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Snapshot Reviews in Emerging Fields

Diffusion in High Entropy Alloy Systems – *A Review*

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ABSTRACT

High entropy alloys (HEAs) represent a class of multicomponent alloys that have garnered significant attention within materials community over the past two decades, largely due to their potential for high-temperature applications. It is essential to comprehend the diffusion behavior within these systems as it forms the foundational basis for designing and developing materials for specific uses, especially in high-temperature applications where the sluggish diffusion effect plays a pivotal role in enhancing material properties. Nevertheless, the existence and extent of the sluggish diffusion effect in these materials have been vigorously debated. Our understanding of this effect in HEAs remains limited, primarily because practical techniques for determining multicomponent diffusion behavior are lacking. This is also the reason that the data on diffusion in quaternary and higher-order systems are scarce in the literature. This review provides an overview of the present state-of-the-art in diffusion studies within the context of HEAs and explores the potential methodologies. Although the existence of sluggish diffusion in HEAs has been a topic of intense debate, there is currently insufficient experimental evidence to support its presence. Consequently, the review explores potential future research directions that aim to fill the gaps in our understanding of this area.

1. Introduction

The need for a comprehensive understanding of diffusion behavior in multicomponent alloys with non-dilute compositions is evident. The existing challenge arises from the limited availability of practical techniques for determining diffusion coefficients in such systems, particularly in quaternary and higher-order compositions, which necessitates ongoing efforts within the literature. This significance stems from the widespread use of multicomponent materials in various industrial applications, underscoring the fundamental importance of comprehending their diffusion characteristics. While well-established methodologies have successfully measured composition-dependent diffusion coefficients in binary and ternary systems [1,2] it becomes increasingly intricate when extending these analyses to higher-order systems beyond ternary. This complexity arises due to a myriad of constraints encountered in experimental, theoretical, and numerical approaches. Consequently, this review paper's principal objective is to assess the existing diffusion studies and discuss potential methodologies for quantitatively characterizing diffusion in multicomponent non-dilute alloys, commonly denoted as High Entropy Alloys (HEAs).

High Entropy Alloys (HEAs) are multi-principal multicomponent alloys composed of elements in an equimolar or near equimolar ratio. They may exhibit a simple solid solution or a mixture of simple phases [3,4,5]. These alloys have been the subject of significant

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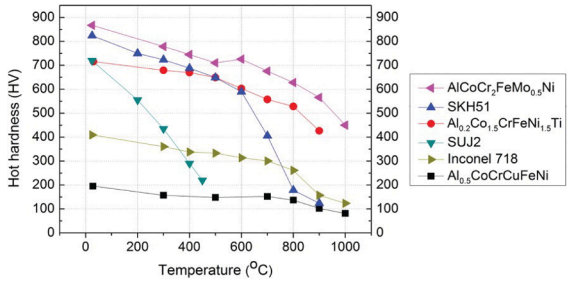

Fig. 1. Hardness as a function of temperature for various HEAs compared to conventional alloys, reprinted with permission from Tsai et al. [11].

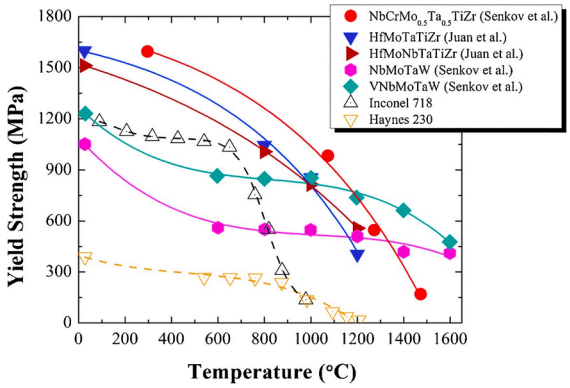

Fig. 2. Yield strength as a function of temperature for various HEAs compared to conventional super-alloys, reprinted with permission from Ye et al. [12].

research interest in the materials community over the past two decades, as they provide many opportunities for designing high-performing alloys with simple microstructures [6,7]. Traditionally, it was believed that an increase in the number of components would increase the complexity of the microstructure. However, the discovery of HEAs has challenged this belief and opened new possibilities for the design of high-performance alloys.

