Modeling Solutions for Grain Boundary Diffusion

Whipple's solution is a solution to coupled differential equations and boundary conditions describing grain boundary diffusion. The solution provides concentration as a function of position (x,y) in the geometric condition where the grain boundary is modeled as a slab of width 2a centered at x=0. The solution has the condition that at y=0, $c=c_0$ at all times, i.e. it is a constant source solution. It accounts for diffusion from the surface directly into bulk from the surface, as well as fast diffusion along the grain boundary, where it then diffuses out of the grain boundary slab into the volume, laterally. The solution assumes the source is diffusing into a semi-infinite grain bounday/material. **[RTP Whipple, Philosophical Magazine, 45 (1954); 1225.]**

The solution is a function of several dimensionless variables, which themselves are a function of x,y,t, and several diffusion coefficients, which are functions of activation energy, the material's melting temperature and the diffusion anneal temperature. It is easiest to obtain contour plots of concentration if the final solution is of the form $c_g(x,y)$, which is best accomplished by defining several values as constants at the beginning of the worksheet. T_m, D_0, and Q_0 are material constants, and can be adjusted based on the system being modeled. T_0 and t are the diffusion time and temperature, and should be adjusted based on the expected diffusion anneal time/temperature for which the solution is being modeled. In this particular worksheet I am modeling magnesium self diffusion at diffusion temperature 250 °C for various times.

Input Constants

Melting temp in °C $\quad T_m := 650$

Diffusion temp in °C $\quad T_0 := 250$

Diffusion time in sec $\quad t := 60 \cdot 5$

Volume Diffusion: Pre-Exponential and Activation Energy in nm^2/sec and J/K-mol

$D_0 := 4.2 \cdot 10^{13} \qquad Q_0 := 127000$

As determined by Arrhenius fit to Shewmon and current SIMS data, obtained from ORNL Diffusion Group internal website

Defining the volume coefficient is based on a typical Arrhenius equation, with a material-dependent activation energy and pre-exponential, as deinfed above. Temperature needs to be in K for this equation, hence T_0+273. The grain boundary diffusion coefficient has similar relationships, yet the pre-exponent and activation energies are not accurately known. Thus, an equation provided by Gjostein (assuming 0.5 nm grain boundary slab width) was used to estimate D_{gg}. The grain boundary half width is also defined here for use in later calculations.

Defining Diffusion Coefficients

In nm^2/sec

$$D_{vol} := D_0 \cdot \exp\left[\frac{-Q_0}{8.314 \cdot (273 + T_0)}\right]$$

$$D_{gb} := 3 \cdot 10^{13} \cdot \exp\left[-8.96 \cdot \frac{(273 + T_m)}{(273 + T_0)}\right]$$

[NA Gjostein, in *Diffusion*, American Society of Metals, Metals Park, OH (1973), 241.]

$a := 0.25$ grain boundary half width (nm)

It is most convenient to model grain boundary diffusion equations as functions of a set of dimensionless variables, originally proposed by Whipple in 1954 (see reference above). These definitions have been used to describe grain boundary diffusion ever since. In this model, the grain boundary diffusion is modeled at a constant z (can be imagined as a cross-section). The grain boundary is infinite in the y direction, which is also primary diffusion direction.

Defining Dimensionless Variables

$$\Delta := \frac{D_{gb}}{D_{vol}}$$ ratio of grain boundary to volume diffusion coefficient

$$\eta(y) := \frac{|y|}{\sqrt{D_{vol} \cdot t}}$$ diffusion depth, normalized by sqrt(Dt)

$$\xi(x) := \frac{(|x| - a)}{\sqrt{D_{vol} \cdot t}}$$ lateral diffusion distance (out of grain boundary into volume), normalized by sqrt(Dt)

$$\beta := \frac{(\Delta - 1) \cdot a}{\sqrt{D_{vol} \cdot t}}$$ essentially Δ, which is described above, normalized by sqrt(Dt). grain bounday width term also present

