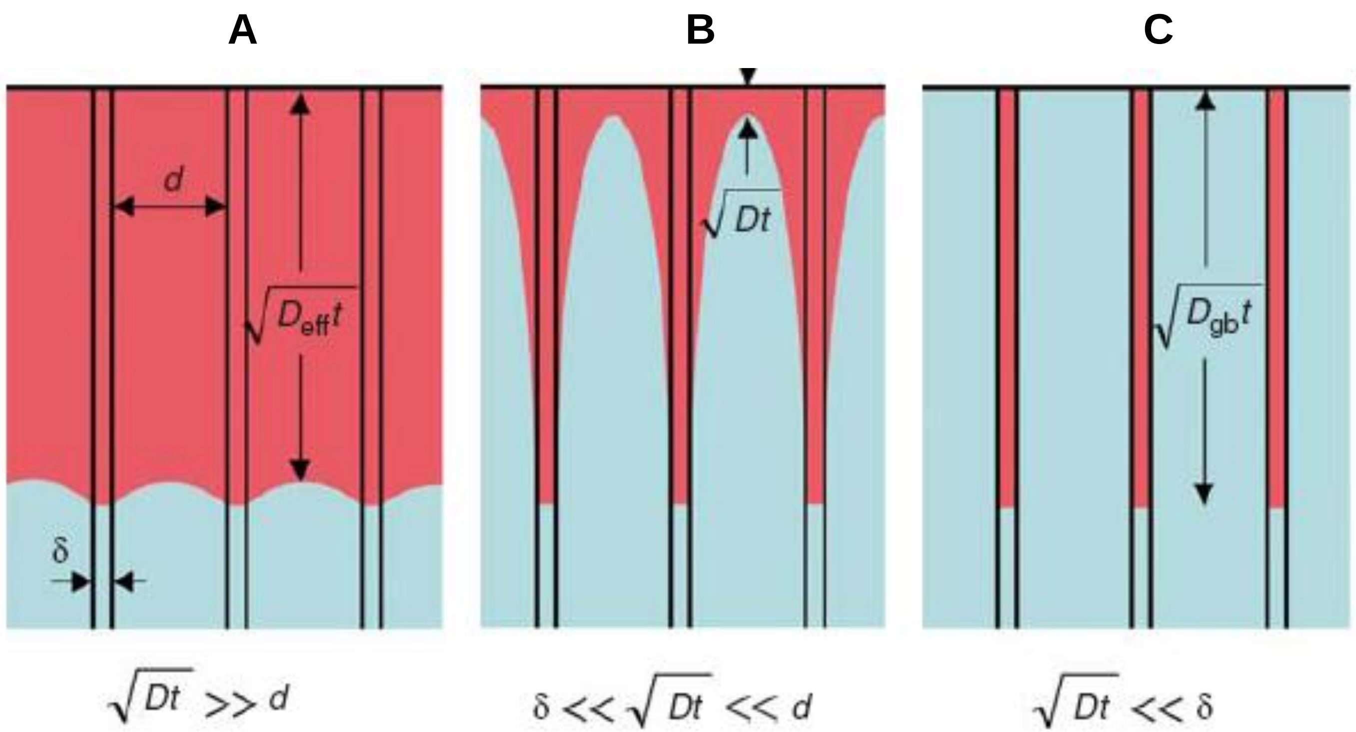
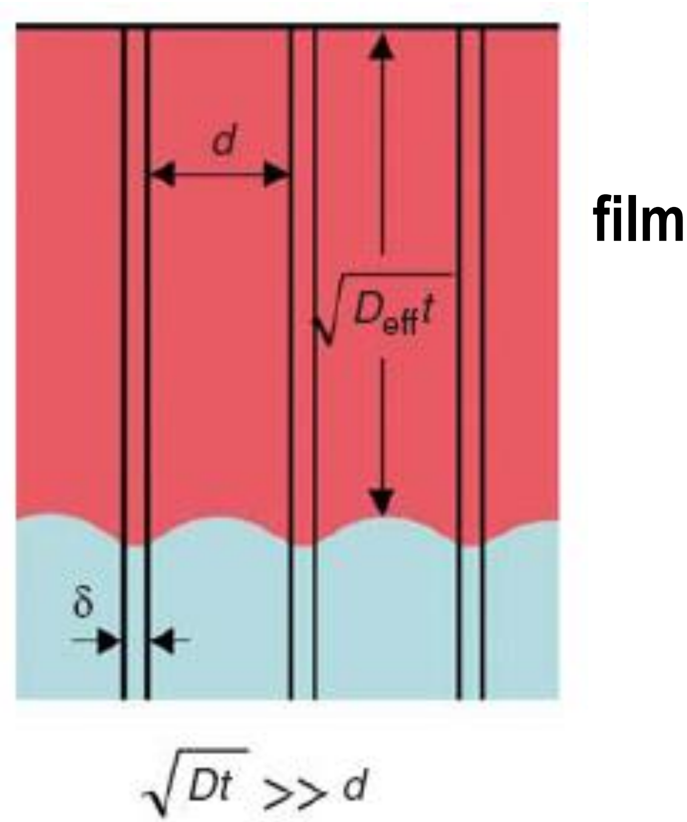


Illustration of polycrystalline diffusion regimes according to Harrison's classification scheme (parallel slab model) [*Trans Far Soc 1961*]. D is the volume diffusion coefficient, D_{gb} is the grain boundary diffusion coefficient, d is the grain size, δ is the grain boundary width, and t is the diffusion time. *[De Souza et al. 2009, MRS Bulletin]*.

- ***More analysis of diffusion regimes by Belova & Murch (Phil Mag 09), Divinski et al. (Z. MetallK 02), book by Kaur, Mishin & Gust (Wiley, 3rd ed.)***

A-Kinetics in Thin Films

- Conflicting limiting conditions for A-kinetics and thin films
  1. $\sqrt{Dt}$ >> d
     - Sufficient lateral diffusion from GB
  2. $6\sqrt{D_{eff}t} \leq t_{film}$
     - Diffusion cannot extend beyond film thickness
- Grain size related to film thickness when grain growth saturates in thin film due to dimensional constraints (C.V. Thomson, Annu. Rev. Mat. Sci. 2000): $d \approx 2 \cdot t_{film}$
- Either grains or diffusion distance will be too large, cannot satisfy both conditions!



$$D_{eff} = -\frac{1}{4t}\left[\frac{\partial(lnC)}{\partial(x^2)}\right] \text{ (Gaussian)}$$

$$D_{eff}^{Hart} = fD_{gb} + (1-f)D$$

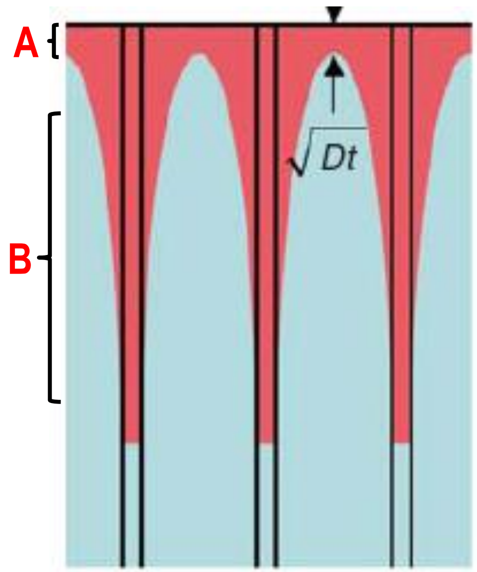
*f = volume fraction of grain boundaries

