Impurity and Tracer Diffusion Studies of Magnesium and its Alloys

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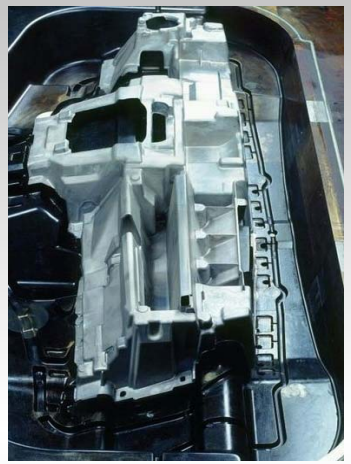
Program Introduction

- DOE Integrated Computational Materials Engineering (ICME) program:
  - initiate and coordinate a multiorganizational effort to develop an integrated suite of validated computational materials modeling tools that are linked to analysis systems used in manufacturing and engineering design [*].
  - provide a quantitative linkage between the processing, microstructure, and properties of a material for desired application (e.g., Mg-based light metal alloys used in the automotive industry).
  - Knowledge of fundamental materials properties, thermodynamics, and kinetics in the form of reliable databases are the foundations of an ICME approach

[*] J. Allison, D. Backman, and L. Christodoulou, *J. Met.*, p. 25 (Nov. 2006).

Mg and Mg Alloys

- Base of lightweight structural materials
- Typical alloying elements (Al, Zn, Mn) do not add significant weight
- Among most abundant elements available, ability to maintain cost effectiveness
- Easily machined and formed by casting or hot forming
- Applications in Automotive, Aerospace and Electronic industries



