Tracer Diffusivity Data Collection and Reporting; Examples from the Mg-based systems

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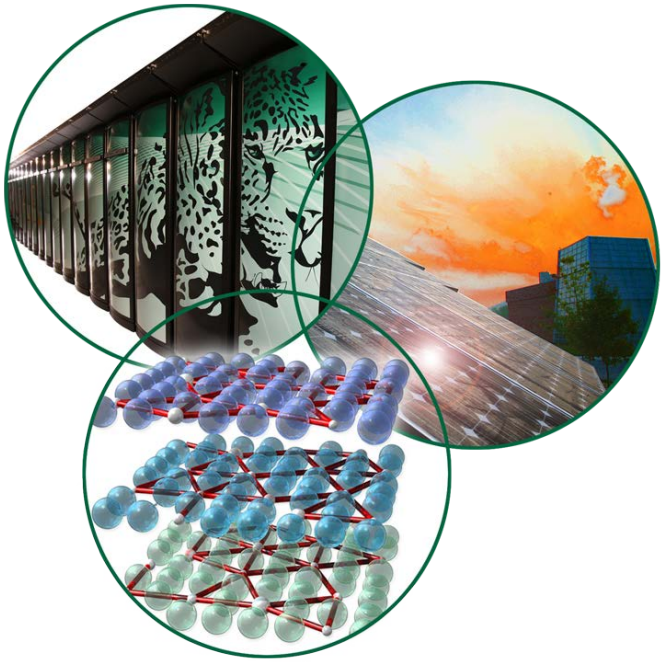


11th NIST Diffusion Workshop
Gaithersburg, MD, May 8-9, 2013

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

Outline: Process Flow

- Overall Goals
  - Project goals
  - Diffusion goals
- System/phase, composition
- Alloy processing
- Composition analysis
- Phase analysis

- Tracer Diffusion Steps
  - Experimental annealing technique
    - Mg (capsule) design
    - Temperature calibration
    - Capsule/sample preparation
  - Pre-annealing
    - Homogenization anneal
    - Pre-diffusion anneal
    - Sample polishing/technique
  - Isotope deposition technique
    - UHV sputtering system design
    - Isotope foil (Mg-25) bonding
    - Sputter deposition technique
  - Tracer diffusion anneal
    - Temperature-time output

- SIMS (system details)
  - Optimizing conditions for accurate analysis
  - Depth profiles (raw data) of annealed samples
- Data Analysis
  - Thick film solution
  - Fitted parameters

Project Goals

- To develop a Mg tracer diffusion database for Mg, Zn, Al in magnesium-rich alloys for incorporation in the Magnesium Integrated Computational Engineering (ICME) project
  - From tracer data, the complete L_{ij} matrix of phenomenological coefficients can be computed in line with Onsager's formalism (e.g., Manning relations)
- Major focus was on developing tools, techniques and procedure for the SIMS-based thin-film stable-isotopic technique for tracer studies in Mg alloys
  - Many details of our experiments and procedures are available on our public website: http://www.ornl.gov/sci/diffusion/index.html

Onsager Diffusion Formalism

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

$$J_k = -\sum_i L_{ki}^n \,\mathrm{grad}(\mu_i) \qquad \sum_k J_k = -J_v$$

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

$$L_{ii} = \frac{C_i D_i^*}{kT}\left(1 + \frac{2C_i D_i^*}{M_0 \sum_k C_k D_k^*}\right) \qquad L_{ij} = \frac{2C_i D_i^* 2C_j D_j^*}{kT M_0 \sum_k C_k D_k^*} \qquad i \neq j$$

- Chemical potentials from thermodynamic database

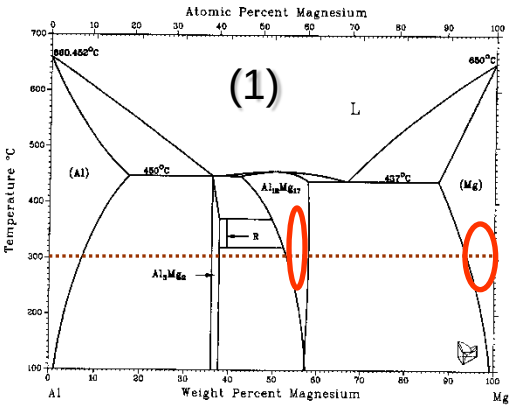
➢ *Cross-terms are not ignored as in Darken (correlation effects influence cross-terms)*

➢ *Tracer diffusion data is independent of thermodynamic database*

Types of Diffusion Activities

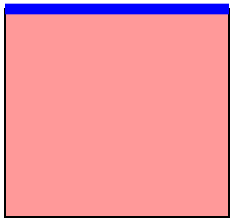
- Tracer diffusion studies in Mg using stable isotopes/SIMS
  - *Focus of this talk*
- Diffusion couple (interdiffusion) studies
  - Discussed by Prof. Sohn (UCF)
- Grain boundary diffusion studies (limited- not discussed)
  - MathCad model
- Diffusion modeling (limited – not discussed)
  - MD simulation, polycrystalline modeling

Tracer Diffusion: SIMS-based thin-film stable-isotope technique



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

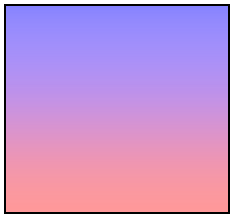
(2)



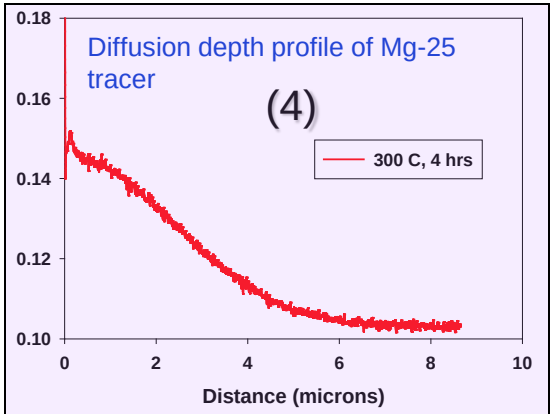
T_o

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

(3)



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

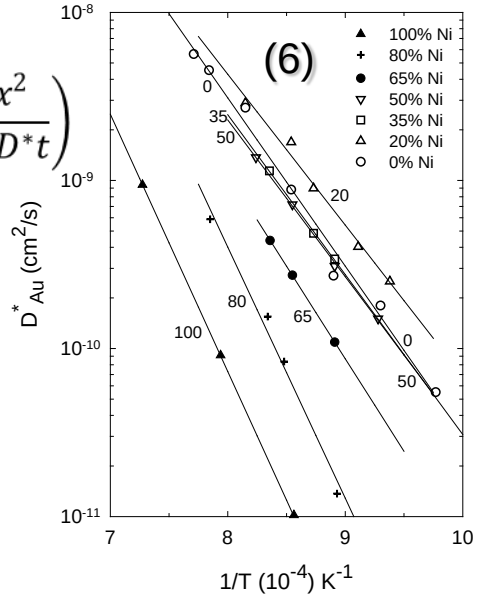


(4) Measure depth profile of isotope or isotope ratio with SIMS

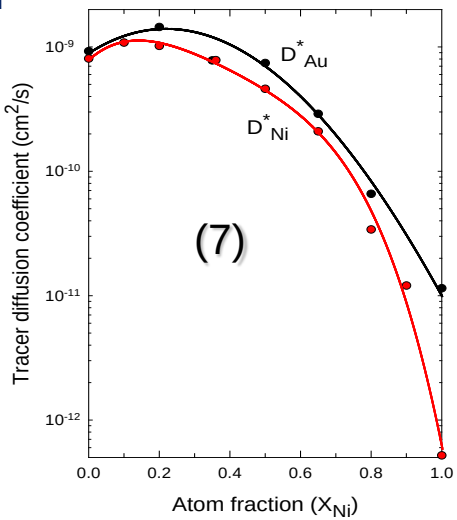
(5)

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

(5) Fit depth profile data for isotope in (4) with above thin-film solution to extract tracer diffusivity D^*.



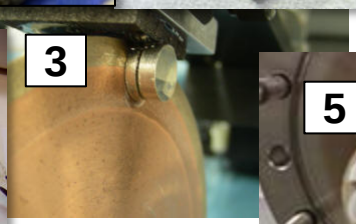
(6) Repeat for different temperatures and compositions to check for Arrhenius fits (e.g. Au in Au-Ni alloys, *Kurtz et al., Acta Met.'55*)

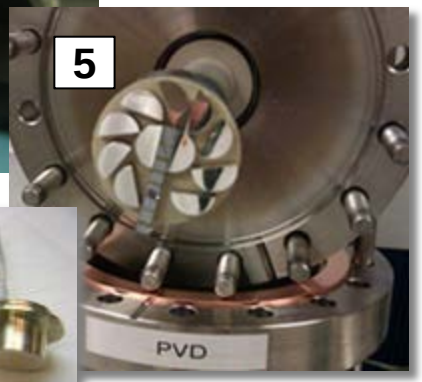


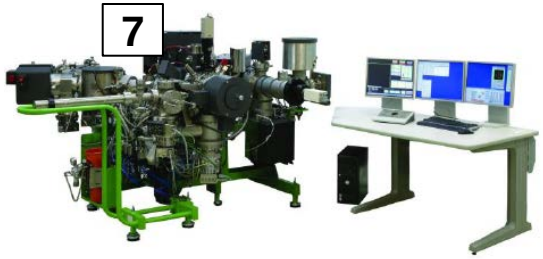
(7) Fit using suitable polynomials for functional form of isotopic diffusivity $D_k^*(X_1, X_2, \ldots, T)$ (e.g. Au-Ni tracer diffusion at 900°C, *Reynolds et al. Acta Met. '57*)

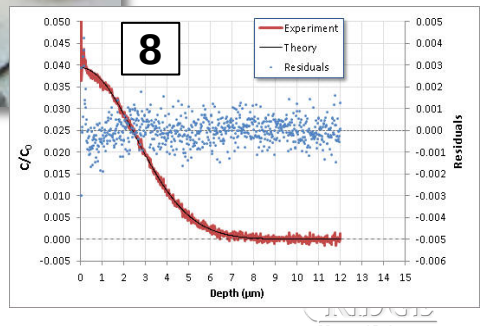
Process Sequence

1. Single phase alloy extrusion
2. Homogenization and grain-growth anneal
3. Sectioning
4. Conditioning anneal
5. Polishing/Coating
6. Annealing
7. SIMS profiling
8. Analysis









Processing steps involved co-ordination between partners

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE

- Annealing
- Analysis
- Modeling

THE UNIVERSITY OF NEWCASTLE AUSTRALIA

Theory

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

UNIVERSITY OF CENTRAL FLORIDA

- Coating
- Interdiffusion
- Analysis

ORNL project Coordination

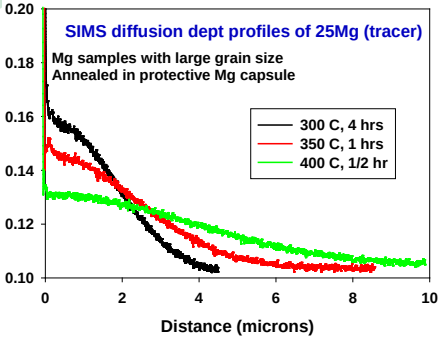
VirginiaTech
Invent the Future

- SIMS
- XPS
- Characterization

Magnesium Elektron
SERVICE & INNOVATION IN MAGNESIUM

- Material casting
- Extrusion

ICME-CI



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Mg-Al-Zn (MAZ) alloy synthesis (Mg-Elektron) & characterization

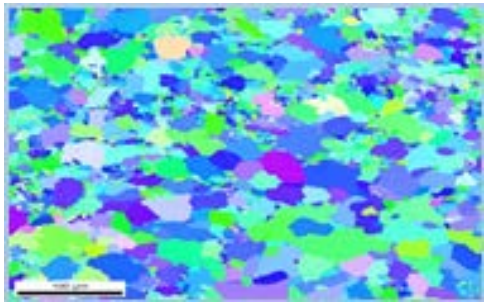
		Nominal composition (weight %)			Chemical analysis (weight %)						
Alloy	**Phase**	**Mg**	**Al**	**Zn**	**Al**	**Zn**	**Mn**	**Ca**	**Pb**	**Si**	**Fe**
MA1	α	99	1	0	0.97	0.0049	0.0054	0.0026	0.0021	0.0031	0.003
MA3	α	97	3	0	2.81	0.0035	0.0054	0.0036	0.0001	0.0043	0.0053
MA6	α	94	6	0	6.73	0.0056	0.0056	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: Mg17Al12; δ: MgZn

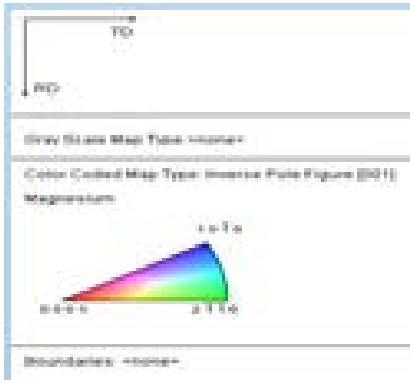
Other elements detected in trace amounts are Cu (<20 ppm), Sn (<20 ppm), Ni (<5 ppm), Zr (< 10 ppm) (ppm = parts per million).

