

Supplementary

Pseudo-binary and Pseudo-ternary diffusion couple methods for estimation of the diffusion coefficients in multicomponent systems and high entropy alloys

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S1. The conventional method of estimating the diffusion coefficients in the multicomponent system and difficulties with the increase in the number of components

The interdiffusion coefficients ($\tilde{D}$) and the interdiffusion flux ($\tilde{J}_i$) of component i in an n component system are related for constant molar volume by [3,4]

$$\tilde{J}_i = -\sum_{j=1}^{n-1} \tilde{D}_{ij}^n \frac{1}{V_m} \frac{dN_j}{dx} \quad (\text{S1a})$$

$$\sum_{i=1}^n \tilde{J}_i = 0 \quad (\text{S1b})$$

$\frac{dN_j}{dx}$ is the composition (atomic or mole fraction) gradient of component j , where x is the position parameter. V_m is the molar volume. n^{th} component is considered as the dependent variable. Irrespective of the number of components in a system, the interdiffusion flux of component i can be expressed as [3,4]

$$\tilde{J}(Y_{N_i}^*) = -\frac{N_i^+ - N_i^-}{2tV_m} \left[(1 - Y_{N_i}^*) \int_{x^-}^{x^*} Y_{N_i} dx + Y_{N_i}^* \int_{x^*}^{x^+} (1 - Y_{N_i}) dx \right] \quad (\text{S1c})$$

where $Y_{N_i} = \frac{N_i - N_i^-}{N_i^+ - N_i^-}$ is the composition normalized variable.

Binary system

As already explained in the manuscript, Equation S1a in a binary system simplifies to

$$\tilde{J}_i = -\tilde{D} \frac{1}{V_m} \frac{dN_i}{dx} \quad (\text{S2a})$$

It has only one interdiffusion coefficient at a particular composition at the temperature of interest irrespective of the diffusion profile of a component used for the estimation. Additionally, one can even estimate the intrinsic diffusion coefficients at the Kirkendall marker composition following [17]

$$D_i = \frac{1}{2t} \left(\frac{\partial x}{\partial N_i} \right)_K \left[N_i^+ \int_{x^-}^{x^K} Y_{N_i} dx - N_i^- \int_{x^K}^{x^+} (1 - Y_{N_i}) dx \right] \quad (\text{S2b})$$

Ternary system

In a ternary system, Equation S1a can be written as

$$V_m \tilde{J}_1 = -\tilde{D}_{11}^3 \frac{dN_1}{dx} - \tilde{D}_{12}^3 \frac{dN_2}{dx} \quad (S3a)$$

$$V_m \tilde{J}_2 = -\tilde{D}_{21}^3 \frac{dN_1}{dx} - \tilde{D}_{22}^3 \frac{dN_2}{dx} \quad (S3b)$$

$$\tilde{J}_1 + \tilde{J}_2 + \tilde{J}_3 = 0 \quad (S3c)$$

Here $\tilde{D}_{ii}^3$ are the main interdiffusion coefficients, which are associated with the concentration gradients of the same component. $\tilde{D}_{ij}^3$ are the cross interdiffusion coefficients, which are associated with the concentration gradients of another component. Component 3 is the dependent variable [3,4]. In a ternary system, two diffusion couples are required to intersect at a composition at which these diffusion coefficients can be estimated. The composition of intersection can be found by plotting the composition profiles on Gibb's triangle [3,4]. This is shown in Figure 5a. At the composition of the intersection from two diffusion couples, we can write

$$V_m \tilde{J}_1 \Big|_{DF_1} = -\tilde{D}_{11}^3 \left(\frac{dN_1}{dx} \right)_{DF_1} - \tilde{D}_{12}^3 \left(\frac{dN_2}{dx} \right)_{DF_1} \quad (S4a)$$