Mg alloy instrument panel casting

Mg alloy wheel

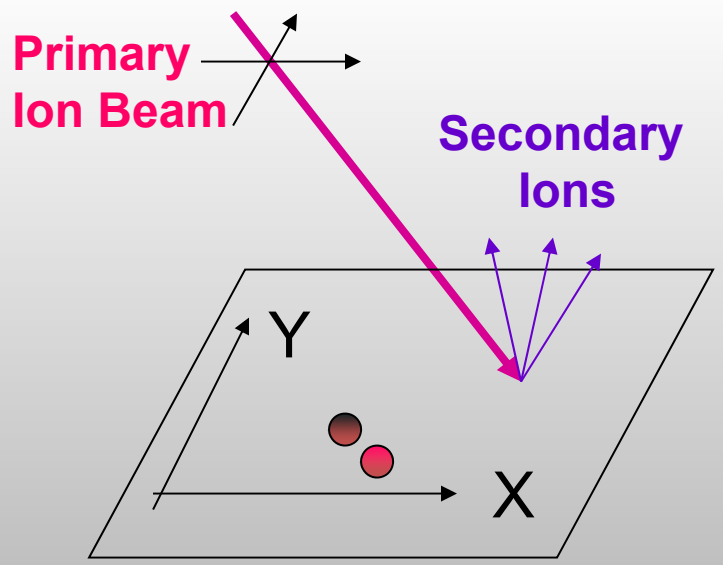
Project Introduction

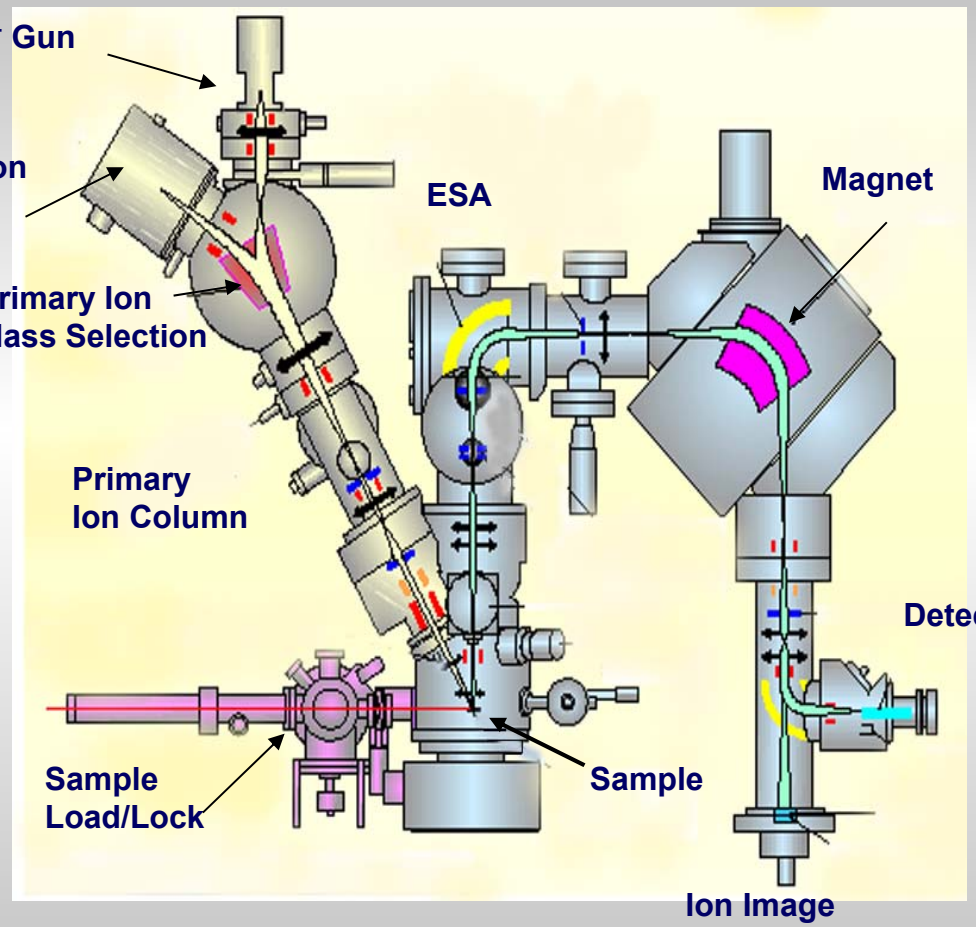
- Currently developing a diffusion database in Mg-based light metal alloy systems
- Homogeneous single-phase samples in Mg and its alloys prepared using induction melting followed by prolonged annealing and hot rolling to desired shapes
- Impurities, stable and enriched unstable isotopes of various elements (e.g., Mg, Al, Zn, Mn, etc) deposited as thin films then diffusion annealed
- Measurement of diffusion profiles conducted using depth profiling capability of secondary ion mass spectroscopy (SIMS)
- Diffusion constants fed into Mg-ICME databases

