Chapter 5

Diffusion
Why Study Diffusion?

- Materials of all types are often heat-treated to improve their properties.
- A heat treatment almost always involve atomic diffusion.
- Often an enhancement of diffusion rate is desired.
- Using mathematics of diffusion and appropriate diffusion constants, we can predict:
  1. Heat-treating temperatures
  2. Times
  3. Cooling rates

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Why Study Diffusion?

- Diffusional processes are often utilized to introduce impurity atoms into silicon semiconductors.

  ✓ Knowledge of time & temperature dependences of appropriate diffusion parameters is necessary.

- Heat treatment of steels involves diffusion.

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5.1 Introduction

- **Diffusion**: phenomenon of material transport by atomic motion.

- **Topics to be discussed**:
  1. atomic mechanisms by which diffusion occurs
  2. mathematics of diffusion
  3. influence of temperature and diffusing species on rate of diffusion
5.1 Introduction

- **Diffusion couple**: joining bars of two different metals together so that there is intimate contact between the two faces;

- **Figure 5.1**: Cu–Ni diffusion couple before a high-temperature heat treatment.
5.1 Introduction

- This couple is heated for an extended period at an elevated temperature and cooled to RT.

- Figure 5.2:
  - Pure Cu and Ni at the two extremities of the couple
  - separated by an alloyed region.
  - Concentrations of both metals vary with position
5.2 Diffusion Mechanisms

- **Diffusion**: stepwise migration of atoms from lattice site to another.
- Atoms in solid materials are in constant motion, rapidly changing positions.
5.2 Diffusion Mechanisms

For an atom to make such a move, two conditions must be met:

1. An empty adjacent site
2. Atom must have sufficient energy to break bonds with its neighbor and then cause some lattice distortion during the displacement.
5.2 Diffusion Mechanisms

- At a specific temperature some small fraction of total number of atoms is capable of diffusive motion, by virtue of magnitudes of their vibrational energies.
- This fraction increases with rising temperature.
5.2 Diffusion Mechanisms

Vacancy Diffusion

- **Vacancy diffusion**: interchange of an atom from a normal lattice position to an adjacent vacant lattice site or vacancy, Figure 5.3a.
5.2 Diffusion Mechanisms
Vacancy Diffusion

- Extent to which vacancy diffusion can occur is a function of number of these defects
- Diffusion of atoms in one direction opposes motion of vacancies
5.2 DIFFUSION MECHANISMS

Interstitial Diffusion

Figure 5.3b: atoms that migrate from an interstitial position to a neighboring empty one.
5.2 DIFFUSION MECHANISMS

Interstitial Diffusion

In most metal alloys, interstitial diffusion occurs much more rapidly than diffusion by vacancy mode, because:

- Interstitial atoms are smaller and thus more mobile
- More empty interstitial positions than vacancies

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5.3 Steady-State Diffusion

- When an atom moves into a vacancy,
  - a new hole is opened. In turn, this may receive an atom from any of the neighboring sites.
  - As a result, a vacancy makes a random walk through a crystal.
- Same random walk mechanism may be described for a C atom moving among Fe atoms from interstice to interstice.
- Diffusion is a time dependent process
5.3 Steady-State Diffusion

Example: assume there is a C atom per 20 unit cells of FCC Fe at point (1), and only 1 C atom per 30 unit cells at point (2), which is one mm away.

✓ Since there are random movements of C atoms at each point, we will find a net flux of C atoms from (1) to (2).

This net flow of atoms is called diffusion.
5.3 Steady-State Diffusion

- Flux $J$ of atoms (atoms/m$^2$.s) is proportional to concentration gradient, (Fick’s 1$^{\text{st}}$ law)

$$J = -D \frac{dC}{dx}$$

- $D$ = diffusion coefficient (m$^2$/s), vary with:
  1. nature of solute atoms
  2. nature of solid structure
  3. change in temp

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5.3 Steady-State Diffusion

Note the following:

- Higher temp provide higher D, because atoms have higher thermal energies and therefore greater probability of being activated over the energy barrier between atoms.

- C has a higher D in Fe than does Ni in Fe because C atom is a small one.

- Cu diffuses more readily in Al than in Cu because Cu-Cu bonds are stronger than Al-Al bonds.
5.3 Steady-State Diffusion

Note the following:

- Atoms have higher D in BCC Fe than in FCC Fe because former has a lower atomic PF.
- FCC structure has larger interstitial holes, however, passageways between holes are smaller than in BCC structure.
- Diffusion proceeds more rapidly along grain boundaries.

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5.3 Steady-State Diffusion

Example Problem 5.1

Diffusion Flux Computation

A plate of iron is exposed to a carburizing (carbon-rich) atmosphere on one side and a decarburizing (carbon-deficient) atmosphere on the other side at 700 °C. If a condition of steady state is achieved, calculate the diffusion flux of carbon through the plate if the concentrations of carbon at positions of 5 and 10 mm beneath the carburizing surface are 1.2 and 0.8 kg/m³, respectively. Assume a diffusion coefficient of $3 \times 10^{-11}$ m²/s at this temperature.
5.4 Non-Steady-State Diffusion

- Diffusion flux and concentration gradient at some particular point in a solid vary with time (F5.5)
- Fick’s 2\textsuperscript{nd} Law:

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]

**Figure 5.5:** Concentration profiles for non-steady-state diffusion taken at three different times, \(t_1\), \(t_2\), and \(t_3\).
5.4 Non-Steady-State Diffusion

Boundary & Initial conditions (Figure 5.6):
1. For $t = 0$, $C = C_o \ @ 0 \leq x \leq \infty$
2. For $t > 0$, $C = C_s$ (constant surface concentration) \ @ \ x = 0, \ C = C_o \ \text{at} \ x = \infty$

Figure 5.6 Concentration profile for nonsteady-state diffusion; concentration parameters relate to Equation 5.5.

