

## **Lecture 6: Diffusion in binary substitutional materials (alloys):**

### **Kirkendall Effect and Darken's equation**

#### **Today's topics**

- Understand the basic concepts of vacancy, substitutional diffusion, Kirkendall effect and its implication in alloy practice.
- What is the major difference between interstitial diffusion and substitutional diffusion in terms of "diffusion coefficient".
- Understand Darken's equation and interdiffusion coefficient,  $\tilde{D}$ .

**Short history:** Although atomic diffusion in solids is far slower than that in gases and liquids, such diffusion does take place, and it is related to various processes such as recrystallization, precipitation, and oxidation (as we will learn throughout this course). The study of diffusion in solids was initiated just 100 years ago when Sir Roberts-Austen discovered the diffusion phenomenon of gold in solid lead in 1896.

#### **About vacancies:**

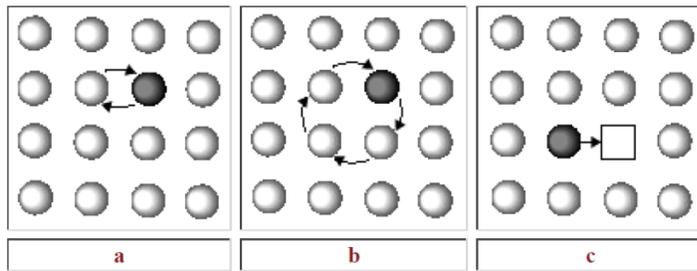
Vacancies are missing atoms in a crystal structure. For a perfect, pure crystal containing a mole of atoms ( $6.023 \times 10^{23}$ ), there is only one distinguishable way in which the atoms can be arranged. The introduction of a single vacancy enables a very large number of alternative arrangements, thus causing great increase in *configurational entropy* ( $\Delta S$ ). This thermodynamically favors the formation of a vacancy. However, on the other hand, vacancies are defects and the associated defect energy (enthalpy of formation,  $\Delta H$ ) opposes their formation, i.e.,  $\Delta G = \Delta H - T\Delta S$  must be  $< 0$ . A compromise is reached whereby there is an equilibrium concentration of vacancies. Thereby, *a perfect crystal is unachievable in all practical circumstances!*

The equilibrium concentration of vacancies is typically  $10^{-6}$ , i.e., one in a million of the sites is vacant, at a temperature close to melting. Pairs of vacancies, called divacancies, also exist but at even lower concentrations. In platinum, the concentration of divacancies has been shown to be about 10% that of monovacancies.

#### **Mechanisms of Substitutional Atom Diffusion:**

Atoms can in principle migrate by exchanging the position directly, with the correlated motion of two adjacent atoms (see Figure 1 below). But this would entail very large local distortions in the crystal (large positive free energy change). These distortions can be reduced by the ring diffusion mechanism as shown in Figure 1 below, although this has the disadvantage that many atoms have

to move in a correlated manner. The ring diffusion is common in liquids and amorphous solids which have more free space.

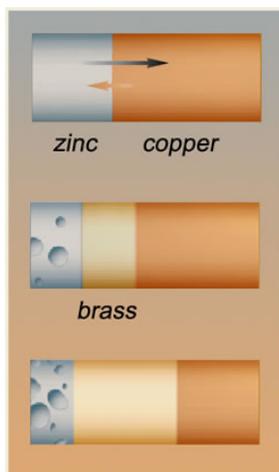


**Figure 1.** The atomic diffusion mechanism showing (a) a direct exchange mechanism, (b) ring mechanism, and (c) vacancy mechanism.

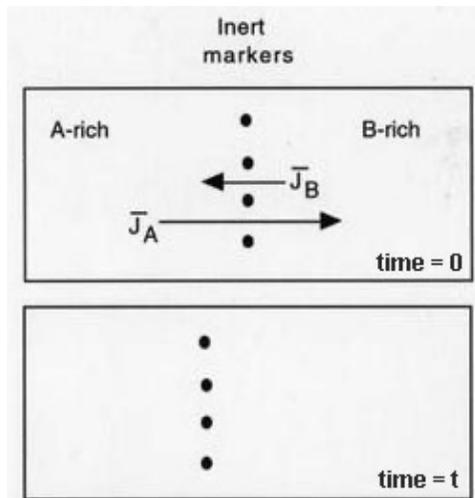
There are many other mechanisms for substitutional diffusion, but the most obvious one involves atoms jumping into vacancy sites (see Figure 1, case c). However, this was not accepted as a viable mechanism for a long time because the concentration of vacancies was intuitively perceived to be too small to give perceptible diffusion. The Kirkendall experiment (in 1942) proves the existence of vacancy diffusion in the vast majority of metallic materials. This is a remarkable example of an experiment which is ingenious, simple and conclusive (see below).

