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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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ABSTRACT

The benefits of using the pseudo-binary and pseudo-ternary diffusion couple methods in multicomponent inhomogeneous systems are demonstrated by estimating different types of composition-dependent diffusion coefficients. These are important for understanding the basic atomic mechanism of diffusion and complex compositional evolutions. These were otherwise considered impossible during the last many decades. Without any options previously, sometimes the average values over a composition range of random choice were estimated, which are not the material constants but depend on the composition range and also the end member compositions. The steps and analyses for utilising the pseudo-binary and pseudo-ternary methods are first described in the Ni-Co-Fe-Mo system by producing the ideal diffusion profiles fulfilling the concepts behind these methods. Following, the discussion is extended to the systems related to medium (Ni-Co-Cr) and high (Ni-Co-Fe-Mn-Al) entropy alloys. In fact, this is the first report showing a correct experimental method that should be followed for the estimation of the interdiffusion and intrinsic diffusion coefficients in inhomogeneous high entropy alloys. In the end, the limitations of following these methods because of the generation of non-ideal diffusion profiles are discussed based on experimental results. The steps are also suggested to avoid such complications. These methods are easy to adopt for research engineers. Most importantly, these give an opportunity to validate the data estimated following newly proposed numerical methods by different groups with experimentally estimated diffusion coefficients, which were not possible earlier.

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1. Introduction

The diffusion community faced an unsolved challenge for almost nine decades after the relations developed based on the Onsager formalism [1,2] for the

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estimation of the diffusion coefficients in inhomogeneous multicomponent material systems [3,4]. The composition dependent diffusion coefficients (not the average over a composition range) could be estimated (experimentally) only in simple binary and ternary systems. These could not be estimated in a system with more than three components fulfilling the mathematical complications and associated stringent experimental requirements [3,4]. The studies in simple binary and ternary systems are useful to develop an understanding of the basic (atomic and phenomenological) diffusion mechanisms. However, these are not useful to relate the diffusion rates of components with microstructural evolution influencing different physical and mechanical properties of multicomponent materials used in various applications. Addition of components might change the diffusion rates significantly because of change in thermodynamic driving forces and concentration of defects assisting the diffusion process. The thrust for the development of new multicomponent material with enhanced properties in various applications has increased manifold especially following the concept behind the high entropy alloys (HEA) [5–7]. Therefore, today, the need for effective approaches for the measurement of diffusion rates of components in these complex systems is even more important.

Recently, Paul and his group have established the concept of the pseudo-binary (PB) [8] and pseudo-ternary (PT) methods [9] by extending the benefits of diffusion studies in binary and ternary systems to complex multicomponent systems. The concepts of these methods are established following a completely different notion that was followed in the diffusion community during the last nine decades. Previously, the experiments were conducted such that all the components were forced to develop the diffusion profiles. This led to the impossible situation in a system with more than three components because of complications of the equations which cannot be fulfilled [3,4]. The difficulties associated with the previously followed conventional methods are explained in the supplementary file. On the other hand, the experiments in the newly developed methods are designed such that only two components in PB and three components in PT diffusion couples are expected to develop the diffusion profiles keeping all other components constant. These reduce the mathematical complications for the estimation of diffusion coefficients such that composition dependent diffusion coefficients can be estimated in multicomponent systems.

These approaches are still at the nascent stage. The PB method is used in very few systems [10–14] and the PT method is just proposed [9]. These have the potential to become methods of choice in future if the steps for utilising these techniques to study the role of alloying in the multicomponent system are established. A very important step of normalisation of the composition profiles for the estimation of the data and also to facilitate the comparison of the estimated data in different conditions are to be demonstrated. These are discussed first with the help of experiments conducted in the NiCoFeMo quaternary system. The main advantage of conducting experiments on this system can be realised from the

fact that the melting of an alloy with the desired composition is easier in the absence of relatively volatile components. Subsequently, we have extended our analysis in the concentrated single-phase high entropy alloys (HEA), which have garnered enormous attention with the aim of developing new materials. Unfortunately, very few (purely) experimental interdiffusion studies are conducted until now and various issues with the analyses or comparison are already reported [15,16]. In this article, we have demonstrated the steps/tricks to be followed with respect to the experiments for the estimation of the diffusion coefficients. The studies reported here will set the guidelines for diffusion studies in multicomponent materials (in general) in various systems of practical applications, which could not be done during last many decades following the previously followed conventional experimental methods. It should be noted here that the aim of this article is not to estimate diffusion coefficients in a particular system but to demonstrate the newly established methods in various systems with a different number of components.

2. Results and discussion

In this section, we shall first discuss the concept behind designing the samples for PB and PT methods with the aim of systematic comparison because of alloying. At first, we have considered the NiCoFeMo system in which volatile components are not present and therefore, it is easy to prepare the alloys with almost the desired compositions without many trials. This is an important step for the estimation of the data with minimum error. The material system is related to various types of Inconel alloys. Following, the analysis is extended to the high entropy alloys (HEA) with a higher number of components. The experimental methods conducted in this study are discussed in the supplementary file.

2.1. The concept and practice of following the pseudo-binary (PB) method

In this section, we demonstrate the use of the PB method in multicomponent systems. In the beginning, the diffusion coefficients are estimated in the Ni-Fe and Ni-Co binary systems following the conventional method. Subsequently, the PB method is utilised to estimate the data in Ni-Co (Fe fixed) and Ni-Fe (Co fixed) ternary systems and Ni-Co (Fe, Mo fixed) and Ni-Fe (Co, Mo fixed) quaternary systems, which are not possible following the conventional methods. The estimated data are then compared to examine the role of alloying on diffusion coefficients. These analyses are subsequently extended to the systems related to medium and high entropy alloys with a special emphasis on the strategy of designing experiments for estimation of the intrinsic diffusion coefficients with minimum error.

2.1.1. The conventional binary (CB) diffusion couples in Ni-Co and Ni-Fe systems

Following the relation developed based on the Onsager formalism [1,2], the interdiffusion coefficients (\tilde{D}) and the interdiffusion flux (\tilde{J}_i) of component i in a n component system are related by [3,4]

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

$\frac{dN_j}{dx}$ is the composition (atomic or mole fraction) gradient of component j , where x is the position parameter. V_m is the molar volume. Which is considered as the constant since the variation of the lattice parameters with the composition in multicomponent systems is generally not available. This does not affect significantly unless there is a very high non-ideality in the molar volume variation [17]. This relation is applicable when the vacancy concentration is in equilibrium in the presence of enough sources and sinks [3]. The interdiffusion fluxes, when estimated with respect to the composition profiles of different components, are related by

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

The interdiffusion flux of component i (for constant molar volume) can be estimated from its composition profile utilising [18,19]

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

N_i^- is composition at the left-hand side and N_i^+ is composition at the right-hand side of the diffusion couple of component i . x is the position parameter and t is the time of annealing at the temperature of interest. $Y_{N_i} = (N_i - N_i^-) / (N_i^+ - N_i^-)$ is the composition normalised variable.

In a binary system of components 1 and 2, Equation (1) reduces to

$$\tilde{J}_1 = -\tilde{D}(1) \frac{1}{V_m} \frac{dN_1}{dx} \quad (3a)$$

$$\tilde{J}_2 = -\tilde{D}(2) \frac{1}{V_m} \frac{dN_2}{dx} \quad (3b)$$

$$\tilde{J}_1 + \tilde{J}_2 = 0 \quad (3c)$$

Since $N_1 + N_2 = 1$ and $dN_1 + dN_2 = 0$, we have $\tilde{D}(1) = \tilde{D}(2)$. Therefore, the same value of interdiffusion coefficient at the particular composition for the temperature of the experiment is estimated irrespective of the component (1

or 2) considered for the analysis. By utilising the Equations (2) and (3), this can be estimated directly from [18,19]

$$\tilde{D} = \frac{1}{2t} \left(\frac{dx}{dY_{N_i}} \right)_{x^*} \left[(1 - Y_{N_i}^*) \int_{x^{-\infty}}^{x^*} Y_{N_i} dx + Y_{N_i}^* \int_{x^*}^{x^{+\infty}} (1 - Y_{N_i}) dx \right] \quad (4)$$

A typical binary diffusion couple of Ni and Ni_{0.9}Fe_{0.1} is shown in Figure 1(a), which is annealed at 1100°C for 100 h. Before estimation of the data, it is very important to follow certain steps correctly for smoothening the composition profiles measured in EPMA fulfilling the Equations (3)–(4). This is even more important in the case of PB and PT couples as explained in the next part of this discussion. As shown in Figure 1, the open symbols are the measured compositions of different components at various locations. These are then smoothened individually for different components for a continuous variation. Since these are smoothened individually, the summation of compositions of components 1 and 2 at various locations may not be equal to one after this step ($N_T = N_1 + N_2 \neq 1$). Therefore, as a next mandatory step, the composition profiles should be divided by N_T (*i.e.* N_i/N_T) so that we have $N_T = N_1 + N_2 = 1$ after this normalisation. Then only $\tilde{J}_1 = -\tilde{J}_2$ (see Equation (3c)) will be fulfilled and therefore the same interdiffusion coefficients will be estimated irrespective of the composition profiles considered for the estimation. Otherwise, wrongly it will give two different values of the interdiffusion coefficients at one particular composition. These are then converted to Y_{N_i} vs. x

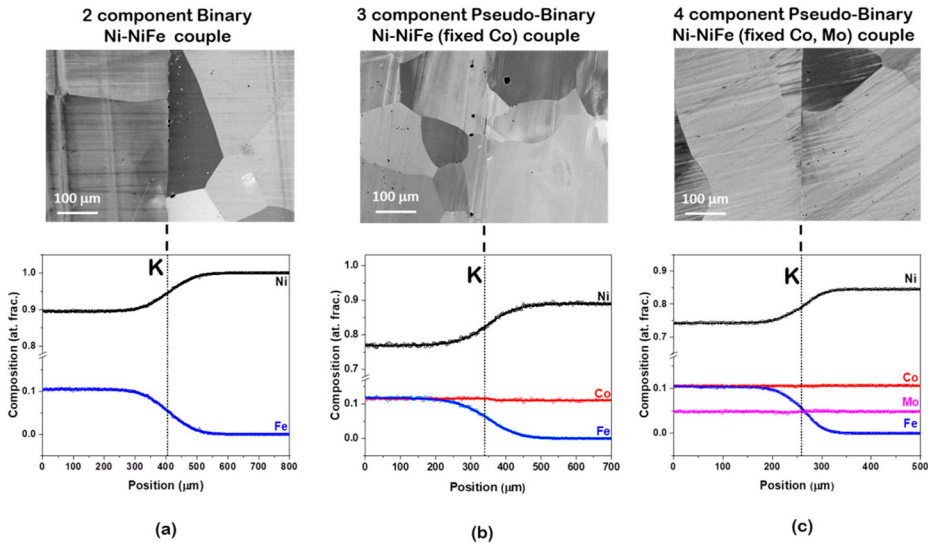


Figure 1. Microstructure and composition profiles of (a) Binary Ni-Ni_{0.9}Fe_{0.1} (b) 3 component PB Ni_{0.9}(Co_{0.1})-Ni_{0.8}Fe_{0.1}(Co_{0.1}) and (c) 4 component PB Ni_{0.85}(Co_{0.1}Mo_{0.05})-Ni_{0.75}Fe_{0.1}(Co_{0.1}Mo_{0.05}) diffusion couples annealed at 1100°C for 100 h. The locations of the Kirkendall marker planes are indicated by 'K'.

and $(1 - Y_{N_i})$ vs. x considering any one of the components. Utilising these plots, the diffusion coefficients are estimated following Equation (4). The estimated variations of the interdiffusion coefficients in the Ni-rich side of the Ni-Fe and Ni-Co binary alloys are shown in Figure 2. A previous study by Jung et al. [20] in the binary Ni-Co system reporting very similar values are incorporated for comparison.

