Phase diagram determination by diffusion couple technique

- Diffusion couples combined with some equilibrium alloys could be very useful to determine a ternary phase diagram, which otherwise needs many alloys to melt.

- Before going to explain the procedure, it is necessary to learn drawing the diffusion path on a phase diagram.

- When a composition profile developed in a ternary interdiffusion zone is plotted on a Gibb’s triangle it is called diffusion path.

- Note that the procedure of drawing the diffusion path is formulated and should be followed without asking for logic at every step.
For the sake of explanation, let us consider a hypothetical phase diagram and a diffusion couple.

- There are many compounds, \( \alpha, \beta, \ldots, \gamma \) are present.

- There are few two phase equilibrium regions, for example, between \( \delta \) and \( \sigma \), \( \lambda \) and \( \mu \). There are also few three phase equilibrium regions, for example between \( \beta, \delta \) and \( \sigma \).

- Two phase equilibriums are connected by the tie lines and three phase equilibrium regions are kept blank.
Now suppose alloy Z is coupled with pure A and different phases evolve in the interdiffusion zone separated by planar or wavy interface.

Practice to draw the diffusion path is presented step by step:

If composition in the $\alpha$ phase varies towards A rich side as shown in the figure diffusion path should be drawn as straight line, as shown by $ab$.

Since the phases $\delta$ and $\sigma$ are separated by a wavy interface, the solid diffusion path line should intersect the tie lines as shown by $bc$.

Then composition profile goes through the $\sigma$ phase as shown by $cd$.

Following precipitates of the $\pi$ phase appears and again after that the $\sigma$ phase exists. That means the diffusion path should enter the two phase equilibrium region as shown by $def$ and should come back again to the $\sigma$ phase and continues up to $fg$.

Phase $\sigma$ and $\pi$ are separated by a straight interface. So diffusion path should go parallel to the tie lines as shown by $gh$ and it should be drawn by the dotted line.

$ij$ shows the three phase equilibrium region, starting from one phase $\pi$ goes to two phase region $\lambda$ and $\mu$.

$jk$ shows the phase mixture of $\lambda$ and $\mu$. The location of the line depends on the relative amounts of the phases.
$kl$ shows transition of one three phase equilibrium to another three phase equilibrium.

$lm$ shows the path for two phase equilibrium to the $\gamma$ phase.

Following diffusion path goes through the $\gamma$ phase, as shown by $mn$.

- Further, as shown by the blue dotted line, diffusion path should at least intersect ones the line connecting between $Z$ and $A$. For any deviation it will move away from the straight line, however, because of mass balance it has to go to opposite direction also.
Let us study the diffusion path between the alloy R and S.

Alloy R is a mixture of $\alpha$ and $\mu$. Alloy S is the mixture of $\beta$ and $\gamma$. In the interdiffusion zone another phase T evolves.

So first the diffusion path from R will continue to the same two phase mixture region, however the volume fractions could be different, which makes the line to go to a certain direction.

At the interface of R and T, three phases are in equilibrium, however, it moves from a two phase region to a single phase T. So the diffusion path has to enter the phase region of T as it is shown.

Composition might change within T. Further at the interface of T and alloy S, the system is in three phase equilibrium.

It moves from single phase to two phase equilibrium.
We can see now, what will happen when different diffusion couples are made in this system.

When Ag is coupled with Fe$_{80}$Ti$_{20}$, which is basically a phase mixture of Fe and Fe$_2$Ti phases, interdiffusion will not occur because Ag can stay with these two phases in equilibrium.
When Ag is coupled with Fe$_{30}$Ti$_{70}$, which is basically a phase mixture of $\beta$-Ti and FeTi phases, phase mixture of TiAg and FeTi grows in the interdiffusion zone.

It goes through two three phase equilibriums. At one interface, Ag is in equilibrium with (TiAg + FeTi). At another interface, $\beta$-Ti and FeTi is in equilibrium with TiAg.
From one diffusion couple and subsequent annealing one can get idea about the phase boundary compositions in a ternary phase diagram.

For example, we take c as thin film and sandwich between A and B.

From the composition analysis of the diffusion couple annealed at different annealing times, we can determine the phase boundary compositions.

Very close to the phase boundary of $\alpha_1$ and $\alpha_2$, composition of phase boundary of the miscibility gap can be determined.
Similarly, if thin foil of Ni is sandwiched between V and Cr, phase boundary compositions of different phases can be determined after annealing for increasing times.

However, just the diffusion couples may not be enough to develop complete phase equilibria.

We may need to melt few selected alloys, as shown by the dots in the phase diagram, to establish the complete phase diagram.

So diffusion couple combined with equilibrated alloy helps to construct the ternary phase diagram with certain degree of confidence.

Determination of the phase diagram with just equilibrated alloy could be very tiresome and time consuming.