Diffusion Measurements using SIMS

Secondary Ion Mass Spectrometer

Spatial Resolution: ca. 1 mm
Depth Resolution: 10 nm



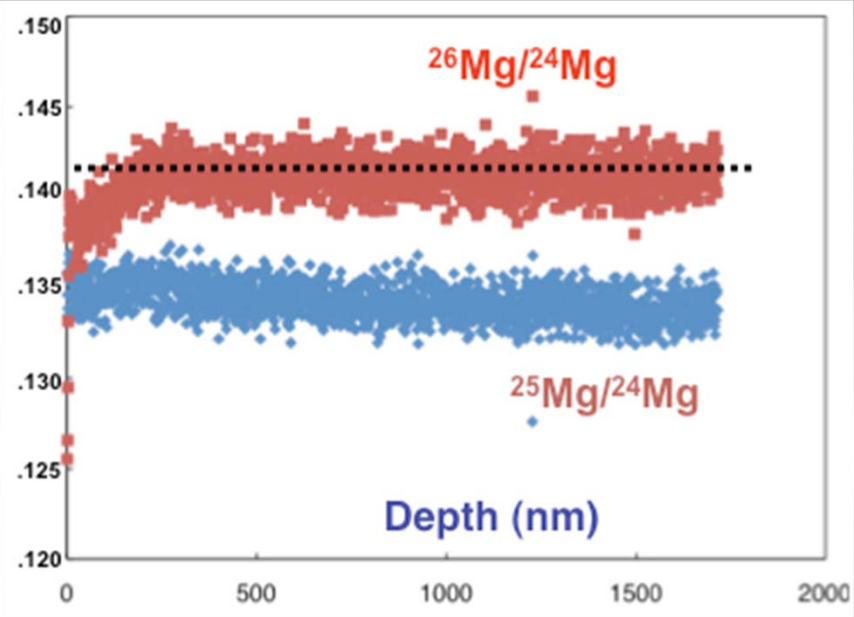


Preliminary Characterization of Mg-Alloys
Isotopic Ratios Measured by SIMS

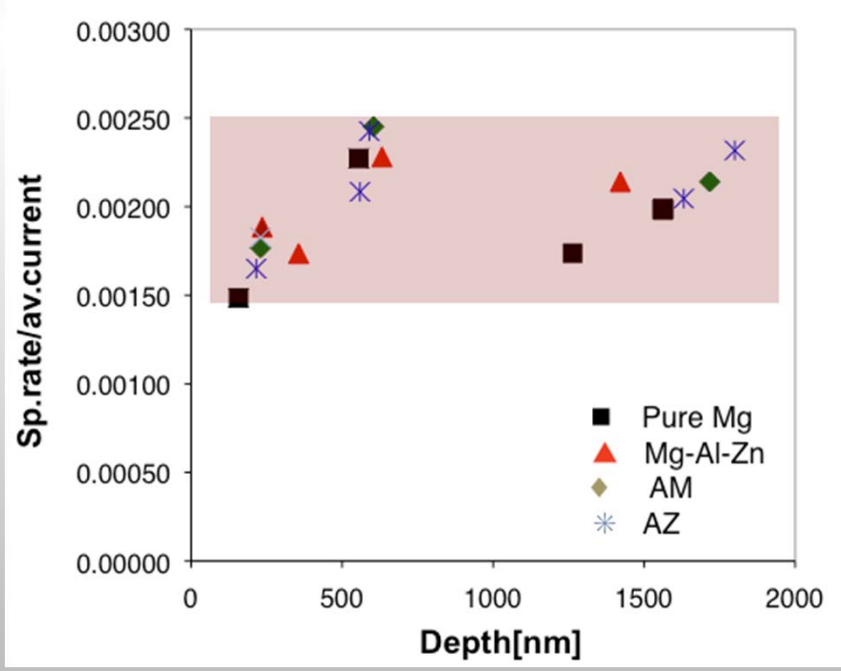
	25Mg/24Mg ratio (SD)	26Mg/24Mg ratio (SD)
Reference value	0.127	0.139
Mg	0.129 (<0.001)	0.138 (<0.001)
Mg-Al-Zn	0.130 (<0.001)	0.139 (<0.001)
AZ31B-2	0.129 (<0.001)	0.138 (<0.001)
AM60B-2	0.130 (<0.001)	0.139 (<0.001)

- Cameca3f SIMS
  - ✓ O_2 primary beam
  - ✓ 10kV (5.5kV on the sample) primary
  - ✓ 20nA beam current
  - ✓ Detection area was circular with 60 micrometers diameter.
  - ✓ High mass resolution was used

SIMS: Sputtering Depth and Rate (CAMECA 3F SIMS)

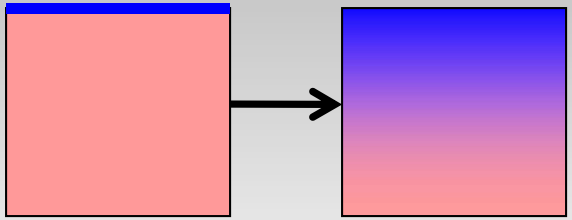


- Isotope ratio remains relatively constant as a function of sputtering depth for a given specimen.



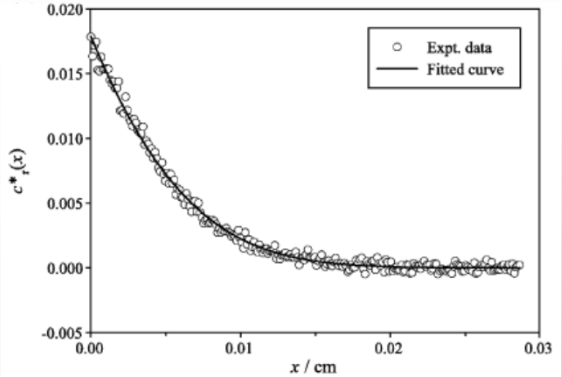
- Sputtering rate varies (25%) randomly (not as a function of composition).
- Requires profilometry for every specimen measured.

Procedure for Tracer and Impurity Diffusion Measurements



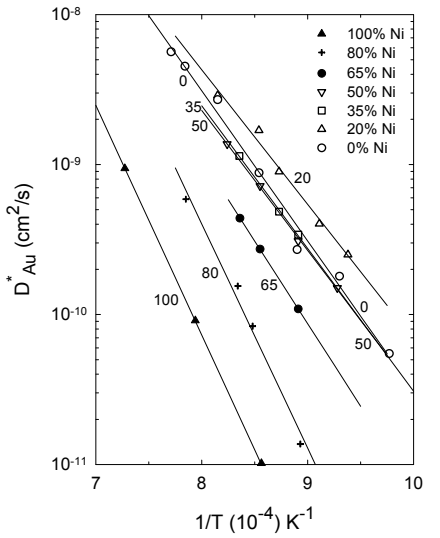
- Single phase alloy sample
- Deposition of thin film
- Anneal at T_o
- Measure depth profile with SIMS
- Fit data to thin film solution to extract D (impurity or tracer)