Alloy Processing

- Based on discussion with Mg-Elektron
  - Molten alloys were cast in a graphite crucible about 1.5" diameter, 4" height.
    - Pure Fe is also a good container for liquid Mg
  - Air cooled.
  - After casting (assuming rapid cooling), the outer skin was removed with a lathe.
  - Sample was warmed around 400ºC for approx. 1 hr in a furnace.
  - Cast ingot was then extruded in the warm condition to final rod dimensions using appropriate dies (~9mm diameter)
  - Do not expect C in alloy but we have not analyzed.

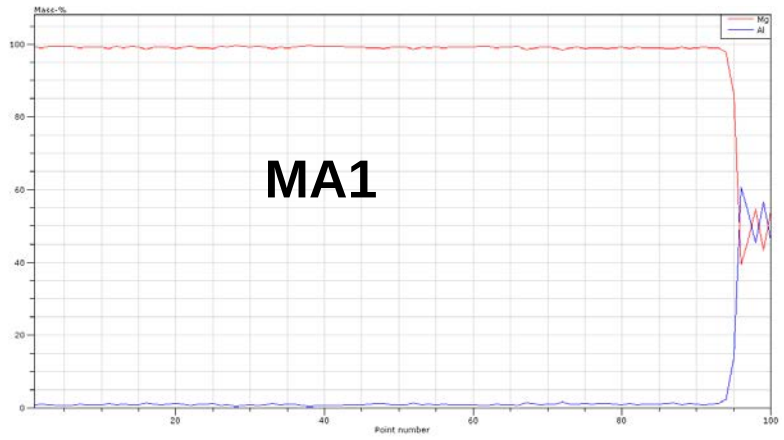


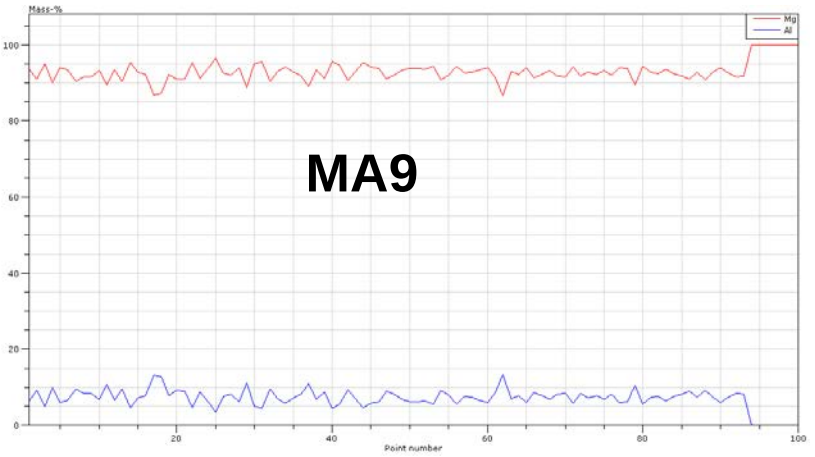
As-extruded microstructure (EBSD), mean grain size ~10 μm, broad distribution

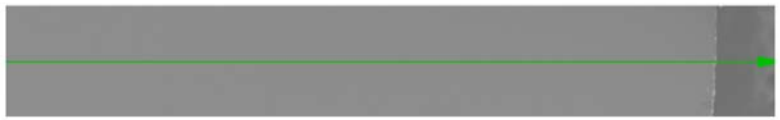


Nominal Composition Analysis of Extruded Rods

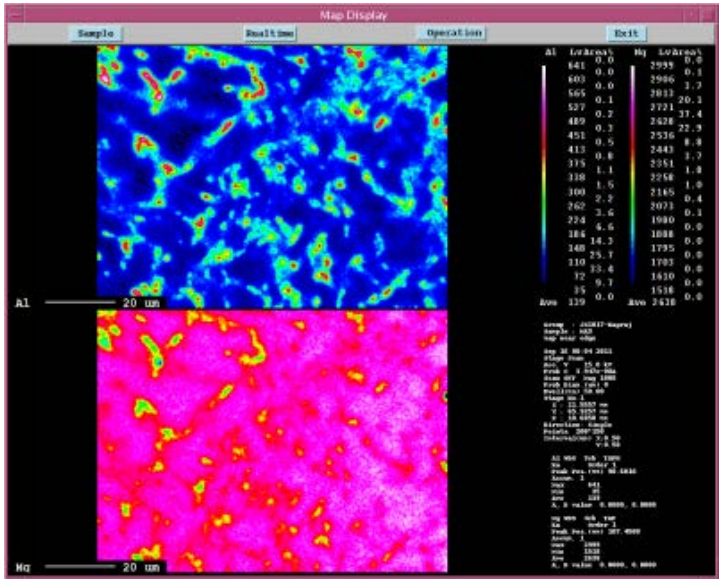
- To look at the uniformity across each sample, line scans were performed using the FEI Quanta 600 FEG with a Bruker EDS system at Virginia Tech.
- Analysis on samples polished using a 0.02um silica final step.
- SEM/EDS analysis
  - 20kV accelerating voltage and 5.0 μm for the spot size.
  - Working distance approx. 11mm.
  - Line scans of four to five millimeters from center to edge