B-Kinetics in Thin Films

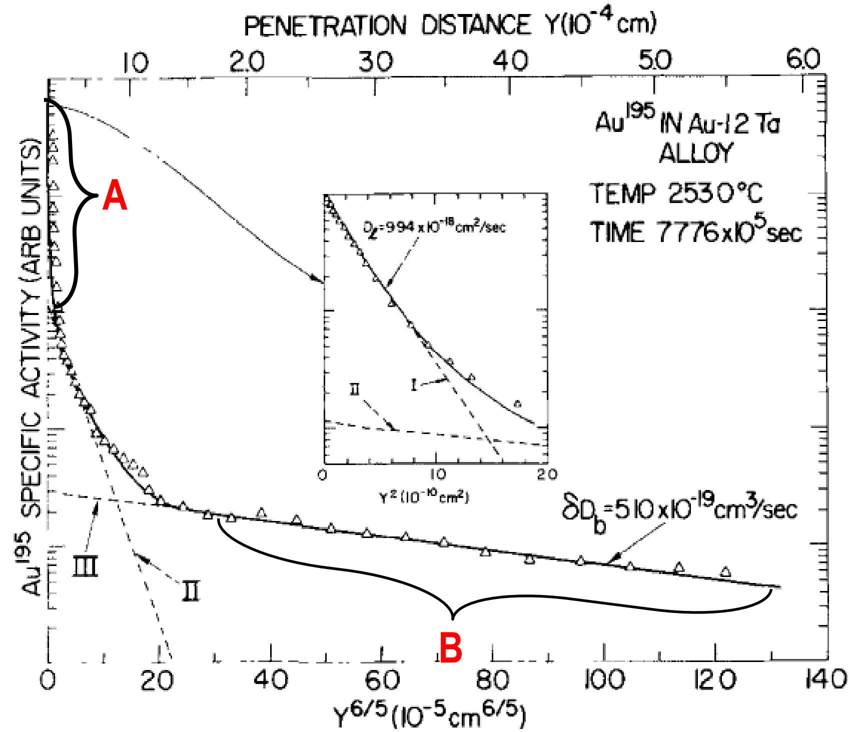
A: D = - $\frac{1}{4t}\left(\frac{\partial ln(C)}{\partial x^2}\right)$

B: $s\delta D_{gb}$ =

$0.66\sqrt{\frac{D}{t}}\left(\frac{\partial ln(C)}{\partial x^{6/5}}\right)^{-5/3}$



$\delta << \sqrt{Dt} << d$

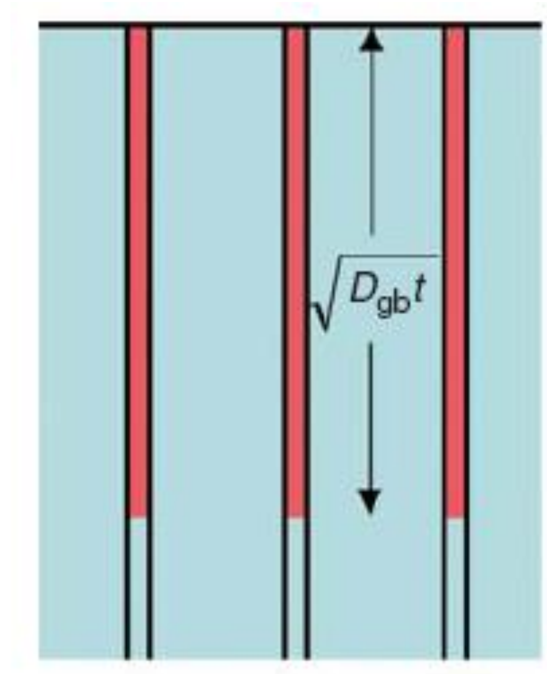


[Gupta (1977), Met. Trans. A, vol. 8A]

- **Realistic diffusion anneal times and temperatures**
  - Relatively easy to satisfy δ << $\sqrt{Dt}$ << d with thin film restrictions
- **Dual analysis – extract both D and $s\delta D_{gb}$ (s = impurity segregation factor, δ =grain boundary width) from separate regions**

C-Kinetics in Thin Films

- **Volume diffusion negligible, diffusant confined to grain boundary**
- **Can extract D_{gb} directly, not convoluted as $s\delta D_{gb}$ in regime B**
- **Very low volume fraction of GB**
  - **Difficult to detect such low concentrations with SIMS**
- **Requires extremely low diffusion times and temperatures**



$$\sqrt{Dt} << \delta$$

$$D_{gb} = -\frac{1}{4t}\left(\frac{\partial ln(C)}{\partial x^2}\right)$$

Objective

- **Develop a method to determine the grain boundary diffusion coefficient (D_{gb}) in thin films, and use it to find the self-D_{gb} in Mg and/or Al impurity D_{gb} for incorporation into the Mg- Integrated Computational Materials Engineering (ICME) project**

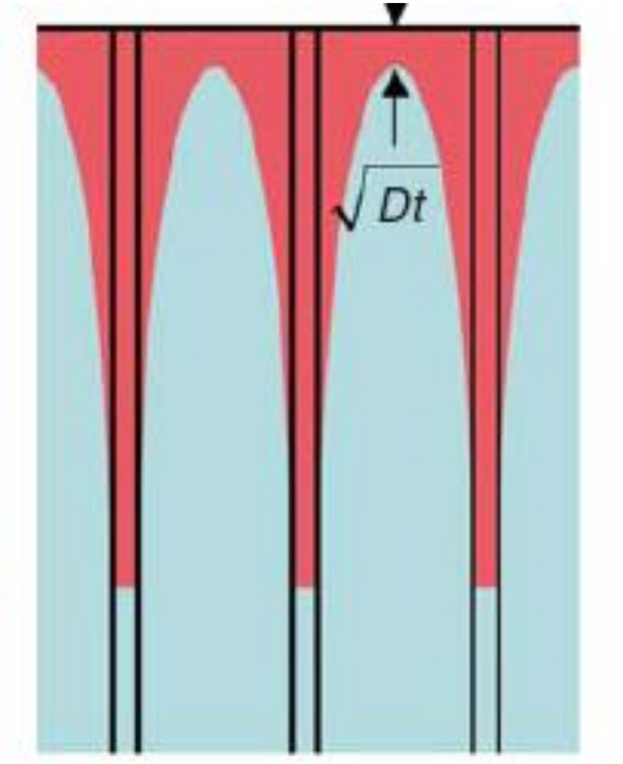
Approach/Strategy

- **Determine suitable diffusion conditions and thin film morphologies consistent with Harrison B-kinetics**
- **Measure tracer diffusion coefficients in Mg thin films using secondary ion mass spectrometry (SIMS) X**
- **Correlate diffusion coefficients with grain boundary orientations determined by EBSD X**

B-kinetics Limiting Conditions

1) $\delta << \sqrt{Dt} << d$

- $\frac{d}{\sqrt{Dt}} = \Lambda \geq 10$
  - **Ensure appreciable diffusion out of grain boundary into grains**
- $\frac{\delta}{2\sqrt{Dt}} = \alpha \leq 0.1$
  - **Avoids overlap of diffusion profiles from opposite boundaries into a single grain**