$$V_m \tilde{J}_2 \Big|_{DF_1} = -\tilde{D}_{22}^3 \left(\frac{dN_2}{dx} \right)_{DF_1} - \tilde{D}_{21}^3 \left(\frac{dN_1}{dx} \right)_{DF_1} \quad (S4b)$$

$$V_m \tilde{J}_1 \Big|_{DF_2} = -\tilde{D}_{11}^3 \left(\frac{dN_1}{dx} \right)_{DF_2} - \tilde{D}_{12}^3 \left(\frac{dN_2}{dx} \right)_{DF_2} \quad (S4c)$$

$$V_m \tilde{J}_2 \Big|_{DF_2} = -\tilde{D}_{22}^3 \left(\frac{dN_2}{dx} \right)_{DF_2} - \tilde{D}_{21}^3 \left(\frac{dN_1}{dx} \right)_{DF_2} \quad (S4d)$$

After estimating the interdiffusion fluxes following Equation S4, the four interdiffusion coefficients can be estimated.

One of the main problems of the ternary system is that we cannot predict the diffusion path of a diffusion couple *a priori*. This can be explained based on the experimental results reported by Ugaste et al. in the Ni-Co-Fe system, as shown in Figure S1 [35].

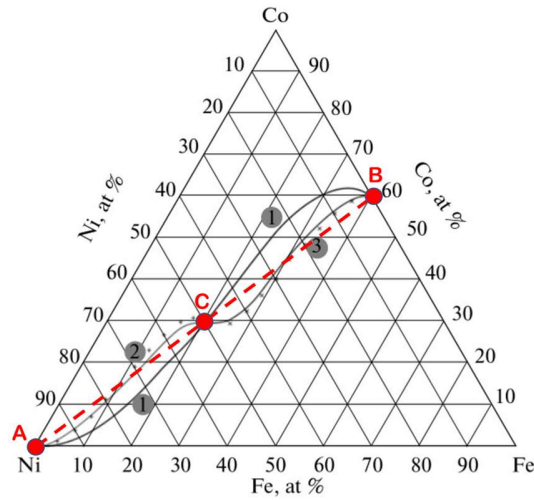


Figure S1: Diffusion paths in Ni-Co-Fe system between different end-member alloys annealed at 1100°C for 196 hrs [35].

Figure S1 indicates when A and B are coupled (number 1), it follows a typical serpentine diffusion path on Gibb's triangle. Subsequently, A and B are coupled with C which is located at the intersection of tie line connecting A and B and the diffusion path of the diffusion couple of the same alloys. Instead of following the same diffusion paths, both the diffusion couples (number 2: diffusion couple A/C, number 3: diffusion couple C/B) follow completely different diffusion paths. A rudimentary analysis by Rönkä et al. [34] indicates that the diffusion path of a diffusion couple depends strongly on the intrinsic diffusion coefficients of the end member compositions. Therefore, there is a high chance of finding a different diffusion path when the end member compositions are changed. Over the decades, the interdiffusion coefficients are determined in many ternary systems. A common practice is to mention the estimated diffusion coefficients on Gibb's triangle, as compiled in Ref [20]. Looking at the data, one can immediately notice that these are generated randomly since there is no control over the intersection composition of two diffusion

couples. Therefore, it is very difficult to study the change in diffusion coefficients even after systematic change in compositions of the end members in a ternary system. This is considered as one of the major drawbacks of studying interdiffusion in a ternary system following the conventional method.