During the last decade, the definition of HEAs has evolved, and at present, they are defined as alloys containing four or more principal components, with their concentration ranging from 5 to 35 atomic %. HEAs are thought to possess high configurational entropy, which helps stabilize these alloys' simple phases. However, the study reported by Zhang et al. [8] proposed that the entropy of mixing alone may not consistently lead to a reduction in Gibbs free energy. Otto et al. [9] also suggested that increased configurational entropy might not stabilize the single phase in all alloys, as its effect may not be substantial enough to overcome the driving forces that promote the formation of secondary phases. Furthermore, recent research [9,10] indicates that the enthalpy of mixing also plays a significant role in the stabilization of these HEAs. Nevertheless, one of the most fascinating aspects of these alloys is their exceptional properties, including good thermal stability, high hardness and wear resistance, excellent high-temperature strength, and corrosion resistance. Numerous studies have reported these properties and plotted for comparison against conventional alloys in Figs. 1 and 2 from Tsai et al. and Ye et al., respectively [11,12].

The outstanding properties of HEAs offer new possibilities for applications in the aerospace, automotive, and energy industries. When first reported, these remarkable properties were initially attributed to a hypothesized set of fundamental phenomena known as the four core effects, which included the high entropy effect, severe lattice distortion, the cocktail effect, and sluggish diffusion kinetics [6]. Since the origin of HEAs, these core effects have been heavily debated in the community, and most of the recent literature disputes the existence of the suggested initial four core effects.

While there are ongoing debates regarding these four core effects, further research is needed to enhance our understanding and develop a more comprehensive knowledge base of HEAs' behavior and potential applications. Among these four effects, sluggish diffusion kinetics is believed to be responsible for the structural and thermal stability and exceptional mechanical properties observed in these systems. Currently, sluggish diffusion behavior in HEAs is the most controversial topic in the research community regarding this class of materials, as reported in several studies [13,14,15,16].

The hypothesis of sluggish diffusion was first proposed in 2004, based purely on qualitative observations of slow precipitation, grain growth, and phase transformation kinetics in these alloys [3,17,18,19]. Table 1 summarizes the main findings of studies [3,17,18,19] used to hypothesize the sluggish diffusion behavior in HEAs. According to some researchers, the formation of coarser precipitates and the phase transformations in HEAs requires a cooperative motion and redistribution of different elements, which is hindered by the distorted lattices observed in these alloys. This led to the development of the sluggish diffusion hypothesis.

Table 1
Key findings of the reports which hypothesized sluggish diffusion behavior in HEAs.

System	Key Findings	Ref.
CuCoNiCrAl$_x$Fe	The ultra-finely spaced and modulated structure was observed in the as-cast CuCoNiCrAlFe equimolar alloy, resulted from spinodal decomposition within which crystallites precipitated at sizes of only several nanometers. On the contrary, similar nanocrystalline structures are rarely seen in the corresponding states of conventional alloys or bulk amorphous alloys, which require special heat treatments to produce nano sized precipitates. Based upon that they have concluded the sluggish diffusion behavior in HEAs.	[3]
AlxCoCrCuFeNi	Ultrafine precipitates were observed in the matrix of the AlxCoCrCuFeNi alloy system. These precipitates are nanoscale in size but not as coarse as those often found in traditional cast alloys. Based upon that they have concluded the sluggish diffusion behavior in HEAs.	[17]
(AlCrMoSiTi)N	A reactive DC magnetron sputtering technique is used to deposit nitride films from a single equiatomic AlCrMoSiTi target. The as-deposited phase, grain size, and lattice constant of the coatings remain unchanged even after annealing in vacuum at 1173 K for 5 h. The high mixing entropy and sluggish diffusion of the multi-component coatings are believed to contribute to the thermal stability of the microstructure.	[18]
Al0.5CoCrCuFeNi	A set of thermo-mechanical treatments were conducted to investigate the stability of the phases in the high-entropy alloy Al0.5CoCrCuFeNi. The phase constitution in the alloy after annealing at 1100 °C was found to be identical to that in the as-cast alloy. The slow diffusion kinetics were thought to account for the retention of these phases in the annealed alloy, which is like quenching from high temperatures to room temperature. Based upon that they have concluded the sluggish diffusion behavior in HEAs.	[19]

Subsequently, many authors have utilized this postulation to explain various phenomena observed in their studies, such as high creep resistance and slow oxidation resistance [19,20,21,22,23,24,25,26,27,28].