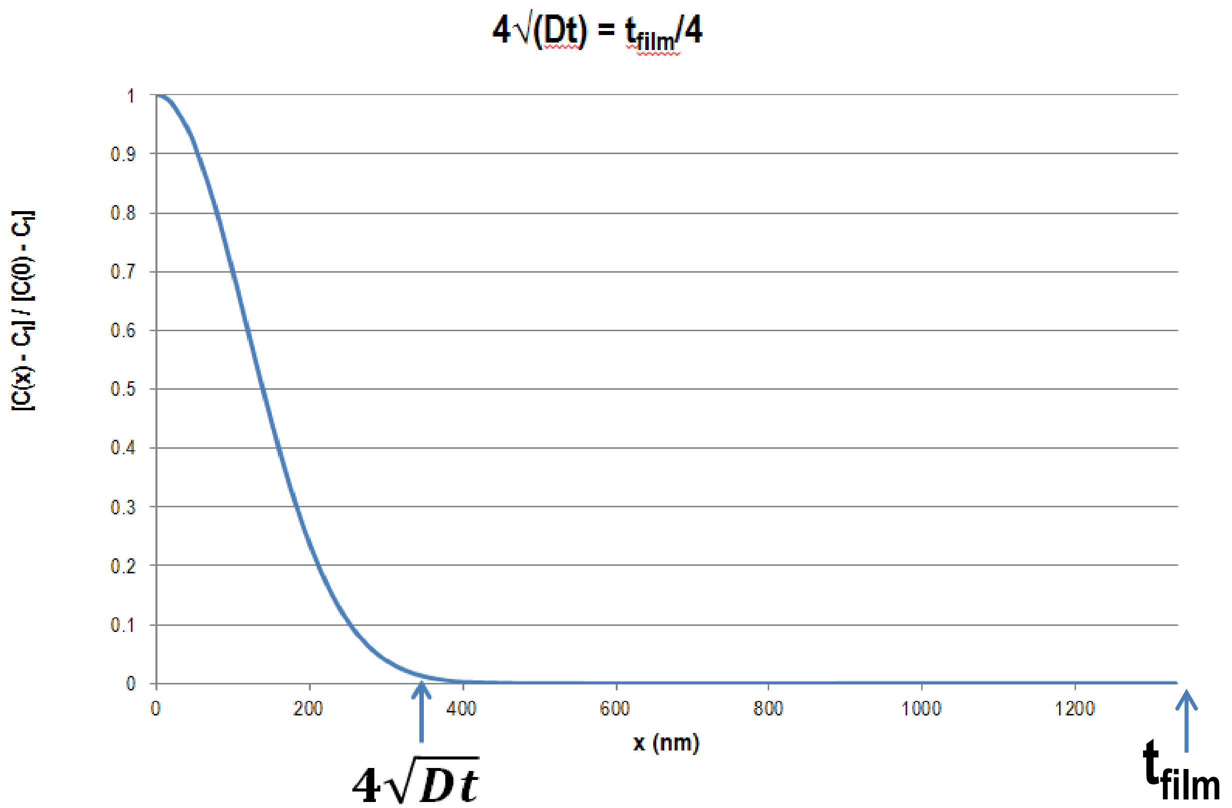


$\delta << \sqrt{Dt} << d$

***$\delta \approx 0.5$ nm in fcc materials**

Thin Film Geometry Requirement

2) $4\sqrt{Dt} \approx \frac{t_{film}}{4}$



- **Bulk diffusion negligible at x= $4\sqrt{Dt}$**
- **Set $4\sqrt{Dt}$ equal to ¼ t_{film} so that both (bulk and GB tail) regions are measureable**

Thin-film Approximation Requirement

3) $\sqrt{Dt} >> t_{tracer}$ (thickness of tracer layer on film)

Let $\frac{\sqrt{Dt}}{t_{tracer}} = \lambda \geq 5$

- Needs to be met in order to use the thin-film solution, which is more convenient

- Can use thick-film solution (more complex) if this condition is not met

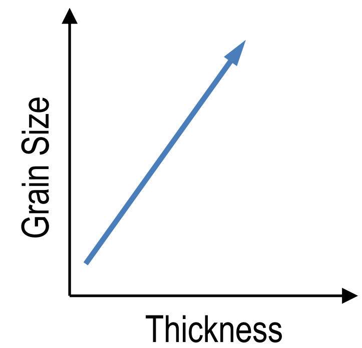
Limiting conditions

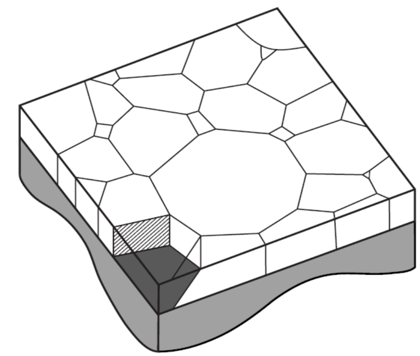
(1) $\delta << \sqrt{Dt} << d$ (2) $4\sqrt{Dt} \approx \frac{t_{film}}{4}$ (3) $\sqrt{Dt} >> t_{tracer}$

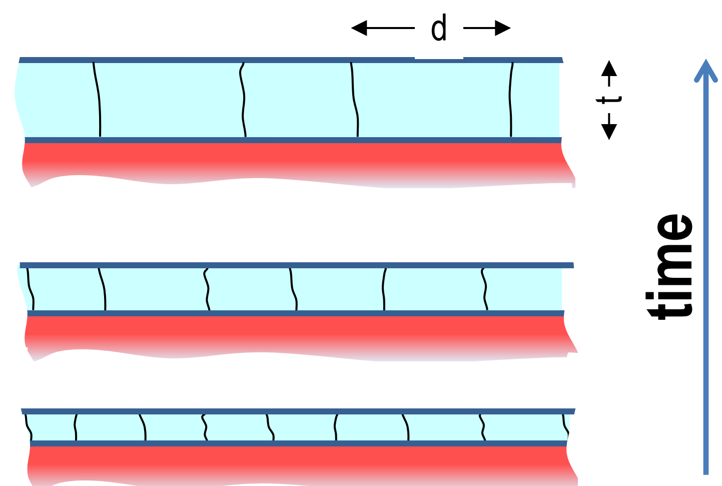
- Set up an Excel spreadsheet:
  - *Input:* temperature, diffusivity (D), film thickness (t_{film})
  - *Outputs:* diffusion time (t), minimum grain size (d), tracer thickness (t_{tracer})
- Easy to obtain conditions to satisfy all requirements:
  - Diffusion temperature range: 175 - 250^{o}C
  - Diffusion time: >10 min (exact time depends on temperature)
  - Mg film thickness: 500 – 2000 nm
  - Tracer film thickness: 10 nm

Proposed Experimental Design: Mg thin films

- Deposit Mg films (0.2, 0.6, and 1.8 µm thick) on single crystal Si wafers
  - Heated and non-heated substrates
- Anneal at various conditions
  - Specific times and temperatures
- Characterize grain size and orientations with EBSD or FIB
- Grain growth study to determine conditions for pre-annealing films that will be used for diffusion studies
  - Want equilibrium with grain boundaries normal to surface, and $d \approx 2 \cdot t_{film}$



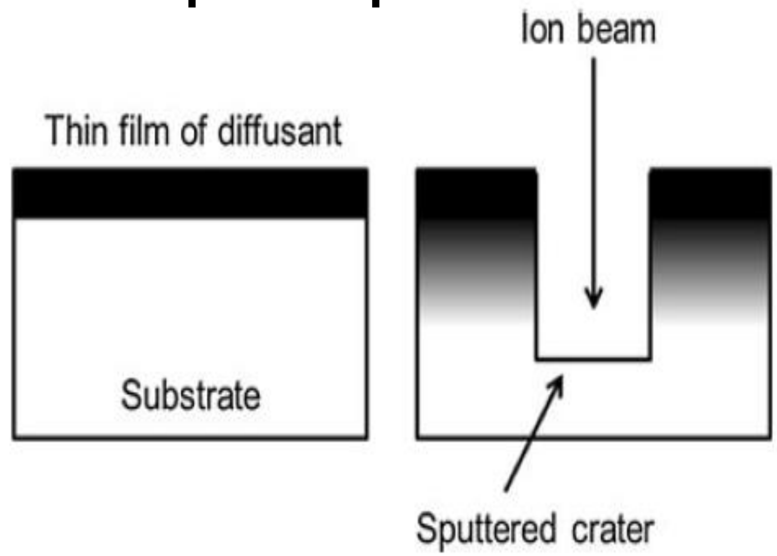




[Thompson (1990), Annu. Rev. Mater. Sci., vol. 20]

Experimental Design: SIMS-based Thin Film Technique

- Deposit thin ^{25}Mg tracer or Al impurity film (~10 nm)
- Diffusion anneal ($150^0C < T < 300^0C$, time varies with T and t_{film})
- Measure depth profile of isotope ratio using SIMS
- Analyze concentration profile to extract D in near surface region and $s\delta D_{gb}$ or δD_{gb} in tail region using appropriate solution fits
- Repeat at multiple temperatures to obtain Arrhenius fits

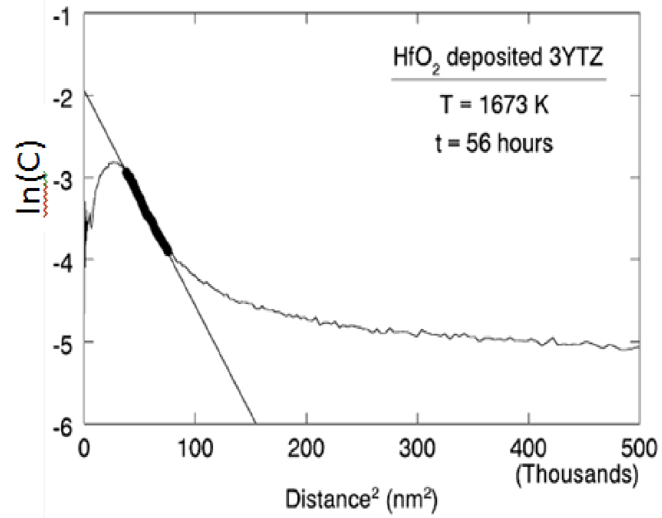


Cameca ims7f-Geo (Virginia Tech)

Dual Analysis from SIMS data (e.g. YTZ thin film)