The intrinsic diffusion coefficients at the Kirkendall marker plane can be estimated (considering a constant molar volume) following [19,21]

$$D_i = \frac{1}{2t} \left(\frac{\partial x}{\partial N_i} \right)_K \left[N_i^+ \int_{x^{-\infty}}^{x^K} Y_{N_2} dx - N_i^- \int_{x^K}^{x^{+\infty}} (1 - Y_{N_2}) dx \right] \quad (i = 1, 2) \quad (5)$$

where $Y_{N_2} = (N_2 - N_2^-)/(N_2^+ - N_2^-)$ and $1 - Y_{N_2} = (N_2^+ - N_2)/(N_2^+ - N_2^-)$. This is true when the composition profile is plotted such that $N_2^+ > N_2^-$. This further means that the composition of component 1 in the right-hand side of the diffusion couple is higher than the composition of the same component in the left-hand side of the diffusion couple.

The Kirkendall marker location can be detected easily by analysing the micro-structural evolution in the interdiffusion zone. It is already known based on theoretical and experimental analysis that the marker plane demarcates the growth from different sides of a diffusion couple [3,4,22]. As shown in Figure 1, this plane is located at the composition of $N_{Fe} = 5.3$ at%, in the Ni/Ni_{0.9}Fe_{0.1} binary diffusion couple. Following the intrinsic diffusion coefficients are

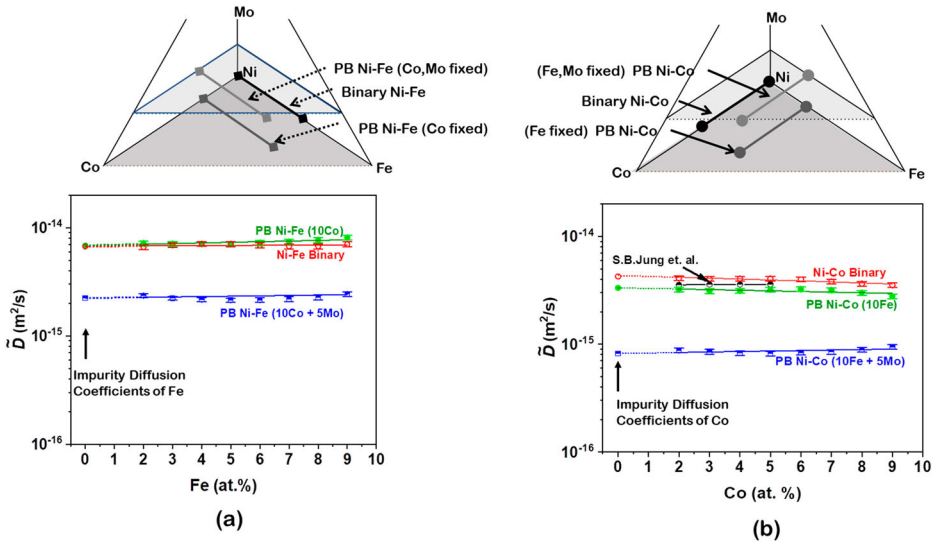


Figure 2. The estimated interdiffusion and impurity diffusion coefficients in (a) binary Ni-Fe, PB Ni-Fe(Co) and PB Ni-Fe (Co,Mo) (b) binary Ni-Co, PB Ni-Co(Fe) and PB Ni-Co (Fe,Mo) diffusion couples. All the couples are annealed at 1100°C for 100 h.

estimated utilising Equation (5) as $D_{\text{Ni}} = 1.02 \times 10^{-15} \text{ m}^2/\text{s}$ and $D_{\text{Fe}} = 7.28 \times 10^{-15} \text{ m}^2/\text{s}$.

One can even estimate the impurity diffusion coefficients by extending the plot of interdiffusion coefficients vs. composition to pure components. For example, the impurity diffusion coefficient of component 2 in pure component 1 can be estimated as $D_{2(1)}^{\text{imp}} = \lim_{N_2 \rightarrow 0} \tilde{D}$ and similarly, the impurity diffusion coefficient of component 1 in pure component 2 can be estimated as $D_{1(2)}^{\text{imp}} = \lim_{N_1 \rightarrow 0} \tilde{D}$. Since the interdiffusion coefficients are estimated in the Ni-rich of the Ni-Fe and Ni-Co binary alloys, we can estimate the impurity diffusion coefficients of Fe *i.e.* $D_{\text{Fe(Ni)}}^{\text{imp}}$ and Co *i.e.* $D_{\text{Co(Ni)}}^{\text{imp}}$ in Ni. These are estimated at 1100°C by extending the estimated composition dependent interdiffusion coefficients to Fe and Co composition of zero, as shown in Figure 2. These are estimated as $D_{\text{Fe(Ni)}}^{\text{imp}} = 6.71 \times 10^{-15} \text{ m}^2/\text{s}$ and $D_{\text{Co(Ni)}}^{\text{imp}} = 4.25 \times 10^{-15} \text{ m}^2/\text{s}$. The reported values available in the literature following the direct radiotracer method at the same temperature are $D_{\text{Fe(Ni)}}^{\text{imp}} = 10^{-4} \exp(-269400(J/\text{mol}))/RT = 5.6 \times 10^{-15} \text{ m}^2/\text{s}$ and $D_{\text{Co(Ni)}}^{\text{imp}} = 2.77 \times 10^{-4} \exp(-285100(J/\text{mol}))/RT = 3.9 \times 10^{-15} \text{ m}^2/\text{s}$ [23–25]. These are very close to the estimated values in this study considering that two different types of measurement techniques are followed.

2.1.2. The pseudo-binary (PB) diffusion couples in three and four components NiCoFeMo system

In a pseudo-binary (PB) diffusion couple, only two components (1 and 2) are expected to develop the diffusion profiles keeping all other components constant such that $(dN/dx)_{3,4,\dots,n} = 0$ and $(\tilde{J})_{3,4,\dots,n} = 0$. In such a condition, Equation (1) reduces to a situation similar to the binary system as expressed in Equation (3). At this point, it should be noted here that although two components develop the diffusion profiles other components are also present in the alloy. In a n components system, we can express the relations between the compositions with respect to the atomic fraction (or the mole fraction) $N_1 + N_2 + N_3 \dots + N_n = 1$. However, since only two components develop the diffusion profiles, we have $dN_1 + dN_2 = 0$ in the interdiffusion zone. Therefore, following the similar logic of Equation (3), we have $\tilde{D}(1) = \tilde{D}(2)$. It means that one can estimate the interdiffusion coefficients utilising any one of the composition profiles for the estimation of the same value at various compositions.

One may estimate the interdiffusion coefficients utilising the composition profile of any one of the components directly or after modifying the profiles such that components which are kept constant are added in a particular fashion depending on the type of materials studied (random solid solution or the intermetallic compound [8]). To clarify further, in a random solid solution, the modified compositions of the diffusion components can be calculated following $M_i = N_i/N_v = N_i/(1 - N_f)$, where N_i is the composition of one of the variable components i and $N_v = N_1 + N_2$ is the total of variable compositions in a

PB diffusion couple. $N_f = N_3 + N_4 \dots N_n$ is the total of compositions which are kept as the constant. Therefore, in the PB diffusion couple, this leads to $M_1 = N_1/(N_1 + N_2)$ and $M_2 = N_2/(N_1 + N_2)$ such that we have $M_1 + M_2 = 1$. One can then estimate the interdiffusion coefficients following

$$\tilde{D} = \frac{1}{2t} \left(\frac{dx}{dY_{M_i}} \right) \left[(1 - Y_{M_i}^*) \int_{x^{-\infty}}^{x^*} Y_{M_i} dx + Y_{M_i}^* \int_{x^*}^{x^{+\infty}} (1 - Y_{M_i}) dx \right], \quad (6a)$$

where $Y_{M_i} = (M_i - M_i^-)/(M_i^+ - M_i^-)$ is the modified composition normalised variable.

These will give the same value of the interdiffusion coefficients at a particular (modified) composition even if one estimates directly from the composition profiles without any modification since

$$Y_{N_i} = \frac{N_i - N_i^-}{N_i^+ - N_i^-} = \frac{\frac{N_i}{N_v} - \frac{N_i^-}{N_v}}{\frac{N_i^+}{N_v} - \frac{N_i^-}{N_v}} = \frac{M_i - M_i^-}{M_i^+ - M_i^-} = Y_{M_i}$$

$$\frac{dY_{N_i}}{dx} = \frac{dY_{M_i}}{dx}$$

Therefore, the value of the estimated data is not affected by the modification method. However, it should be noted here that this modification is mandatory if the interdiffusion flux is estimated, which is expressed as

$$\tilde{J}(Y_{M_i}^*) = -\frac{M_i^+ - M_i^-}{2tV_m} \left[(1 - Y_{M_i}^*) \int_{x^{-\infty}}^{x^*} Y_{M_i} dx + Y_{M_i}^* \int_{x^*}^{x^{+\infty}} (1 - Y_{M_i}) dx \right] \quad (6b)$$

In this equation, the interdiffusion flux value would be estimated wrongly if N_i is used instead of M_i . The modified compositions consider only the components which participate for the evolution of the interdiffusion flux and therefore $\tilde{J}_1 + \tilde{J}_2 = 0$ is fulfilled in a PB diffusion couple. The intrinsic fluxes of the components [3] should be rewritten with respect to the modified compositions as

$$J_i = -\frac{1}{2tV_m} \left[M_i^+ \int_{x^{-\infty}}^{x^K} Y_{M_2} dx - M_i^- \int_{x^K}^{x^{+\infty}} (1 - Y_{M_2}) dx \right] \quad (7a)$$

where J_i is the intrinsic flux of component i ($= 1, 2$). $Y_{M_2} = (M_2 - M_2^-)/(M_2^+ - M_2^-)$ and $1 - Y_{M_2} = (M_2^+ - M_2)/(M_2^+ - M_2^-)$. This is true when the composition profile is plotted such that $M_2^+ > M_2^-$. This further means that the modified composition of component 2 in the right-hand side of the diffusion couple is higher than the modified composition of the same component in the left-hand side of the diffusion couple. This fulfils the relation between the interdiffusion and intrinsic fluxes $\tilde{J}_1 = M_2J_1 - M_1J_2$ or $\tilde{J}_2 = M_1J_2 - M_2J_1$.