Until recently, only a few studies have been conducted on diffusion in HEAs, and the debate has centered around whether diffusion in HEAs is sluggish or not [13,14,15,16,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48,49,50,51,52,53,54,55,56,57,58,59,60,61,62]. Since most materials used in various applications are multicomponent alloys, it is essential to understand the multicomponent effects in interdiffusion processes to control various processing and development of new alloys for specific applications. Thus, it is appropriate to postulate that the diffusional interactions among constituent components play crucial roles in determining the diffusion behavior of multi-component, non-dilute alloy systems such as HEAs.

In view of the above discussion, the primary purpose of this review paper is to conduct a thorough evaluation of existing diffusion studies and potential methodologies in HEAs. To accomplish this goal, the review is organized as follows. First, we provide a concise overview of the theoretical foundations of diffusion. Second, we scrutinize the various potential methodologies for investigating multicomponent diffusion in the context of HEAs, encompassing experimental, numerical, and theoretical approaches. Third, we critically assess diverse diffusion studies conducted on HEAs as documented in the literature, specifically the bulk and grain boundary diffusion. Finally, we summarize our examinations and deliberate on future directions for research.

2. Diffusion – Theoretical foundations

Diffusion in solids occurs when vacancies move through the crystalline lattice of a pure metal or alloy in the absence of any chemical gradient or when two different solid materials having different chemistries are placed in close contact at moderate to high temperatures, resulting in a net flow of matter in such a way that it decreases or equalizes the chemical potential gradients. The gradient in the chemical potential is the driving force for diffusion which in turn may arise from the gradient in concentration, temperature, stress, electric field, and/or magnetic field. In an alloy system, the gradient in the chemical potential can be related to the concentration gradients through appropriate thermodynamic relations. Concentration gradients also play a very crucial role in various processes involving multicomponent diffusion.

2.1. Diffusion in a binary system

The vigor of diffusion is generally estimated in terms of the diffusion flux or diffusive flow. Fick [63] showed that the diffusion flux is proportional to the concentration gradient for the diffusion of a particular component along its concentration gradient. In other words, the flux of a component only depends upon its own concentration gradient in a binary system which is expressed as:

$$J_i = -D\frac{\partial C_i(x,t)}{\partial x} \tag{1}$$

where J_i is the flux of component *i*, D is the proportionality constant known as the diffusion coefficient, and $\frac{\partial C_i}{\partial x}$ is the concentration gradient of component i at position x and time t. The negative sign on the right-hand side of Eq. (1) denotes that the diffusion is occurring down the concentration gradient.

2.2. Diffusion in a multicomponent system

Onsager [64] expanded Fick's work [63] to include multicomponent systems, where the flux of a component is influenced not only by its own concentration gradient, but also by the concentration gradients of the other components in the system. Expression of Fick's law extended to the multicomponent system in which the flux of a component i with respect to the laboratory-fixed frame of reference is related to the linear combination of the concentration gradients is given by [64]:

$$\widetilde{J}_i = -\sum_{j=1}^{n} \widetilde{D}_{ij} \frac{\partial C_j}{\partial x} \tag{2}$$

where $\widetilde{J}_i$ is the interdiffusion flux of component *i*, and $\widetilde{D}_{ij}$ are n^2 interdiffusion coefficients known as partial interdiffusion coefficients [65]. These coefficients account for the contribution of a concentration gradient of component *j* to the interdiffusion flux of the component *i*. When $i = j$, $\widetilde{D}_{ij}$ is called a main interdiffusion coefficient and when $i \neq j$, it is called the cross or interactive interdiffusion coefficient which quantifies the diffusional interactions. $\frac{\partial C_j}{\partial x}$ is the concentration gradient of component *j* with respect to the distance coordinate *x*.

