Dissecting the Diffusion Genome

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Outline

• Diffusion Genome – definition within MGI context

• Components of the diffusion genome
  – Formalism: robust and general
  – From formalism to database: a case for tracer
  – Types of diffusion data
    • Volume: tracer (radioisotopes, SIMS), interdiffusion/intrinsic, others
    • Grain boundary/interfaces
    • Theoretical
  – Data infrastructure & dissemination
  – Effective Diffusion

• Final remarks
MGI Goals

• 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.
Diffusion Database vs Genome

- **A diffusion database** typically provides the bulk diffusion coefficient of a component as a function of composition and temperature for the selected phase.

- **A diffusion genome** is a science and knowledge-base system of *fundamental* diffusion information that includes databases:
  - Provides raw/fundamental diffusion data or “protodata” and details on methods and techniques used preferably in a universally acceptable data format.
  - 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) diffusion data.
  - Can be improved over time and adapted as desired.
  - Database approach/es constructed from the genome must be rigorous and be adaptable to materials of arbitrary complexity.
Components of the Diffusion Genome: Formalism

Fick’s First Law (1855):

\[ J_i = -D_i \frac{dC_i}{dx} \]

Because it does not recognize all of the driving forces, direct and indirect, acting on species \( i \), Fick’s First Law is frequently insufficient as a condition for describing fluxes.
The Onsager (1929, 1931) Flux Equations of irreversible processes (Nobel prize in chemistry, 1968) provide a general formalism through the postulate of linear relations between fluxes and driving forces:

\[ J_i = \sum J_{ij} X_j \]

- \( L_{ij} \) : the phenomenological coefficients (independent of driving force)
- \( X_j \) : the driving forces (e.g. gradients in the chemical potential, electric field etc.)

Knowledge of the \( L \) matrix in a material would provide all possible kinetic information. But the \( L \) matrix is not directly measurable and so relations are sought between it and the measurable tracer diffusion coefficients in homogeneous systems.

Obtaining the \( L \) matrix from other types of diffusion coefficients (e.g., interdiffusion coefficients) is very difficult without simplifying assumptions.
Tracer diffusion coefficients provide the natural basis of a kinetics database.

They are measurable, can be accurately determined, and when this is impossible or difficult (e.g., Al, because of the lack of isotopes), they can be estimated through a combination of first principles calculations and Kinetic Monte Carlo calculations.

Tracer diffusion coefficients can be converted to the desirable Onsager phenomenological coefficients (L matrix) in metallic alloys and intermetallics via the approximate Manning relations or the almost rigorous Moleko-Allnatt-Allnatt relations (work in progress).
Onsager Diffusion Formalism

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

\[ J_k = - \sum_i L_{ki}^n \text{grad}(\mu_i) \quad \sum_k J_k = -J_v \]

• \( L_{ki} \)'s obtained from tracer diffusion data using Manning relations:

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

• Chemical potentials from thermodynamic database

➢ Cross-terms are not ignored as in Darken (correlation effects influence cross-terms)
Tracer Diffusion Measurements: Thin Film Approach

(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., Mg\(^{25}\)) on annealed sample

(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 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)
Availability of stable isotopes & SIMS means that tracer measurements are more affordable and safe, but cannot avoid working with radioactive isotopes in some cases, e.g., Al, Nb, Mn, etc., since these elements are monoisotopic.
Diffusion Data: Bulk

- **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 (e.g., Mg alloys)

- **Only the tracer diffusion coefficient is unique; rest are matrices**
Obtaining tracer data from interdiffusion/intrinsic data

• The conversion of interdiffusion/intrinsic diffusion coefficient matrices to the tracer coefficients (and vice versa) can be done using the Manning or MAA formalisms, provided the thermodynamics are readily available and robust.

