Self-Diffusion Studies in Mg using Secondary Ion Mass Spectrometry

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Outline

• Introduction
• Secondary Ion Mass Spectrometry (SIMS)
• Initial and induced surface topography
  – Instrumental description
  – Reduction of sputter topography
  – Large diffusion depths
• Sputter deposition system
• Modeling
• Summary/Conclusions
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

- Mg-ICME cyber infrastructure for exchanging data and models between collaborators.

- Advance scientific understanding in Mg cast & wrought alloys for structural applications, processing-structure-property relations, corrosion, crash energy management, fatigue performance, design optimization.

- Education of high-caliber materials science & engineering students and professionals in the U.S. and abroad.
Why use SIMS for Tracer Diffusion?

Stable Isotopes and SIMS

- Historically tracer diffusion studies have been performed using radioactive tracers.
- Use of stable isotopes (instead of radioactive isotopes) has a dramatic effect on safety and reduced costs.*
- SIMS gives a direct in-depth measurement of isotopic tracer diffusion.
- Advancements in Secondary Ion Mass Spectrometry (SIMS) for the accurate detection of trace levels of stable isotopes permits well-known thin film solution to be utilized.
- SIMS system at VT measures isotopic ratio as a function of depth or at any point in sample.

Al and Mn are monoisotopic; hence still need radioactive isotopes for these elements.
Elements of Tracer Diffusion Measurements: Thin Film

(1) Prepare single phase alloy sample (e.g., Mg-5%Al) at \( T_0 \)

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

(3) Anneal at \( T_0 \) for desired times (mins to hrs) to cause isotope to diffuse inwards

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

(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

(7) Fit using suitable polynomials for functional form of isotopic diffusivity \( D_k^*(X_1, X_2, \ldots, T) \)
Secondary Ion Mass Spectrometry (SIMS)
Principle

Impact of a primary ion triggering off cascades of atomic collisions.
- Incident ion
- Sample atoms
- Successive sites of displaced atoms
- Positive and negative secondary ions giving chemical and isotopic composition of the sample
- Electron
SIMS Technique

<1 x 10^{-9} \text{ torr}

Sample

MASS SPECTROMETER

M^+ M^- M^0

Extraction

Mass Spectra

Most Common

concentration

depth

Depth Profile

Mass filtered ion Image
What we would like to confirm

Will the SIMS thin film tracer diffusion technique using stable isotopes as tracers give diffusivities in Mg that are similar to those in the literature obtained through radioactive isotope measurements?

- Mg self-diffusion and impurity diffusion data in literature
- Self-diffusion data mostly from 600-1000 K
- Need to address SIMS related issues to assure most accurate profiles
VT – Nanoscale Characterization and Fabrication Labs

Centralized characterization lab for VT and other research institutions

- LEO 1550 FESEM
- FEI Helios 600 Dual Beam (FIB+SEM)
- FEI Quanta 600 Environmental SEM
- VG 350 FE-Auger
- Cameca 7f Geo SIMS
- Phi Quantera XPS
- Veeco AFM
- FEI Titan 300 TEM

http://www.ictas.vt.edu/facilities/ncfl.shtml
Issues - Initial surface roughness

- Typically metallic materials will start with significant initial surface roughness.
- Roughness is carried through resulting in a loss of depth resolution.
- After sputtering roughness will be worse than initial roughness.
- Need to assure that initial surface is smooth because depth resolution can be no better than initial surface finish.

From Wilson, et. al., 1989
Issues - Sputter-induced roughness

• Roughness formed during the sputtering process will lead to decreased depth resolution
• Especially a problem when sputtering polycrystalline materials such as metallic films
• Worsens with larger depths
• Can easily see min-max roughness of > 5 \(\mu m\)
• Methods to minimize
  – Eucentric rotation
  – Optimized analytical conditions

From Wilson, et. al., 1989
Cameca IMS 7f-Geo

- Range of energy/angle combinations available
- Continuous primary beam current monitor
- High mass resolution to separate $^{25}$Mg$^+$ from $(^{24}$Mg + $^1$H)$^+$ -- $\sim$4000 m/$\Delta$m
- Oxygen leak to increase steady state concentration of oxygen at specimen surface
- Dual Faraday cups for high precision stable isotope measurements
Why we care about angle, energy and O-leak

• For certain metallic matrices (especially those that readily oxidize) it is possible to reduce or eliminate sputter topography by selection of optimal conditions
  – Primary ion species (O$_2^+$, Ar$^+$, Cs$^+$, etc.)
  – Primary ion energy
  – Primary ion bombardment angle
  – Oxidative environment (O-leak)
Primary beam trajectory

- Impact angle on Cameca is dependant on primary/secondary beam energies
- +/+ or -/- gives retarding field effect
- +/- or -/+ gives accelerating field effect
Cameca IMS Primary Ion Angle