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



(*De Souza et al., Sol. State Ionics '05)*

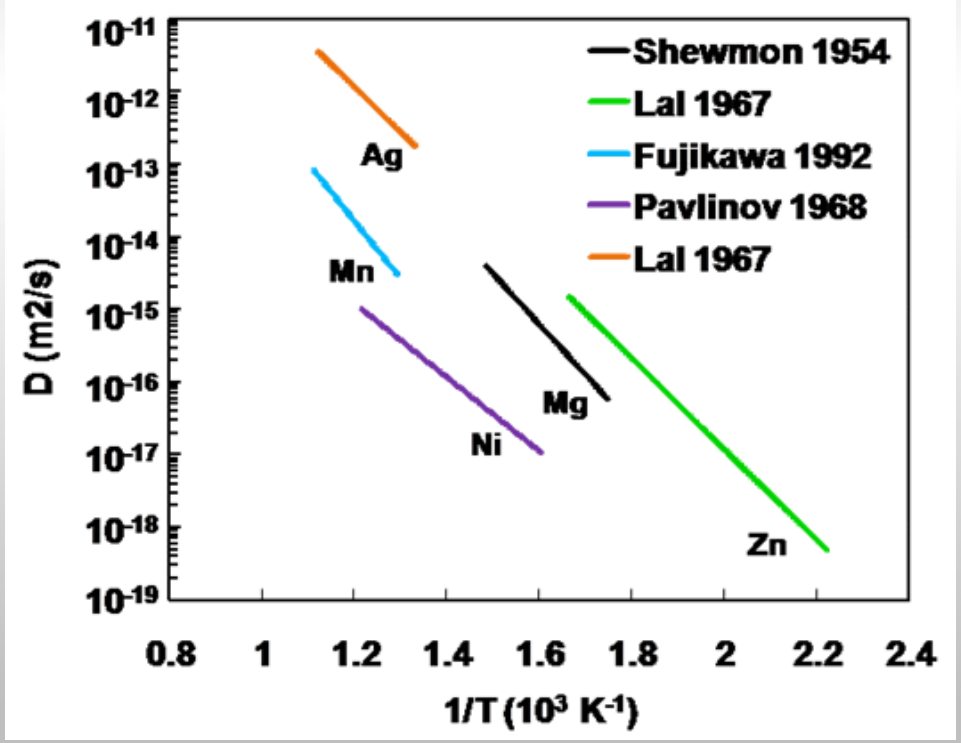
- Repeat for different temperatures and compositions to check for Arrhenius fits



Kurtz et al., Acta Met.'55)

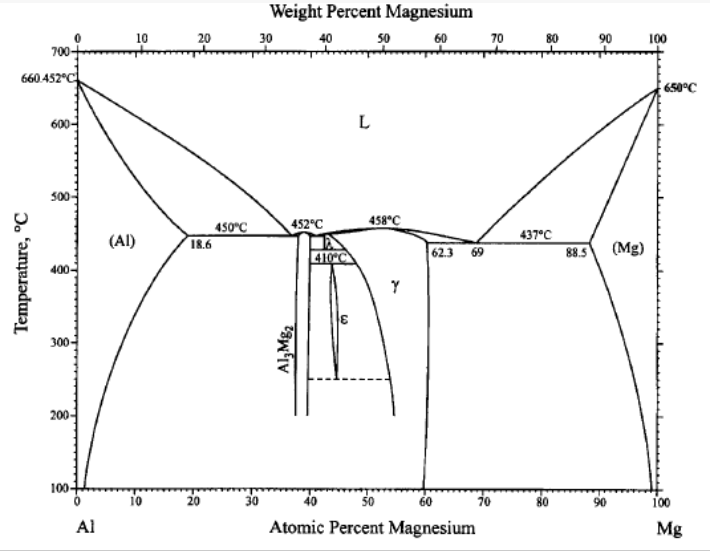
Diffusion in Mg

- No previous diffusion data for Al in Mg available (to our knowledge)



Al-Mg Annealing Times and Temperatures

- **Based on the self-diffusion coefficient of Mg[*], estimated the time for diffusion anneals at three different temperatures so that SIMS profiles at dilute solution limit can be carried out**



