

Topic 4: how do point defects diffuse?

Overview

Mass transport in solids, where different chemical species diffuse in a material due to random motion with or without a driving force, is a fundamental kinetic process for a wide variety of materials problems: growth of precipitates in nearly every advanced structural alloy from steels to superalloys, sintering of powders to make advanced ceramics, degradation of materials from irradiation, creep, recrystallization, corrosion, charge/discharge cycles in batteries, electromigration, and more. Fundamentally, all of the atomic-scale processes involved in mass transport require *defects*: interstitials for “small” impurity atoms, or vacancies and interstitials for substitutional solutes. The atomic-scale mechanisms can be very simple (site-to-site hopping for interstitial atoms) to increasingly complex mechanisms (vacancy-mediated to interstitialcy-mediated), and can be influenced by defect concentrations, temperature, strain, doping (!), and the presence of additional defects. The complexity of transport makes both experiments and modeling difficult, but the centrality to materials science and engineering provides a continuing driving force for its study. An entire course could be dedicated to this topic; here, we will consider a few of the defect specific aspects of diffusion applied to a relatively recent discovery: the “nano” Kirkendall effect.

Reading

For this topic, you will want to read the original discovery of the Kirkendall effect (a seminal result in diffusion, which took a long time to be accepted! See this history lesson), and a recent review paper covering some of the aspect of the application of the Kirkendall effect to the processing of nanoparticles. For the application part, you will also want to review results about diffusivity in semiconductors.

- A. D. Smigelskas and E. O. Kirkendall, “Zinc Diffusion in Alpha Brass,” *Trans. AIME* **171**, 130-142 (1947). Available on Google Drive.
- Z. Yang, N. Yang, and M.-P. Pileni, “Nano Kirkendall Effect Related to Nanocrystallinity of Metal Nanocrystals: Influence of the Outward and Inward Atomic Diffusion on the Final Nanoparticle Structure.” *J. Phys. Chem. C* **119**, 22249-22260 (2015): doi:10.1021/acs.jpcc.5b06000
- Yoonkook Son, Yeonguk Son, Min Choi, Minseong Ko, Sujong Chae, Noejung Park, and Jaephil Cho, “Hollow Silicon Nanostructures via the Kirkendall Effect.” *Nano Lett.* **15**, 6914-6918 (2015): doi:10.1021/acs.nanolett.5b02842
- T. Y. Tan, U. Gösele, “Diffusion in Semiconductors” in *Diffusion in Condensed Matter: Methods, Materials, Models*. (Springer, 2005). Chapter 4: doi:10.1007/3-540-30970-5_4

Team assignment

The development of hollow binary alloys nanoparticles—either ordered intermetallics or compound semiconductors—is complicated by the multiple components involved. After reviewing the literature on using the Kirkendall effect to design hollow nanoparticles, identify a possible new compound semiconductor or intermetallic to target for nanoparticle development.

1. Putting aside the issues of how you could *synthesize* your particular alloy, select a compound

semiconductor or ordered intermetallic and propose a possible approach to create a hollow nanoparticle.

2. Does your selection require a solid solution before heating, or a core-shell design?
3. Any other considerations for processing that you think could help your design?

Prelecture questions

1. Diffusion mechanisms for solutes are sometimes inferred from the experimental activation barrier Q for diffusion, where $D = D_0 \exp(-Q/k_B T)$. Briefly explain how you might decide what type of diffusion mechanism a species had, based on the diffusion barrier.
2. Is it possible to get the Kirkendall effect if solutes diffuse via a different mechanism rather than vacancy-mediated diffusion? Justify your answer.
3. If a solute B in matrix A can occupy both substitutional sites B_A and interstitial sites B_i , then more complicated diffusion profiles are possible. Assume that the interstitial species is mobile, while the substitution is not. Consider the Frank-Turnbull mechanism, where an interstitial solute and a vacancy can combine to make a substitutional solute (and vice versa); if this reaction is in local equilibrium, vacancies are able to maintain global equilibrium, and B_i is a slower moving species than the vacancies, write the diffusivity of solute B in terms of defect concentrations and transport coefficients. Be sure to specify whether your concentrations are the local concentrations, or the thermodynamic equilibrium concentrations.

Suggested background

These may help you think about the papers and questions raised; you may want to look beyond these, too.

- Course webnotes:
 - 3.2.1 Atomistic mechanisms
 - 3.2.2 Self-diffusion
 - 3.2.3 Impurity diffusion
- Prof. Helmut Mehrer, “Diffusion: Introduction and Case Studies in Metals and Binary Alloys” (sections 1.1-1.3, 1.5-1.8) from *Diffusion in Condensed Matter: Methods, Materials, Models*. (Springer, 2005). Chapter 1: doi:10.1007/3-540-30970-5_1
- Prof. Manfred Martin, “Diffusion in Oxides” (sections 5.3) from *Diffusion in Condensed Matter: Methods, Materials, Models*. (Springer, 2005). Chapter 5: doi:10.1007/3-540-30970-5_5
- Slides (on Google Drive):
 - Diffusion

Note: If you are interested in more of the theory of mass transport, you should read Allnatt and Lidiard, *Atomic Transport in Solids*. (Cambridge Univ. Press, 1993) doi:10.1017/CBO9780511563904. This is *the* background reference for the theory of diffusion in solids. It has the two different (equivalent and related) approaches to understanding diffusion and goes from atomic-scale mechanisms to macroscale diffusion.

Discussion: Oct. 1-3, 2024