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5.4 Non-Steady-State Diffusion

\[ \frac{C_x - C_o}{C_s - C_o} = 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \]
Example Problem 5.2
Non-steady-State Diffusion Time Computation

For some applications, it is necessary to harden the surface of a steel above that of its interior. One way this may be accomplished is by increasing the surface concentration of carbon in a process termed carburizing; steel piece is exposed, at an elevated temperature, to an atmosphere rich in a hydrocarbon gas, such as methane (CH₄).

Consider one such alloy that initially has a uniform carbon concentration of 0.25 wt% and is to be treated at 950°C. If the concentration of carbon at the surface is suddenly brought to and maintained at 1.20 wt%, how long will it take to achieve a carbon content of 0.80 wt% at a position 0.5 mm below the surface? The diffusion coefficient for carbon in iron at this temperature is 1.6 × 10⁻¹¹ m²/s; assume that the steel piece is semi-infinite.
Example Problem 5.3
Non-Steady-State Diffusion Time Computation II

The diffusion coefficients for copper in aluminum at 500 and 600°C are $4.8 \times 10^{-14}$ & $5.3 \times 10^{-13}$ m$^2$/s, respectively. Determine the approximate time at 500°C that will produce the same diffusion result (in terms of concentration of Cu at some specific point in Al) as a 10-h heat treatment at 600°C.
5.5 Factors Influencing Diffusion

**Diffusing Species**

Magnitude of diffusion coefficient $D$ is indicative of rate at which atoms diffuse

**Table 5.2 A Tabulation of Diffusion Data**

<table>
<thead>
<tr>
<th>Diffusing Species</th>
<th>Host Metal</th>
<th>$D_0$ (m²/s)</th>
<th>Activation Energy $Q_a$ (kJ/mol)</th>
<th>$Q_a$ (eV/atom)</th>
<th>Calculated Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>$\alpha$-Fe (BCC)</td>
<td>$2.8 \times 10^{-4}$</td>
<td>251</td>
<td>2.60</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>$\gamma$-Fe (FCC)</td>
<td>$5.0 \times 10^{-5}$</td>
<td>284</td>
<td>2.94</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>$\alpha$-Fe</td>
<td>$6.2 \times 10^{-7}$</td>
<td>80</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>$\gamma$-Fe</td>
<td>$2.3 \times 10^{-5}$</td>
<td>148</td>
<td>1.53</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>Cu</td>
<td>$7.8 \times 10^{-5}$</td>
<td>211</td>
<td>2.19</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>Cu</td>
<td>$2.4 \times 10^{-5}$</td>
<td>189</td>
<td>1.96</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>Al</td>
<td>$2.3 \times 10^{-4}$</td>
<td>144</td>
<td>1.49</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>Al</td>
<td>$6.5 \times 10^{-5}$</td>
<td>136</td>
<td>1.41</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>Al</td>
<td>$1.2 \times 10^{-4}$</td>
<td>131</td>
<td>1.35</td>
<td></td>
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<tr>
<td>Cu</td>
<td>Ni</td>
<td>$2.7 \times 10^{-5}$</td>
<td>256</td>
<td>2.65</td>
<td></td>
</tr>
</tbody>
</table>
5.5 Factors Influencing Diffusion

Diffusing Species

- The diffusing species as well as the host material influence the diffusion coefficient.

- **Example:** there is a significant difference in magnitude between self-diffusion and carbon inter-diffusion in iron at 500°C

  - $D$ value being greater for carbon inter-diffusion ($3.0 \times 10^{-21}$ vs. $2.4 \times 10^{-12}$ m$^2$/s).

- Self-diffusion occurs by a vacancy mechanism

- Carbon diffusion in iron is interstitial
5.5 Factors Influencing Diffusion

Diffusing Species

Temperature dependence of the diffusion coefficients is

\[ D = D_o e^{-Q/RT} \]

\[ \ln(D) = \ln(D_o) - \frac{Q}{RT} \]

\[ \log(D) = \log(D_o) - \frac{Q}{2.3R} \left( \frac{1}{T} \right) \]

- \(D_o\) = temp independent pre-exponential, m\(^2\)/s
- \(Q\) = activation energy for diffusion (J/mol, cal/mol, eV/atom)

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Example Problem 5.4
Diffusion Coefficient Determination

Using the data in Table 5.2, compute the diffusion coefficient for magnesium in aluminum at 550°C.
Example Problem 5.5
Diffusion Coefficient Activation Energy and Pre-exponential Calculations

In Figure 5.8 is shown a plot of the logarithm (base 10) of the diffusion coefficient vs. reciprocal of absolute temperature, for the diffusion of copper in gold. Determine values for the activation energy and the pre-exponential.

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Design Example 5.1
Diffusion Temperature–Time Heat Treatment Specification

The wear resistance of a steel gear is to be improved by hardening its surface. This is to be accomplished by increasing carbon content within an outer surface layer as a result of carbon diffusion into the steel; carbon is to be supplied from an external carbon-rich gaseous atmosphere at an elevated and constant temperature. The initial carbon content of steel is 0.20 wt%, whereas surface concentration is to be maintained at 1.00 wt%. For this treatment to be effective, a carbon content of 0.60 wt% must be established at a position 0.75 mm below the surface. Specify an appropriate heat treatment in terms of temperature and time for temperatures between 900 and 1050°C. Use data in Table 5.2 for the diffusion of carbon in iron.
Home Work Assignments

- 7, 10, 13, 17, 21, 27, 31, D1
- Due Sunday 20/10/2013
- Quiz on Tuesday 22/10/2013

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