Temperature (°C)	Time (hr)
300	2
350	0.5
400	0.5

[*] S. Fujikawa, *J. Jap. Inst. Light Metals, 42 (1992) 822.*

Deposition of Diffusion Source: Al-Mg System

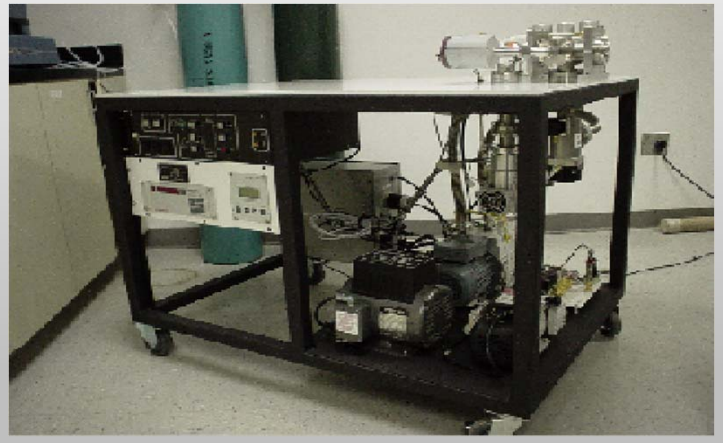
- Pure Mg (99.9%) disks were coated with a thin film (500nm) of pure Al (99.9%)
- The Mg substrates were RF plasma cleaned in situ prior to deposition and an Al layer was deposited by DC magnetron sputtering from pure Al targets
- The depositions were performed in 4 mTorr of Ar and a deposition chamber pressure around 10^{-8} Torr was obtained prior to performing the depositions

UCF Sputter system

Diffusion Anneal

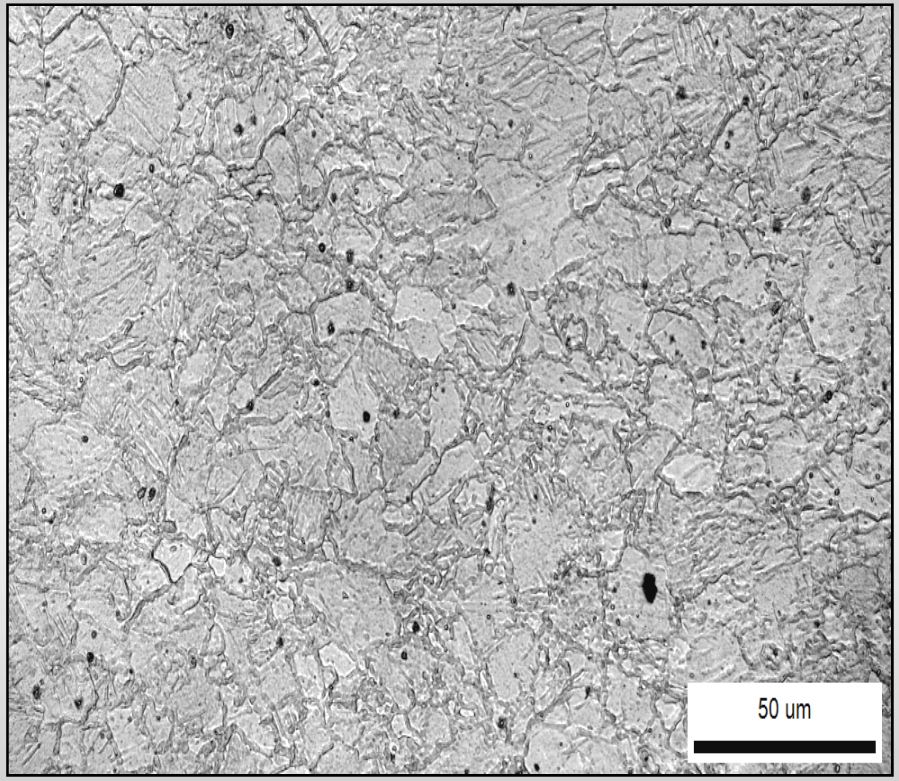
- Samples encapsulated in quartz capsules that were evacuated to 10^{-6} Torr and backfilled with Ar-H_2 mixtures
- Annealed in a furnace with independent thermocouple reading, then broken in ice water for rapid quenching