Based on the Gibbs-Duhem [66] constraint applied to the partial molar volumes $\overline{V}_i$, for an *n*-component system there exist (*n*-1) independent concentration gradients and (*n*-1) independent fluxes in Eq. (2), and those constraints are described as

$$\sum_{i=1}^{n} \overline{V}_i \frac{\partial C_j}{\partial x} = 0 \tag{3}$$

$$\sum_{i=1}^{n} \overline{V}_i \widetilde{J}_i = 0 \tag{4}$$

In the present context, partial molar volumes are assumed constant and equal. Thus, by utilizing this assumption on Eq. (3), Eq. (2) can be reduced to:

$$\widetilde{J}_i = -\sum_{j=1}^{n-1} \widetilde{D}_{ij}^{n} \frac{\partial C_j}{\partial x} \, (i = 1 \text{ to } n-1) \tag{5}$$

where $\widetilde{D}_{ij}^{n}$ are experimentally measurable interdiffusion coefficients and the superscript '*n*' denotes that *n* is treated as the dependent component. Thus, there are $(n\text{-}1)^2$ independent interdiffusion coefficients, which are practical or experimentally measurable. These experimentally measurable interdiffusion coefficients are related to partial interdiffusion coefficients [65] as:

$$\widetilde{D}_{ij}^{n} = \widetilde{D}_{ij} - \widetilde{D}_{in} \tag{6}$$

In a volume fixed frame of reference, these interdiffusion coefficients are related to the atomic mobilities as [67,68]:

$$\widetilde{D}_{ij}^{n} = \sum_{p=1}^{n} (\delta_{pi} - x_i) x_p M_p \left(\frac{\partial \mu_p}{\partial X_j} - \frac{\partial \mu_p}{\partial X_n} \right) \tag{7}$$

where δ_{pi} and x_i represent the Kronecker delta and mole fraction of the i^{th} component, respectively. M_p denotes the mobility of the component *p* and $\left(\frac{\partial \mu_p}{\partial X_j} - \frac{\partial \mu_p}{\partial X_n} \right)$ correspond to the thermodynamic factor.

This atomic mobility is further related to the tracer diffusivity (D_p^*), gas constant (R) and temperature (T) as [67,68]:

$$D_p^* = M_p RT \tag{8}$$

There is ample literature available on the determination of diffusion coefficients in binary systems and somewhat moderate data are available for ternary systems; however, for higher-order systems published information is limited due to complexities involved in such experimental studies. As the number of components increases in a system, thermodynamic interactions among the components become influential, impacting the diffusion behavior of each component. In a multicomponent system, a component's interdiffusion flux is influenced by its concentration gradient and the gradients of the other components. These cross effects, known as diffusional interactions, have a significant role in governing the interdiffusion behavior of constituent elements. The importance of diffusional interactions is illustrated in Fig. 3, which depicts a schematic of a ternary system comprising of red, blue, and yellow coloured atoms,

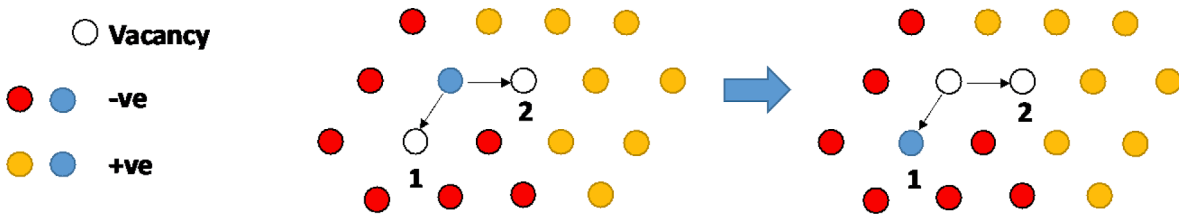

Fig. 3. Schematic showing the significance of the diffusional interactions.

along with vacancies. Consider the scenario where blue atoms exhibit a negative diffusional interaction with red atoms and a positive diffusional interaction with yellow atoms. In multicomponent systems, it is expected that atom jumps will be biased towards neighbouring atoms with highly negative thermodynamic interactions or diffusional interactions with the jumping atom, rather than those with less negative or more positive thermodynamic interactions. Thus, the most probable jump of the blue atoms is towards the vacancy, surrounded by the red atoms. The blue atom jumping to the site nearest the red atoms, as opposed to the sites nearest the yellow atoms, results in a lower net thermodynamic penalty and is therefore preferred. These interactions are important in understanding and controlling various diffusion-governing processes such as homogenization, grain growth, precipitation, dissolution, and many more. Although diffusional interactions are important in the context of multicomponent systems, the literature suggests that these terms are ignored or while studying multicomponent diffusion.