Therefore, the intrinsic diffusion coefficients should be estimated by modifying Equation (5) as

$$D_i = \frac{1}{2t} \left(\frac{\partial x}{\partial M_i} \right)_K \left[M_i^+ \int_{x^-}^{x^K} Y_{M_2} dx - M_i^- \int_{x^K}^{x^+} (1 - Y_{M_2}) dx \right] \quad (i = 1, 2) \quad (7b)$$

This satisfies the relation between the interdiffusion and intrinsic diffusion coefficients $\tilde{D} = M_2 D_1 + M_1 D_2$. Our extensive analysis indicates that this modification strategy suits well in all types of PB and PT couples (incremental or with pure components as the end members) for the estimation and comparison of all types of diffusion coefficients in random alloys.

The composition profile of a three component PB diffusion couple is shown in [Figure 1\(b\)](#), in which Ni and Fe develop the diffusion profiles keeping Co as the constant. Similarly, the composition profiles of four component PB couple is shown in [Figure 1\(c\)](#), in which Ni and Fe develop the composition profiles keeping Co and Mo as the constants. ‘K’ indicates the location of the Kirkendall marker planes. Similar examples in which Ni and Co develop the diffusion profiles keeping Fe (in three component – PB couple) and Fe and Mo (in four component PB couple) are also developed (see supplementary file). All the experiments are conducted at 1100°C and annealed for 100 h. It can be seen clearly that all the couples show ideal PB diffusion couple features fulfilling: (i) the compositions of components are the same (or very close) which supposed to remain constant at the ends of diffusion couple, additionally, (ii) there are no signs of uphill diffusion in any of these components.

As described in the previous section (while demonstrating the steps to be followed to estimate the diffusion coefficients in a binary system), the experimentally measured profiles are smoothened first individually which may lead to the total of compositions $N_T = \sum_{i=1}^n N_i \neq 1$. These are then normalised by N_i/N_T such that we have $\sum_{i=1}^n N_i = 1$. This is a mandatory step to utilise all the equations for the estimation of the diffusion coefficients even in the PB method. It should be noted here that this step does not change the nature of the diffusion profiles but make sure that after smoothening the profiles of different components individually $\sum_{i=1}^n \tilde{J}_i = 0$ is fulfilled. Following, the modified composition profiles of the diffusing components are calculated for the estimation of the composition dependent interdiffusion coefficients, as shown in [Figure 2](#). It can be seen that the interdiffusion coefficients of Ni-Fe do not change much in the presence of Co; whereas, the interdiffusion coefficients of Ni-Co decreases a bit in the presence of Fe. There is a significant decrease in interdiffusion coefficients in both the cases in the presence of Mo. This is further explained in the discussion section.

Next, we extend our analysis for the estimation of the intrinsic diffusion coefficients. It should be noted here that these parameters could be estimated previously only in a binary system following the conventional method [3,4].

One of the major advantages of this PB method is that these parameters now can be estimated in a multicomponent system with any number of components facilitating basic understanding of the atomic mechanism of diffusion. We have already explained the estimation of these parameters in the Ni-Fe binary system in the previous section. As an example, the location of the Kirkendall marker planes in three components Ni-Fe (Co fixed) and four components Ni-Fe (Co, Mo fixed) PB couples are indicated in [Figure 1](#). The estimated intrinsic diffusion coefficients utilising Equations (7b) are listed in [Tables 1](#) and [2](#). These are also estimated in the Ni-Co (Fe) and Ni-Co (Fe, Mo) diffusion couples. It can be seen that the location of the Kirkendall marker planes for the compositions of Fe and Co in binary systems are different with respect to the modified compositions of the same components. Therefore, we cannot compare the data since the intrinsic diffusion coefficients might change with compositions in a particular diffusion couple. However, the marker plane locations with respect to the modified compositions in 3 component and 4 component PB couples are more or less the same and, therefore, we can compare the estimated data. It can be clearly seen that the addition of Mo decreases the intrinsic diffusion rates of both Ni and Fe or Co in both types of PB couples.

One important point with the comparison of the estimated data in different binary and PB couples should be described here. We designed the alloys with a fixed range of 10 at.% Fe (in Ni-Fe binary and PB couples) and 10 at.%Co (in Ni-Co binary and PB couples) irrespective of the content of other components which are kept constant. These lead to a different range of the diffusing components in the diffusion couple when we compare $\Delta N_i = N_i^+ - N_i^-$ and $\Delta M_i = M_i^+ - M_i^-$. For example, if we consider the 3 component PB couple with end member compositions Ni(0.1Co) and Ni0.1Fe

Table 1. Estimated diffusion coefficients at the Kirkendall marker plane positions in the Ni-Fe(Co, Mo) PB system at 1100°C.

	Composition (K plane)		\tilde{D}^k ($\times 10^{-15}$ m ² /s)	D_{Ni} ($\times 10^{-15}$ m ² /s)	D_{Fe} ($\times 10^{-15}$ m ² /s)
	N_{Fe}	(M_{Fe}) at. %			
Binary NiFe	5.3		6.95 ± 0.3	1.02 ± 0.05	7.28 ± 0.37
PB NiFe (Co Fixed)	6.2	(6.88)	7.29 ± 0.3	2.56 ± 0.13	7.64 ± 0.38
PB NiFe (Co, Mo Fixed)	5.6	(6.58)	2.02 ± 0.1	1.41 ± 0.06	2.06 ± 0.10

Table 2. Estimated diffusion coefficients at the Kirkendall marker plane positions in the Ni-Co(Fe, Mo) PB system at 1100°C.

	Composition (K plane)		\tilde{D}^k ($\times 10^{-15}$ m ² /s)	D_{Ni} ($\times 10^{-15}$ m ² /s)	D_{Co} ($\times 10^{-15}$ m ² /s)
	N_{Co}	(M_{Co}) at. %			
Binary NiCo	5.02		4.10 ± 0.2	10.7 ± 0.6	3.75 ± 0.19
PB NiCo (Fe Fixed)	5.9	(6.55)	2.99 ± 0.1	2.79 ± 0.14	3.01 ± 0.15
PB NiCo (Fe, Mo Fixed)	5.5	(6.47)	0.82 ± 0.05	0.17 ± 0.01	0.86 ± 0.04

(0.1Co), we have

$$\begin{aligned}\Delta M_{\text{Ni}} &= M_{\text{Ni}}^+ - M_{\text{Ni}}^- = \frac{N_{\text{Ni}}^+}{(N_{\text{Ni}} + N_{\text{Fe}})} - \frac{N_{\text{Ni}}^-}{(N_{\text{Ni}} + N_{\text{Fe}})} = \frac{0.9}{0.9} - \frac{0.8}{0.9} = 1 - 0.8889 \\ &= 0.1111.\end{aligned}$$

The same in a 4 component Ni(0.1Co, 0.05Mo) and Ni-0.1Fe(0.1Co, 0.05Mo) diffusion couple leads to

$$\begin{aligned}\Delta M_{\text{Ni}} &= M_{\text{Ni}}^+ - M_{\text{Ni}}^- = \frac{N_{\text{Ni}}^+}{(N_{\text{Ni}} + N_{\text{Fe}})} - \frac{N_{\text{Ni}}^-}{(N_{\text{Ni}} + N_{\text{Fe}})} = \frac{0.85}{0.85} - \frac{0.75}{0.85} \\ &= 1 - 0.8824 = 0.1176.\end{aligned}$$

Therefore, the 3 and 4 component PB couples have a comparable composition range of 11.11 and 11.76 at.% compared to the 10 at.% range in the binary couples. We have the same equivalent composition in the Ni-rich side since we have $N_i^+ = M_i^+$, the difference in the composition range is created because of $N_i^- \neq M_i^-$ in different couples. Although we do not have control over the location of the Kirkendall marker plane since the addition of a component may influence the diffusion rates of different components differently, still there could be a chance of even closer compositions of the marker planes if the same equivalent composition range would be maintained, especially when we compare the binary and PB couples. This would be true (at least in these examples) since there is not much variation in the estimated interdiffusion coefficients in a particular diffusion couple with the change in Fe or Co, as can be seen in [Figure 2](#) and also because of small composition (or modified composition) range used in this study. The chance of finding a difference in location of the Kirkendall planes increases when the composition range of a diffusion couple is high. Because of the same reason, we have compared the interdiffusion coefficients with respect to Fe and Co composition variations instead of modified composition variations. As described in the next section, we have conducted the experiment in the medium and high entropy alloys keeping the range of modified compositions as fixed.

Similar to the binary systems, we have estimated the impurity diffusion coefficients of the components in different alloys by extending the interdiffusion coefficients measured in PB couples, as shown in [Figure 2](#). These values are listed in [Tables 3](#) and [4](#). It should be noted here that this is an additional advantage of following this PB method. It can be seen that, as expected, the impurity diffusion coefficients decrease significantly especially in the presence of Mo.

Table 3. Impurity diffusion coefficients $D_{\text{Fe}}^{\text{imp}}$ estimated in the Ni-Fe(CoMo) system at 1100°C.

	Impurity Diffusion Coefficients $D_{\text{Fe}}^{\text{imp}}$ ($\times 10^{-15}$ m ² /s)
Binary NiFe	6.71 ± 0.3
PB NiFe (Co Fixed)	6.84 ± 0.3
PB NiFe (Co, Mo Fixed)	2.24 ± 0.1

Table 4. Impurity diffusion coefficients $D_{\text{Co}}^{\text{imp}}$ estimated in the Ni-Co(FeMo) system at 1100°C.

	Impurity Diffusion Coefficients $D_{\text{Co}}^{\text{imp}}$ ($\times 10^{-15}$ m ² /s)
Binary NiCo	4.25 ± 0.2
PB NiCo (Fe Fixed)	3.33 ± 0.1
PB NiCo (Fe, Mo Fixed)	0.82 ± 0.04

2.1.3. The diffusion analysis in the systems related to medium and high entropy alloys

Tsai et al. conducted the PB method in the FeNiCoCrMn system to conclude that diffusion rates decrease with the increase in the number of components [12]. Paul [15] raised serious doubts about their analysis and quality of the data published. Their logic of following such an analysis [26] was further refuted by Paul and Divinski [16]. Kulkarni and Chauhan [27] estimated the average of main and cross interdiffusion coefficients in a four-component system. Unfortunately, by mistake, they compared the data in a ternary system measured at a different temperature to make a wrong conclusion on sluggish diffusion [16]. Additionally, the limitations of estimating the average diffusion coefficients are discussed in detail in Ref. [16]. Previously, there was no other option other than estimating these average values. In this manuscript, we have demonstrated the advantages of utilising the PB method for the estimation of the composition dependent diffusion coefficients. At present no other purely experimental studies are available on the estimation of the composition dependent interdiffusion coefficients, although, the composition dependent tracer diffusion coefficients were reported recently by Gaertner et al. [28]. At present, various theoretical analyses are being established [29–31]. Ideally, the veracity of these methods should be checked with the help of diffusion coefficients estimated following purely experimental methods. This was not possible earlier since the composition dependent diffusion coefficients could not be estimated in a system with more than three components. Therefore, the importance of these new methods demonstrated in this article is unquestionable.