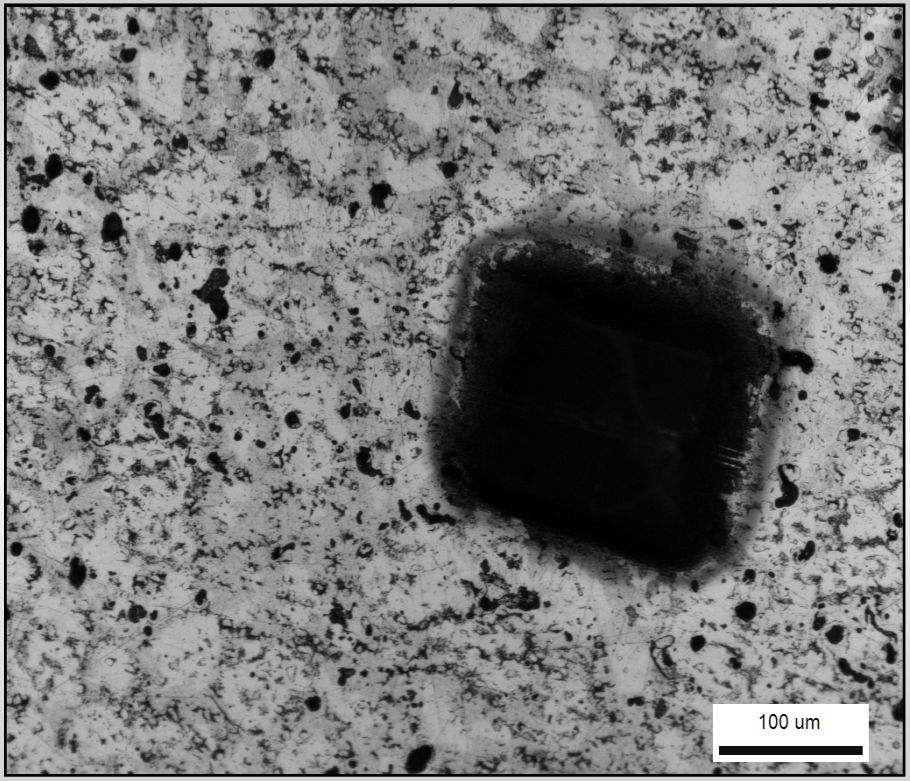
Vacuum system



Sealed quartz capsule with sample

Pure Mg Characterization

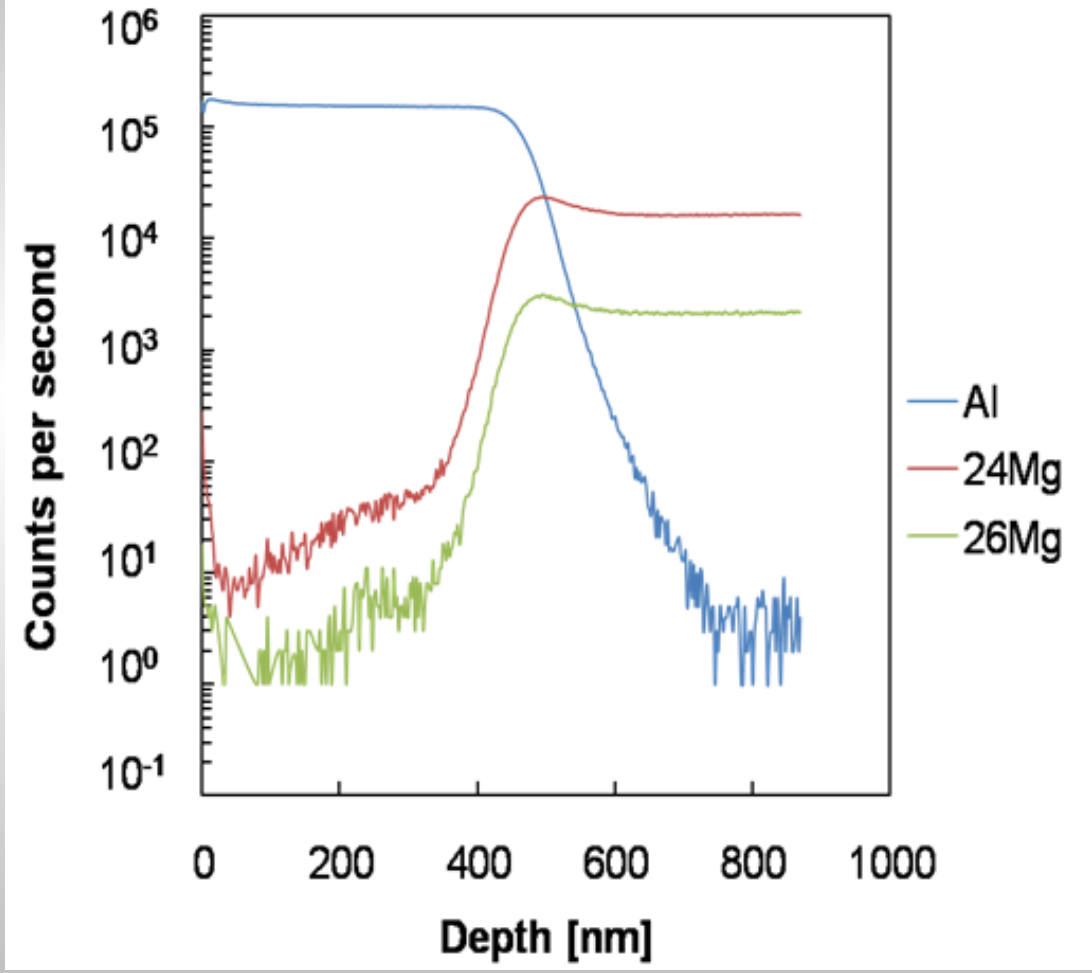