  - E.g., in Mg-Al, tracer coefficient for Mg can be measured while that for Al may be obtained using measured interdiffusion/intrinsic data and thermodynamics:

\[
\tilde{D} = (X_{\text{Mg}} D^*_{\text{Al}} + X_{\text{Al}} D^*_{\text{Mg}}) \phi \ S
\]

• Preferably, experimental (e.g., activities) thermodynamic data that has been assessed should be used.

• This somewhat makes the tracer diffusion database dependent upon the thermodynamics, so as far as possible, significant tracer data should be collected for as many components as possible.

• Use of proprietary thermodynamic databases for such conversions or MGI in general is likely to be problematic.
Bulk (tracer) Diffusion: Orientation dependence

- In some compounds, e.g., YBCO, anisotropy can be 100X
- Functional applications may require orientation-dependent data

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

![SIMS diffusion dept profiles of 25Mg (tracer)]

Mg samples with large grain size
Annealed in protective Mg capsule

- 300 C, 4 hrs
- 350 C, 1 hrs
- 400 C, 1/2 hr

![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.

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

- Depending upon spot size (1 – 50 µm) and grain size, either individual single crystal diffusivity or average diffusivity can be measured with SIMS
Diffusion Data: Grain boundary

Experimental grain boundary diffusion measurements require use of tracers (radioactive or stable isotopes).

Lij’s for grain boundaries can be obtained similar to bulk but less rigorous.

Harrison’s classification scheme for diffusion in polycrystalline materials.

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, $d_b$ is the grain boundary width, and t is the diffusion time. [DeSouza, Martin et al., MRS Bulletin, vol. 34, Dec 2009].
Grain boundary diffusion using thin films & stable isotopes/SIMS/Atom Probe

Graph of $\ln(c_{avg}(y))$ vs. $y^{6/5}$, based on the averaged Suzuoka solution. 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, as noted by the subscripts. $D_{vol} = 0.396, 2.004, 8.683, \text{and} 32.911 \text{ nm}^2/\text{sec}$, respectively; $D_{gb} = 5.937 \times 10^4, 1.624 \times 10^5, 4.033 \times 10^5, \text{and} 9.221 \times 10^5 \text{ nm}^2/\text{sec}$, respectively.
Theoretical prediction of tracer diffusivity

Molecular dynamics (regular, basin constrained, etc.) (EAM potentials)

Determination of saddle point and attempt frequencies:
- Harmonic Transition State Theory
- + Nudged Elastic Band method
- or First Principles (ab initio) methods.

Diffusion mechanisms

Jump rates catalogue

Kinetic Monte Carlo (KMC).

Jump rates catalogue

Long time limit (supercomputer)

Tracer diffusion coefficients.
Diffusion data: Theoretical

In solid-state diffusion, the movement of atoms normally takes place by discrete jumps or hops (the ‘hopping model’).

Diffusion coefficients such as the tracer diffusion coefficient are then partitioned as:

\[ D_j^* = f_j \left( Z c_v w_j a^2 \right) \]

The correlated part expresses the correlations or memories between the directions of successive jumps of a given atom. These correlations result from the continued proximity of a defect to a particular atom and from differences in atom-defect exchange frequencies e.g. on different sublattices.

Sometimes the correlated part can be ignored \((as\ in\ the\ Darken\ assumption)\). Other times, it changes the tracer diffusion coefficient by many orders of magnitude and cannot be ignored!!

First principles calculations can provide the uncorrelated part.

Kinetic Monte Carlo calculations can provide the correlated part.
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)

\[ D_{eff} (Hart) = \frac{gb + (1 - f)D}{D_{gb}D} \]

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

\[ D_{eff} (Maxwell) = \frac{D_{gb}[(3 - 2f)D + 2fD_{gb}]}{fD + (3 - f)D_{gb}} \]
Effective Diffusion: Multiscale Monte Carlo model

3-D polycrystalline grain structure and mean-square displacement (MSD) of random walkers with time (MCS).