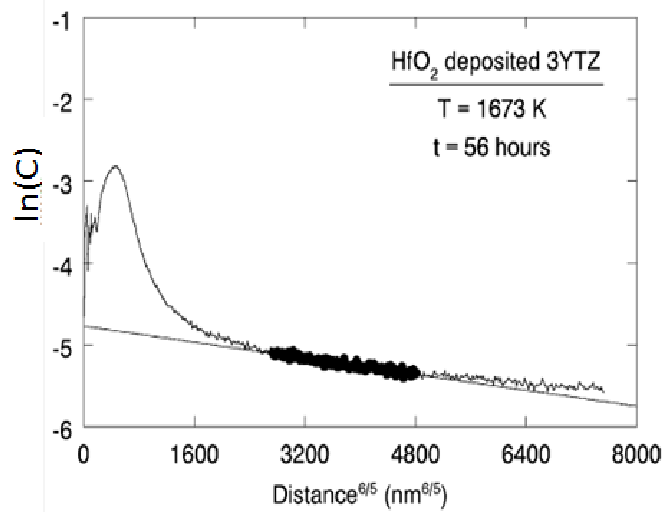
$$D = -\frac{1}{4t}\left(\frac{\partial \ln(C)}{\partial x^2}\right)$$

- **Bulk impurity diffusivity of Hf in YTZ in near surface region**
  - C = Relative Intensity ($^{178}Hf/^{91}Zr$)



$$s\delta D_{gb} = 0.66\sqrt{\frac{D}{t}}\left(\frac{\partial \ln(C)}{\partial x^{6/5}}\right)^{-5/3}$$

- **Triple product in tail region**
  - Least-squares non-linear fit or other algorithm also possible to fit data



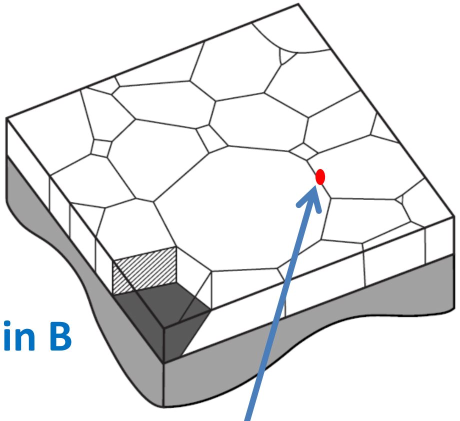
[Swaroop, *et al.* (2005), Acta Mat., vol. 53]

Notable Obstacles with SIMS for GB impurity diffusivity measurements

- SIMS result in B regime gives only $s\delta D_{gb}$
  - Need to separate the three terms by other methods including radiotracer and/or Atom Probe
- Only gives "average" D_{gb} over many grain boundaries
  - More beneficial for MGI if specific data can be obtained for many different grain boundary types (i.e. tilt, twist boundaries, specific misorientation angles, etc.)
- Grain growth is related to grain boundary diffusion
  - Grain growth will occur during diffusion anneal if films are not pre-annealed to achieve equilibrium grain size ($d \approx 2 \cdot t_{film}$)
- ^{25}Mg is naturally occurring in pure Mg (~10%)
  - SIMS needs to detect concentration above background, resolution might not be good enough deep in grain boundary tail region

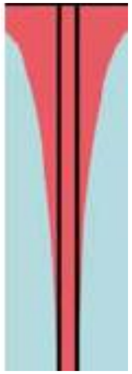
Overcoming SIMS obstacles

- **Atom Probe Tomography to obtain atomic-resolution, 3D map of single grain boundary after diffusion anneal**
  - Option for C-kinetics regime (can extract D_{gb} alone)
  - Grain boundary orientation-specific data
  - Deconvolute $s\delta D_{gb}$ into constituents if B-kinetics
  - Also carry out grain boundary self-diffusivity measurements in B and C to obtain δ
- **NanoSIMS to get concentration profile at a single grain boundary**
  - Used in conjunction with EBSD (electron backscatter diffraction) to associate the D_{gb} found to a single type and orientation of grain boundary
  - Also could be used to deconvolute $s\delta D_{gb}$ into constituents
- **Diffuse ^{25}Mg into pure ^{24}Mg films (~99%) to avoid problem of ^{25}Mg background signal in pure Mg**
  - Currently cost-prohibitive to use thick films of ^{24}Mg with high enrichment (~99%) because of technique used (calutrons) for isotopic enrichment
  - Development of new centrifugation techniques for Mg would have a major impact on cost of Mg isotopes



Location of NanoSIMS crater or Atom Probe Sample (Directly on Grain Boundary)

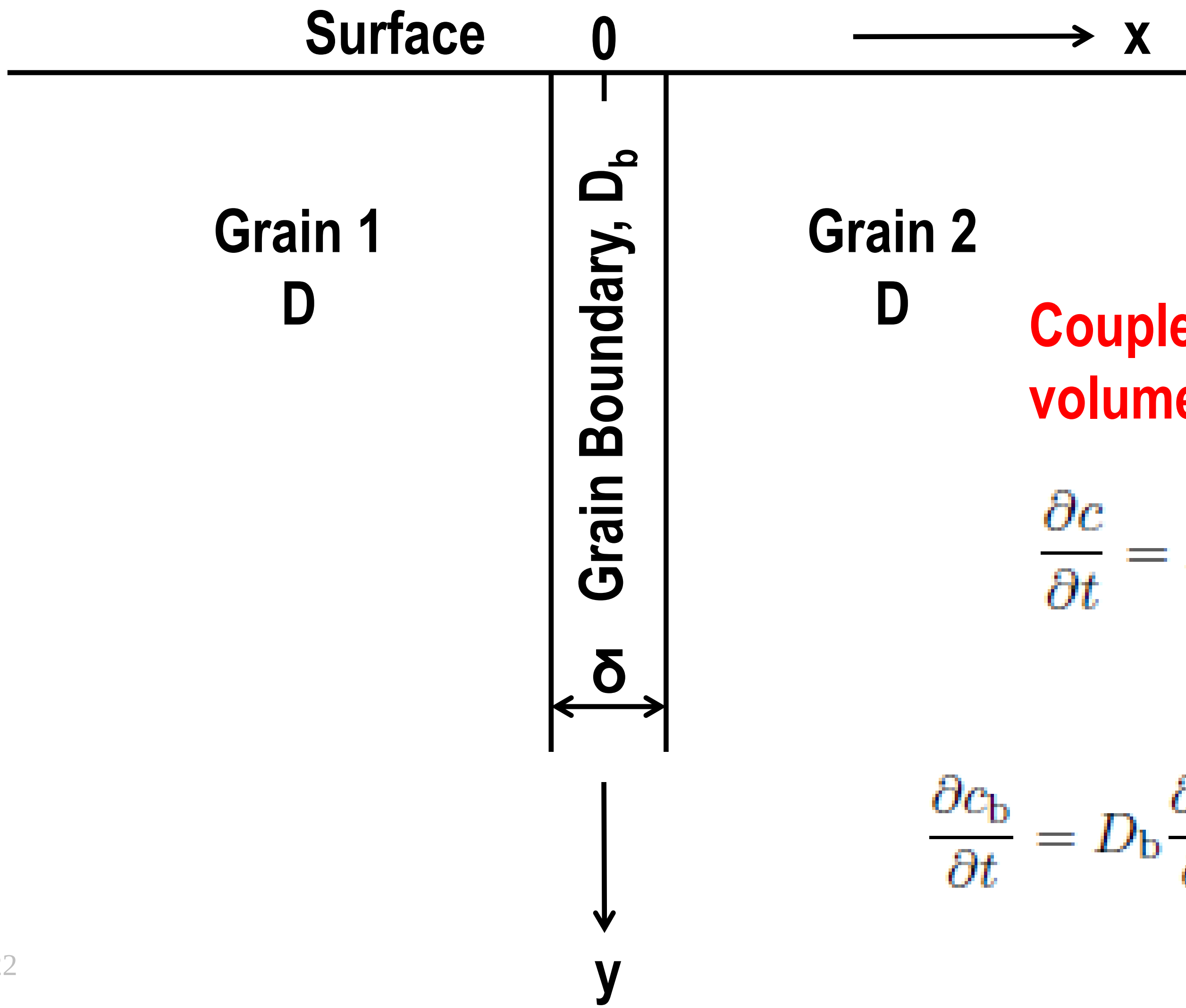
Side View of Hypothetical Atom Probe Map



GB diffusion modeling exercise in Mathcad

- **Single grain boundary**
  - **Fisher/Whipple (constant/infinite source)**
  - **Suzuoka (finite/thin film source)**
- **Multiple grain boundaries**
  - **Averaged Suzuoka (finite source)**
  - **Analyze SIMS signal intensity in tail region**

Fisher's model of an isolated grain boundary



Constant source
$c(x, 0, t) = c_0$ = const.