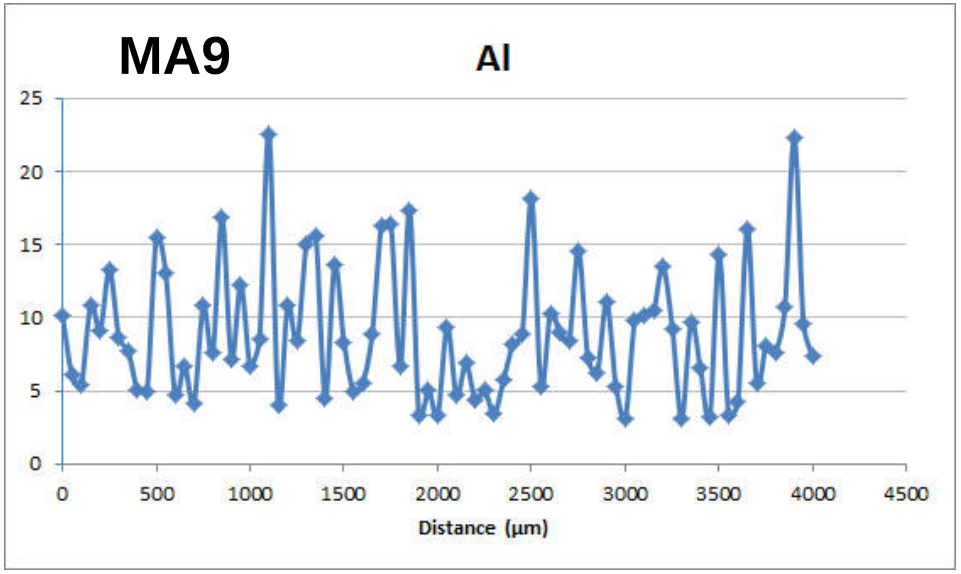


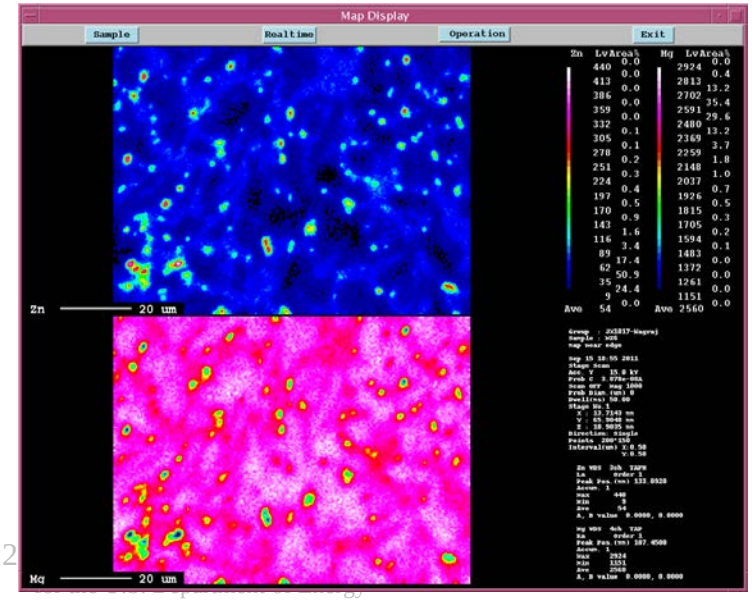


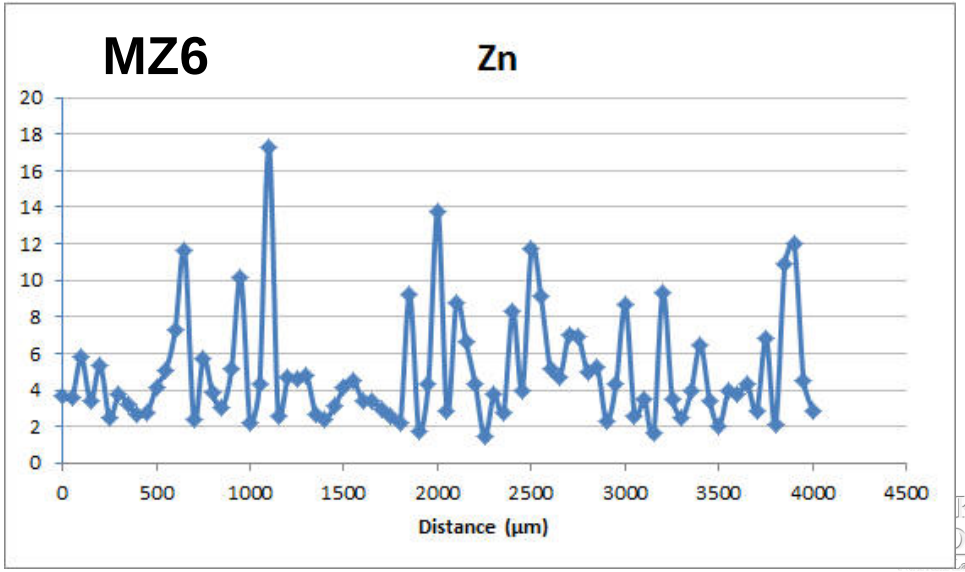


EPMA analysis

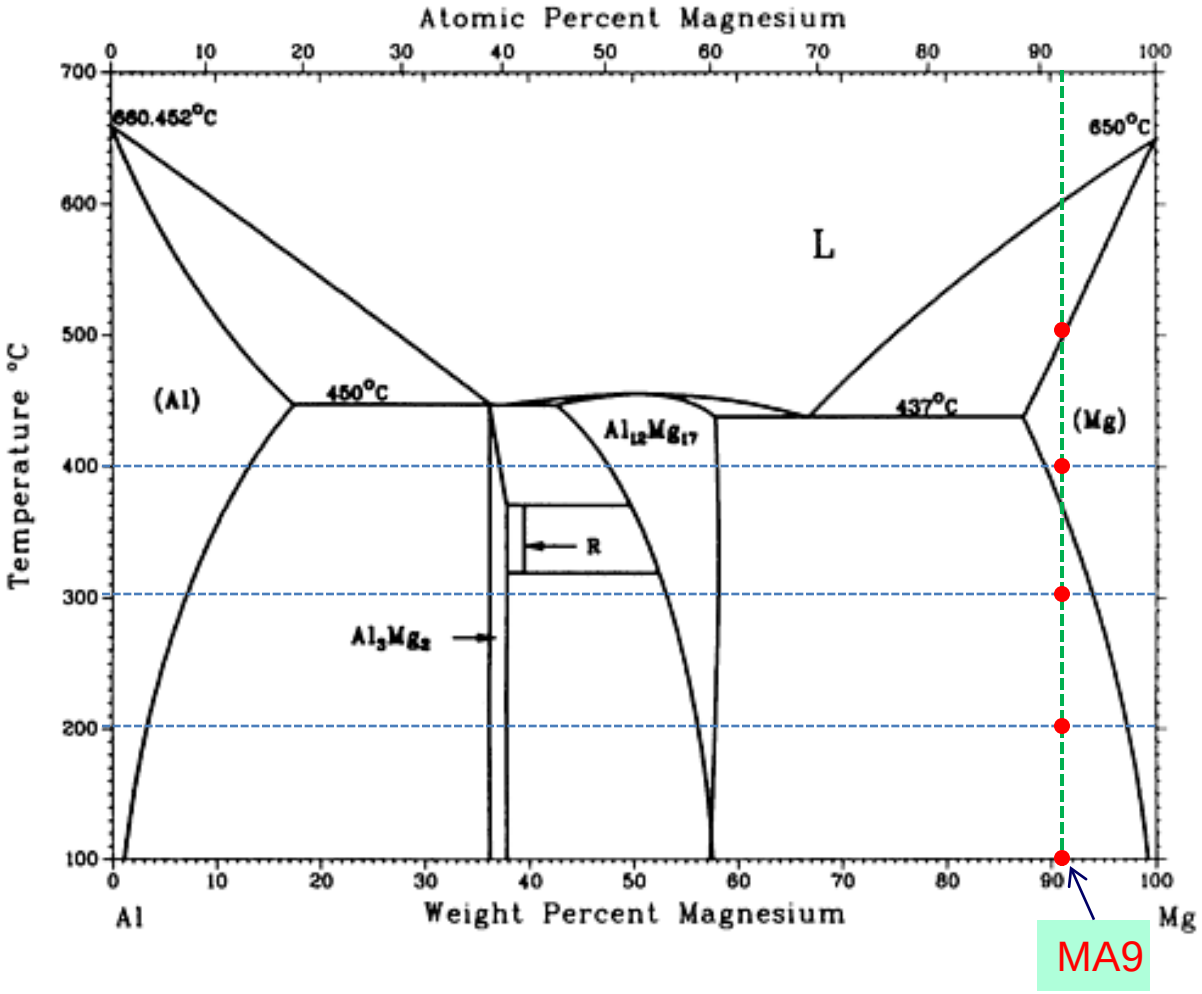






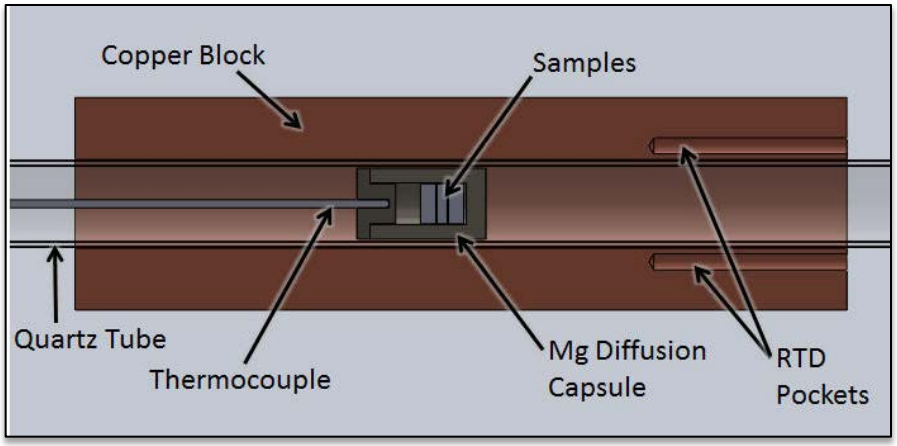


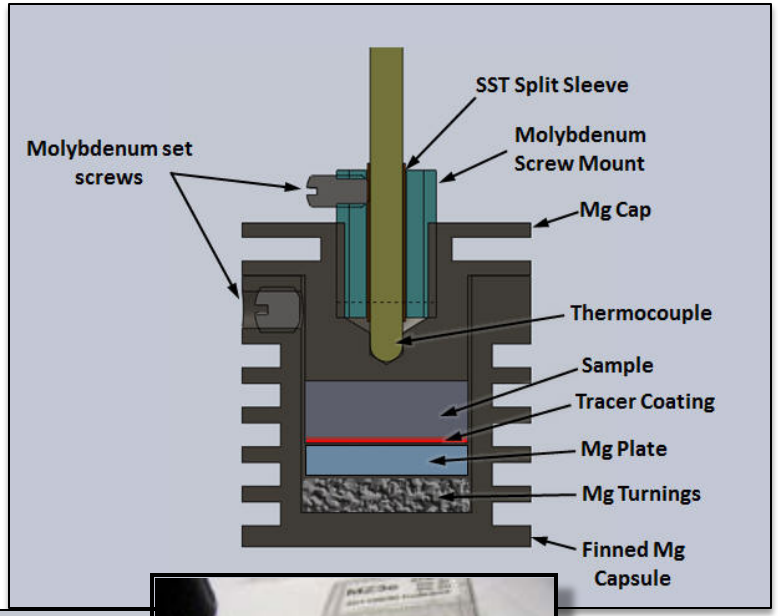
Mg-Al Phase Diagram

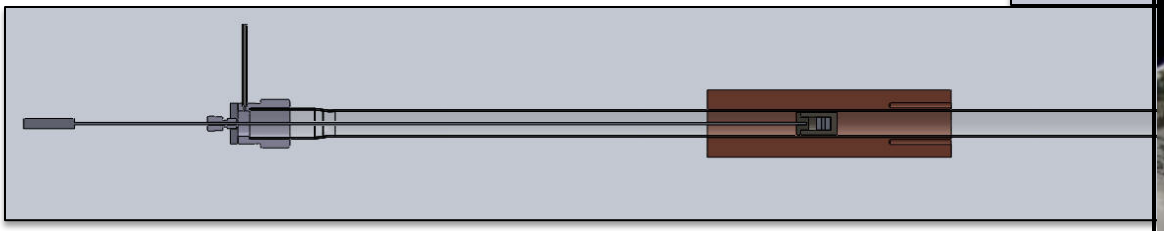


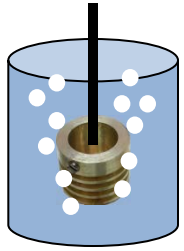
- *$Mg_{17}Al_{12}$ precipitates form during air cooling following warm extrusion*
- *EDS, EPMA analysis made it clear that while compositions were reasonably uniform and close to nominal compositions, samples needed to be homogenized to ensure single phase structures and large grain sizes*

Mg Diffusion Annealing Technique









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

Thermocouple Calibration

- http://www.ornl.gov/sci/diffusion/Experimental/Apparatus/Thermometry.html
  - Includes RTD & Thermocouple specifications
    - RTDs: Omega PR-11-3-100-1/8-18-E-CLA is the 4-wire version of the PR-11-2 and is IEC/DIN Class A accuracy (±0.15°C at 0°C). Note: 4-wire version must be in at least 1/8" OD sheathing.
      - Class **A tolerance:** **ΔT** °C = ± (0.15 + 0.002 • T)
    - TCs: All SST sheathed K-type. Standard limits of error: ±2.2°C or 0.75% (-200°C to 1250°C)
      - TC1 Omega KMQSS-020G-12 Dia:0.020, length: 12«
      - TC2 ...etc.
  - Readout systems for RTD's and thermocouples with reading accuracy
  - Summary of Calibration: ORNL Metrology Lab was used for calibration of TCs and RTDs using NIST traceable standards to within ±1ºC.

- Calibration tests were performed in a furnace with an alumina isothermal block at 400°C, 500°C and 600°C. All probes were within ±1ºC. Equilibration was much slower but there were less thermal gradients using this thermal mass.
- In comparison, probes in a fluidized sand bath with lower thermal mass had lower stability (±2ºC).

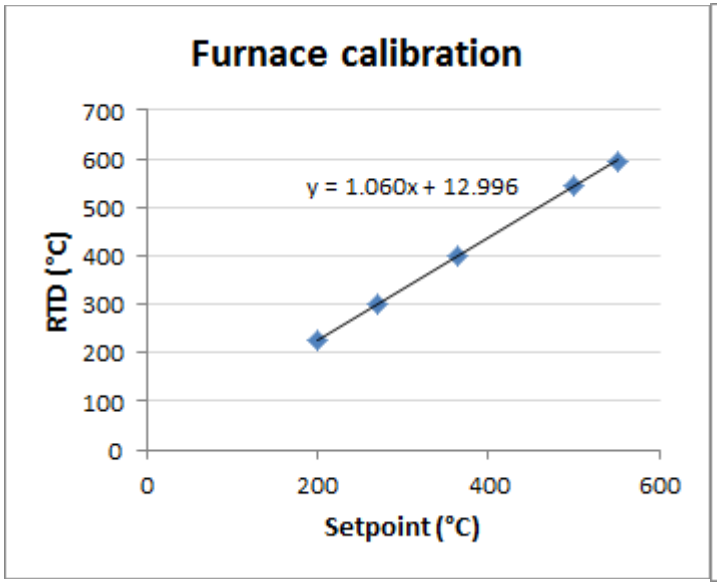
T ºC	0.00	398.60	499.65	600.01
TC1	-0.13	-0.75	0.35	0.63
TC2	0.58	-0.09	0.80	0.65
TC3	0.51	-0.08	0.80	0.63
TC5	0.62	-0.32	0.03	0.15
RTD1	0.45	0.99	1.06	1.34
RTD2	0.28	0.52	0.46	0.83
RTD3	0.11	0.40	0.34	0.72
RTD4	0.28	0.70	0.67	1.14

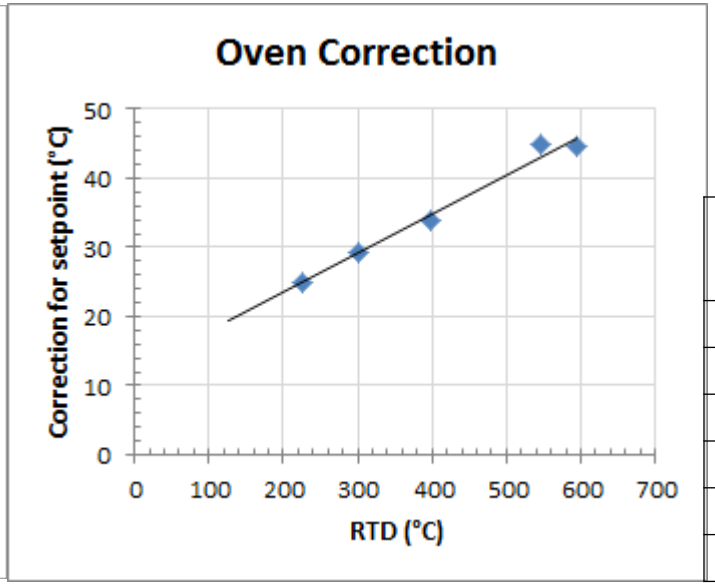
Correction of RTD standard resistance at 0ºC 100.00Ω to their actual resistance (100.056Ω for RTD3) would eliminate the majority of the measured errors (to within 0.1ºC).