- Effective diffusivity increases with decreasing grain size
- Effective diffusivity increases with temperature at a given grain size
Data Infrastructure

• What kind of information should be included while providing diffusion data?
• How should it be stored initially, i.e., data format?
• Can this initial format be easily modified? Queried?
• How should data be disseminated?
• Will it be available to all or only to an exclusive club?
• Data protection, copyright, etc.

Several workshops on MGI

– Others: Brown university, Engineering Conferences International (ECI), MST societies, etc.
Data Infrastructure (contd.)

• Suggestions (from NIST MGI & Diffusion workshop)

  • Elements present
  • Type of diffusivity & other relevant information (e.g., bulk diffusivity, bulk moduli)
  • Experimental or computational method
  • Type of measurement (direct or indirect)
  • Number of phases present

  For each phase present:
  • Phase name, phase composition, phase fraction and errors
  • Crystal structure or amorphous
  • Lattice parameters
  • Temperature/Pressure & errors, standards

  Metadata
  • Type of material, processing history
  • Bulk composition, material impurities
  • Sample preparation
    – Microstructure information: Single crystal, polycrystalline (grain size, dislocation density, texture, etc.)
    – Non-crystalline
  • Data manipulation/analysis details
  • Reporting format (raw data, digitized data, other)
  • References (DOI or text; one must be present)
  • Additional information
ORNL diffusion website: Mg-ICME

Grain Boundary Diffusion

Objective:
The objective of this project is to use the SIMS-based, stable isotope tracer technique to determine grain boundary diffusion coefficients (D_gb) of Al, Zn, and Mg in pure Mg and various Mg-rich alloys composed of these elements.

Background:
Grain boundary (GB) diffusion has important roles in grain growth, creep, and deformation behavior, and is the dominant diffusion process in fine-grained materials. A quantitative description of GB diffusion is also likely to be an integral part of the diffusion equation that is required for accurate computational modeling of evolving microstructures. Traditional GB diffusion experiments are carried out using bicrystals and narrow gap test specimens, which are very expensive, time consuming, and only provide data for a single, specific grain boundary orientation. The SIMS-based, thin film approach is much more representative of GB diffusion in polycrystalline materials. The main drawback to this method is that the probe size (typically 200 μm) is far larger than the grain boundary region (~0.5 μm), meaning that a single SIMS measurement must sample over multiple grain boundaries in order to obtain an appreciable signal. This type of diffusion study needs to be carried out using extremely fine-grained materials, in order to ensure a relatively large surface fraction of grain boundaries, and thus a substantial SIMS signal of the tracer diffusion. It is difficult to obtain and maintain these necessary small grain sizes using bulk samples, because of the possibility of GB diffusion-activated grain growth during the diffusion anneal. Thin film provide the ideal geometry for this condition mainly because small grain sizes can be maintained over the course of diffusion experiments, since grain growth and boundary migration are controlled by the film thickness. As a general rule, average grain sizes in thin films are roughly equal to the film thickness.

Approach:
We will use both a top-down experiment with an analysis based on Gilmer and Farrell’s solutions, as well as a lateral diffusion experiment with the typical SIMS analysis. Both these methods are approaches to overcome the problem that the diffusion would quickly penetrate the entire thickness of the film through the grain boundary under appropriate GB diffusion conditions. The Gilmer-Farrell solution accounts for buildup of diffusion in the grain boundary region due to a reflecting boundary condition at the top of the film, whereas the lateral method provides the same, unobstructed diffusion length that the ‘semi-infinite’ solutions (Somorjai) can be applied. We will be inverting for the grain boundary diffusion experiment under conditions consistent with Harrison’s B-Simons regime, as this will provide an appreciable diffusion signal for SIMS measurements, and can be accomplished with reasonable Mg thin film thicknesses. We will begin with Al diffusion studies into pure Mg films, sputtered on thermally oxidized Si substrates (~500 μm SiO2). The thermal oxide is intended to act as a diffusion barrier to satisfy the reflecting boundary condition for the Gilmer-Farrell analysis, and eliminate surface-interface diffusion effects with the lateral diffusion experiments. Once we have confirmed the proper methodology to extract D_gb from the experiment, similar involving 75Mg as a tracer into ~2.5 μm pure Mg films. This is necessary due to the ~10% background signal of 26Al in commercially pure Mg. By increasing the 26Mg level in the film from ~6% to ~99.9%, the SIMS signal of the 25Mg diffusion increases by a factor of 200, allowing detectable concentrations in the grain boundary region. In the future, further studies involving Al, Mg, and Zn diffusion into co-sputtered Mg-rich alloy films may be completed.