Coupled Equations for volume and gb diffusion

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right)$$

$$\text{where } |x| > \delta/2$$

$$\frac{\partial c_{\mathrm{b}}}{\partial t} = D_{\mathrm{b}}\frac{\partial^2 c_{\mathrm{b}}}{\partial y^2} + \frac{2D}{\delta}\left(\frac{\partial c}{\partial x}\right)_{x=\delta/2}$$

Whipple (exact) solution for Mg: constant source (Phil Mag 1954)

- **Bamboo microstructure in thin film coincides very well with some of the more common mathematical solutions to the gb diffusion equations.**
  - **These solutions are all functions both volume and grain boundary diffusivities (D and D_{gb}, respectively), which are dependent on diffusion temperature.**
  - **Because the grain boundary diffusivity is unknown, it was estimated based on an empirical relation derived for the general situation of grain boundary self-diffusion in hcp metals**
  - **Volume diffusion is calculated by an Arrhenius relation using parameters determined from previous ^{25}Mg self-diffusion experiments.**
- **The various solutions are also functions of several dimensionless variables, Δ, η, ξ, and β, which were originally defined by Whipple.**

$$\Delta = \frac{D_{gb}}{D} \quad \eta = \frac{y}{\sqrt{Dt}} \qquad \xi = \frac{x-a}{\sqrt{Dt}} \qquad \beta = \frac{(\Delta-1)a}{\sqrt{Dt}}$$

  - **where a is the grain boundary half-width (assumed to be 0.25 nm), and t is the diffusion time in seconds.**

➢ ***Whipple solution is not relevant to the SIMS gb study – only an exercise***

  ➢ **Single grain boundary cannot be probed, expensive to have infinite (thick) source isotope**

Whipple solution: Mg material constants

$D_0 = 4.2 \times 10^{13}$ nm^2/s $Q_0 = 127{,}000$ J/K-mol

- From Arrhenius fit to Shewmon (high T) and ORNL SIMS (low T) data

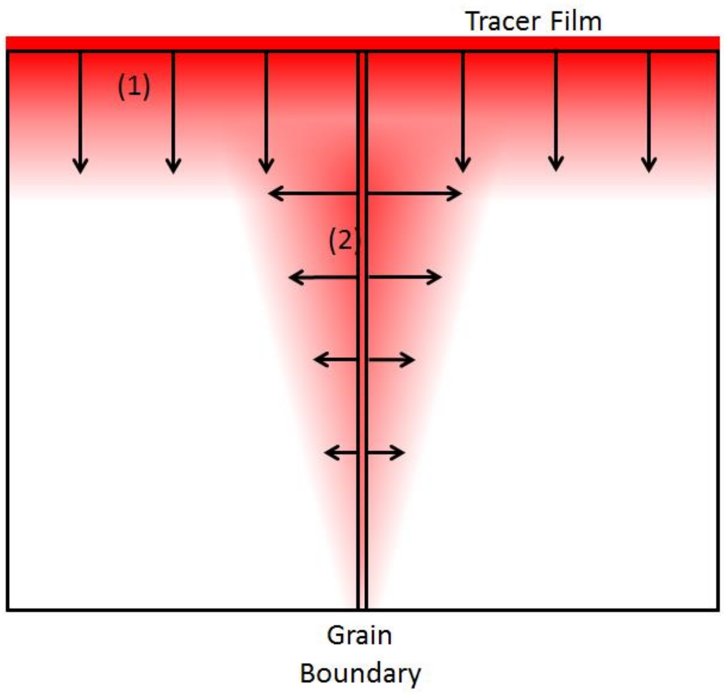
$$D_{vol}(T) = D_o \exp\left[\frac{-Qo}{8.314(273+T)}\right]$$

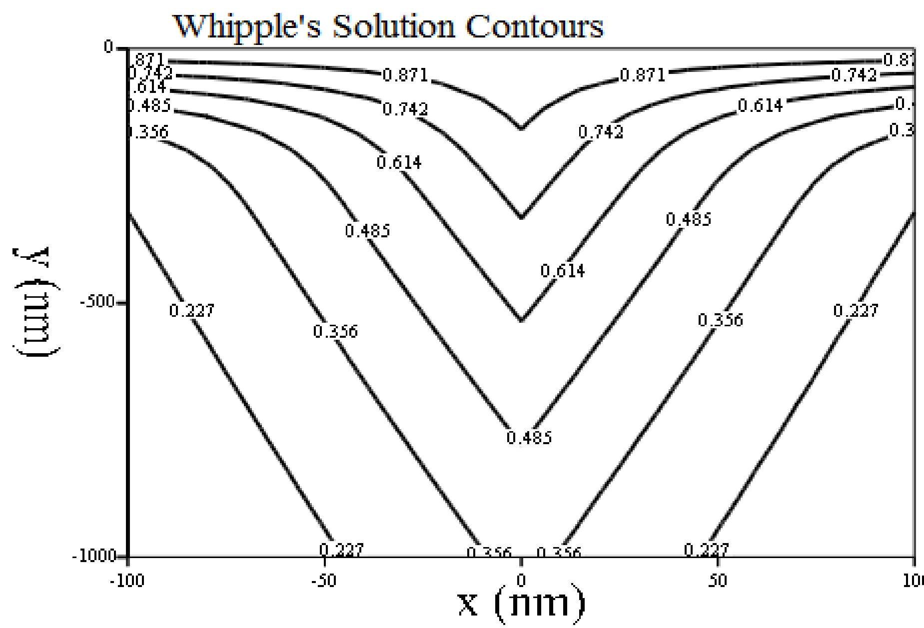
$$D_{gb}(T) = 3.10^{13} \exp\left[-10.27\frac{(273+T_M)}{(273+T)}\right]$$

- General empirical relation derived from multiple hcp gb diffusion studies (Gust et al. J. Physiq. 1985)

a = 0.25 nm (grain boundary half width)

Whipple solution for Mg (infinite source, constant surface concentration boundary condition)