Furnace Calibration

- MTI GSL-1100 Tube Furnace (up to 1200 C) with a quartz tube and temperature controller for heat treatment of magnesium alloys.
- A copper heater block with a 17.5 mm pocket for the 17 mm OD quartz enclosure and two 1/8" RTDs is used for rapid and accurate equilibration of Mg samples at desired heat treatment temperatures.
- For temperature control, we use an internal K-type thermocouple that is calibrated with Class-A RTDs that are in turn calibrated at the ORNL Metrology Laboratory.

MTI GSL-1100 Tube Furnace.

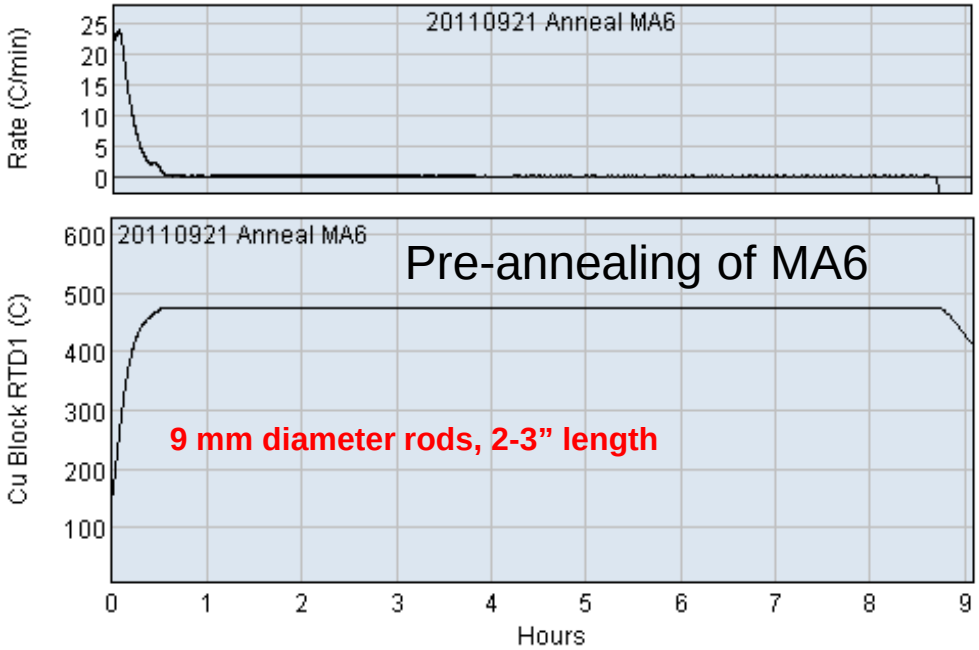


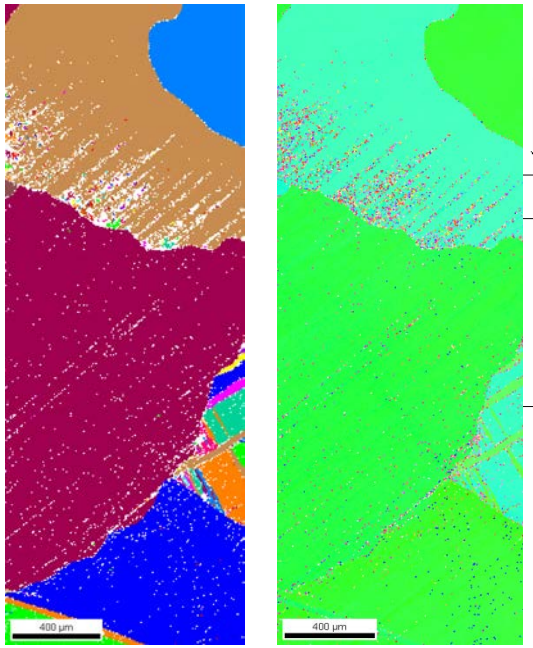


Desired T	Setpoint
200	176
225	200
250	224
300	271
350	318
400	336

High-temperature Homogenization & Grain Growth Annealing

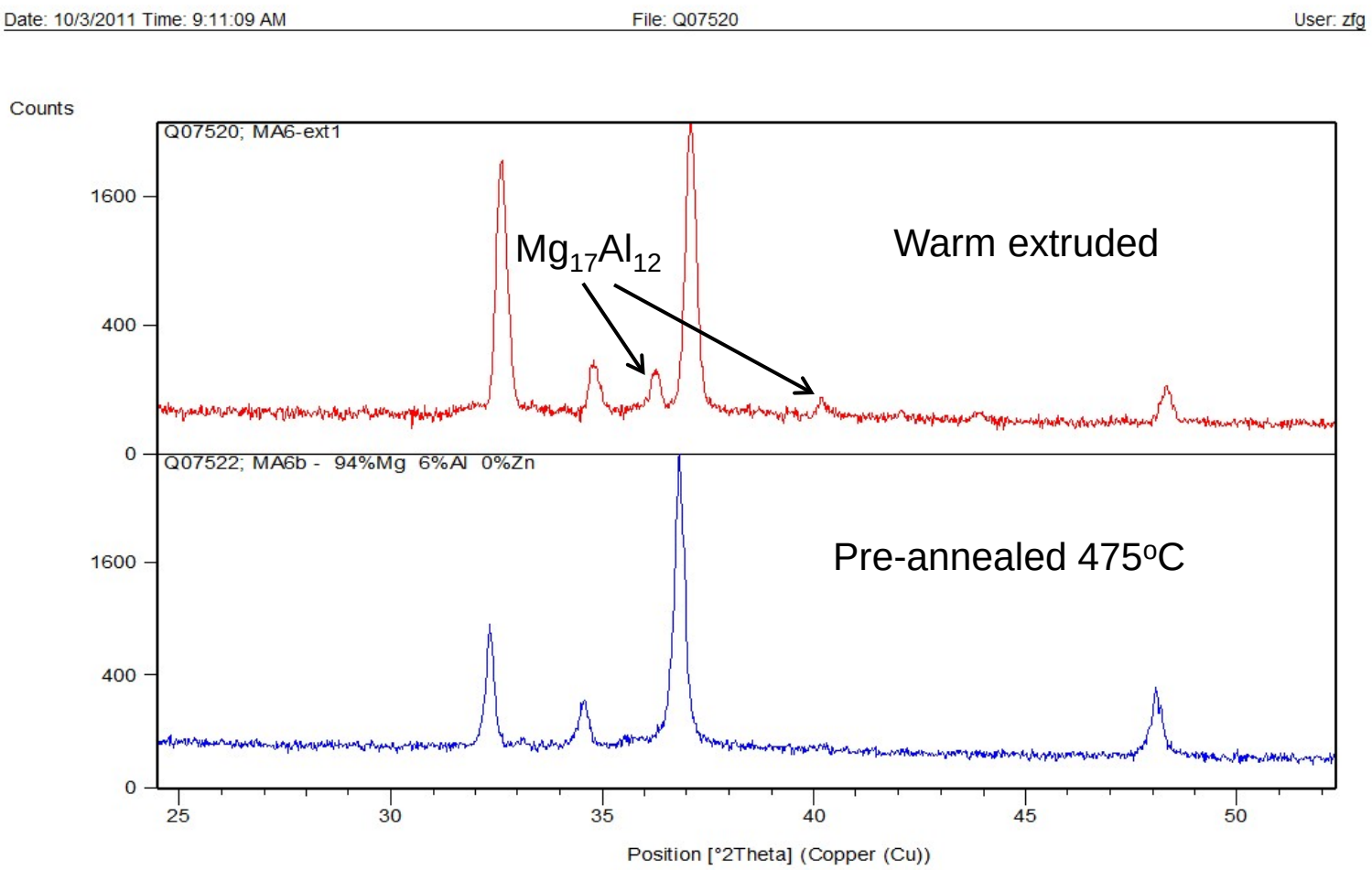
Alloy	Melting temperature onset -solidus (°C)	Pre-annealing temperature (°C)
MA1	630	575
MA6	530	475
MZ3	560	510





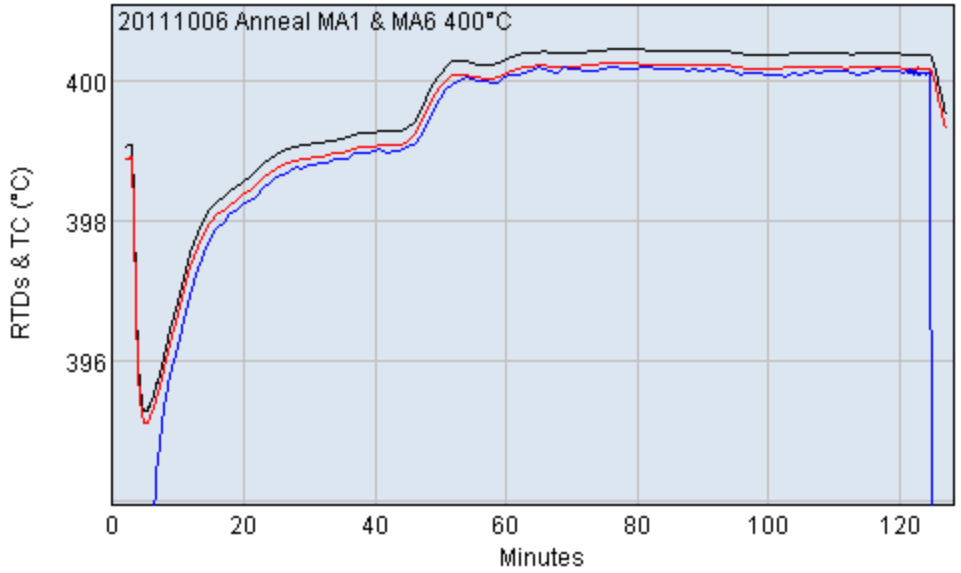
Electron Backscatter Diffraction (EBSD) map (inverse pole figure – top right) of grain orientations in a pure polycrystalline Mg rod after an annealing treatment at 545°C for 14.5 hours. Figure on the top left is the identical grain structure map with enhanced contrast.