Average grain size <20μm

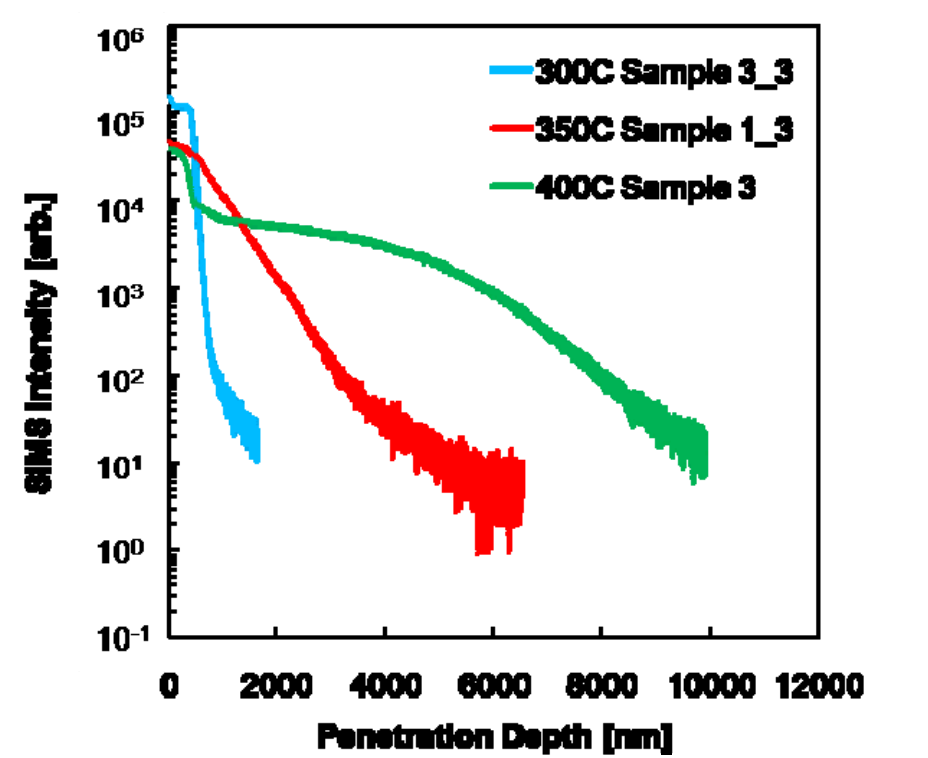
SIMS spot size, 150μm
(Al-Mg 400° C annealed sample)