Because of limitations with conventional SIMS probe sizes, in order to probe individual grain boundary diffusivities, OAKR is exploring the use of the Atom Probes that provides the concentration-depth profiles of isotopes along and adjacent to individual grain boundaries. The advantage of this technique is that the specific grain boundary properties (~1 degree of freedom that defines the grain boundary) are simultaneously obtained along with the SIMS isotopic profiles. Thus this technique provides an unparalleled level of grain boundary diffusion information that is yet to be explored. Research on the use of Atom Probes for such studies is being considered at the present time. In addition, OAKR is interested in acquiring a NanosIMS instrument which provides probe diameters of ~100 nm. This would enable measurements of the averaged isotopic concentration profiles in the grain boundary and grains adjacent to an individual grain boundary as opposed to the also:

- Atom Probes technical memo.pdf

Further Details & Progress:

- 20120091 Irvine's formula solution with full accounting integral close.
- 20120090 Smallest power (pdf / pdf)
- 20120093 GB: Solutions Grain HGUP Mg (pdf / Adobe) & Al Impurity (pdf / Adobe)
- 20120092 GB Solutions Mathcad (pdf / Adobe)
- 20120095 GB Solution including Wall Diff.
- 20120096 Proposed methods for GB studies using thin films (pdf / pdf) - Ethan Ambrosek (see also June 2012 report)
- 20120097 Thin Film GB Diffusion Project (pdf / pdf) - Ethan Ambrosek

ORNL Diffusion website (contd.)

Section on Grain Boundary Diffusion (summer project by Univ. of Wisconsin student)

- Provides some details of objectives, background, procedures, and progress
- Includes relevant literature references, and theoretical contributions by team
- Will include raw data, processed data, and results
- Updated as and when data is gathered and analyzed (sometimes daily)
Final Remarks

• Construction of the Diffusion Genome is a good test-case for other physical properties needed for the MGI.

• Use of the rigorous Onsager formalism for multicomponent diffusion leads to the choice of the tracer diffusion coefficient as the appropriate kinetic parameter for database development.

• Complexity of diffusion information (bulk, orientation dependence, grain boundary diffusion, etc.) can be best analyzed with tracer measurements supplemented with theoretical (first principles/KMC) computations.

• Significant theoretical challenges remain for developing rigorous relations between the tracer diffusivities and the Lij’s in multicomponent systems.

• Further development of theory for composition dependence of diffusivities is still needed (e.g., intermetallic compounds, solute diffusion).

• Development of a universal data entry format would be very helpful for MGI; however, providing raw data along with sufficient details (metadata) can still proceed in the interim.

• Implementation of MGI will require a long-term commitment by program offices within the federal agencies. Need to develop tracer diffusion capabilities!
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End
SIMS Measurements capture anisotropy in Mg self-diffusion

- Large green grain has 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)

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

Extruded rod annealed at 545°C for 14.5 hrs
Tracer Diffusion Benefits - contd.

Grain boundary diffusion using films: Harrison B (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
Tracer Diffusion Benefits - contd.

Data for stoichiometric compounds

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


May be easier to prepare “thin-film” compounds to measure tracer diffusivities

Magnetron Co-sputtering System