It should be noted here that we are not aiming to study the effect of entropy because of alloying on diffusion rates in this particular study. This needs

additional experiments and the knowledge of other details such as the thermodynamic driving forces. Our aim of this study is to demonstrate a correct method that should be followed which is important at this stage to lay the foundation for future studies.

2.1.3.1. The pseudo-binary (PB) method in NiCoCr system. Ni-Co-Cr alloys fall in the category of medium entropy alloy [5] and a base alloy of various multi-component HEAs in which other components such as Fe, Mn, Al are added with the aim of achieving different desirable properties. It is already demonstrated that equiatomic medium entropy NiCoCr alloy possesses better mechanical strength compared to equiatomic high entropy NiCoCrFeMn alloy [32,33]. In this study, we first demonstrate an approach of estimating the interdiffusion and intrinsic diffusion coefficients in Ni-Co-Cr alloy following the PB method. Before considering the ternary system, we first produced a Ni-Co diffusion couple with pure end members for comparison. The composition

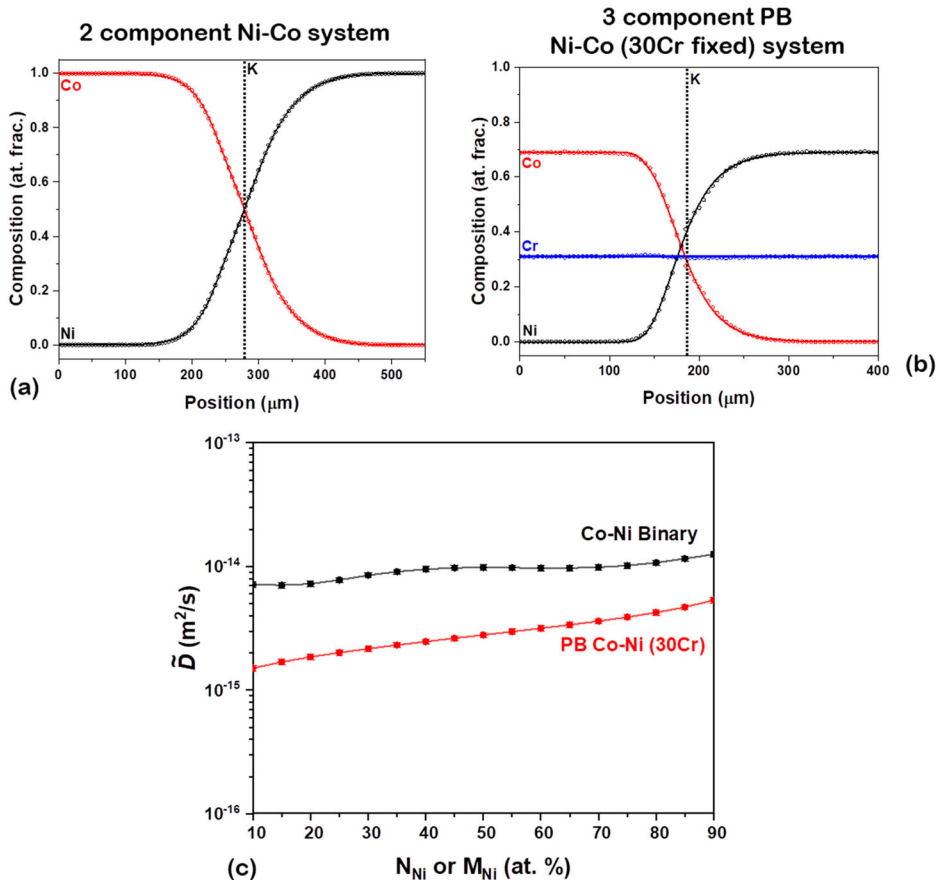


Figure 3. Composition profiles of (a) The binary Ni-Co, (b) pseudo-binary Ni-Co(30at.%Cr) diffusion couples annealed at 1200°C for 50 h 'K' indicates the locations of the Kirkendall marker planes and (c) the comparison of the estimated interdiffusion coefficients.

profile and the location of the marker plane are shown in [Figure 3\(a\)](#). This experiment is conducted at 1200°C and annealed for 50 h. With respect to the composition profile of Ni, we have $N_{Ni}^- = 0$ and $N_{Ni}^+ = 1$ in the binary diffusion couple. Therefore, the interdiffusion coefficients in the binary Co-Ni diffusion couple when plotted such that $N_{Ni}^+ > N_{Ni}^-$ can be estimated utilising Equation (4) from [3]

$$\tilde{D} = \frac{1}{2t} \left(\frac{dx}{dY_{Ni}} \right)_{x^*} \left[(1 - Y_{Ni}^*) \int_{x^-}^{x^*} Y_{Ni} dx + Y_{Ni}^* \int_{x^*}^{x^{+\infty}} (1 - Y_{Ni}) dx \right] \quad (8)$$

The intrinsic diffusion coefficients can be estimated utilising Equation (5) from [3]

$$\begin{aligned} D_{Ni} &= \frac{1}{2t} \left(\frac{\partial x}{\partial N_{Ni}} \right)_K \left[N_{Ni}^+ \int_{x^-}^{x^K} Y_{Ni} dx - N_{Ni}^- \int_{x^K}^{x^{+\infty}} (1 - Y_{Ni}) dx \right] \\ &= \frac{1}{2t} \left(\frac{\partial x}{\partial N_{Ni}} \right)_K \left[\int_{x^-}^{x^K} Y_{Ni} dx \right] \end{aligned} \quad (9a)$$

$$\begin{aligned} D_{Co} &= \frac{1}{2t} \left(\frac{\partial x}{\partial N_{Co}} \right)_K \left[N_{Co}^+ \int_{x^-}^{x^K} Y_{Ni} dx - N_{Co}^- \int_{x^K}^{x^{+\infty}} (1 - Y_{Ni}) dx \right] \\ &= \frac{1}{2t} \left(\frac{\partial x}{\partial N_{Ni}} \right)_K \left[\int_{x^K}^{x^{+\infty}} (1 - Y_{Ni}) dx \right] \end{aligned} \quad (9b)$$

Since $N_{Ni} + N_{Co} = 1$, $dN_{Ni} + dN_{Co} = 0$.

Following we extend our analysis in PB Ni-Co(Cr) diffusion couple with the aim of keeping a certain percentage (30 at.%) of Cr fixed in both the diffusion couples. This is shown in [Figure 3\(b\)](#). This experiment is conducted at 1200°C and annealed for 50 h. A significant decrease in the interdiffusion zone length gives an indication of the decrease in interdiffusion coefficients in the presence of Cr. We prepared the alloys such that the alloy in one end is free from Co and the alloy in another end is free from Ni. The advantage of following such a strategy can be realised immediately especially for the estimation of the intrinsic diffusion coefficients. The modified compositions of Ni can be expressed as $M_{Ni} = N_{Ni}/(N_{Co} + N_{Ni})$ leading to $M_{Ni}^- = N_i^-/(N_{Co} + N_{Ni}) = 0/0.7 = 0$ and $M_{Ni}^+ = N_i^+/(N_{Co} + N_{Ni}) = 0.7/0.7 = 1$. Similarly, we have $M_{Co}^- = 1$, $M_{Co}^+ = 0$.

Utilising these, the interdiffusion coefficients can be estimated from (following Equation (6a))

$$\tilde{D} = \frac{1}{2t} \left(\frac{dx}{dY_{M_{Ni}}} \right) \left[(1 - Y_{M_{Ni}}^*) \int_{x^-}^{x^*} Y_{M_{Ni}} dx + Y_{M_{Ni}}^* \int_{x^*}^{x^{+\infty}} (1 - Y_{M_{Ni}}) dx \right], \quad (10)$$

where $Y_{M_{Ni}} = (M_{Ni} - M_{Ni}^-)/(M_{Ni}^+ - M_{Ni}^-)$.

Similarly, the intrinsic diffusion coefficients following Equation (7) and utilizing the modified compositions can be estimated from

$$D_{Ni} = \frac{1}{2t} \left(\frac{dx}{dM_{Ni}} \right)_K \left[M_{Ni}^+ \int_{x^{-\infty}}^{x^K} Y_{M_{Ni}} dx - M_{Ni}^- \int_{x^K}^{x^{+\infty}} (1 - Y_{M_{Ni}}) dx \right]$$

$$= \frac{1}{2t} \left(\frac{dx}{dM_{Ni}} \right)_K \left[\int_{x^{-\infty}}^{x^K} Y_{M_{Ni}} dx \right] \quad (11a)$$

$$D_{Co} = \frac{1}{2t} \left(\frac{dx}{dM_{Co}} \right)_K \left[M_{Co}^+ \int_{x^{-\infty}}^{x^K} Y_{M_{Ni}} dx - M_{Co}^- \int_{x^K}^{x^{+\infty}} (1 - Y_{M_{Ni}}) dx \right]$$

$$= \frac{1}{2t} \left(\frac{dx}{dM_{Ni}} \right)_K \left[\int_{x^K}^{x^{+\infty}} (1 - Y_{M_{Ni}}) dx \right] \quad (11b)$$

The relations for the intrinsic diffusion coefficients have only one part compared to two parts (inside the bracket) because of preparing the end member alloys such that in one end Co is not there and at another end, Ni is not there in the PB Ni-Co(Cr) diffusion couple. Therefore, the error in the estimation of the intrinsic diffusion coefficients is expected to be less compared to the incremental diffusion couple. This is a good strategy to follow especially in a multi-component system. The estimated interdiffusion coefficients following Equation (8) in Ni-Co binary diffusion couple and following Equation (10) in PB Ni-Co (Cr) diffusion couple are compared in Figure 3(c). It can be seen that there is a decrease in interdiffusion coefficients because of Cr addition. Similarly, the estimated intrinsic diffusion coefficients in binary Ni-Co couple following Equation (9) and in PB Ni-Co (Cr) couple following Equation (11) are listed in Table 5. It can be seen that the interdiffusion coefficients decrease over the whole composition range because of Cr addition. There is a significant difference in the compositions of the Kirkendall marker plane at which the intrinsic diffusion coefficients are estimated. However, if we still compare the data as listed in Table 5, it can be seen that the diffusion rates of both the components are affected equally because of the presence of Cr.