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



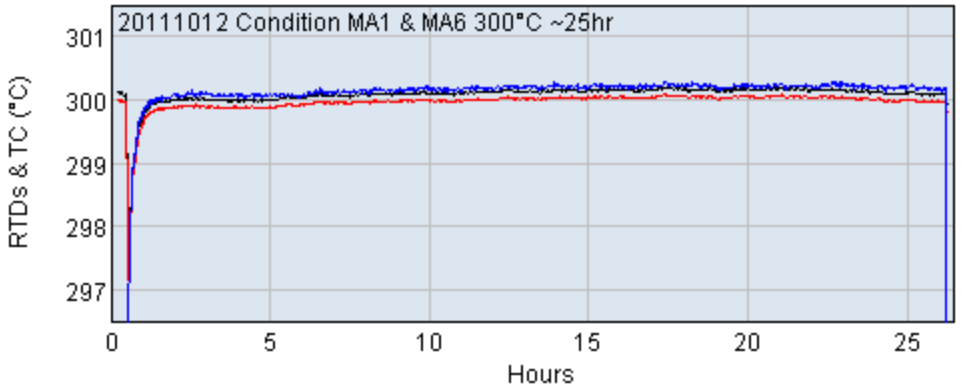
➢ ***Precipitate phase dissolved during pre-annealing at 475°C, 8 hrs***

Conditioning Anneal at Tracer Diffusion Temperatures



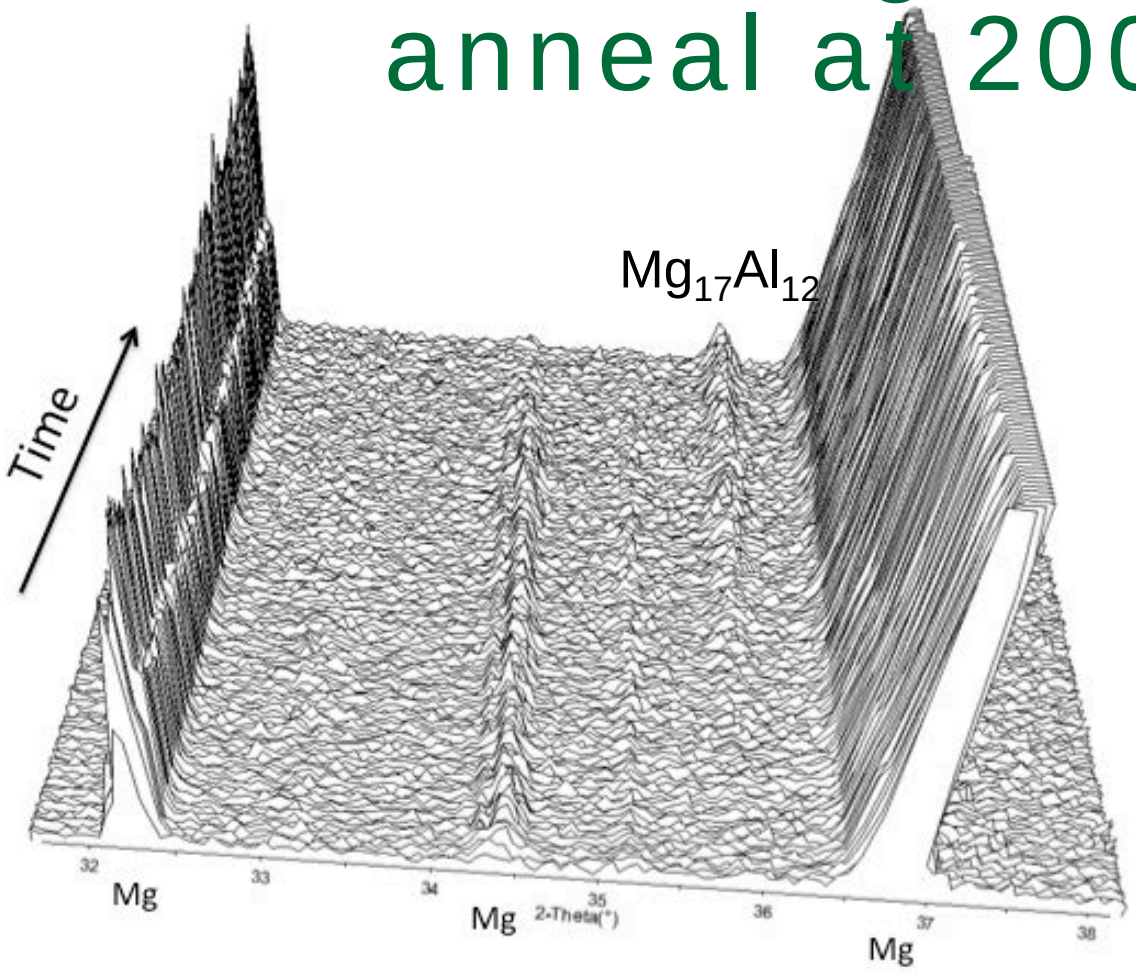
MA1 & MA6:

400°C, ~2 hrs
(tracer diffusion annealing time: 30 mins)



300°C, ~25 hrs
(tracer diffusion annealing time: 4 hrs)

MA6 XRD during conditioning anneal at 200°C



200°C, 24 hrs

- Weight fraction of $Mg_{17}Al_{12}$ precipitate is still increasing with time
- Current tracer diffusion experiments at ≥ 250°C (single phase)

➢ ***At temperatures ≥ 250°C no precipitate phase was observed***

➢ ***Only at 200°C precipitate phase was observed***

Polishing Mg: Art or Science?

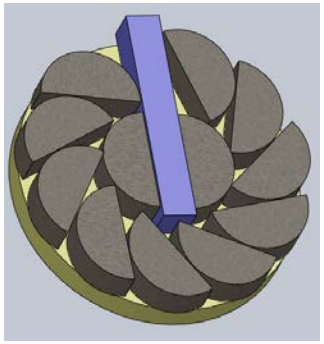
E.g.: Virginia Tech recipe (ORNL, UCF recipes are different …)

Graduate student notes (detailed polishing procedure) …

➢ ***Virginia Tech recipe used DI water rather than a non-aqueous solution medium for polishing***

UHV Deposition System for Mg
(Coffey/Dein: UCF)

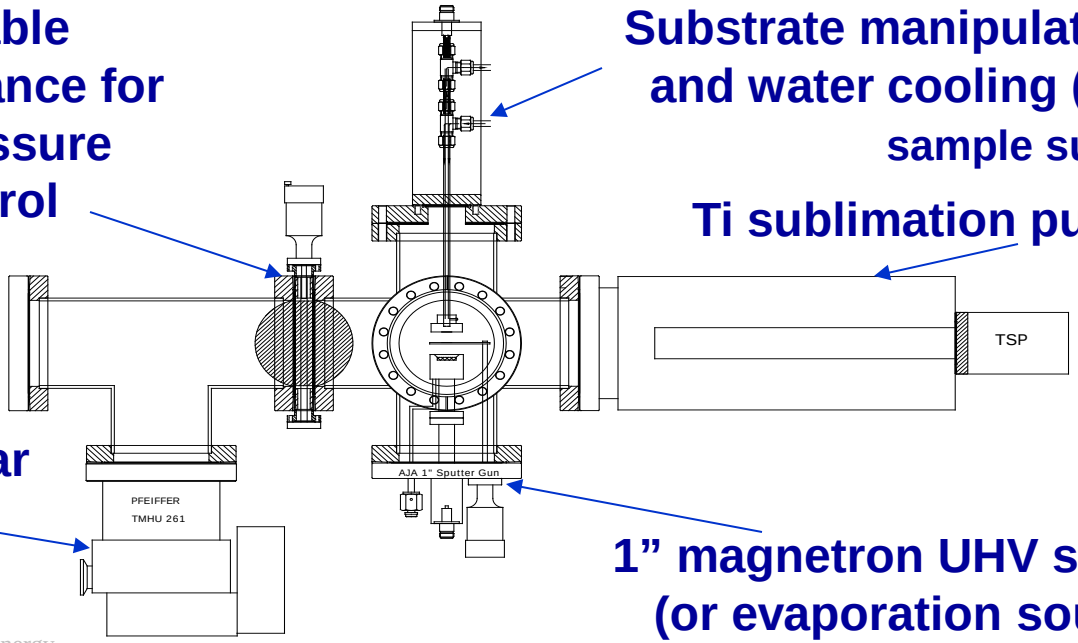
- **Short target-substrate spacing for high deposition rates (~ 10 x increase).**
- **UHV bake-able vacuum components and pumping (~10^4 x improvement):**
  - **< 1E-8 Torr *(even better vacuum levels attainable with longer and higher temperature baking)***
- **Hot metal getter purification of Ar process gas at point-of-use.**
- **All metal-sealed Ar process gas handling components.**
- **Shielding in chamber to provide "getter sputtering" for further increased purity**



Variable conductance for Ar pressure control

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

Ti sublimation pump for water vapor



Turbomolecular pump for Ar

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

Isotopic Foil: Specs

ASSAY

Element: Magnesium
Symbol: Mg
Isotope: 25
Series: NB
Batch: 158543

ISOTOPIC ANALYSIS

Isotope	Atomic Percent	Precision plus/minus
24	1.83	0.07000
25	97.86	0.06000
26	0.31	0.01000

The limits quoted above are an expression of the precision of this measurement only. The error is estimated at less than 1% from known sources of systematic errors.

Internal Use Only
Date Entered: 12/13/1994
Last Change: 08/30/2011 02:31:55 PM
By: AUU

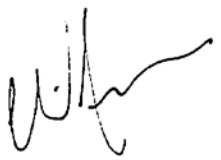
SPECTROGRAPHIC ANALYSIS (SSMS)

Element: ppm	Element: ppm	Element: ppm	Element: ppm
Ag:	I:	Rh:	Tc:
Al: 20	In:	Ru:	Te:
As:	Ir:	S: 20	Th:
Au:	K: 20	Sb:	Ti: <1
B: 5	Li:	Sc:	Tl:
Ba:	Mg: M	Se:	U:
Be:	Mn: 1	Si: 20	V: 1
Bi:	Mo: 5	Sn:	W:
Br:	N:	Sr:	Zn: 3
C:	Na: 200	Ta:	Zr: 1
Ca: 5	Nb:		
Cb:	Ni: 3		
Cd:	O:		
Cl: 5	Os:		
Co: <1	P: 20		
Cr: 1	Pa:		
Cs:	Pb:		
Cu: 10	Pd:		
F:	Pm:		
Fe: 20	Po:		
Ga:	Pt:		
Ge:	Ra:		
Hf:	Rb:		
Hg:	Re:		

LANTHANIDES and ACTINIDES

Am:	La:
Bk:	Lu:
Ce:	Md:
Cf:	Nd:
Cm:	Np:
Dy:	Pr:
Er:	Pu:
Es:	Sm:
Eu:	Tb:
Fm:	Y:
Gd:	Yb:
Ho:	Tm:

* Symbols: M - major; T - trace; I - interference; < - less than; </= less than/equal to; ~ approximately; nd - not detected.
* Elements listed above without values were not detected or would calculate less than 10 ppm.
* Request No. 34262; Requisition No. 9503
* This analysis reflects enrichment and impurity levels prior to conversion/fabrication.
* <- No spectrum line visible. Probably absent, definitely less than value given.
* <T- Present but less than value given.
* The spectrographic results reported herein are semi-quantitative estimates and should not be interpreted or construed to be precise quantitative determinations.