As-Deposited Al films



- **SIMS depth profile for as-deposited Al film on pure Mg disk**

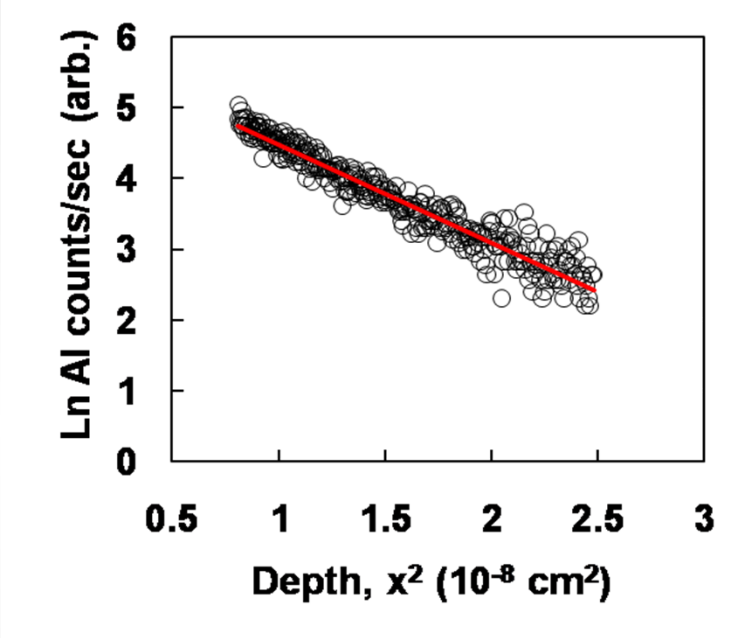
SIMS Depth Profiles Al-Mg



- Increase in penetration depth with increasing temperature

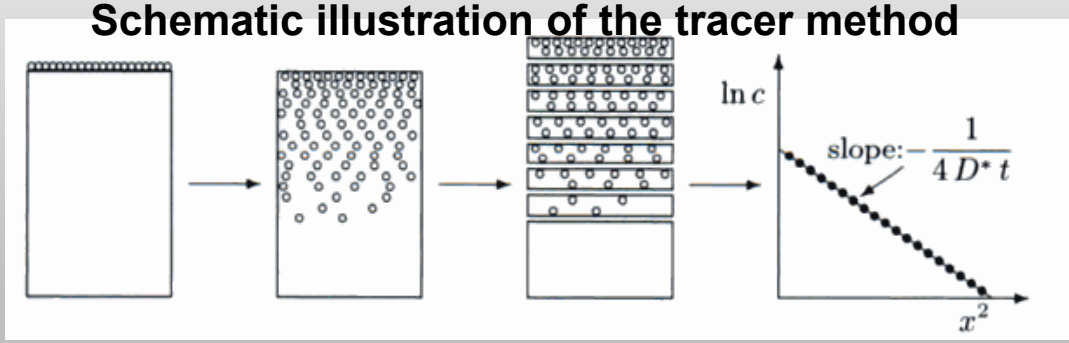
- Sample is lightly polished after annealing to reduce surface roughness for SIMS analysis
- Anneals performed at 300°C, 350°C and 400°C
- Depth profiles conducted of several samples at each temperature as well as multiple spots on the same sample for statistical reliability

Impurity Diffusion Coefficient Extraction



- Data from depth profile plotted as Ln(C) vs. x^2
- Slope of plot used to calculate diffusion coefficient

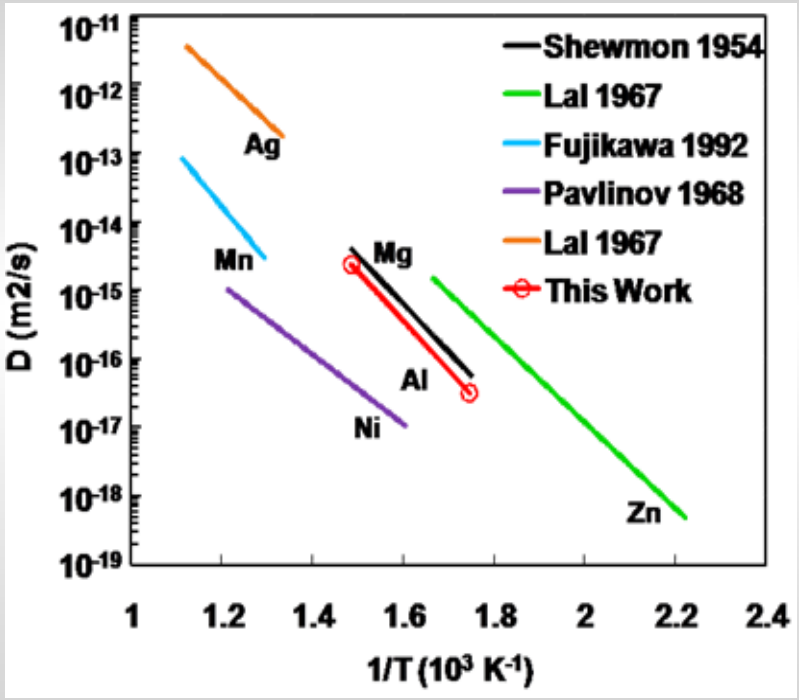
Schematic illustration of the tracer method



Diffusion in Condensed Matter, Paul Heitjans, Jörg Kärge 2nd Ed.

Concluding Remarks

- 300°C (2 samples, 5 spots)
  D=2.99 (+/-0.39)x10^{-17} m^2/s
- 400°C (3 samples, 3 spots)
  D=2.15 (+/-0.86)x10^{-15} m^2/s
- Analysis being conducted at 350°C



Future Work

- Zn and Mn impurity diffusion in Mg
- Stable isotopes of Mg and Zn for tracer diffusion experiments in Mg and Mg alloys

Acknowledgements

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