2.1.3.2. The pseudo-binary (PB) method in AlMnNiCoFe system. Very recently, Tsai et al. [34] have shown a superior property in the AlMnNiCoFeCr alloys. However, we concentrated our studies in a five component system in the

Table 5. Estimated diffusion coefficients at the Kirkendall marker plane positions in the Ni-Co(Cr) system at 1200°C.

	Composition (K plane)		\tilde{D}^k ($\times 10^{-15}$ m ² /s)	D_{Co} ($\times 10^{-15}$ m ² /s)	D_{Ni} ($\times 10^{-15}$ m ² /s)
	N_{Co}	(M_{Co}) at. %			
Binary Co-Ni	49.8		9.78 ± 0.4	10.4 ± 0.50	9.07 ± 0.46
PB Co-Ni (Cr Fixed)	27.7	(39.6)	3.11 ± 0.2	3.13 ± 0.17	3.08 ± 0.15

absence of Cr since one of the alloys do not produce a single phase with 10 at.% Al and equiatomic compositions of the rest of the components. Theoretically one can study diffusion in the presence of a phase mixture; however, intentionally, we are avoiding it since the determination of a composition profile in such a situation includes additional error leading to uncertainty in the estimated diffusion coefficients. Further, in this study, our aim is just to show the correct method in a multicomponent HEA. For the sake of comparison, studies are conducted in 3 component 0.10Al-0.10Mn(Ni) and 5 component 0.10Al-0.10Mn(NiCoFe) systems. The composition profiles of the components and the locations of the Kirkendall marker planes are shown in Figure 4(a,b). These are generated at 1100°C after annealing for 25 h. Following a similar approach as described earlier, the interdiffusion coefficients are estimated and shown in Figure 4(c). We found very similar values of the interdiffusion

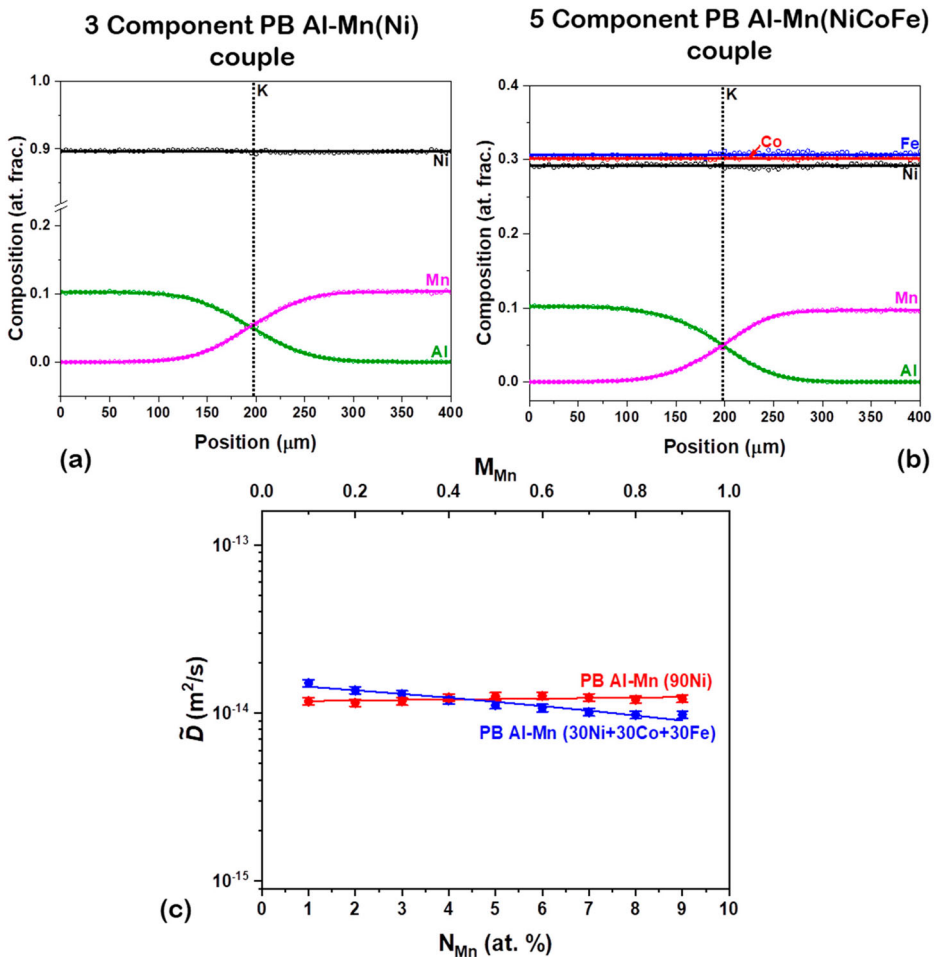


Figure 4. Composition profiles of (a) Al-Mn(Ni), (b) Al-Mn(NiCoFe) PB couples annealed at 1100°C for 25 h 'K' indicates the locations of the Kirkendall marker planes and (c) the estimated interdiffusion coefficients.

coefficients in 3 and 5 component systems and therefore we can conclude that the diffusion rates do not change much because of Co and Fe addition. The same is confirmed by repeating the experiments. Following, the intrinsic diffusion coefficients were estimated as listed in Table 6. It can be seen that there is not much difference in the estimated intrinsic diffusion coefficients as well. The diffusion coefficient of Al increases and the diffusion coefficient of Mn decreases slightly. However, most importantly, it must be apparent that we are able to estimate the composition dependent diffusion coefficients even in a five component system following the PB method, which would not be possible following the conventional method available earlier.

2.2. The concept and practice of following the pseudo-ternary (PT) method

We have demonstrated the estimation of the composition dependent interdiffusion, intrinsic diffusion and impurity diffusion coefficients in the multicomponent system following the PB method in the previous section. These would be impossible following the conventional method. These parameters are important for understanding the underlying atomic mechanism of diffusion. However, the diffusion process in the multicomponent system is far more complex if more than two components are allowed to diffuse. One has to know diffusional interactions among various components *i.e.* the main and the cross interdiffusion coefficients [3].

In this section, we first demonstrate the estimation of these parameters following a conventional ternary (CT) method in a three-component NiCoFe system. Following, we extend our analysis by PT method in a four-component NiCoFeMo system to study the influence of Mo alloying in NiCoFe on composition dependent main and cross interdiffusion coefficients. This would not be possible following the conventional method which was utilised during the last nine decades since it cannot handle more than three components because of stringent mathematical and experimental complexities.

2.2.1. The conventional ternary (CT) diffusion couples in Ni-Co-Fe system

In a ternary system, Equation (1) reduces to

$$\tilde{J}_1 = -\tilde{D}_{11}^3 \frac{1}{V_m} \frac{dN_1}{dx} - \tilde{D}_{12}^3 \frac{1}{V_m} \frac{dN_2}{dx} \quad (12a)$$

Table 6. Estimated diffusion coefficients at the Kirkendall marker plane positions in the Al-Mn (NiCoFe) system at 1100°C.

	Composition (K plane)		\tilde{D}^k ($\times 10^{-14}$ m ² /s)	D_{Al} ($\times 10^{-14}$ m ² /s)	D_{Mn} ($\times 10^{-14}$ m ² /s)
	N_{Al}	(M_{Al}) at. %			
PB Al-Mn (Ni Fixed)	4.83	(48.3)	1.44 ± 0.09	1.39 ± 0.07	1.49 ± 0.07
PB Al-Mn (Ni,Co,Fe Fixed)	5.46	(54.6)	1.39 ± 0.07	1.63 ± 0.08	1.19 ± 0.06

$$\tilde{J}_2 = -\tilde{D}_{21}^3 \frac{1}{V_m} \frac{dN_1}{dx} - \tilde{D}_{22}^3 \frac{1}{V_m} \frac{dN_2}{dx} \tag{12b}$$

$$\tilde{J}_1 + \tilde{J}_2 + \tilde{J}_3 = 0 \tag{12c}$$

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 a Gibb’s triangle [35–37].

A set of diffusion couples (DF1 and DF2) are prepared in the Ni-rich corner of the Ni-Co-Fe system. The experimentally measured and smoothed profiles developed at 1100°C after annealing for 100 h are shown in Figure 5 (a). These are normalised following the steps as discussed during the demonstration of binary and PB diffusion couples. The composition of intersection is found on Gibb’s triangle as $N_{Ni} = 0.93$, $N_{Co} = 0.030$ and $N_{Fe} = 0.040$. The interdiffusion fluxes at this composition are estimated utilising Equation (2). Considering Co as the dependent variable, we have two independent

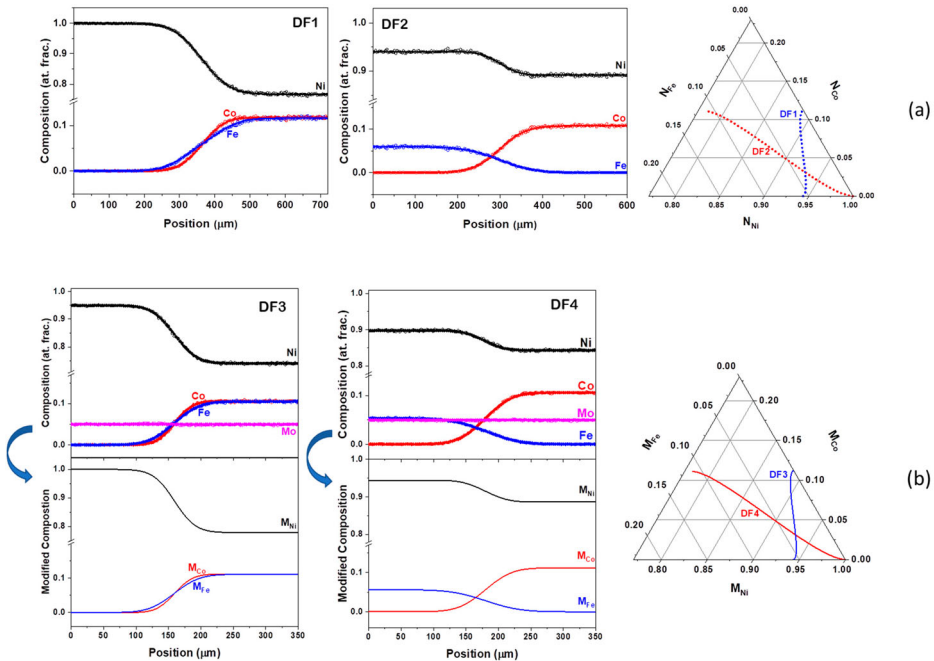


Figure 5. Composition profiles of (a) Ternary and (b) Pseudo-Ternary diffusion couples annealed at 1100°C for 100 h.

interdiffusion fluxes for components Co and Fe from one diffusion couple. Similarly, we estimate two other interdiffusion fluxes of these components at the same composition from another diffusion couple. By relating these four interdiffusion fluxes in Equations (12a,b), we can estimate four interdiffusion coefficients at the composition of the intersection. These are listed in Table 7. It should be noted here that we can estimate the interdiffusion coefficients considering any other component as the dependent variable if stability equations [37] (as mentioned in the supplementary file) are fulfilled. Moreover, different types of interdiffusion coefficients are related by simple equations [3,4]. Now we extend our analysis to the four component Ni-Co-Fe-Mo system to estimate the effect of the presence of Mo on the estimated diffusion coefficients following the PT method.