Mg Foil Sputter Target Preparation (UCF: Coffey/Dein)

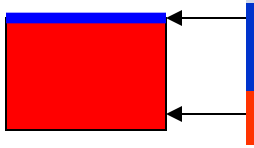
- **Notes (Dein): Sputter target preparation/bonding procedure …**

➢ **Indium used for bonding Mg isotopic foil to sputter gun**

Conditions for Isotopic Deposition

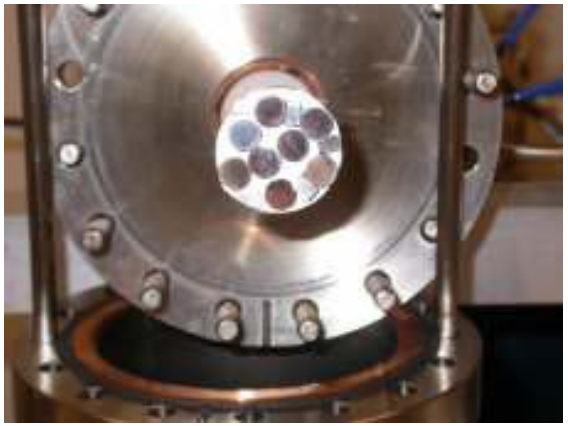
Pre-sputter cleaning of native oxide followed by deposition

- System pressure 1.2E-8 Torr
- RF pre-clean: 126 Watts RF, 20 Sccm Argon @ 5 mTorr for 60 seconds.
- Magnesium Deposition: 50 Watts DC, 20 Sccm Argon @ 5 mTorr for 50 seconds.
  - Detailed steps described on website



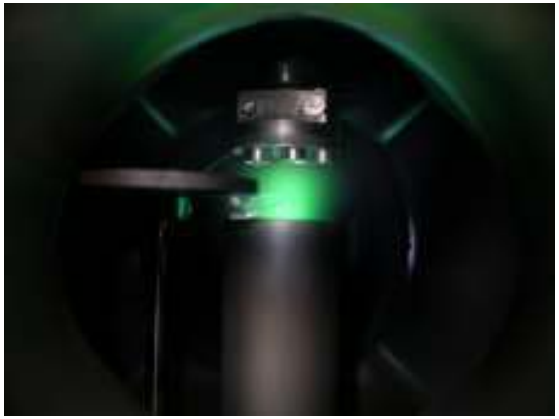
Initial Isotope Concentrations

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



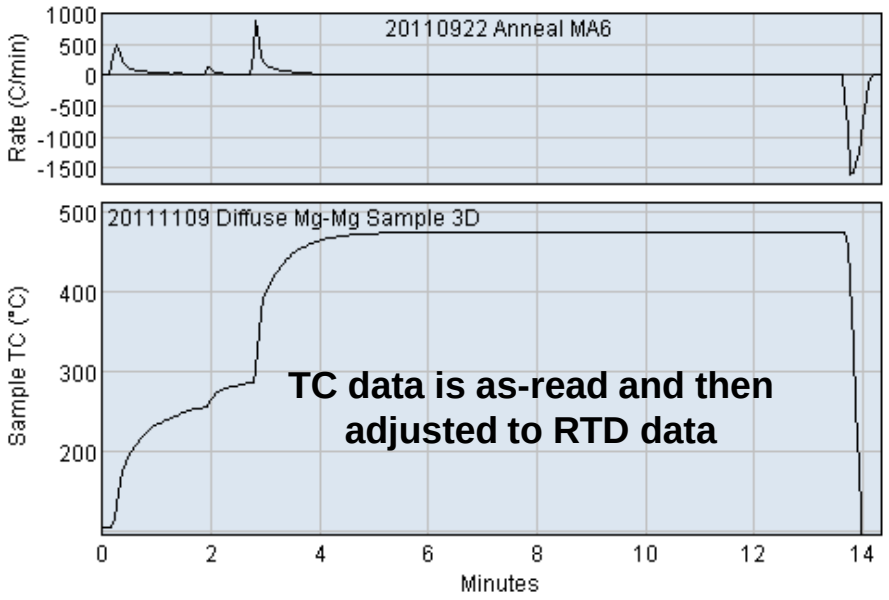
Mg samples within ~1 inch circle

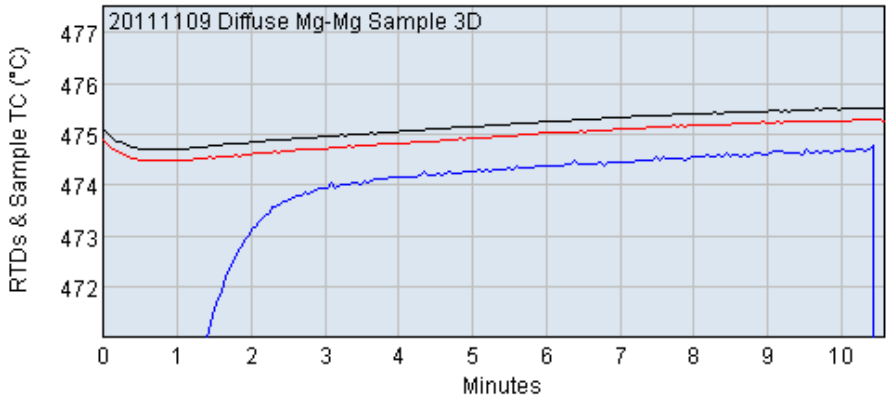
RF sputter pre-clean



Mg-25 deposition

Diffusion Annealing





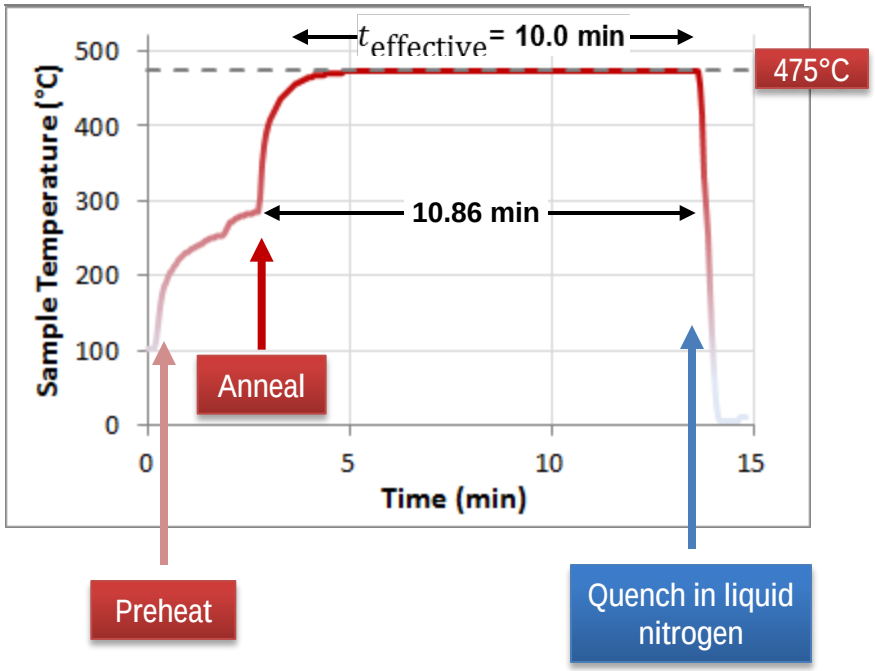
E.g.: MA6, 475°C, 10 mins – Warmack notes

- Use finned Mg diffusion capsule (20111012) for lighter mass and faster equilibration. Standard Thermolyne furnace setup set at 435°C to obtain 475°C on copper block.
- Practice with dummy sample and get about -7% time correction for 10 minutes in the Cu block.
- Load Mg Sample 3D (should have ~150nm Mg-25) using filings obtained from sample Mg rods (Alfa lot F29X155), a 1-mm Mg section (same material), and the sample facing the Mg section.
- Pump and purge 3X with 4%H2/He. Insert into preheating section and then into Cu block region for ~10min. The sample TC (TC3) and the back TC (TC4) agreed to within 0.1°C and read lower than the RTDs by an average of 0.8°C.
- Withdraw and immediately plunge into LN_2 until room temperature (~20sec).
- The total time in the Cu block was 10.8min with a maximum sample temperature of 474.7°C (measured by TC3), so the calculated diffusion time is 10.0min or 0.166hr. Of the total time, the contribution to the effective diffusion for time spent below 300C is less than 0.01%.

Temperature profile correction

- Effective time at annealing temperature can be calculated using the actual profile and the activation energy (Rothman 1984) using numerical integration
- 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

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

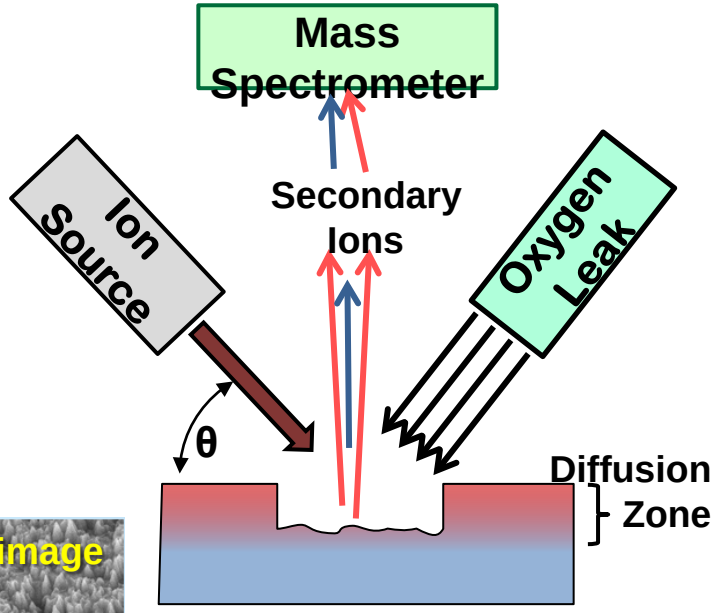


Cameca ims7f-Geo

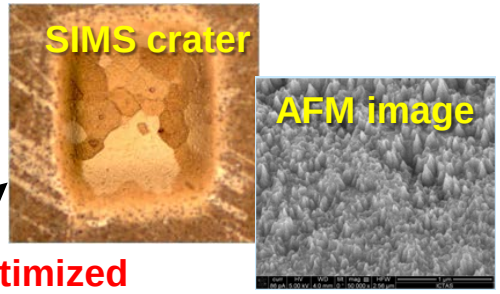
Secondary Ion Mass Spectrometry (Hunter, VT)

SIMS primary ion sputtering conditions for a 1 μm Mg polycrystalline film deposited on a Si wafer

- Roughness increases with sputter depth for polycrystalline samples due to grain orientation
- Oxygen leak creates an amorphous oxide surface to reduce grain orientation effects
- Also, energy and angle are optimized to reduce roughness

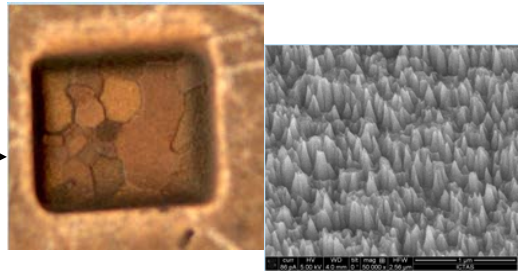


Energy, kV	O-leak	Angle	Roughness, nm
Unsputtered			7.2
3	yes	37	10.7
2	yes	40.6	10.7
3	yes	40.6	12.2
3	yes	46	17.4
3	no	46	30.7
5	no	44	37.7