The intrinsic fluxes and the intrinsic diffusion coefficients in a ternary system are related as [3, 4]

$$V_m J_1 = -D_{11}^3 \frac{dN_1}{dx} - D_{12}^3 \frac{dN_2}{dx} \quad (\text{S5a})$$

$$V_m J_2 = -D_{21}^3 \frac{dN_1}{dx} - D_{22}^3 \frac{dN_2}{dx} \quad (\text{S5b})$$

$$V_m J_3 = -D_{31}^3 \frac{dN_1}{dx} - D_{32}^3 \frac{dN_2}{dx} \quad (\text{S5c})$$

We need to determine six intrinsic diffusion coefficients in a ternary system. One can write three equations for three components in one couple at the Kirkendall marker plane position. Therefore, we need two diffusion couples for six equations so that six intrinsic diffusion coefficients can be estimated. Since the diffusion parameters are material constants and the values change with the change in composition, a major constraint is automatically introduced that the Kirkendall marker plane position should be found at the composition of intersection in both the diffusion couples at which six equations can be written in two different diffusion couples. We have already discussed above that the diffusion path of a particular diffusion couple cannot be predicted *a priori*. It is almost impossible to design two diffusion couples in which the marker plane can be located at the composition of an intersection unless found incidentally. Therefore, it is almost impossible to estimate the intrinsic diffusion coefficients in a ternary system.

Quaternary and multicomponent system

The relations between the interdiffusion fluxes and the interdiffusion coefficients in a quaternary system can be written based on Equation S1 as

$$V_m \tilde{J}_1 = -\tilde{D}_{11}^4 \frac{dN_1}{dx} - \tilde{D}_{12}^4 \frac{dN_2}{dx} - \tilde{D}_{13}^4 \frac{dN_3}{dx} \quad (\text{S6a})$$

$$V_m \tilde{J}_2 = -\tilde{D}_{21}^4 \frac{dN_1}{dx} - \tilde{D}_{22}^4 \frac{dN_2}{dx} - \tilde{D}_{23}^4 \frac{dN_3}{dx} \quad (\text{S6b})$$

$$V_m \tilde{J}_3 = -\tilde{D}_{31}^4 \frac{dN_1}{dx} - \tilde{D}_{32}^4 \frac{dN_2}{dx} - \tilde{D}_{33}^4 \frac{dN_3}{dx} \quad (\text{S6c})$$

$$\tilde{J}_1 + \tilde{J}_2 + \tilde{J}_3 + \tilde{J}_4 = 0 \quad (\text{S6d})$$

Therefore, we need to estimate the nine interdiffusion coefficients in a quaternary system. We can write three equations in one diffusion couples. Therefore, we need three diffusion couples to intersect at one common composition so that we can write a total of nine equations at the same composition but in three different couples. However, because of the complicated nature of the diffusion paths, it is impossible to design three couples such that these would intersect at one composition in a four-component space. In fact, one can easily intersect two couples in a ternary system on Gibb's triangle, as shown in this article Figure 6. However, it is difficult to intersect even two couples in a four-component space, as explained in the schematic diagram in Figure S2, since diffusion paths get an extra degree of freedom to deviate. Following the same line of discussion, it must be clear that the estimation of the diffusion coefficients will be even more difficult with the increase in the number of components.

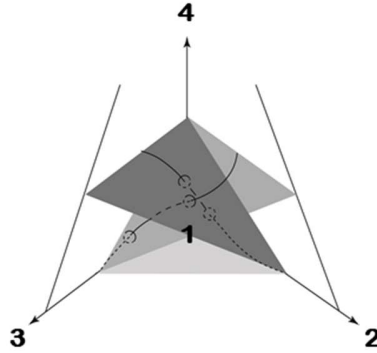


Figure S2: Diffusion paths of two diffusion couples in a four-component space.

Therefore, we can conclude that we can estimate both the interdiffusion and intrinsic diffusion coefficients following straightforward method in a binary system. We can even estimate the tracer diffusion coefficients if the thermodynamic parameters are known. In a ternary system, the experimental method is a bit more tedious since we need two diffusion couples to intersect at one composition. We do not have much control over the composition

of the intersection since the diffusion path is not known *a priori*. Therefore, we have difficulties to generate the interdiffusion coefficients systematically. Moreover, we cannot estimate the intrinsic diffusion coefficients. In a quaternary or multicomponent system, we cannot estimate any diffusion coefficients in an inhomogeneous material following the conventional methods.