-10kV
+5kV
+1kV
-5kV
Oxygen Leak

- Jet of O\textsubscript{2} is directed at the sample surface
- Increases the steady state oxygen concentration at the surface
- Leads to a rapid stabilization of the ion yield
- Rapid ion yield stabilization decreases depth required for steady state condition
Effect of Oxygen Leak

- Caused by the depth required for the oxygen to reach a “steady-state” condition
- As energy increases surface transient increases
- Lower energy leads to higher steady state oxygen concentration
- Oxygen leak increases steady state oxygen concentration by ~10x in Mg
- High oxygen concentration is desired to maximize oxidation of metal
High precision isotope analysis on Cameca 7f-geo

Experimental conditions:
- Analysis area size ~15x15µm²
- High mass resolution

Sample:
- Si quartz disk

Analysis on different spots over a 15mm Ø:

Std. dev. over 14 spots: 0.25 permil (0.025 %)

• In depth profile mode
  - Sub-permil isotopic ratios difficult/impossible (crater depths, changing signals, etc, lower signal)
  - Precision is 0.5 – 1 % (5-10 permil)
  - For tracer analysis higher precision gives larger dynamic range and better diffusion coefficient measurement
SIMS sputtering for depth profiling

Unsputtered Surface (2 μm Mg film deposited on Si)

SEM

AFM -- $R_a \sim 7$nm
SIMS sputtering for depth profiling

“Typical” conditions
5kV at 45° no oxygen leak

SEM

AFM -- $R_a \sim 40$nm
SIMS sputtering for depth profiling

2 µm thick Mg film deposited on silicon

Unsputtered
$R_a \sim 7 \text{ nm}$

“Typical” SIMS conditions
$R_a \sim 40\text{ nm}$

Improved SIMS conditions
$R_a \sim 10\text{ nm}$
## Summary roughness data for crater at ~2 µm depth

<table>
<thead>
<tr>
<th>Impact Energy, kV</th>
<th>O-leak</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsputtered</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- 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

<table>
<thead>
<tr>
<th>Impact Energy, kV</th>
<th>O-leak</th>
<th>Angle</th>
<th>Avg. Roughness, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>no</td>
<td>44</td>
<td>37.7</td>
</tr>
</tbody>
</table>

O-leak pressure measured in main chamber

- Optimized conditions gave crater roughness of ~10 nm at ~2 µm depth
- But typical conditions gave ~38 µm
Effect of Sputter Topography on Depth Resolution

As deposited Al film on Mg

Steeper depth profile means higher depth resolution and more accurate profile

Typical conditions

Improved conditions

IMS7f improved conditions
Issue with high temperature anneal

- High temperature anneal can give diffusions of 10’s of μm
- Maximum SIMS depth profile depth ideally < 5 μm
- Lateral resolution of SIMS (5-10 μm) does not allow measurements on the cross section

Concentration in atom fractions, plot of 25Mg for initial film thickness of 100 nm (enriched to 98%)
Possible approach for deep diffusions

Magnification = $1 / \sin(\theta)$

For a 30 μm diffused layer polished at 1 degree this gives

$t = 30 \, \mu m$, $\theta = 1 \, \text{deg}$; $d = 1720 \, \mu m$; Mag $=1752/30 \sim 57x$
UHV System for Mg stable isotope deposition (UCF)

- 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.
XPS of UHV deposited Mg film

Mg2p core level spectra

Sample #1

Composition (at.%) vs Depth (nm)

Binding Energy (eV)
Simulation of Tracer Diffusion

Calculated diffusion profiles for Mg single crystal with tracer layer

- Objective is to provide guidance on the choice of diffusion anneal parameters and in the interpretation of results
- Finite difference modeling of diffusion profiles
  - tracer film thicknesses
  - time
  - temperature
- Simulations will be extended to three dimensional grain structures
  - Grain boundary and triple line diffusivities will be obtained using molecular dynamics simulations

<table>
<thead>
<tr>
<th>Location</th>
<th>(^{24}\text{Mg})</th>
<th>(^{25}\text{Mg})</th>
<th>(^{26}\text{Mg})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Material</td>
<td>0.7899</td>
<td>0.1001</td>
<td>0.1100</td>
</tr>
<tr>
<td>Tracer Deposit</td>
<td>0.0180</td>
<td>0.9787</td>
<td>0.0033</td>
</tr>
</tbody>
</table>
Summary

• SIMS conditions have been found that minimize sputter topography - addressing the major error source for tracer diffusion measurements using SIMS

• Next steps
  – Deposition and annealing of $^{25}\text{Mg}$ tracer layers on single crystal Mg substrates
  – Deposition and annealing of $^{25}\text{Mg}$ tracer layers on polycrystalline Mg
  – Deposition and annealing of $^{25}\text{Mg}$ tracer layers on polycrystalline Mg alloy substrates
  – Working out method to measure large diffusion depths
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