In the context of HEAs, sluggish diffusion is a vague term as the cross-terms are extremely important during multicomponent interdiffusion. As suggested by Onsager [64], flux of a component not only depends on its own concentration gradient but also on the gradients of the other components present in the system. Thus, sluggish diffusion is expected to play a crucial role in governing diffusion behavior in HEAs. It is also possible that certain HEA systems may experience "faster" diffusion behavior due to unaccounted and unexpected interactions between constituent elements. In light of this, the next section is dedicated to the potential methodologies available in the literature to investigate the multicomponent interdiffusion behavior relevant to HEAs.

3. Methodologies for determining diffusion coefficients in multicomponent systems

This section addresses the spectrum of approaches for investigating multicomponent diffusion within the realm of HEAs. This entails a holistic examination of early experimental, computational, and theoretical methods, as well as a thorough exploration of the most recent experimental techniques. By encompassing this wide range of approaches, our research aims to provide a well-rounded and up-to-date understanding of the intricate diffusion phenomena that characterize HEAs.

3.1. Tracer diffusion experiments

Tracer diffusion method stands as a cornerstone in providing fundamental diffusion data essential for understanding material transport phenomena. This method involves introducing a trace amount of a specific element or isotope, known as the tracer, into a host material. By monitoring the movement of the tracer over time, one can derive crucial information about the diffusion behavior within the material. The tracer diffusion method enables investigation of key parameters such as diffusion coefficients and concentration profiles, and an understanding of how species migrate through a given material. This method's precision and versatility make it an invaluable source for basic diffusion data [69].

The field of reliable diffusion studies on solids has significantly benefited from radiotracer techniques, as extensively documented [37,38,39,40,41,42,43,44,45,46,47,48]. Radiotracer studies often outperform other techniques. A notable advantage is the straightforward examination of self-diffusion or impurity diffusion using radioisotopes of matrix atoms, allowing the determination of the tracer self-diffusion or impurity diffusion coefficient. Tracer diffusion experiments enable the investigation of diffusion in chemically homogeneous solids without complications from chemical gradients. The experimental method involves preparing a flat, strain-free surface of the diffusion sample. Tracers are deposited onto the polished surface through liquid solution, evaporation or electrodeposition methods. Following deposition, an isothermal diffusion annealing is performed in an encapsulated environment. The corresponding tracer concentrations can be expressed as a thin-film solution of the continuity equation [69]:

$$C_{(x,t)} = \frac{M}{\sqrt{\pi D t}} exp\left(-\frac{x^2}{4Dt}\right) \tag{9}$$

where 'M' is the initial amount of the tracer, 'C' is the concentration of the tracer in the sectioned layer at position 'x', 'D' is the tracer diffusion coefficient and 't' is the time.

3.2. Experimental approaches that gives average or part of interdiffusion coefficients

Dayananda-Sohn analysis

Dayananda and Sohn [70] devised a technique which involves examining the interdiffusion fluxes to obtain an estimate of the average interdiffusion coefficients in a multicomponent system. This technique allows determination of interdiffusion coefficients within specific composition ranges of interest. It relies on a single diffusion couple and considers the moments of interdiffusion fluxes relative to the Matano plane.

The Dayananda-Sohn analysis uses a generic equation as follows:

$$\int_{x_1}^{x_2} \widetilde{J}_i (x - x_0)^r \mathrm{d}x = -\sum_{j=1}^{n-1} \overline{\overline{D}}_{ij}^{n} \int_{C_j(x_1)}^{C_j(x_2)} (x - x_0)^r \mathrm{d}C_j \tag{10}$$

In this equation, $\widetilde{J}_i$ represents the interdiffusion flux of component i, $(x - x_0)^r$ is the moment of the flux about the Matano plane, $\overline{\overline{D}}_{ij}^{n}$ denotes the average interdiffusion coefficient assumed constant over the selected composition range between $C_j(x_1)$ and $C_j(x_2)$ within the diffusion zone. The equation integrates the flux moments and the concentration changes to obtain the average interdiffusion

coefficients.