S2 Experimental procedure

The alloys used for preparing different types of diffusion couples were melted using the pure (99.9-99.95 wt.%) components in an arc melting furnace. To make sure the homogeneity, these alloy buttons were remelted at least five times after changing the side. These were then annealed at $1200 \pm 5^\circ\text{C}$ ($1473 \pm 5\text{ K}$) for 50 h in high vacuum ($\sim 10^{-4}\text{ Pa}$) for better homogenization. The compositions were then measured at many spots randomly in an EPMA (Electron Microprobe Analyzer). The deviations from the average compositions were found to be within $\pm 0.1\text{ at.}\%$. These were sliced with $\sim 1\text{ mm}$ thickness in EDM (electro discharge machine) and prepared metallographically for flat and smooth surfaces. Two foils were then coupled in a special fixture for producing the diffusion couples and annealed at the desired temperature for a certain period of time, which are mentioned in the article. The details of the diffusion couple technique is described in Chapter 3 in Ref. 4. After the diffusion annealing, the samples were cross-sectioned, to prepare metallographically. The diffusion profiles were then measured in EPMA with pure components as standards.

S3 Co-Ni binary and PB diffusion couple profiles

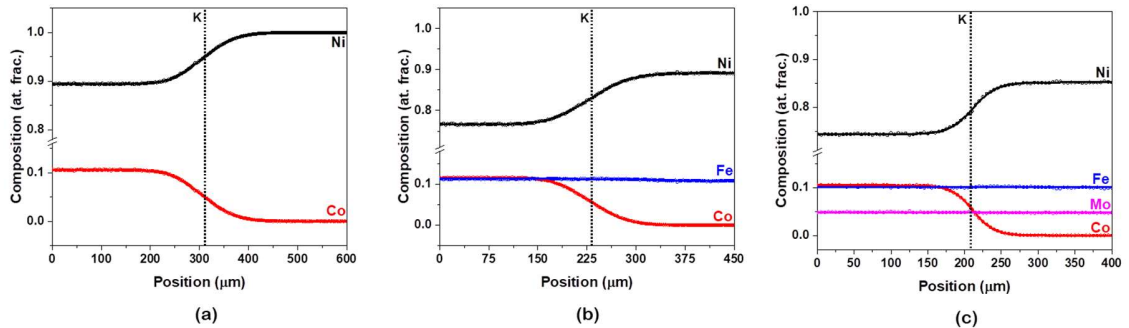


Figure S3 Composition profiles of (a) Binary Ni-Ni_{0.9}Co_{0.1}
(b) 3 component PB-Ni_{0.9}(Fe_{0.1})-Ni_{0.8}Co_{0.1}(Fe_{0.1}) and

(c) 4 component PB-Ni_{0.85}(Fe_{0.1}Mo_{0.05})-Ni_{0.75}Co_{0.1}(Fe_{0.1}Mo_{0.05}) diffusion couples annealed at 1100°C for 100 hrs. The location of the Kirkendall marker planes are indicated by "K". These are developed at 1200±5°C (1473±5 K) after annealing for 50 h.

S4 Stability Equations

A particular component (k) in a conventional ternary (i,j,k) or pseudo-ternary system can be considered as the dependent variable if the estimated diffusion coefficients fulfil the conditions [3]

$$\tilde{D}_{ii}^k + \tilde{D}_{jj}^k > 0 \quad (S7a)$$

$$(\tilde{D}_{ii}^k + \tilde{D}_{jj}^k)^2 \geq 4(\tilde{D}_{ii}^k \tilde{D}_{jj}^k - \tilde{D}_{ij}^k \tilde{D}_{ji}^k) \quad (S7b)$$

$$(\tilde{D}_{ii}^k \tilde{D}_{jj}^k - \tilde{D}_{ij}^k \tilde{D}_{ji}^k) \geq 0 \quad (S7c)$$