The Whipple solution for concentration as a function of position - $c_g(x,y)$ - defined assuming c_0 = 1. For c_0 other than one, the corresponding contour plot can be interpreted as contours of constant c_g/c_0 as opposed to constant c_g. Some example calculations are listed to the right, to ensure the function works properly.

$$c_w(x,y) := \operatorname{erfc}\left(\frac{\eta(y)}{2}\right) + \frac{\eta(y)}{2 \cdot \sqrt{\pi}} \cdot \int_1^{\Delta} \frac{\exp\left[\frac{-(\eta(y))^2}{4\sigma}\right]}{\sigma^{\frac{3}{2}}} \cdot \operatorname{erfc}\left[\left[\frac{1}{2} \cdot \left(\frac{\Delta - 1}{\Delta - \sigma}\right)^{\frac{1}{2}}\right] \cdot \left[(\xi(x)) + \frac{\sigma - 1}{\beta}\right]\right] d\sigma$$

Example Calculations

$c_w(10,10) = 0.985$

$c_w(10,100) = 0.88$

$c_w(10,500) = 0.749$

$c_w(10,1000) = 0.625$

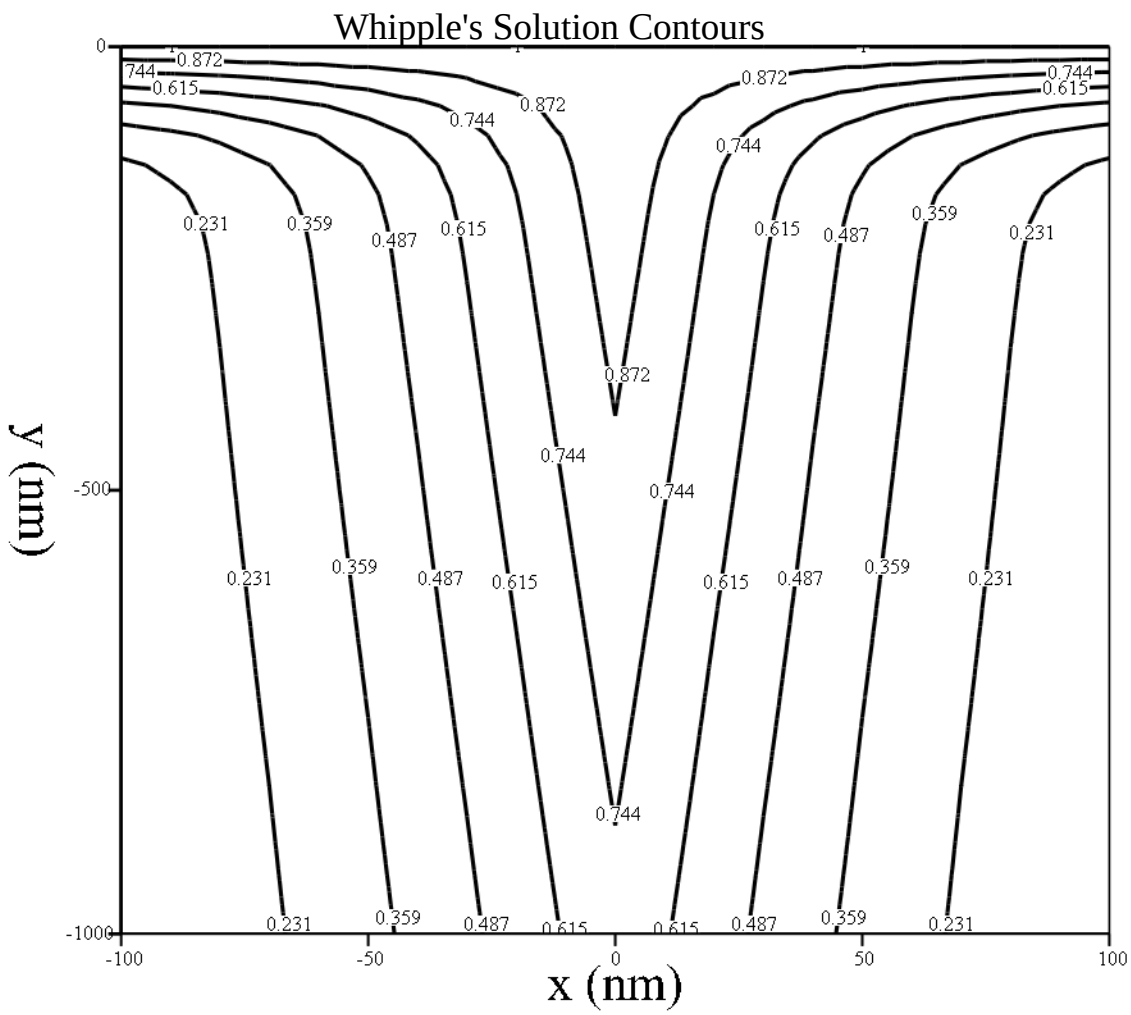
$c_w(10,2000) = 0.431$

$c_w(20,2000) = 0.368$

$c_w(100,2000) = 0.062$

Contours of constant concentration - $c_g(x,y)=C$ - Constant souce of diffusant at concentration $c_0=1$ at y=0 for t>0. Diffusion "into" the volume or grain boundary from the source occurs in the +y direction, and diffusion out of the grain boundary into the volume occurs in the +x direction. (would also occur in the -x direction, if it were plotted). The integral in Whipple's solution does not converge for all values of x and y at a particular time and temperature, so the contour plot is slightly limited in what portion of the volume it can show.

The constant source is at y=0 and the grain boundary is centered at x=0



c_w

