Additional reading for Lecture 7: experimental measurement of interdiffusion co-efficient

Comments:
• It is possible to measure the interdiffusion co-efficient by determining the variation of $X_A$ or $X_B$ after annealing a diffusion couple for a given time such as that depicted by real experimental data in the plot next slide.

• In cases where interdiffusion co-efficient can be assumed constant, the value of interdiffusion co-efficient can be deduced by solving the Fick’s second law for the interdiffusion case as we learned in Lecture 4 (See the very last part of the Lecture note, where unvarying interdiffusion co-efficient assumed).

• However, if interdiffusion co-efficient is not constant (i.e., changing with annealing time as indeed demonstrated in the example shown below), we should use graphical solutions of Fick’s second law to get the value of interdiffusion co-efficient --- that’s exactly what we learn from Lecture 7 --- the Matano method.
real data obtained from copper/zinc binary inter-diffusion upon annealing: Zinc concentration profiles after different times of anneals at 1,053 K.


The average of the diffusivity at 26% Zinc concentration at 1,053 K was $\tilde{D} \times 10^{-13}$ m$^2$/s. Inter-diffusion coefficient $\tilde{D}$ is composition dependent, i.e., varying with annealing time as evidenced here; $\tilde{D}$ increases gradually with $X_{Cu}$, simply because zinc has faster diffusion than copper, and $\tilde{D} = x_{Cu}D_{Zn}^c + x_{Zn}D_{Cu}^c$. 

Original interface between Cu and brass (40%Zn)

Copper (Cu)  Brass (initially at 40% Zn, 60% Cu)
The experiments shown in the last slide were carried out by Kirkendall, and first published in 1942: E.O. Kirkendall, "Diffusion of Zinc in Alpha Brass," *Trans. AIME*, 147 (1942), pp. 104-110. Following this observation, Kirkendall performed the famous “Kirkendall Effect” experiment and published that result in 1947: A.D. Smigelskas and E.O. Kirkendall, "Zinc Diffusion in Alpha Brass," *Trans. AIME*, 171 (1947), pp. 130-142.

From the data in the last slide, the average of the diffusivity ($\tilde{D}$) at 26% Zinc concentration at 1,053 K was $3.8 \times 10^{-13}$ m$^2$s$^{-1}$.

Diffusion coefficient is a function of composition fraction (composition dependent), which in turns varies with annealing time as evidenced here; $\tilde{D}$ increases gradually with $X_{\text{copper}}$, simply because zinc has faster diffusion than copper, and, $\tilde{D} = x_{\text{Cu}}D_{\text{Zn}} + x_{\text{Zn}}D_{\text{Cu}}$. 

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General practices:

- For a given crystal structure, **interdiffusion co-efficient** at the melting point is roughly constant. Therefore if adding B to A decreases the melting point, **interdiffusion co-efficient** will increase at a given temperature, vice versa.

- For a given solvent and temperature, both **interstitial** and **substitution diffusion** are more rapid in a **bcc** lattice than a **close-packed** lattice. For example, for the diffusion of carbon in iron at 910 degree C, the intrinsic diffusion coefficient in alpha-iron (with **bcc** lattice) is about 100 times larger than that in gamma-iron (with **fcc** lattice, close-packed). Similarly for the self-diffusion coefficient of iron atom in alpha-iron is about 100 times larger than that in gamma-iron. The reason for this huge difference lies in the fact that the **bcc** structure is more open and the diffusion process requires less lattice distortion (enthalpy or thermodynamically favored).

![Body centered cubic (bcc) lattice](image1.png) ![Face centered cubic (fcc) lattice](image2.png)