Optimized

Typical



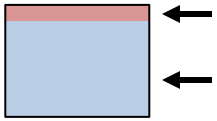
O-leak pressure = 2 x 10^{-6} torr

Virginia Tech. VT

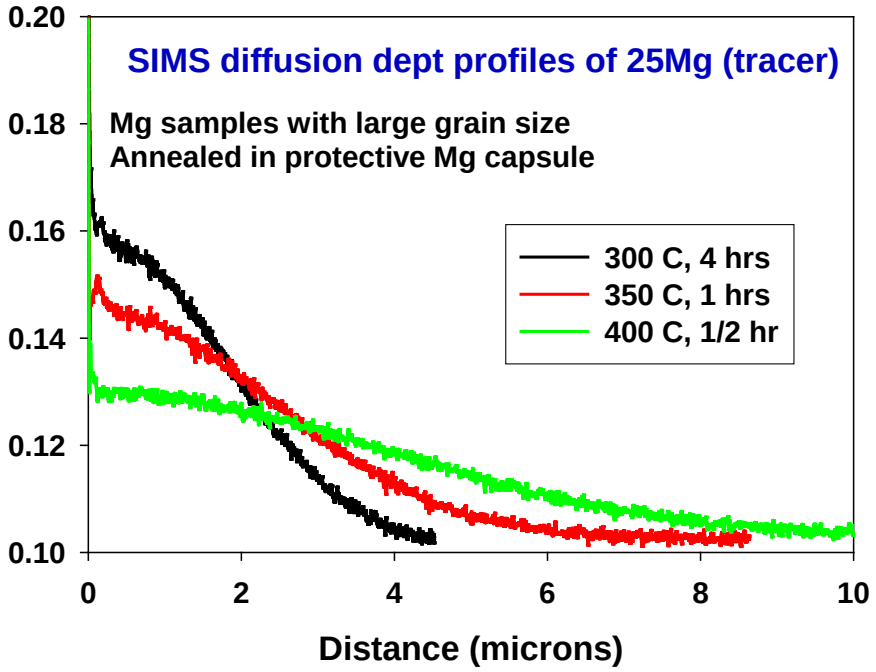
OAK RIDGE National Laboratory

Experimental Mg self-diffusion

Initial

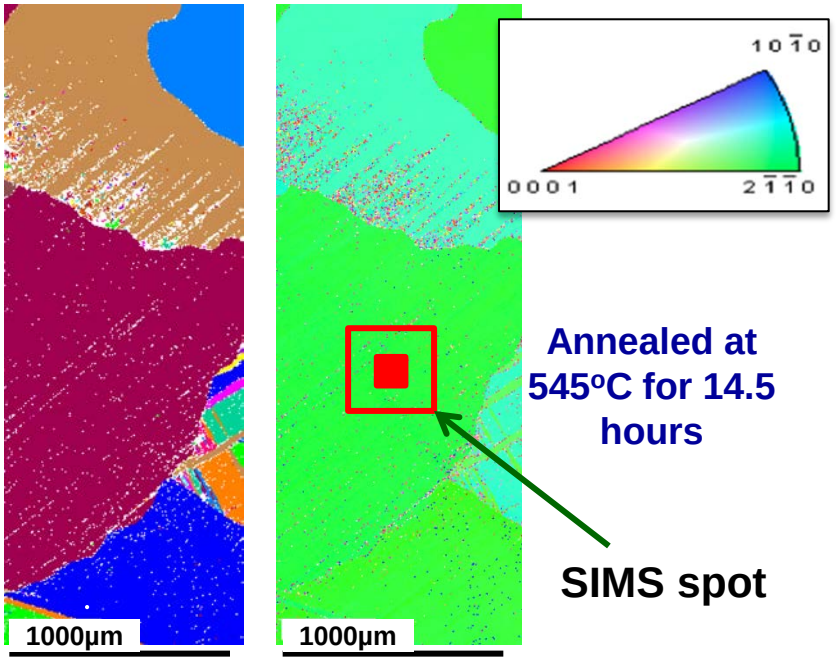


	^{24}Mg	^{25}Mg	^{26}Mg
Tracer	0.018	0.979	0.003
Bulk	0.790	0.100	0.110



SIMS concentration depth profiles of ^{25}Mg

Annealing produces large grains



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.

➢ *Optimized SIMS profiles within single grains yield more accurate bulk diffusivities*

Data Analysis in Excel

Raw SIMS data (optimized conditions)

Spot 1						
24Mg(X)	24Mg(Y)	25Mg(X)	25Mg(Y)	26Mg(X)	26Mg(Y)	x(μm)
0.003884	266703.8	0.009224	84019.23	0.014564	40882.69	0.009224
0.019905	290283.7	0.025245	56293.27	0.030585	37967.31	0.025245
0.035925	269951.9	0.041265	50060.58	0.046606	36200.96	0.041265
0.051946	259058.7	0.057286	49317.31	0.062626	34927.88	0.057286
0.067967	249701.9	0.073307	47454.81	0.078647	33794.23	0.073307
0.083987	244408.7	0.089328	46521.15	0.094668	33266.35	0.089328
0.100008	242367.3	0.105348	46428.85	0.110689	33397.12	0.105348
0.116029	242917.3	0.121369	47680.77	0.126709	34092.31	0.121369
0.13205	245866.3	0.13739	48531.73	0.14273	34150	0.13739
0.14807	245672.1	0.15341	48185.58	0.158751	33623.08	0.15341
0.164091	243240.4	0.169431	47445.19	0.174771	33375.96	0.169431
0.180112	241197.1	0.185452	46381.73	0.190792	33100	0.185452
0.196132	240343.3	0.201473	46304.81	0.206813	33196.15	0.201473
0.212153	239227.9	0.217493	46258.65	0.222834	32928.85	0.217493
0.228174	238239.4	0.233514	45742.31	0.238854	32811.54	0.233514

SIMS data: (X) indicates position in microns (obtained from the measured sputter rate); (Y) indicates SIMS intensity

Summary of calculations for all SIMS Spots (profiles)

20111007 SIMS Mg-Mg ORNL_350C_1Hr_S2 - nonlinear fit.xlsx

Temperature:	349.8	°C
Time:	0.919	hr
Approx. Film Thickness	100	nm

Mg Abundances			
Isotope	^{24}Mg	^{25}Mg	^{26}Mg
Natural	0.7899	0.1001	0.11
Tracer1	0.018	0.9787	0.0033

		D_0 (cm^2/s)	Q (kcal/mol/T)	Projected D (cm^2/s)
Shewmon 1956 (s.c.)	Mg-25	1.50	136	5.88E-12
Shewmon 1954 (p.c.) + recent	Mg-25	0.33	125.8	9.24E-12

Fitted parameters:

	D (cm^2/s)	h (nm)	AB_{Mg25}	RMS*	Lower (μm)	Upper (μm)
Spot 1	9.49E-12	140.9	0.1041	5.50E-04	1	100
Spot 2	9.22E-12	142.6	0.1043	5.71E-04	1	100
Spot 4	9.04E-12	138.9	0.1039	5.95E-04	1	100
Average	**9.25E-12**	140.8	0.1041			
s.d.	2.4%	1.3%	0.2%			

Diffusion length 3.5 μm or 24.9 x film thickness

* RMS of the residuals of C/C_0 between prescribed depths for fitting

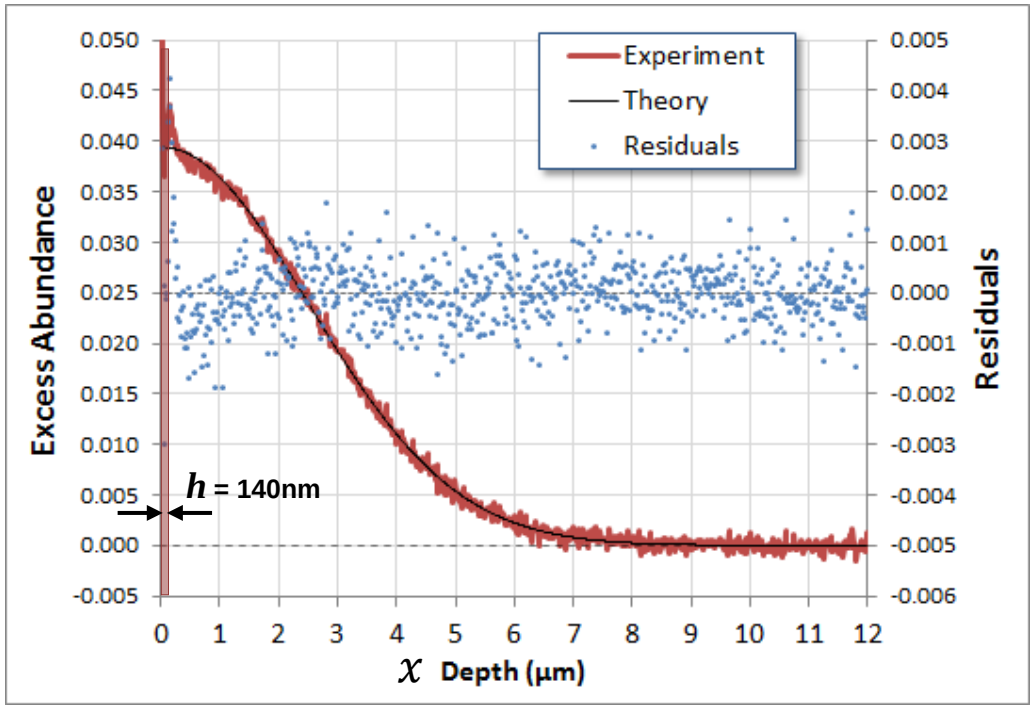
$$\sum_x \left\{ \left[\frac{S_{tracer}(x)}{\sum S_{all\ isotopes}(x)} - A \right] - \frac{(A_{tracer} - A_{natural})}{2} \left[\mathrm{erf}\left(\frac{h-x}{2\sqrt{Dt}} \right) + \mathrm{erf}\left(\frac{h+x}{2\sqrt{Dt}} \right) \right] \right\}^2$$

Excel's Solver add-in feature is used to minimize the sum of the square of the residuals above, where S is the SIMS signal as a function of depth, x, for each of the tracer or impurity isotopes, A_{tracer} is the abundance of the tracer isotope (e.g., Mg-25), $A_{natural}$ is its abundance in the bulk material, time, t, the diffusion coefficient, D, and an initial tracer film of thickness, h. The fitted parameters are D, h and A, which corresponds to the measured apparent abundance of the tracer isotope in the bulk. (The Gaussian formulation can also be used to an accuracy of better than 1% for a diffusion length > 10 times the film thickness.)

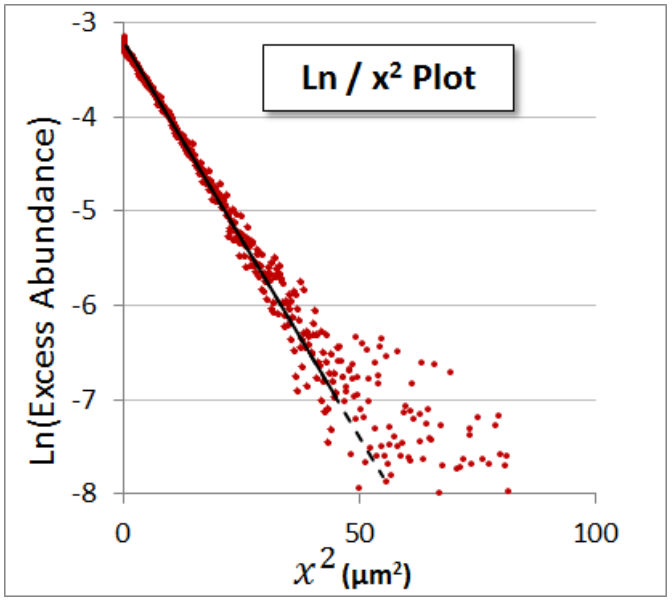
Solver must be manually initiated in each of the worksheets when the data is dropped into the worksheet or when the fitting limits are changed.