Suzuoka's solution is solved the exact same way as Whipple's, but is based on the boundary conditions of an instantaneous source. The solution is of the same form as Whipple's, using the same dimensionless variables as defined above for the Whipple solution. The Suzuoka solution can be obtained by a simple transformation of Whipple's solution through the operator $-(Dt)^{1/2}(\delta/\delta\eta)$ and replacing the value c_0 with M, M being the total amount of diffusant available through the instantaneous source (i.e. product of $c_0 * t_{source}$)

This solution is conventionally broken down into c_1 and c_2 where c_1 accounts for direct volume diffusion from the source, and c_2 accounts for diffusion from the grain boundary into the volume.

Defining M

tracer thickness (in nm) $\quad t_M := 20$

tracer concentration (in atoms/nm^3) $\quad c_M := \dfrac{1.738 \cdot 6.02 \cdot 10^2}{24.305}$ $\quad$ for pure element (Mg) film as tracer: ρN_A/(molar mass)

M - amount of tracer per area (atoms/nm^2) $\quad M := t_M \cdot c_M$

Suzuoka's Solution

$$c_1(y) := \frac{M \cdot \exp\left[\dfrac{-\left(\eta(y)^2\right)}{4}\right]}{\sqrt{\pi \cdot D_{vol} \cdot t}}$$

$$c_2(x,y) := \frac{M}{\sqrt{\pi D_{vol} \cdot t}} \cdot \int_1^{\Delta} \left(\frac{\eta(y)^2}{4 \cdot \sigma} - \frac{1}{2}\right) \cdot \frac{\exp\left[\dfrac{-\left(\eta(y)^2\right)}{4 \cdot \sigma}\right]}{\sigma^{\frac{3}{2}}} \cdot \mathrm{erfc}\left[\frac{1}{2} \cdot \left(\frac{\Delta - 1}{\Delta - \sigma}\right)^{\frac{1}{2}} \cdot \left(\xi(x) + \frac{\sigma - 1}{\beta}\right)\right] d\sigma$$