### **The Kirkendall effect**

Discovered in 1942, the *Kirkendall effect* describes what happens when two solids diffuse into each other at different rates. The boundary between two metals, zinc and copper for example, is formed by a growing layer of alloy -- brass, in this case -- which expands in the direction of the faster-moving species, zinc. The atoms of the two solids don't change places directly; rather diffusion occurs where voids open, making room for atoms to move in --- a vacancy diffusion.



For a general case, the Kirkendall experiment considers a diffusion couple as illustrated below, between A and B, where the diffusion rates of the two species are different ( $|J_A| > |J_B|$ ). Since the diffusion fluxes are different, there will be a net flow of matter past the inert markers, causing the couple to shift bodily with respect to the markers. *This can only happen if diffusion is by a vacancy mechanism. A direct exchange mechanism does not allow the fluxes to be different.*



The diffusion couple is created by welding together A and B, with inert markers placed at the weld junction. The markers are in the form of wires extending out of the diffusion couple and attached to the laboratory bench. The whole specimen therefore translates along the bench as diffusion proceeds because the flux of A is larger than that of B. Given that there is a net flow of matter, there will be an equal and opposite net flow of vacancies which condense to form pores, as discussed depicted earlier above for the zinc-copper diffusion.

**About Kirkendall:** The Kirkendall effect was named after Ernest Kirkendall (1914 - 2005). He discovered the effect in 1942. The *Kirkendall effect* has important practical consequences. One of these is the prevention or suppression of voids formed at the boundary interface in various kinds of alloy to metal bonding. Ernest Kirkendall was born in Michigan in 1914. He graduated from Wayne College (later Wayne University) in 1934, was awarded a master's degree in 1935 and a doctor of science in 1938 from the Metallurgy Department at the University of Michigan. He was an instructor at Wayne University from 1937 to 1941 and an assistant professor from 1941 to 1946, during which time he published two milestone papers

- E.O. Kirkendall, "Diffusion of Zinc in Alpha Brass," Trans. AIME, 147 (1942), pp. 104-110.
- A.D. Smigelskas and E.O. Kirkendall, "Zinc Diffusion in Alpha Brass," Trans. AIME, 171 (1947), pp. 130-142.

From 1947 to 1965, he served as secretary of AIME; he then became a manager at the United Engineering Trustees. He concluded his career as a vice president of the American Iron and Steel Institute from 1966 and 1979.

The above descriptions were referenced from:

- 1 *Prof. Harry Bhadeshia, phase transformation course website, Department of Materials Science & Metallurgy, University of Cambridge.*
- 2 *Hideo Nakajima, The Discovery and Acceptance of the Kirkendall Effect: The Result of a Short Research Career, (the journal) JOM, 49 (6) (1997), pp. 15-19.*

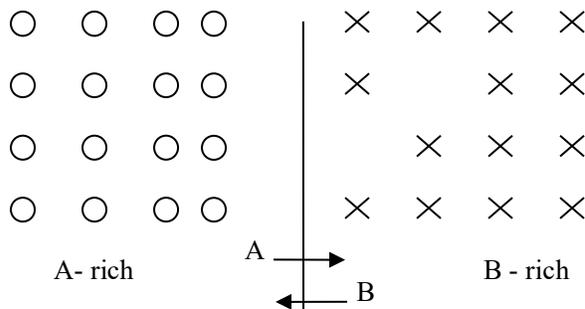
Now let's learn to understand the Kinetics of Kirkendall effect based on what we have already learned on the Fick's law and diffusion coefficient:

In general,  $D_A \neq D_B \Rightarrow D_A^C \neq D_B^C$ , and as learned from last Lecture,

$$D_A^C = D_A \left\{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right\} = D_A \left\{ 1 + \frac{d \ln \gamma_B}{d \ln x_B} \right\}$$

$$D_B^C = D_B \left\{ 1 + \frac{d \ln \gamma_B}{d \ln x_B} \right\} = D_B \left\{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right\}$$

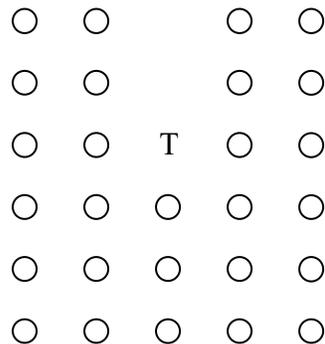
In a substitutional alloy, A & B move in the same lattice. Let's consider a diffusion couple as follows.



Let  $D_A > D_B$ , more A diffuses from left to right than B diffuses from right to left, therefore, vacancy must move from right to left.

**Grain boundary, crystalline defects (including dislocation) provide the source and sink for vacancies.** See the additional reading for more about these basic concepts and application in real-world materials science and engineering.

For example, an edge dislocation can be viewed as an extra partial atomic plane, atoms can be removed from or added to the end of the plane, creating or removing a vacancy.



Vacancy flux from right to left  $\rightarrow$  lattice plane move from left to right.

Vacancy is created on the left by removing atomic plane.