Fitting of diffusion depth profiles

Example: SIMS measured excess 25Mg tracer after 350°C ~1hr



Log-linearized plot has fitting problems at low signal levels



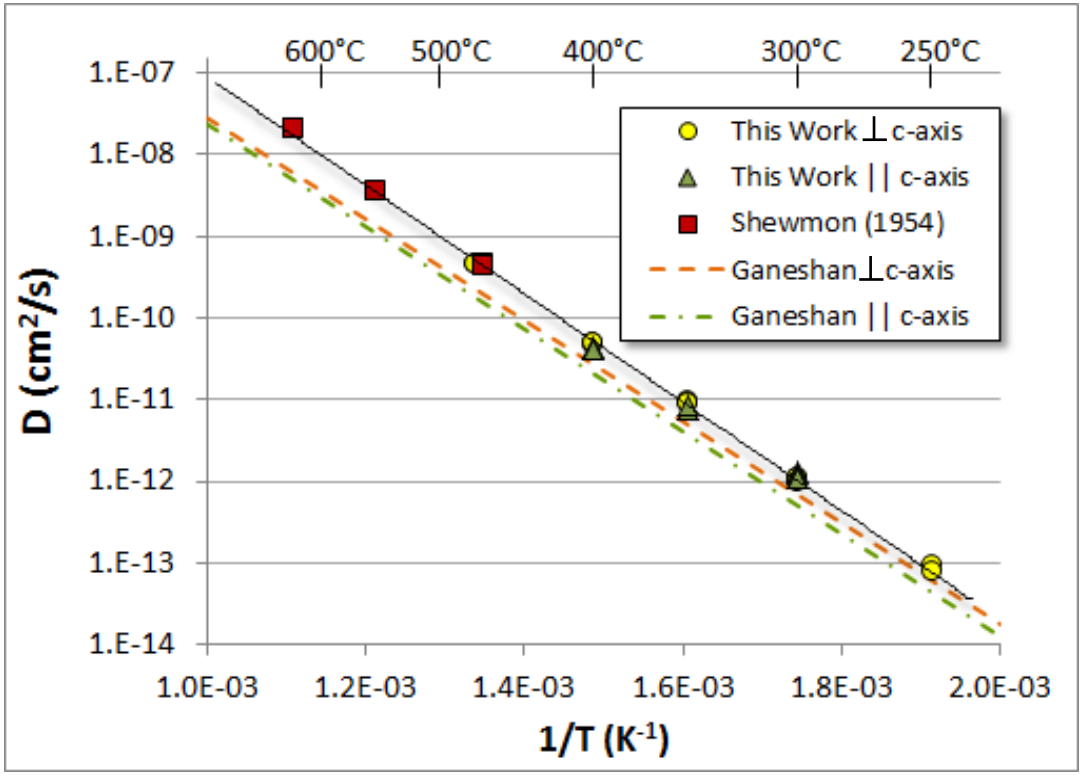
Replace concentration with abundance: $C(x,t) - C_1 = \frac{(C_0 - C_1)}{2}\left[\mathrm{erf}\left(\frac{x+h}{2\sqrt{Dt}}\right) - \mathrm{erf}\left(\frac{x-h}{2\sqrt{Dt}}\right)\right]$

Nonlinear fit of D, h and A by minimizing the sum of the square of the residuals:

$$\sum_x \left\{\left[\frac{I_{tracer}(x)}{\sum I_{all\ isotopes}(x)} - A\right] - \frac{(A_{tracer} - A_{natural})}{2}\left[\mathrm{erf}\left(\frac{x+h}{2\sqrt{Dt}}\right) - \mathrm{erf}\left(\frac{x-h}{2\sqrt{Dt}}\right)\right]\right\}^2$$

Excess Abundance: **Experiment** **Theory**

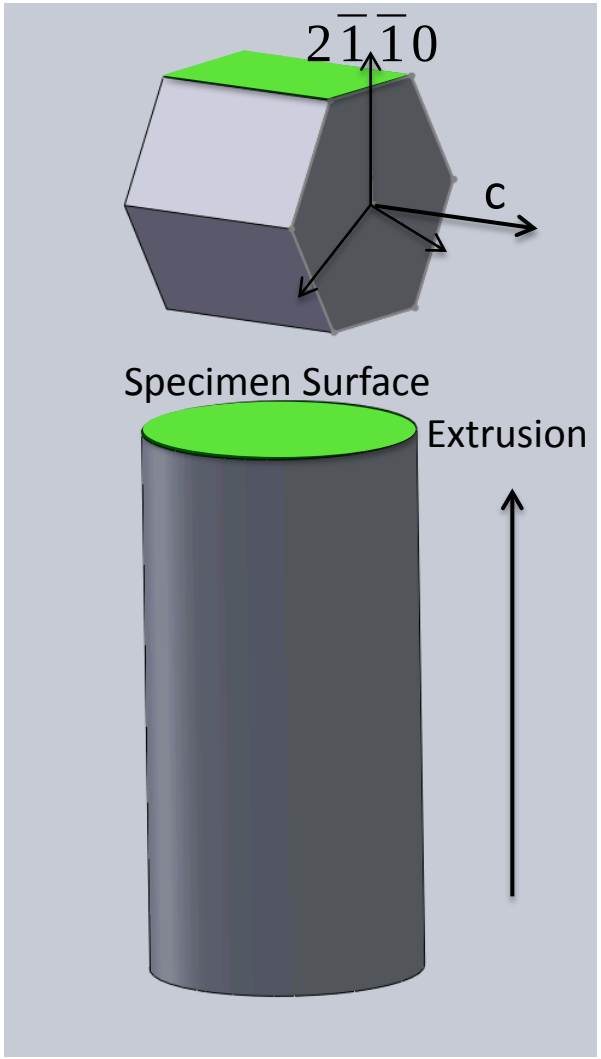
Mg self-diffusion coefficients

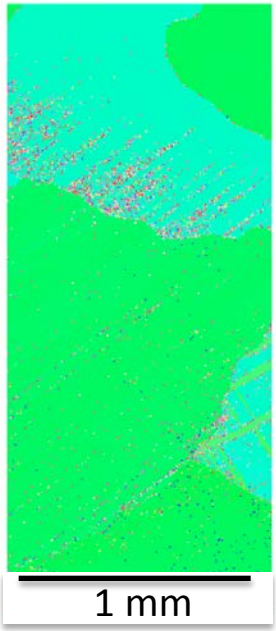


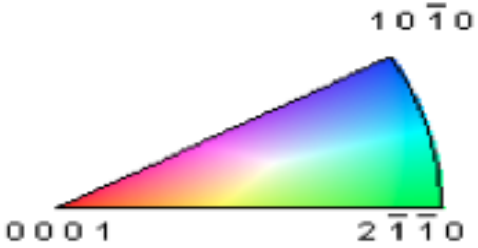
- Standard deviation (SD) for samples perpendicular to c-axis (or along the extruded rod axis) based on 2-3 SIMS depth profile measurements per sample was found to be <6% (temperatures from 300-475°C); however, SD for sample at the lowest temperature 250°C was 10% (only 2 SIMS depth profiles)
- SD for samples along the c-axis (or diffusion normal to the rod axis) was higher (~14%) due to the limited number (2) of SIMS profiles per sample.

- ***Experimental results consistent with polycrystalline radiotracer measurements***
- ***Tracer diffusivities in directions parallel to rod axis (normal to c axis) appear to be higher (at higher temperatures) compared to diffusivities for samples normal to rod axis (orthogonal or parallel to c axis) though more work is needed at lower temperatures due to large scatter.***

Measurements can capture anisotropy in Mg diffusion







Extruded rod annealed at 545°C for 14.5 hrs

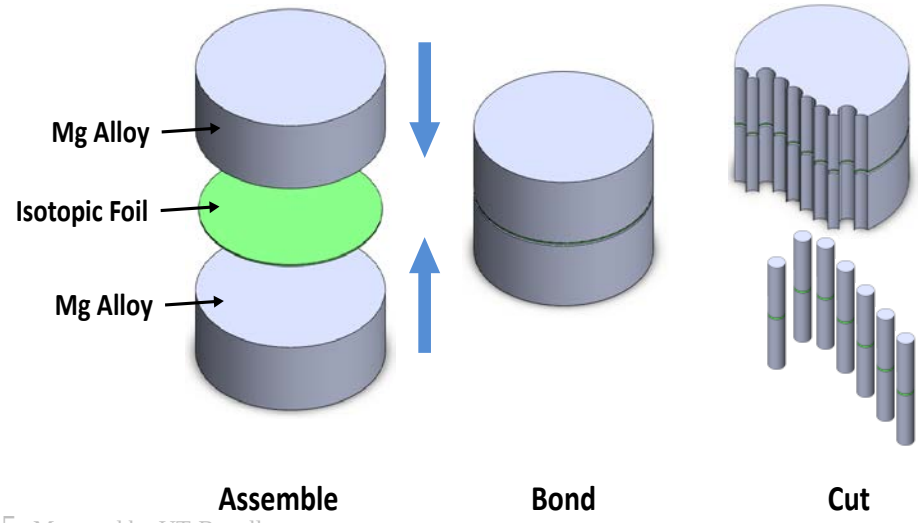
- **Large green grain has $2\bar{1}\bar{1}0$ direction normal to specimen surface**
- **Measured diffusion coefficient is normal to c-axis; shows slightly higher value than that measured parallel to c-axis (section surface parallel to rod axis)**
- **Consistent with known anisotropy in diffusion in magnesium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

Summary

- Established SIMS based tracer diffusion technique to facilitate diffusion database development for MGI
- Described process flow/steps for conducting SIMS-based tracer diffusion experiments.
- Several developments/techniques developed along the way
    - UHV sputter deposition system & deposition procedure
    - SIMS optimized conditions for Mg
    - Mg sample preparation & annealing technique
    - Data analysis and reporting on diffusion website
    - New interdiffusion analysis (Belova et al.)

Future Work

- Current project has ended but tracer diffusion approach would be suitable for building the Diffusion Genome for the MGI
- NiAl, Ni_3Al tracer diffusion studies in the presence of magnetic fields (ongoing ORNL LDRD project)
- Interest in tracer diffusion studies in Mg-liquids relevant for phase field solidification modeling of Mg die casting (DOE proposal pending)



Schematic Mg-alloy sample assembly for high temperature isotopic tracer diffusion measurements using the long capillary method.

Isotopic Phenomenological Diffusion Formalism (new)

Belova et al. (Newcastle, Australia), "Simultaneous Measurement of Tracer and Interdiffusion Coefficients: An Isotopic Phenomenological Diffusion Formalism for the Binary Alloy," submitted to Phil. Mag.

- SIMS technique is capable of analyzing diffusion profiles over a broad length scale, and it can routinely determine concentrations from the matrix level down to ppm/ppb levels.
- SIMS technique permits different isotopes to be distinguished in concentration profiles.
- Onsager phenomenological formalism is developed further for isotopic interdiffusion.
  - The present study addresses the binary alloy case of such a formalism by making use of the general linear response expressions for the Onsager phenomenological transport coefficients
  - In the case of a binary diffusion couple, the new isotopic interdiffusion formalism provides the means to obtain tracer diffusion coefficient(s) together with the interdiffusion coefficient as functions of composition in the diffusion zone in a single straightforward experiment.
  - To apply this formalism, the diffusion couple has to be prepared with essentially different isotopic compositions (abundances) of a given atomic component and cross-section or angle-polish SIMS needs to be used.

Acknowledgements

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Carol Schutte (Materials Technology - Team Lead) and William Joost (Lightweight Materials): Vehicle Technologies Program, DOE
Joe Carpenter: Former program manager, Automotive Lightweight Materials Program, DOE
Phil Sklad, Dave Warren: Automotive Lightweight Materials Program, ORNL