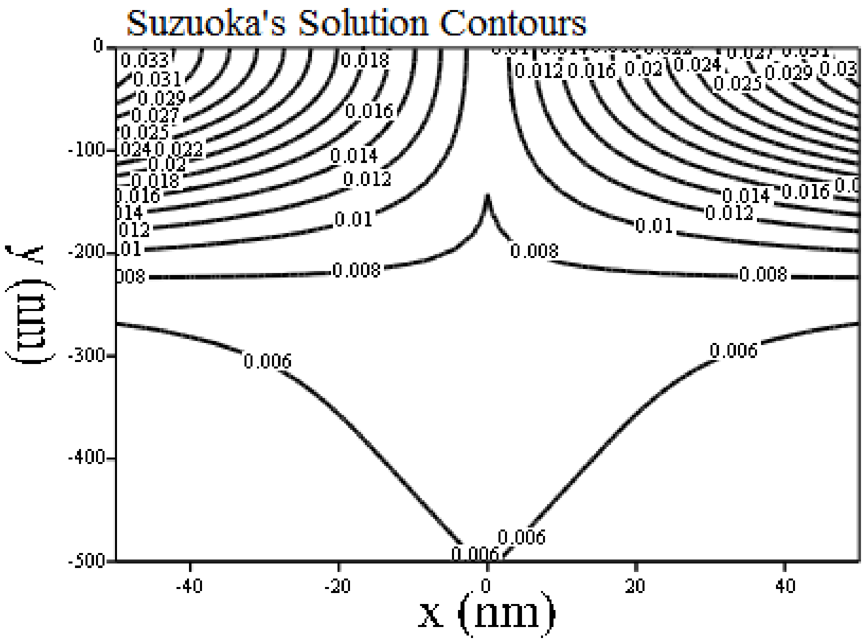




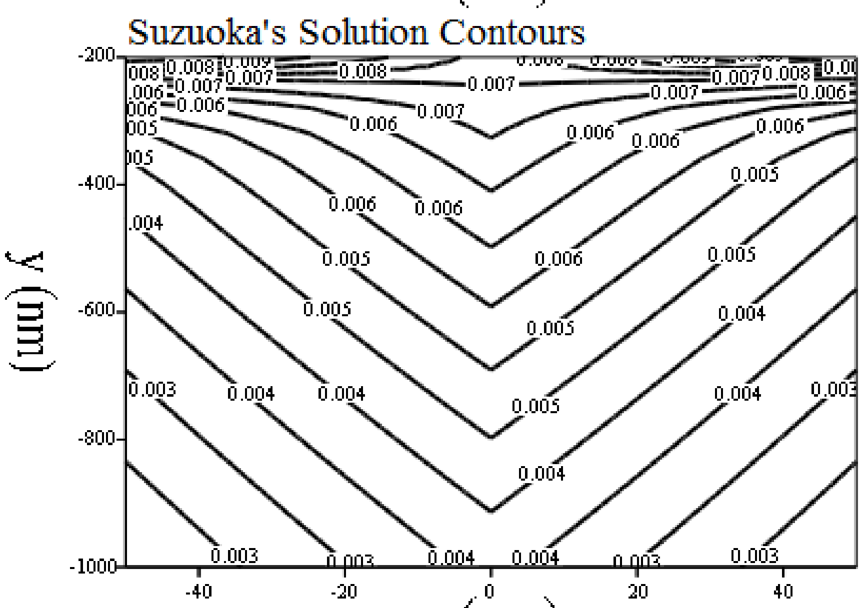
Depiction of idealized grain boundary diffusion model with the diffusion flux in the down direction. Region (1) consists of direct volume diffusion and region (2) of lateral diffusion into the volume from the grain boundary

Concentration contour plot, based on Whipple's solution. The grain boundary is at x=0 and the orientation of the sample is identical to that in the left figure. Diffusion parameters: 10 minutes at 250°C

Suzuoka solution: instantaneous, finite source (Phys Soc Jpn 1964)



(a)



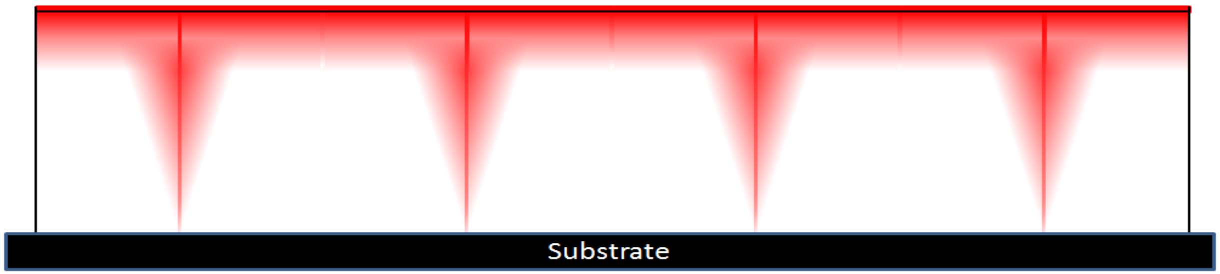
(b)

Concentration contour plots using Suzuoka's instantaneous source solution

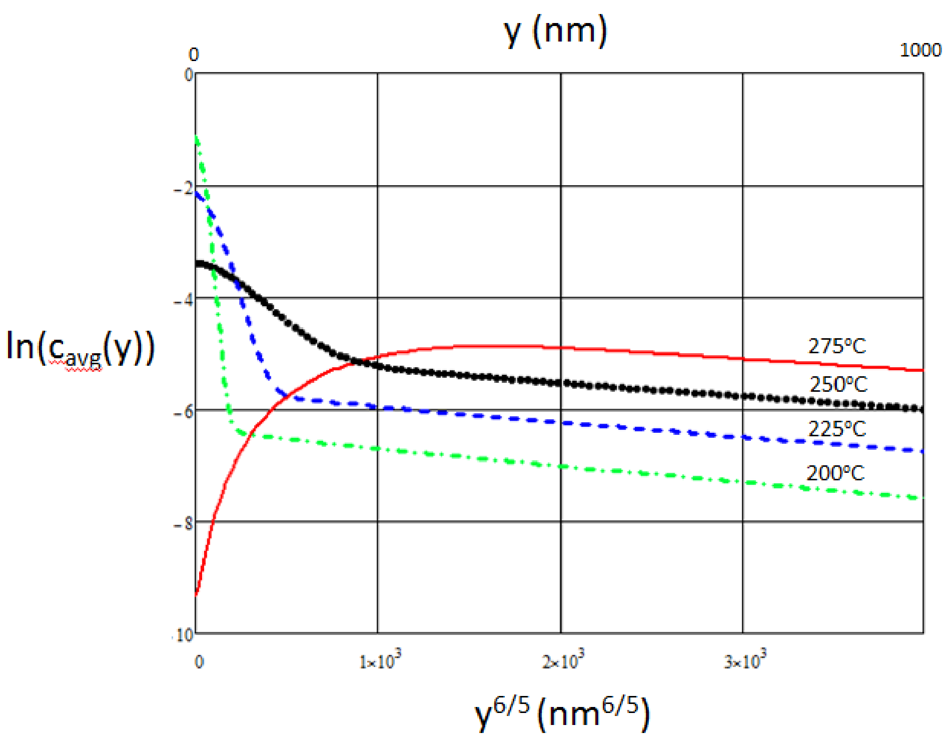
- Plot (a) shows the near-surface and transition regions from 0 to 500 nm in diffusion depth,
- Plot (b) shows the deeper grain boundary diffusion tail region from 200 to 1000 nm

➢ *Suzuoka solution is also not relevant to the SIMS gb study – (single grain boundary cannot be probed)*

Averaged Suzuoka solution for SIMS



Depiction of the geometric condition of multiple parallel grain boundaries



Graph of $\ln(c_{avg}(y))$ vs. $y^{6/5}$, based on the averaged Suzuoka solution for Mg. Y-range is 0-1000 nm, finite tracer thickness is 10 nm, grain size is 500 nm, and diffusion conditions are 10 minutes at 200, 225, 250, and 275°C

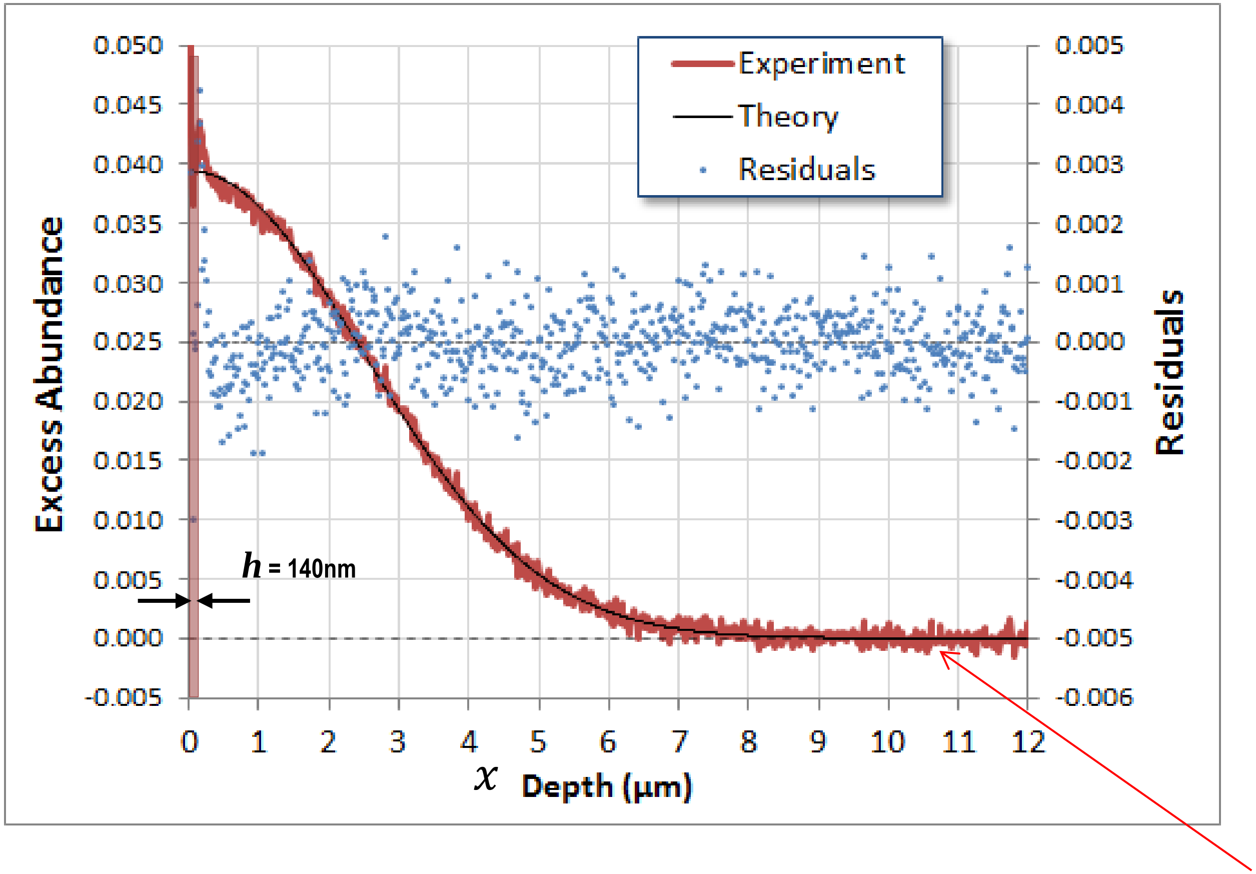
- ***Average Suzuoka solution is relevant to SIMS gb diffusion study (SIMS probe size ~10 μm, grain size ~0.5 - 2 μm)***

