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.

E.O. Kirkendall, "Diffusion of Zinc in Alpha Brass," *Trans. AIME,* 147 (1942), pp. 104-110

Original interface between Cu and brass (40%Zn)

Copper (Cu)

Brass (initially at 40% Zn, 60% Cu)
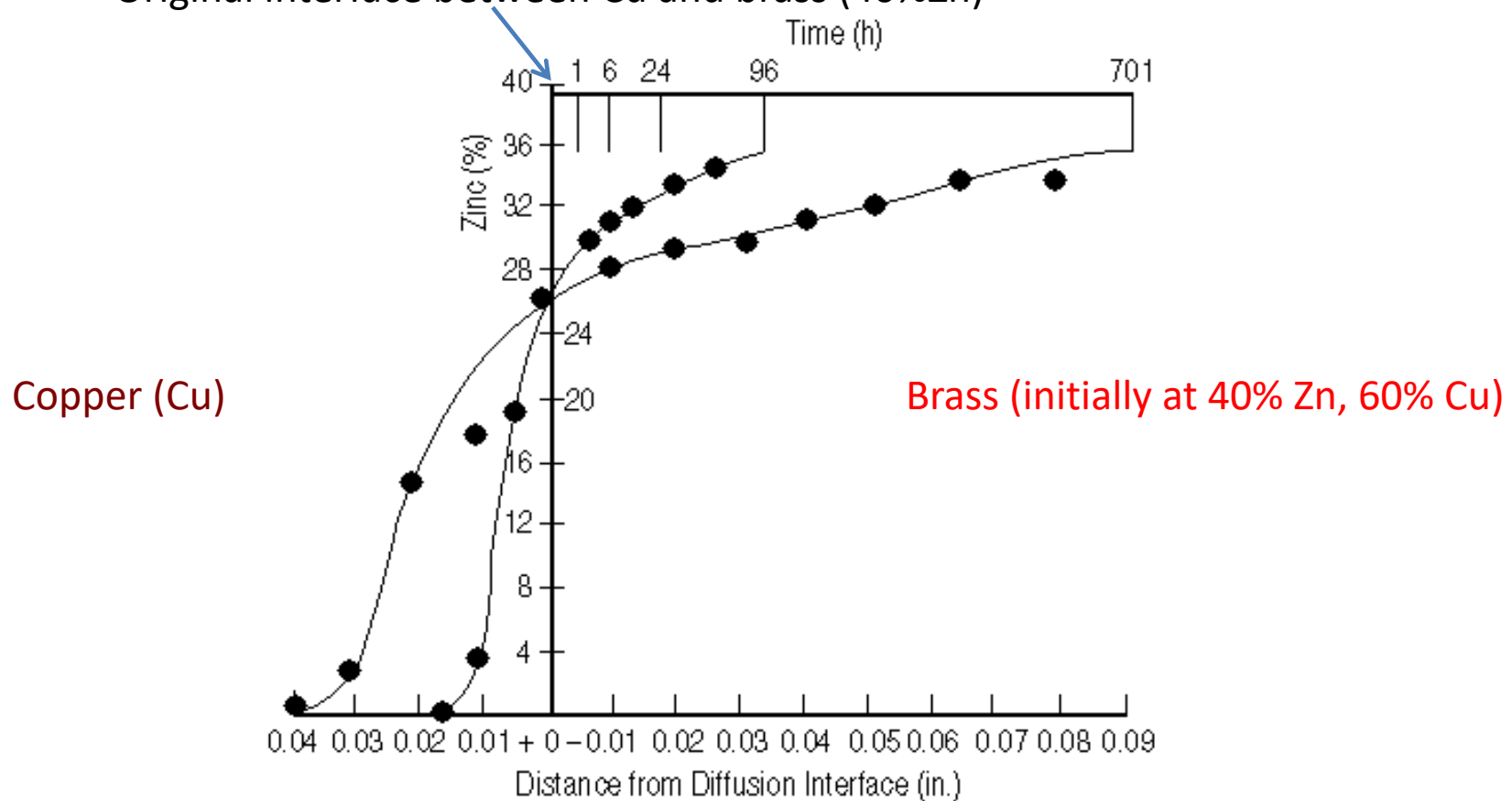
The average of the diffusivity at 26% Zinc concentration at 1,053 K was $\tilde{D}$ 3.8 X 10^{-13} m^2 s^{-1}. Inter-diffusion coefficient $\tilde{D}$ is composition dependent, i.e., varying with annealing time as evidenced here; $\tilde{D}$ increases gradually with X_{Cu}, simply because zinc has faster diffusion than copper, and, $\tilde{D} = x_{Cu} D_{Zn}^{c} + x_{Zn} D_{Cu}^{c}$.

The experiments shown in the last slide was 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.

Ernest Kirkendall

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 X 10^{-13} $m^2s^{-1.}$
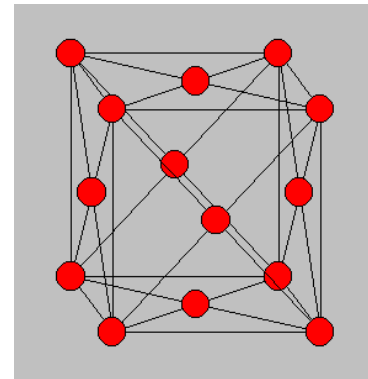
Diffusion coefficient is a function of composition fraction (composition dependent), which in turns varies with annealing time as evidenced here; $\tilde{D}$ increases gradually with **X**$_{copper}$, simply because zinc has faster diffusion than copper, and, $\tilde{D} = x_{Cu}D_{Zn}{}^{C} + x_{Zn}D_{Cu}{}^{C}$.

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 <u>interstitial</u> and <u>substitution diffusion</u> 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).
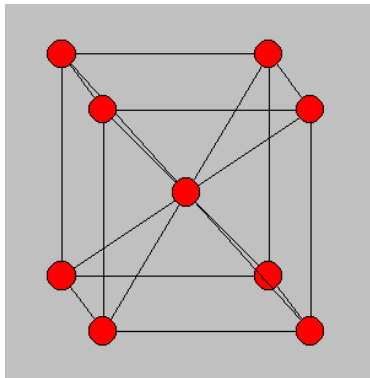
Body centered cubic (bcc) lattice   Face centered cubic (fcc) lattice