It is important to note that the Dayananda-Sohn analysis has limitations in that it only provides the average interdiffusion coefficient within a defined composition range in a system comprising of any number of elements. As the number of components increases, the errors in the estimation also increase. These average effective diffusion coefficients are not inherent material properties; their values are contingent upon the specific diffusion couples, including their compositions and diffusion path. No correlation with mobilities nor tracer diffusion coefficients has been established. While the method is suitable for qualitatively examining diffusion phenomena, it should be noted that even cross-correlations may be inaccurately assessed. Cermak and Rothova [71] suggested that reducing the compositional range for the estimation of the averaged effective interdiffusion coefficient to a very small value enables the estimation of values close to those actually determined at the point of intersection of diffusion paths from two different diffusion couples. However, a study by Cheng et al. [72] demonstrated that this approach is not applicable for determining composition-dependent diffusion coefficients as suggested by Cermak and Rothova.

Pseudo-Binary diffusion couple approach

Paul have introduced a methodology known as the pseudo binary diffusion couple approach [73], which involves utilizing a simplified multicomponent flux equation to investigate diffusion behavior in a multicomponent system. The pseudo binary diffusion couple approach is a technique employed to determine diffusion coefficients in a multicomponent system, focusing on scenarios where only two components exhibit concentration gradients while the remaining components either have negligible or zero concentration gradients across the diffusion zone. This type of situation occurs when only two of the components develop concentration gradients [74].

To grasp the essence of this methodology, let's consider a diffusion couple within a quinary system composed of components 1 to 5. Within the diffusion zone, only the concentrations of components 1 and 2 undergo variation, while components 3, 4, and 5 maintain constant concentrations. When there are no notable diffusional interactions in the system, uphill diffusion regions do not emerge. Consequently, components 3, 4, and 5 exhibit concentration gradients of zero throughout the diffusion zone.

In this scenario, the interdiffusion fluxes of components 1 and 2 can be expressed as:

$$\widetilde{j}_1 = -\widetilde{D}^2_{11}\frac{\partial C_1}{\partial x} \text{ and } \widetilde{j}_2 = -\widetilde{D}^1_{22}\frac{\partial C_2}{\partial x} \tag{11}$$

where $\widetilde{j}_1$ and $\widetilde{j}_2$ represent the interdiffusion fluxes of components 1 and 2, respectively, $\frac{\partial C_1}{\partial x}$ and $\frac{\partial C_2}{\partial x}$ are the concentration gradients of components 1 and 2 in the x-direction, and $\widetilde{D}^2_{11}$ and $\widetilde{D}^1_{22}$ are the main interdiffusion coefficients. These coefficients describe the diffusion of component 1 with component 2 treated as the dependent component and the diffusion of component 2 with component 1 treated as the dependent component, respectively. The validity of this equation is contingent upon the interdiffusion fluxes of components 3, 4, and 5 ($\widetilde{j}_3, \widetilde{j}_4$, and $\widetilde{j}_5$) being zero across the entire diffusion zone.

By using this pseudo binary diffusion couple approach, the main interdiffusion coefficients between the two varying components can be determined at each composition plane within the diffusion zone. The two interdiffusion coefficients should be equal if the molar volume remains constant with composition.

It is important to note that the pseudo-binary approach cannot be applied if one of the constant components develops maximum and minimum concentration profiles. However, in such cases, it is still possible to calculate one main coefficient and one cross coefficient (with one of the two varying components being dependent) at the maximum and minimum positions. This methodology has a further limitation as it provides only one out of sixteen interdiffusion coefficients for a quinary system and one out of nine coefficients for a quaternary system. This approach provides no idea about the cross effects.