SIMS signal intensity in tail region of regime B

- Using averaged Suzuoka solution, we explored the effect of various experimental parameters (temperature, grain size, time) on signal intensity difference (over background)
- Using a conversion ratio based on previous self-diffusion experimental data, we converted the calculated concentration to anticipated SIMS counts.
- Because of the very slight differences in concentration, combined with the unavoidable Gaussian noise (the magnitude of which is roughly proportional to the square root of total counts), we determined that SIMS is feasible for this type of study for impurity or pseudo-impurity grain boundary diffusion experiments only, i.e. there cannot be any substantial background level of the tracer species.
  - This condition is easy to accomplish for the proposed Al into pure Mg experiments
  - This condition will also be satisfied with diffusion of enriched ^{25}Mg tracer into highly enriched ^{24}Mg of the thin film (rather than natural Mg) , where the level of ^{25}Mg has been reduced to negligible levels in the ^{24} Mg thin film.

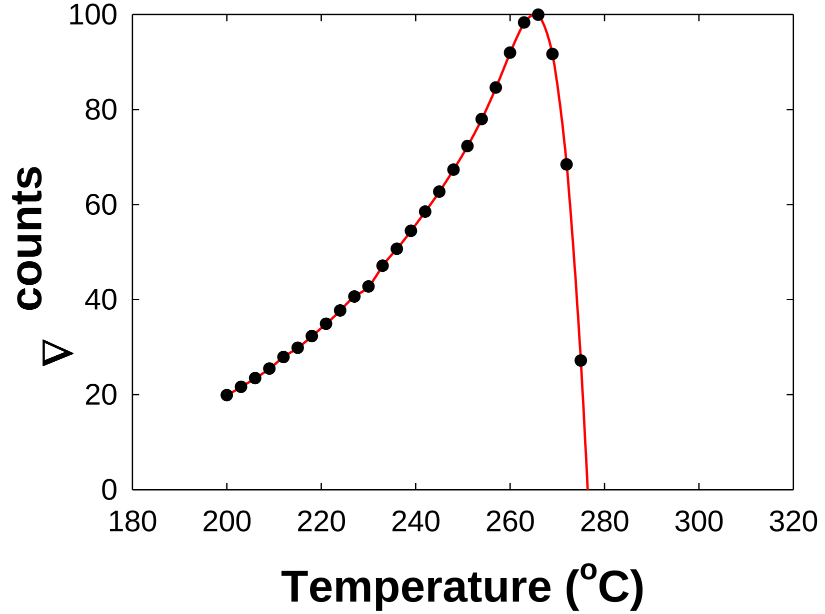
SIMS counts in tail region

Example: SIMS measured excess 25Mg tracer data

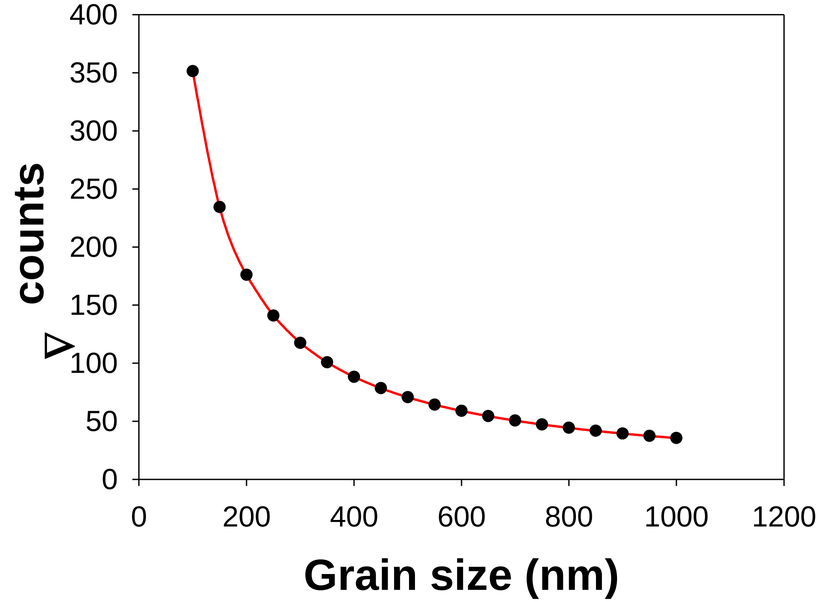


SIMS counts in the tail region (250°C) are ~16,000 counts for a background concentration of ~10% ^{25}Mg in natural Mg

Difference in counts over 100 nm depth in tail (average Suzuoka)



Δcounts is taken as the slope at a depth of 1000 nm to remain in the tail portion of the curve, at constant time of 10 minutes (600 sec).



Δcounts is taken at depth of 1000 nm, with diffusion conditions of 250°C for 10 min

- Difference in counts (hundreds of counts) is comparable to background (Gaussian) signal noise if natural Mg thin film is used
- Hence need to use enriched Mg thin film, i.e., 99.9% of Mg^{24} (0.05% of Mg^{25}) to reduce background signal counts (in tens)

Conclusions

- Explored feasibility of SIMS for grain boundary diffusion studies in magnesium thin films.
  - Suggested experimental conditions based on various requirements to satisfy Harrison's regime B kinetics
- Modeled various gb diffusion solutions for Mg using MathCad software.
  - Averaged Suzuoka solution relevant for SIMS studies
- In order to have sufficient SIMS intensity over background Mg levels in the tail region of regime B, either one needs to conduct impurity gb studies (e.g., Al in Mg), or use isotopically pure Mg^{24} thin films into which the Mg^{25} tracer diffuses.

ORNL diffusion website

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)

Oak Ridge National Laboratory
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

- Diffusion
- Interdiffusion
- Theory
- Communications
- Literature

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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

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Resources

- Team Personnel
- UCF Facilities
- SIMS-XPS VaTech

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

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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Extra Slides

Limiting conditions

- 1) $\delta << \sqrt{Dt} << d$
- 2) $4\sqrt{Dt} \approx \frac{t_{film}}{4}$
- 3) $\sqrt{Dt} >> t_{tracer}$

Input		Input				α ≤ 0.100	
T (^{0}C)	D_v (cm^2/sec)	t_{film} (nm)	[σ] time (min)	d_{max} (nm)	[Λ] d_{min} (nm)	α parameter	[λ] $t_{tracer,\ max}$ (nm)
150	8.70848E-17	200	299.0	400	125	0.020	2.5
175	6.53321E-16	600	358.7	1200	375	0.007	7.5
185	1.37546E-15	1000	473.3	2000	625	0.004	12.5
200	3.96093E-15	600	59.2	1200	375	0.007	7.5