2.2.2. The pseudo-ternary (PT) diffusion couples in the Ni-Co-Fe-Mo system

The concept of the pseudo-ternary (PT) diffusion couples are established based on the expectation that only three components would develop the diffusion profiles keeping all other components the constant in both the diffusion couples. In this study, Mo was kept constant in all the alloys and indeed this component is found to remain constant in both the diffusion couples, as shown in Figure 5(b). These are generated at 1100°C after annealing for 100 h. Following, the concept explained already, we calculate the modified composition profiles after converting the composition to

$$M_i = \frac{N_i}{N_v} = \frac{N_i}{N_{Ni} + N_{Co} + N_{Fe}} \quad (13a)$$

The fixed composition $N_f = N_{Mo}$, such that we have $N_v + N_f = 1$

This leads to

$$M_{Ni} + M_{Co} + M_{Fe} = 1 \quad (13b)$$

The composition and modified composition profiles are shown in Figure 5(b). This intersection is found at $M_{Ni} = 0.93$, $M_{Co} = 0.031$ and $M_{Fe} = 0.039$. The corresponding actual compositions can be recalculated following Equation (13a) as $N_{Ni} = 0.88$, $N_{Co} = 0.030$ and $N_{Fe} = 0.037$ and $N_{Mo} = 0.05$. The interdiffusion fluxes at this composition can be estimated utilising Equation (6b).

Table 7. Interdiffusion coefficients estimated following the ternary and pseudo-ternary methods at 1100°C.

	$\tilde{D}_{NiNi}^{Co} (\times 10^{-15} \text{ m}^2/\text{s})$	$\tilde{D}_{NiFe}^{Co} (\times 10^{-15} \text{ m}^2/\text{s})$	$\tilde{D}_{FeFe}^{Co} (\times 10^{-15} \text{ m}^2/\text{s})$	$\tilde{D}_{FeNi}^{Co} (\times 10^{-15} \text{ m}^2/\text{s})$
Ternary Ni-Co-Fe	4.41 ± 0.22	-2.96 ± 0.16	6.89 ± 0.35	-0.66 ± 0.06
Pseudo-Ternary Ni-Co-Fe (Mo)	0.50 ± 0.03	0.25 ± 0.02	1.79 ± 0.09	0.59 ± 0.04

These are then related by the equations with the interdiffusion coefficients after modifying Equations (12) as

$$\tilde{J}_1 = -\tilde{D}_{11}^3 \frac{1}{V_m} \frac{dM_1}{dx} - \tilde{D}_{12}^3 \frac{1}{V_m} \frac{dM_2}{dx} \quad (14a)$$

$$\tilde{J}_2 = -\tilde{D}_{21}^3 \frac{1}{V_m} \frac{dM_1}{dx} - \tilde{D}_{22}^3 \frac{1}{V_m} \frac{dM_2}{dx} \quad (14b)$$

$$\tilde{J}_1 + \tilde{J}_2 + \tilde{J}_3 = 0 \quad (14c)$$

since $\tilde{J}_4 = 0$ and $(dN_4)/dx = (dM_4)/dx = 0$.

Considering Co as the dependent variable, the estimated interdiffusion coefficients are listed in Table 7. Therefore, we could estimate the main and cross interdiffusion coefficients in a 4 component system, which would be impossible otherwise following the conventional method [38].

3. Discussion

One of the important needs of any type of studies in the multicomponent system is the availability of a method following which one can compare the change in properties because of the addition of components. As explained in Ref. [3,4] (see the supplementary file), the estimation of any diffusion coefficients was not possible experimentally following the conventional method in an inhomogeneous system with more than three components fulfilling the mathematical equations established based on the Onsager formalism. It is almost impossible to intersect the composition profiles of three different diffusion couples at one single composition in a four-component space because of unknown diffusion paths, which cannot be predicted *a priori* [3,37]. The interdiffusion coefficients can be estimated in a ternary system; however, it is very difficult to generate composition dependent interdiffusion coefficients systematically since diffusion paths may follow serpentine, double serpentine or tortuous paths. The composition of the intersection of two diffusion couples (at which these parameters can be estimated) cannot be predicted *a priori* even if a set of diffusion couples are prepared with systematic variations of end member compositions. Different types of diffusion paths are discussed extensively by different research groups [39–42]. Moreover, the intrinsic diffusion coefficients can be estimated only in a binary system but not even in a ternary system since the marker planes should be located at the composition of intersection in both the diffusion couples, which is almost impossible to achieve unless found incidentally in a particular set of diffusion couples [3].

These problems were faced by the diffusion community during the last nine decades. Many attempts were made by various groups for developing new methods but with mixed success. One of the experimental approaches worth

mentioning is the method developed by Dayananda and Shon [43] for the estimation of the average main and cross interdiffusion coefficients over a composition range. The major advantage of this method is that it can be used in a system with any number of components. However, these values are average of a composition range of random choice and therefore do not carry similar importance or the physical significance of the composition-dependent diffusion coefficients. These issues are discussed in detail in Ref. [16]. Still, this method was used frequently since there were no other options for the experimentalists. Many theoretical analyses are also reported from time to time; however, could not be validated because of the lack of experimentally estimated data. In this regard, the PB and PT methods explained in this article solves the unsolved after nine decades. Most importantly, at present, these are the only pure experimental methods following which one can estimate all types of composition-dependent diffusion coefficients in a multicomponent system.

The benefits of following the PB method can be understood immediately based on the estimated diffusion coefficients in the CoNiFeMo system, as shown in Figure 2 and Tables 1 and 2. The estimated diffusion coefficients help to understand the effect of the addition of a component in an alloy systematically. It can be seen that there is not much difference in the estimated interdiffusion coefficients in the presence of Co in the Ni-Fe system. Interdiffusion coefficients of Ni-Co decrease a bit in the presence of Fe. Interdiffusion coefficients decrease significantly in both the systems because of the addition of Mo. This indicates that the addition of Mo might have decreased the concentration of vacancies and/or the thermodynamic forces for diffusion. We could not only measure the composition dependent interdiffusion coefficients very systematically, but we could also estimate the intrinsic diffusion coefficients which would not be possible following the previously available conventional methods even in a ternary system. A similar analysis is followed in the systems related to medium and high entropy for the first time showing the systematic estimation of both the interdiffusion and intrinsic diffusion coefficients.

As already mentioned, one of the main characteristics of the PB diffusion couple is that only two components develop the diffusion profiles. It further means that the experiments are designed such that cross interdiffusion coefficients are forced to zero and the main interdiffusion coefficients of both the components become equal leading to the same value of the interdiffusion coefficients when estimated utilising any of the components. However, the knowledge of the main and cross interdiffusion coefficients are important which highlight the interactions among components and for understanding the compositional (diffusion path) and microstructural evolution. In many systems, in a particular composition range, cross terms might dominate over the main terms [35]. With this need, the concept of the PT diffusion couples is developed utilising which we can estimate both the parameters in a multicomponent system, as already explained in the previous section. We first explained the estimation of the

diffusion parameters in a ternary system (NiCoFe) and then in a quaternary system keeping an additional component (Mo) fixed throughout. As already mentioned, the PT method makes the estimation of these diffusion coefficients possible, which is otherwise impossible in a quaternary system. Similarly, one can follow a similar method in a system with even a higher number of components.

Additionally, the concept of this PT method automatically gives a possibility of designing the experiments such that one can study the influence or the addition of other components on the interdiffusion coefficients systematically. This is explained in Figures 5 and 6. In this study, the end member alloys for the CT and PT diffusion couples are designed with the expectation that we have comparable compositions (and modified compositions) of the intersection. These are indeed found from the Figure 6 at

$$N_{\text{Ni}} = 0.93; N_{\text{Co}} = 0.030; N_{\text{Fe}} = 0.040 \text{ (in CT couple)}$$

$$M_{\text{Ni}} = 0.93; M_{\text{Co}} = 0.031; M_{\text{Fe}} = 0.039 \text{ (in PT couple)}$$

It can be seen that the difference in equivalent compositions of intersections is around 0.1 at.%, which we consider to be very similar. This allows us to compare the data as listed in Table 7 measured by the CT and PT methods. The estimated values indicate that the main and cross interdiffusion coefficients have the opposite sign. One can understand this from Equation (12) considering the sign of composition gradients. For positive values of the main and negative values of cross terms, the total interdiffusion flux will decrease when Ni and Fe diffuse in the same direction *i.e.* when they have the same sign of composition gradients (for example in DF1). This discussion is true for the downhill diffusion of both the components. Similarly, the total interdiffusion flux will increase when they diffuse in the opposite direction *i.e.* when they have the opposite sign of composition gradients (for example in DF2). Since both the cross terms become positive in the presence of Mo in the NiCoFe(Mo) PT diffusion couples, the opposite argument is true in such a situation. Additionally, it is already known that the composition of intersection depends on various factors and not easy to

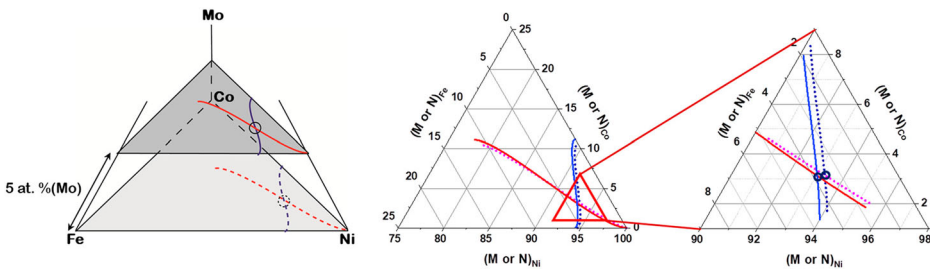


Figure 6. The comparison of compositions of intersections in ternary (dotted lines) and pseudo-ternary (solid lines) diffusion couples annealed at 1100°C for 100 h.

predict [3,4]. However, we managed to get a very close equivalent composition in CT and PT diffusion couples by considering a small composition range and by preparing the end member alloys in a certain way leading to a successful comparison of the data.

4. Conclusions

We have demonstrated the benefits of using newly developed PB and PT methods in few systems for estimation of the composition dependent diffusion coefficients in multicomponent systems which were considered impossible previously based on purely experimental methods. The PB method should be followed with the aim of understanding the atomic mechanism of diffusion by estimating the intrinsic and impurity diffusion coefficients in correlation with thermodynamic driving forces (if known) and concentration of defects assisting the diffusion process. One can even estimate the tracer diffusion coefficients if the thermodynamic parameters are available or estimated. On the other hand, the PT method should be followed to understand the diffusional interactions between components.