Pseudo-Ternary diffusion couple approach

To address the aforementioned limitation, Esakkiraja and Paul [75] introduced a concept referred to as the pseudo-ternary diffusion couple. This approach is an extension of the Kirkaldy-Lane method [76], originally introduced in a ternary system, to a multi-component system. The pseudo-ternary diffusion couple method is akin to the pseudo-binary diffusion couple approach, emphasizing a diffusion couple where only three concentration variables exhibit gradients within the diffusion zone while the other components remain constant. To design this type of diffusion couple, two terminal alloys with distinct compositions for the three components are selected, while the remaining components have identical concentrations in both alloys. It is crucial to ensure that the non-varying components have negligible diffusional interactions to prevent significant concentration gradients resulting from uphill diffusion.

To understand this methodology, let us examine a diffusion couple in a quinary system consisting of components 1 to 5. Only the concentrations of components 1, 2, and 3 within the diffusion zone vary, while components 4 and 5 remain constant. If there are no significant diffusional interactions in the system, uphill diffusion regions do not occur. As a result, components 4 and 5 maintain concentration gradients of zero throughout the diffusion zone.

In this scenario, the interdiffusion fluxes of components 1 and 2 can be expressed as:

$$\widetilde{J}_1 = -\widetilde{D}^3_{11}\frac{\partial C_1}{\partial x} - \widetilde{D}^3_{12}\frac{\partial C_2}{\partial x} \tag{12}$$

$$\widetilde{J}_2 = -\widetilde{D}^3_{21}\frac{\partial C_1}{\partial x} - \widetilde{D}^3_{22}\frac{\partial C_2}{\partial x} \tag{13}$$

In these equations, $\widetilde{j}_1$ and $\widetilde{j}_2$ represent the interdiffusion fluxes of components 1 and 2, respectively, $\frac{\partial C_1}{\partial x}$ and $\frac{\partial C_2}{\partial x}$ are the concentration gradients of components 1 and 2 in the *x*-direction, and $\widetilde{D}^3_{11}$ and $\widetilde{D}^3_{22}$ are the main and $\widetilde{D}^3_{12}$ and $\widetilde{D}^3_{21}$ are the cross interdiffusion coefficients. If the molar volume assumed to be constant then, $\widetilde{J}_3 = -\widetilde{J}_1 - \widetilde{J}_2$ and $\widetilde{J}_4 = \widetilde{J}_5 = 0$, indicating that only two independent interdiffusion fluxes exist in the pseudo-ternary diffusion couple.

Esakkiraja and Paul also propose the possibility of designing another pseudo-ternary diffusion couple with the same three varying concentration variables and at least one common composition within the first couple. Establishing four independent flux equations at the common composition of the two independent diffusion couples makes it possible to evaluate four quinary interdiffusion coefficients. This method offers more comprehensive insights compared to pseudo-binary couples, as it provides information about some of the cross interdiffusion coefficients as well. It is important to note that the effectiveness of this method is exceptionally well when strong diffusional interactions occurring primarily among three or fewer components, which are the components subject to variation within the diffusion zone.

3.3. Computational / theoretical approaches

Calculation of PHAse diagrams (CALPHAD)

In recent years, the CALPHAD approach has gained significant traction in determining atomic mobilities in multicomponent systems [67,68]. By leveraging the principles of thermodynamics and kinetic modeling, CALPHAD approaches offer powerful frameworks to predict diffusion behavior and establish mobility databases for a wide range of material systems. The CALPHAD approach enables the creation of thermodynamic databases that describe the Gibbs free energy functions for different phases and compositions within a material system.

By considering diffusion kinetics, the atomic mobility of each component (M_i) can be determined. These atomic mobilities are often expressed as functions of temperature, incorporating the activation energy for diffusion (Q_i) and the product of the square of the atomic jump distance and jump frequency (M_i°) [77]. The mobility parameters are combined into a single parameter (ΔQ_i) that captures the composition dependence of the atomic mobilities. The composition dependence of the mobility parameters (ΔQ_i) is typically expressed using the Redlich-Kister polynomial [77]. This polynomial considers binary and ternary interaction parameters, reflecting the influence of neighboring components on the diffusion behavior of a particular component. The availability of experimental diffusion data is crucial for accurately determining these interaction parameters, especially in ternary and higher-order systems. Optimization routines are employed to fit the mobility parameters based on the available experimental data, enhancing the accuracy of the mobility databases.