$$c_s(x,y) := c_1(y) + c_2(x,y)$$

Example Calculations

$c_s(10, 500) = 0.23$

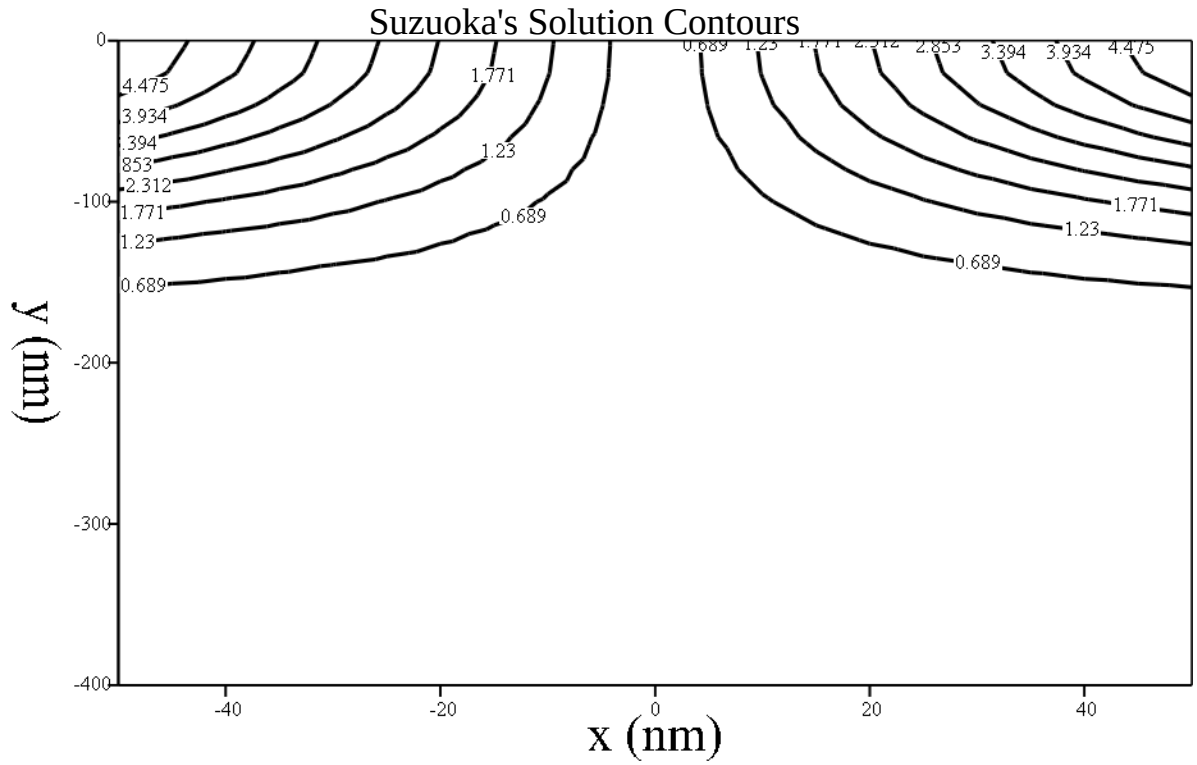
$c_s(10, 100) = 0.651$

$c_s(1, 20) = 0.357$

$c_s(10, 20) = 1.247$

$c_s(1, 2) = 0.36$

Contour plot of Suzuoka's solution, showing contours of constant concentration. Absolute concentration (in atoms/nm^3) are the values shown. The source is at y=0, and there is a grain boundary of width 0.5 nm centered at x=0. The diffusion occurs from the souce into the volume and into the grain boundary in the -y direction, and diffusion occurs from the grain boundary into the volume in both the +x and -x directions.



$\underline{c_S}$

It is most practical to obtain curves based on a solution for the average concentration as a function of depth, that is, $c_{avg}(y)$. To obtain this, the Suzuoka solution is integrated over x and divided by the area it was integrated over. Essentially the standard method to determine the average value of a function.