Vacancy is removed on the right by adding atomic plane.

$\Rightarrow$  Atomic plane move from left to right.

The flux of A has two contributions:

① diffusive flux relative to lattice,  $J_A = -D_A^C \frac{\partial c_A}{\partial x}$

② a flux due to moving of lattice plane  $v \cdot c_A$   
(where  $v$  is the lattice velocity, in unit of length/time)

Then,

$$J_A = -D_A^C \frac{\partial c_A}{\partial x} + c_A \cdot v$$

Similarly,  $J_B = -D_B^C \frac{\partial c_B}{\partial x} + c_B \cdot v$

Assume:  $c_A + c_B = \text{const.}$

In the zone far away from diffusion interface (region),  $J_A + J_B = 0$  ( $J_A = -J_B$ )

So,

$$-D_A^C \frac{\partial c_A}{\partial x} + c_A \cdot v - D_B^C \frac{\partial c_B}{\partial x} + c_B \cdot v = 0$$

Then,  $(c_A + c_B) v = D_A^C \frac{\partial c_A}{\partial x} + D_B^C \frac{\partial c_B}{\partial x}$

Since,  $\frac{\partial c_A}{\partial x} = - \frac{\partial c_B}{\partial x}$  ( $c_A + c_B = \text{const.}$ ), we have

$$(c_A + c_B) v = [D_A^C - D_B^C] \frac{\partial c_A}{\partial x} = [D_B^C - D_A^C] \frac{\partial c_B}{\partial x}$$

Then, we have Lattice velocity:

$$v = \frac{D_A^C - D_B^C}{c_A + c_B} \cdot \frac{\partial c_A}{\partial x} = \frac{D_B^C - D_A^C}{c_A + c_B} \cdot \frac{\partial c_B}{\partial x} \quad (1)$$

now, we have flux of A:

$$J_A = -D_A^C \frac{\partial c_A}{\partial x} + c_A \cdot v$$

$$\begin{aligned}
&= -D_A^C \frac{\partial c_A}{\partial x} + c_A \cdot \frac{D_A^C - D_B^C}{c_A + c_B} \cdot \frac{\partial c_A}{\partial x} \\
&= \frac{-D_A^C c_A - D_A^C c_B + c_A D_A^C - c_A D_B^C}{c_A + c_B} \cdot \frac{\partial c_A}{\partial x} \\
&= -[x_B D_A^C + x_A D_B^C] \cdot \frac{\partial c_A}{\partial x}
\end{aligned}$$

Similarly,

$$J_B = -[x_A D_B^C + x_B D_A^C] \cdot \frac{\partial c_B}{\partial x}$$

Let's introduce the interdiffusion coefficient,  $\tilde{D}$

$$\tilde{D} = x_A D_B^C + x_B D_A^C$$

Now, we have

$$J_A = -\tilde{D} \frac{\partial c_A}{\partial x}, \quad J_B = -\tilde{D} \frac{\partial c_B}{\partial x}$$

**From Lecture 5:**  $D_A^C = D_A \left\{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right\}$ ,  $D_B^C = D_B \left\{ 1 + \frac{d \ln \gamma_B}{d \ln x_B} \right\}$

and  $\left\{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right\} = \left\{ 1 + \frac{d \ln \gamma_B}{d \ln x_B} \right\} = \frac{x_A x_B}{RT} \frac{d^2 G}{dx_A^2} = \frac{x_A x_B}{RT} \frac{d^2 G}{dx_B^2}$

Then, we have

$$\begin{aligned}
\tilde{D} &= x_A D_B^C + x_B D_A^C \\
&= [x_A D_B + x_B D_A] \left\{ 1 + \frac{\partial \ln \gamma_A}{\partial \ln x_A} \right\} = [x_A D_B + x_B D_A] \left\{ 1 + \frac{d \ln \gamma_B}{d \ln x_B} \right\} \quad (2)
\end{aligned}$$

$$= [x_A D_B + x_B D_A] \frac{x_A x_B}{RT} \frac{d^2 G}{dx_A^2} = [x_A D_B + x_B D_A] \frac{x_A x_B}{RT} \frac{d^2 G}{dx_B^2} \quad (3)$$

This is referred to as **Darken's equation**.

With Darken's equation, the diffusion coefficient of A and B are correlated together, reflecting the 'cooperative' diffusion in substitutional alloys, for example as illustrated above in Kirkendall

experiment performed on the zinc-copper alloy diffusion. The interdiffusion coefficient  $\tilde{D}$  is determined by both the diffusion coefficient of A and B, whereas in the case of interstitial diffusion as discussed in the last a few lectures, the diffusion coefficient as used in the Fick's law is determined only by that of A or B.

Interstitial diffusion occurs in some solid crystals, like germanium and silicon, wherein the diamond cubic crystal structure possesses a lot of free space, and the atoms may be forced into interstitial positions during diffusion.