In this study, only the ideal diffusion profiles fulfilling the requirements of the concept behind PB and PT methods are shown. As already mentioned, in an ideal PB couple, only two components should develop the diffusion profiles keeping all other components the constant throughout. Similarly, in an ideal PT couple, only three components are expected to develop the diffusion profiles keeping all other components the constant. These simplify the equations facilitating the estimation of different types of composition-dependent diffusion coefficients.

With respect to the limitations of these studies, there can be mainly two types of problems to be faced leading to the developments of non-ideal diffusion profiles. If these deviations are minor one can still estimate the diffusion coefficients but only after correct normalisation method, which otherwise will lead to the generation of data without any physical significance [15,16]. In the case of severe non-ideal diffusion profiles, experiments should be changed with a different strategy. These are explained in detail below:

(I) *A difference in compositions of the component(s) in the end members which are supposed to remain constant:*

Practically, it is not very difficult to melt an alloy with (almost) the desired composition. However, with the increase in the number of components and in the presence of relatively volatile components during melting, this sometimes becomes a bit difficult. This is the reason that initially we considered the NiCo-FeMo system, which is much easier to handle. This system helped us to demonstrate the concept behind the PB and PT methods by generating ideal diffusion profiles. When we switched to the NiCoFeAlMn HEA, we could not produce the

alloys exactly as desired in the first attempt. In another attempt, we could produce the alloys as desired and subsequently generated a reasonably good PB couple as already shown in Figure 4.

To discuss this problem further, let us consider the Al-Mn(NiCoFe) diffusion couple that was produced first but we did not consider it for the estimation of the diffusion coefficients. This profile is shown in Figure 7(a). The three components Ni, Co, Fe were planned to be kept constant with equal compositions at the ends of diffusion couples. However, one can find a difference in compositions of Ni and Fe at two ends of the diffusion couple. Therefore, it is apparent that Ni and Fe have created a (minor) diffusion profile, which should have influenced the interdiffusion flux of Al and Mn. One of the influences must be clear from the non-symmetric nature of diffusion profiles as marked on the figure, which will lead to $\tilde{J}_{Al} + \tilde{J}_{Mn} \neq 0$. Therefore, these do not fulfil the conditions of the PB diffusion couple of Al and Mn. If the diffusion coefficients are to be estimated utilising these profiles without any correction, these will give two different values at one particular composition. In such a situation, one should not utilise the concept of the PB couple without following a proper normalisation step. As a first step, a fixed and average value of the Fe, Ni, and Co should be plotted, as shown in Figure 7(b). At this point, the total of $N_T = \sum_{i=1}^n N_i \neq 1$. Following the profiles of Al and Mn should be normalised by N_i/N_T leading to

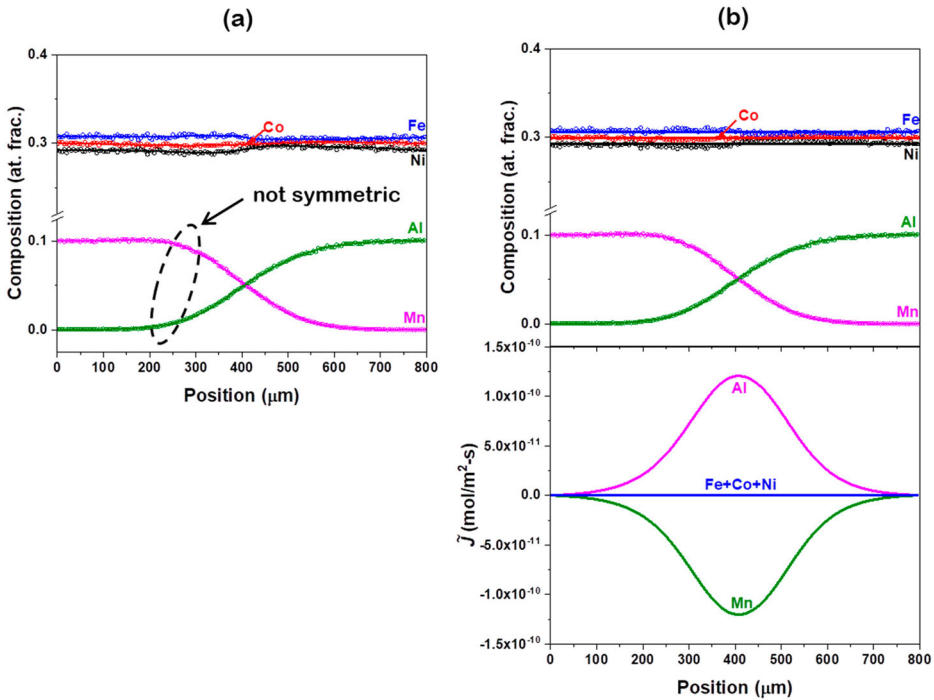


Figure 7. (a) As measured (b) Normalised composition profiles and the interdiffusion fluxes in Al-Mn(NiCoFe) non-ideal pseudo-binary diffusion couple annealed at 1100°C for 50 h.

$M_{Al} + M_{Mn} = 1$, $\tilde{J}_{Al} + \tilde{J}_{Mn} = 0$. This will give the same value of the interdiffusion coefficients (with certain error) at a particular composition irrespective of the composition profile considered. However, we did not estimate data from this couple since we have produced a better diffusion couple after remelting the alloys, as shown in [Figure 4\(b\)](#).

There are practically two ways by which this problem can be avoided since it is very difficult to produce alloys with exactly the desired compositions and without even a very minor deviation. If the deviation is very minor, one can normalise the profiles following the method as described above for the estimation of the diffusion coefficients. In the case of major deviation, the alloys should be remelted for a better average composition. Irrespective of the type of (volatile or non-volatile) components used, one can still produce an alloy with the desired composition if a proper and repeated effort is made. In many applications, alloys are frequently produced with the almost desired composition to achieve a good property balance. There is no reason why it cannot be achieved here. Therefore, this issue is solvable and should not be considered as a real problem.

(II) *Presence of uphill diffusion of the components which are supposed to remain constant:*

As already mentioned, the PB and PT couples are prepared with the expectations that only 2 components in PB and 3 components in PT should produce the diffusion profiles keeping other components as the constant. However, just keeping the compositions of a component the same in both the ends may not produce a constant diffusion profile in the interdiffusion zone. Frequently, the presence of uphill diffusion might be witnessed which is driven by thermodynamic parameters and the diffusion coefficients, which are not known in most of the multi-component systems and therefore cannot be predicted *a priori*. Two pieces of evidence of such type are shown in [Figure 8\(a,b\)](#) in which cross interdiffusion coefficients are not zero because of the presence of uphill diffusion of the components which supposed to remain constant. In [Figure 8\(a\)](#), Mo has a small uphill profile. We, therefore, cannot utilise the equations of PB couple for the estimation of the interdiffusion coefficients using the profiles as it is. In this situation, after following the mandatory step of smoothening (as described previously during the explanation of the CB and PB methods utilising ideal or near ideal profiles), an additional step to be followed to make the Mo profile constant with an average value. Following, the diffusion profiles of Ni and Fe should be modified such that again we have $N_T = \sum_{i=1}^n N_i = 1$ before estimating the interdiffusion coefficients utilising the equations related to the PB method. The modified interdiffusion fluxes are shown on the same plot along with actual interdiffusion fluxes. It can be seen that the difference is not very high and the estimated data may not include a high error. This much difference is also frequently noticed when an experiment is repeated. It also should be noted that there is another source of error automatically included. In the

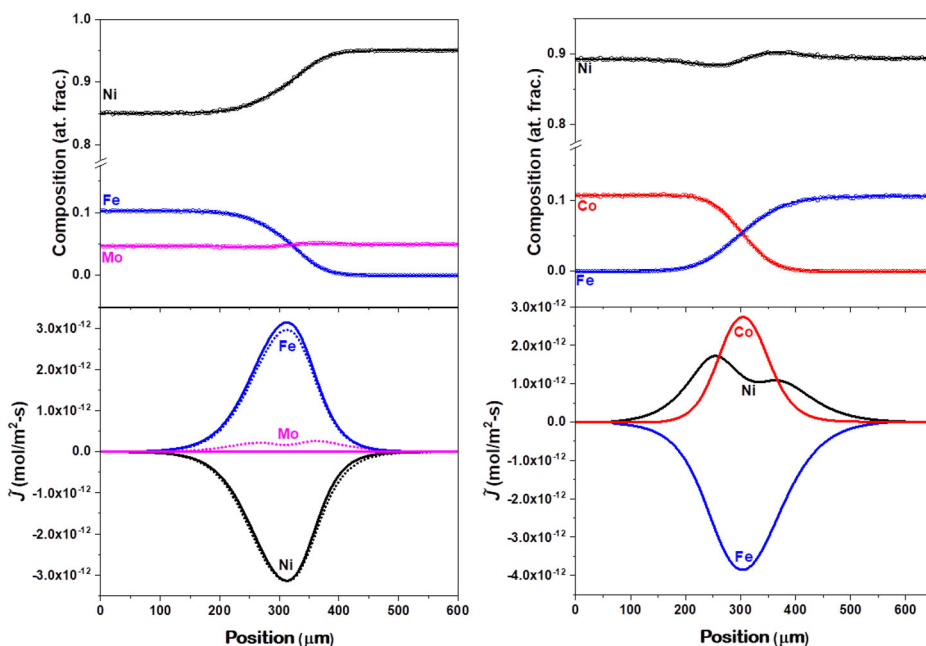


Figure 8. (a) Ni-Fe(Mo) pseudo binary diffusion couple with minor uphill diffusion of Mo showing a small difference between actual (dotted lines) and modified (solid lines) interdiffusion fluxes of Fe and Ni. (b) Fe-Co(Ni) pseudo-binary diffusion couple with major uphill diffusion of Ni. Both the couples are annealed at 1100°C for 100 h.

absence of uphill diffusion, the interdiffusion zone length would be different. We have not estimated the data in this diffusion couple since we have considered only the ideal diffusion profiles to demonstrate the PB and PT methods in this article.

Another profile is shown in Figure 8(b), although Ni is fixed in end member composition, it has the uphill diffusion in the interdiffusion zone. The plot of interdiffusion fluxes shows how this has affected the diffusion profile of Fe and Co differently. The range of uphill diffusion must be clear from the estimated interdiffusion flux of Ni and this profile should not be considered for estimation of the diffusion coefficients by imposing the concept of PB diffusion couple. One should ideally use the conventional ternary method for the estimation of the main and cross interdiffusion coefficients.

The two types of problems discussed with respect to PB couples could be witnessed frequently in various PT couples. We are currently involved in analysing the level of error introduced in such a situation based on theoretical calculations and will be reported in future. These will be analysed based on various non-ideal situations, which are currently being generated by us in many different systems to demonstrate up to what extent of deviation can be considered as minor. It is true that we cannot use these methods when the level of non-ideality because of uphill diffusion is very high. However, we have witnessed several times (not yet

published) that one may get good profiles by avoiding the composition range showing the uphill diffusion.