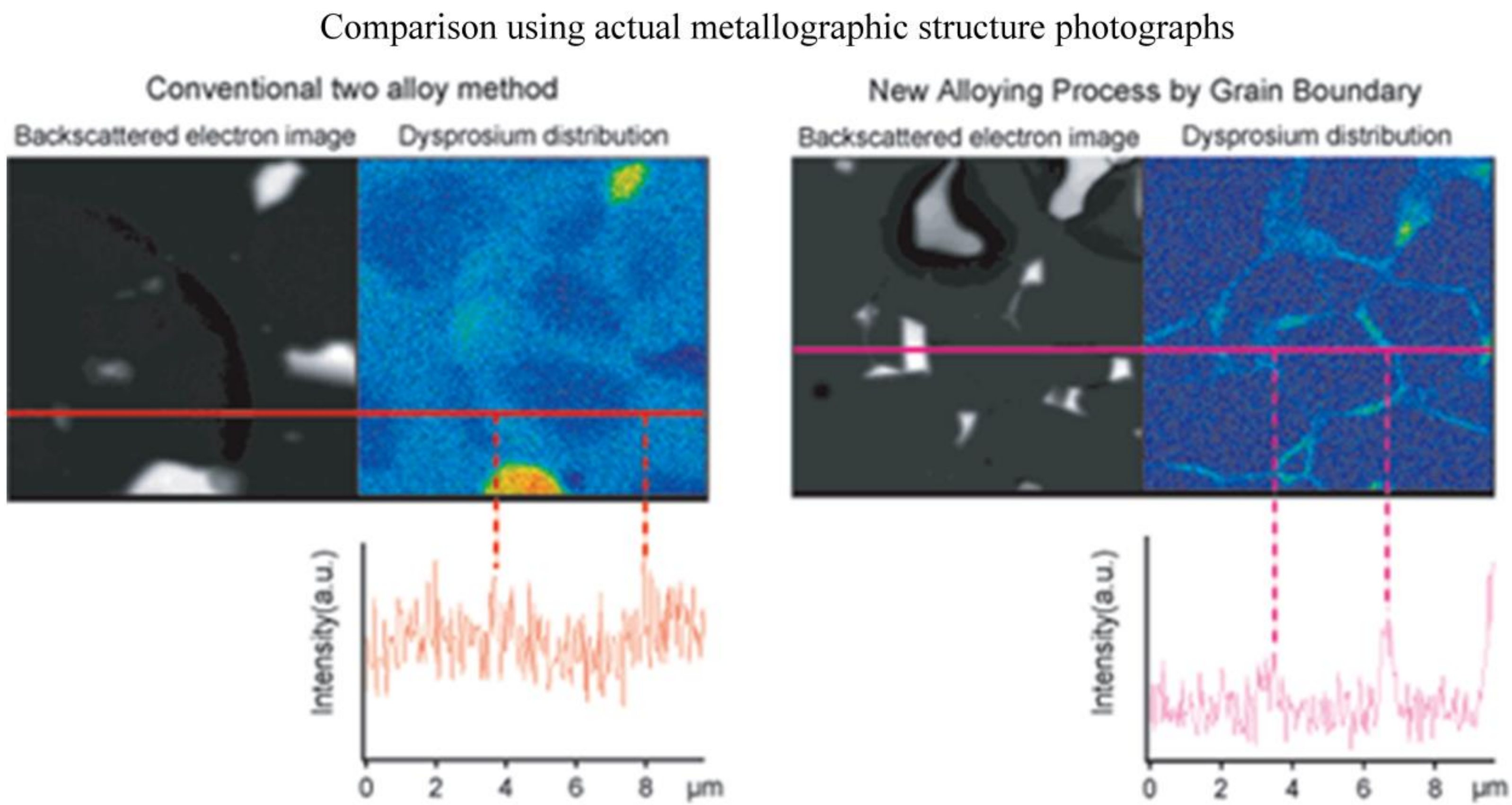
- **Set up an Excel spreadsheet:**
  - ***Input:*** **temperature, diffusivity, film thickness - t_{film}**
  - ***Outputs*****: diffusion time, minimum grain size, max t_{tracer}**

- **Easy to determine conditions to satisfy all requirements**

Role of Dy diffusion in $Nd_2Fe_{14}B$ permanent magnets

- Increase in temperature results in a reduction in intrinsic coercivity (Hc) (and BH_{max}) and hence increases tendency towards demagnetization
- Bulk Dy addition (substitutes for Nd) in the bulk increases coercivity Hc (at temperature) but reduces remanence Br (magnetization)
- Conventional *2-alloy method* (NEO + low melting RE compound) by Shin-Etsu Chemical results in a higher concentration of heavy rare earths (Dy) along the gb but some Dy is also distributed in the bulk due to sintering at high temperatures
    - Enhances coercivity and prevents reduction in remanence simultaneously
- In Shin-Etsu's *GB Diffusion Method*, sintered NEO is coated with Dy compound and heat treated at low temperatures to cause *gb diffusion* (no bulk penetration)
    - More efficient use of Dy
    - Enhances coercivity by ~30% without reduction in remanence over 2-alloy method

Dysprosium Diffusion
(Shin-Etsu)

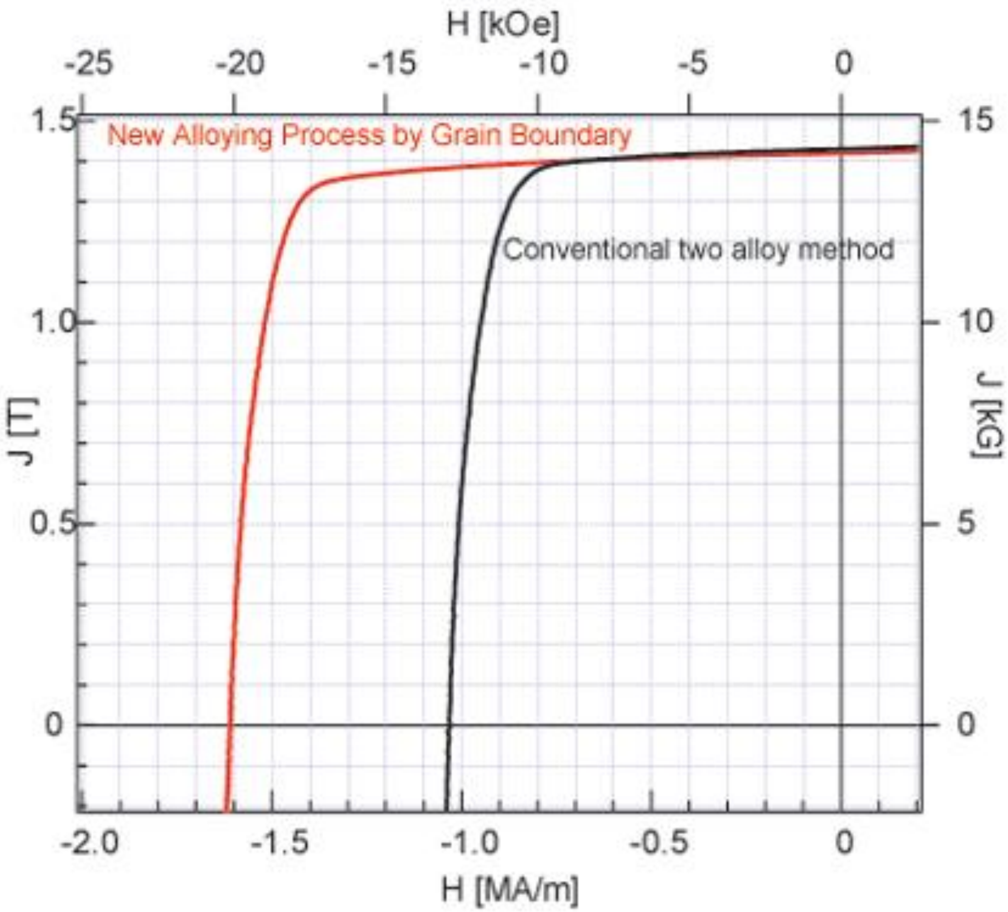


It can be said that the dysprosium is distributed more sharply at the grain boundary with higher concentration in the magnet produced by the new alloying process by grain boundary diffusion.

http://www.shinetsu-rare-earth-magnet.jp/e/rd/grain.html

From Hitachi presentations and catalog

Dysprosium GB Diffusion



- **Dy vapor deposited coating on sintered NEO followed by low temperature grain boundary diffusion**

- ***Dy gb diffusion in NEO magnets enables more efficient use of Dy compared to two-alloy method***
- ***Increase in coercivity (H) without affecting remanence***