One cannot deny the impact of these newly developed methods in diffusion studies, especially because there are plenty of examples in which ideal or near ideal profiles are developed. The main aim of this work is to lay the foundation of the PB and PT methods for the analysis of multicomponent diffusion which was otherwise believed to be impossible during the last many decades. We have successfully demonstrated the benefits of following PB and PT methods in multicomponent diffusion to examine the role of alloying on diffusion coefficients. We have shown the correct analysis in the medium and high entropy alloys for the first time. Additionally, the newly developed numerical methods can be verified with the experimentally estimated diffusion coefficients, which was not possible earlier. Following, these numerical methods can be extended in the case of non-ideal PB and PT diffusion profiles. Most importantly, these PB and PT methods lease a new life in the field of multicomponent diffusion. The dataset generated in a combination of experimental and numerical analysis in different multicomponent systems will help to understand various physical and mechanical properties. This is even more important today because of the thrust of developing new multicomponent materials in various applications.

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References

- [1] L. Onsager, *Reciprocal relations in irreversible processes. I.* Phys. Rev. 37 (1931), pp. 405–426.
- [2] L. Onsager, *Reciprocal relations in irreversible processes. II.* Phys. Rev. 38 (1931), pp. 2265–2279.
- [3] A. Paul, T. Laurila, V. Vuorinen, and S.V. Divinski, *Thermodynamics, Diffusion and the Kirkendall Effect in Solids*, Springer International Publishing, Cham, 2014.
- [4] A. Paul and S. Divinski (eds.), *Handbook of Solid State Diffusion: Volume 1: Diffusion Fundamentals and Techniques*, Elsevier, Amsterdam, The Netherlands, 2017.

- [5] B.S. Murty, J.W. Yeh and S. Ranganathan, *High-entropy Alloys*, Butterworth-Heinemann, Oxford, UK, 2014.
- [6] D.B. Miracle and O.N. Senkov, *A critical review of high entropy alloys and related concepts*. Acta Mater. 122 (2017), pp. 448–511.
- [7] O.N. Senkov, D.B. Miracle, K.J. Chaput and J.-P. Couzinie, *Development and exploration of refractory high entropy alloys—A review*. J. Mater. Res. 33 (2018), pp. 3092–3128.
- [8] A. Paul, *A pseudobinary approach in multicomponent interdiffusion and the Kirkendall effect in multicomponent systems*. Philos. Mag. 93 (2013), pp. 2297–2315.
- [9] N. Esakkiraja and A. Paul, *A novel concept of pseudo ternary diffusion couple for the estimation of diffusion coefficients in multicomponent systems*. Scr. Mater. 147 (2018), pp. 79–82.
- [10] P. Kiruthika and A. Paul, *A pseudo-binary interdiffusion study in the β -Ni(Pt)Al phase*. Philos. Mag. Lett. 95 (2015), pp. 138–144.
- [11] P. Kiruthika, S.K. Makineni, C. Srivastava, K. Chattopadhyay and A. Paul, *Growth mechanism of the interdiffusion zone between platinum modified bond coats and single crystal superalloys*. Acta Mater. 105 (2016), pp. 438–448.
- [12] K.Y. Tsai, M.H. Tsai and J.W. Yeh, *Sluggish diffusion in Co–Cr–Fe–Mn–Ni high-entropy alloys*. Acta Mater. 61 (2013), pp. 4887–4897.
- [13] S. Tripathi, V. Verma, T.W. Brown and K.N. Kulkarni, *Effect of small amount of manganese on the interdiffusivities in Fe–Al alloys*. J. Phase Equilib. Diffus. 38 (2017), pp. 135–142.
- [14] M. Vaidya, G. Mohan Muralikrishna, S.V. Divinski and B.S. Murty, *Experimental assessment of the thermodynamic factor for diffusion in CoCrFeNi and CoCrFeMnNi high entropy alloys*. Scr. Mater. 157 (2018), pp. 81–85.
- [15] A. Paul, *Comments on “sluggish diffusion in Co–Cr–Fe–Mn–Ni high-entropy alloys” by K.Y. Tsai, M.H. Tsai and J.W. Yeh*. Acta Mater. 61 (2013), pp. 4887–4897. Scripta Mater. 135 (2017), pp. 153–157.
- [16] S.V. Divinski, A.V. Pokoev, N. Esakkiraja and A. Paul, *A Mystery of “sluggish diffusion” in high-entropy alloys: The Truth or a Myth?* Diff. Found. 17 (2018), pp. 69–104.
- [17] S. Santra and A. Paul, *Role of the molar volume on estimated diffusion coefficients*. Metall. Mater. Trans. A 46 (2015), pp. 3887–3899.
- [18] F. Sauer and V. Freise, *Diffusion in binären Gemischen mit Volumenänderung*. Z. Elektrochemie 66 (1962), pp. 353–362.
- [19] V.A. Baheti and A. Paul, *Development of different methods and their efficiencies for the estimation of diffusion coefficients following the diffusion couple technique*. Acta Mater. 156 (2018), pp. 420–431.
- [20] S.B. Jung, T. Yamane, Y. Minamino, K. Hirao, H. Araki and S. Saji, *Interdiffusion and its size effect in nickel solid solutions of Ni–Co, Ni–Cr and Ni–Ti systems*. J. Mater. Sci. Lett. 11 (1992), pp. 1333–1337.
- [21] F.J.J. van Loo, *On the determination of diffusion coefficients in a binary metal system*. Acta Metall. 18 (1970), pp. 1107–1111.
- [22] C. Ghosh and A. Paul, *A physico-chemical approach in binary solid-state interdiffusion*. Acta Mater. 55 (2007), pp. 1927–1939.
- [23] H. Bakker, J. Backus and F. Waals, *A curvature in the arrhenius plot for the diffusion of iron in single crystals of nickel in the temperature range from 1200 to 1400°C*. Phys. Status Solidi B 45 (1971), pp. 633–638.
- [24] A.B. Vladimirov, V.N. Kaygorodov, S.M. Klotsman and I.S. Trakhtenberg, *Bulk diffusion of cobalt and tungsten in nickel*. Phys. Met. Metallogr. 46 (1978), pp. 94–101.
- [25] A.D. LeClaire and G. Neumann, *Ni group metals*, in *Diffusion in Solid Metals and Alloys*, H. Mehrer, ed., Springer, Heidelberg, 1990. pp. 132–136.

- [26] K.-Y. Tsai, M.-H. Tsai and J.-W. Yeh, *Reply to comments on “sluggish diffusion in Co-Cr-Fe-Mn-Ni high-entropy alloys”*. Scr. Mater. 135 (2017), pp. 158–159.
- [27] K. Kulkarni and G.P.S. Chauhan, *Investigations of quaternary interdiffusion in a constituent system of high entropy alloys*. AIP. Adv. 5 (2015), p. 097162.
- [28] D. Gaertner, K. Abrahams, J. Kottke, V.A. Esin, I. Steinbach, G. Wilde and S.V. Divinski, *Concentration-dependent atomic mobilities in FCC CoCrFeMnNi high-entropy alloys*. Acta Mater. 166 (2019), pp. 357–370.
- [29] D.L. Beke and G. Erdélyi, *On the diffusion in high-entropy alloys*. Mater. Lett. 164 (2016), pp. 111–113.
- [30] W. Kucza, J. Dąbrowa, G. Cieślak, K. Berent, T. Kulik and M. Danielewski, *Studies of “sluggish diffusion” effect in Co-Cr-Fe-Mn-Ni, Co-Cr-Fe-Ni and Co-Fe-Mn-Ni high entropy alloys; determination of tracer diffusivities by combinatorial approach*. J. Alloys Compd. 731 (2018), pp. 920–928.
- [31] W. Chen and L. Zhang, *High-Throughput determination of interdiffusion coefficients for Co-Cr-Fe-Mn-Ni high-entropy alloys*. J. Phase Equilib. Diffus. 38 (2017), pp. 457–465.
- [32] B. Uzer, S. Picak, J. Liu, T. Jozaghi, D. Canadinc, I. Karaman, Y.I. Chumlyakov and I. Kireeva, *On the mechanical response and microstructure evolution of NiCoCr single crystalline medium entropy alloys*. Mater. Res. Lett. 6 (2018), pp. 442–449.
- [33] Z. Zhang, H. Sheng, Z. Wang, B. Gludovatz, Z. Zhang, E.P. George, Q. Yu, S.X. Mao and R.O. Ritchie, *Dislocation mechanisms and 3D twin architectures generate exceptional strength-ductility-toughness combination in CrCoNi medium-entropy alloy*. Nat. Commun. 8 (2017), p. 14390.
- [34] M.T. Tsai, J.C. Huang, P.H. Lin, T.Y. Liu, Y.C. Liao, J.S.C. Jang, S.X. Song and T.G. Nieh, *Creep of face-centered-cubic {111} and {100} grains in FeCoNiCrMn and FeCoNiCrMnAl alloys: Orientation and solid solution effects*. Intermetallics 103 (2018), pp. 88–96.
- [35] V.D. Divya, U. Ramamurty and A. Paul, *Interdiffusion and solid solution strengthening in Ni-Co-Pt and Ni-Co-Fe ternary systems*. Philos. Mag. 93 (2013), pp. 2190–2206.
- [36] J.S. Kirkaldy, *Diffusion in multicomponent metallic systems*. Can. J. Phys. 35 (1957), pp. 435–440.
- [37] J.S. Kirkaldy and D.J. Young, *Diffusion in The Condensed State*, Institute of Metals United Kingdom 35, 1987.
- [38] R.T. DeHoff and N. Kulkarni, *The trouble with diffusion*. Mater. Res. 5 (2002), pp. 209–229.
- [39] M.S. Thompson and J.E. Morral, *The effect of composition on interdiffusion in ternary alloys*. Acta Metall. 34 (1986), pp. 339–346.
- [40] F.J.J. Loo, G.F. Bastin and J.W.G.A. Vrolijk, *A practical solution for the diffusion equations in binary and multicomponent systems with constant intrinsic diffusion coefficients*. Metall. Mater. Trans. A 18 (1987), pp. 801–809.
- [41] K.J. Rönkä, A.A. Kodentsov, P.J.J. Van Loon, J.K. Kivilahti and F.J.J. Van Loo, *Thermodynamic and kinetic study of diffusion paths in the system Cu-Fe-Ni*. Metall. Mater. Trans. A 27 (1996), pp. 2229–2238.
- [42] Y.E. Ugaste, A.A. Kodentsov and J. Priimets, *Investigation of interdiffusion and kirken-dall effect in the Co-Ni-Fe system: III. Dependence of diffusion parameters on the initial conditions*. Phys. Met. Metallogr. 110 (2010), pp. 485–491.
- [43] M.A. Dayananda and Y.H. Sohn, *A new analysis for the determination of ternary inter-diffusion coefficients from a single diffusion couple*. Metall. Mater. Trans. A 30 (1999), pp. 535–543.