The atomic mobilities obtained from the CALPHAD approach are directly related to tracer diffusivity and interdiffusion coefficients. Tracer diffusivity is expressed as the product of the atomic mobility, the gas constant and the temperature, which was discussed earlier in Eq. (8), and given as:

$$D_p^* = M_p RT$$

In a volume fixed frame of reference, the atomic or component mobility is subsequently linked to the chemical diffusivities, concentration, and thermodynamic factor which can be expressed as discussed previously in Eq. (7) as [77]:

$$\widetilde{D}_{ij}^n = \sum_{p=1}^{n} (\delta_{pi} - x_i) x_p M_p \left(\frac{\partial \mu_p}{\partial X_j} - \frac{\partial \mu_p}{\partial X_n} \right)$$

These chemical diffusivities are further related to the experimental measurable interdiffusivities through the relation described in Eq. (6)

The accuracy of the mobility parameters depends on the availability of experimentally determined and assessed diffusion data, particularly in ternary, quaternary, and quinary systems. The optimization process involves fitting the parameters using available experimental data, improving the accuracy of the mobility databases. The more comprehensive the diffusion data, the higher the accuracy of the determined mobility parameters [78]. Thus, diverse diffusion data across different composition ranges is essential for developing reliable mobility databases based on the CALPHAD approach.

Inverse simulation method

The determination of diffusivities in multicomponent systems through the inverse simulation method involves utilizing experimental data and numerical modeling techniques to estimate diffusion coefficients based on observed concentration profiles [79]. This approach provides valuable insights into the diffusion behavior of complex material systems.

To begin with, the initial step of the inverse simulation method entails collecting experimental data, which includes concentration profiles or the assembly of isothermal diffusion couples for the desired multicomponent system. This typically involves measuring the concentration profiles at various positions and times within the diffusion zone.

Subsequently, an initial set of diffusivities is assumed, and numerical methods are employed to solve the multicomponent diffusion equation, aiming to simulate concentration profiles that closely match the experimental data. The iterative process of the inverse simulation method involves determining the set of diffusion coefficients based on the obtained errors. By minimizing the difference between the simulated and experimental concentration profiles, an optimized set of tracer diffusivities can be calculated.

The optimization process continues until convergence is achieved, indicating that the diffusion coefficients have been accurately

determined. To ensure the reliability of the estimated diffusivities, it is essential to validate them by comparing the simulated concentration profiles with additional experimental data that were not used in the inverse simulation. This validation step enhances the confidence in the obtained diffusion coefficients.

In the absence of comprehensive experimental techniques for determining complete sets of interdiffusion coefficients, computational methods such as the inverse simulation method become crucial. However, it is essential to note that a limitation of the inverse simulation method is the lack of physical significance associated with the diffusivities or atomic mobilities, as they are considered fitting parameters. In multicomponent systems with many parameters involved, multiple sets of solutions can exist, making it challenging to accurately determine the diffusivities. Another constraint associated with the use of inverse simulation methods is the potential for generating multiple solutions, especially when relying solely on interdiffusion data (concentration profiles) as input. Researchers, including Kumar et al. [80], and Xia et al. [81], have explicitly stressed the significance of integrating tracer diffusion coefficients in these analyses.

Manning's model (theoretical approach)

Interdiffusion coefficients described in Eqs. (2) or (5) are phenomenological coefficients. Fundamentally, they are related to the atomic jump frequencies and jump activation energies. Einstein [82] was the first scientist to discover the diffusivity term's fundamental meaning. Later, Manning did extensive theoretical work on diffusion in binary systems and also extended it to multicomponent diffusion in solids [83,84,85]. Manning [65], in his theoretical study, emphasized that cross terms should not be overlooked even in ideal solution cases. He further demonstrated that differences in the jump frequencies of various diffusing species can lead to a net vacancy flow across a fixed lattice plane, resulting in the so-called 'vacancy wind effect.' The effective vacancy concentration seen by diffusing atoms in the direction of the vacancy flow would be different from that in the opposite direction. Manning suggested that this vacancy wind effect can be another driving force influencing diffusion behavior. Manning through his theoretical work [65] developed expressions that relate the main and cross intrinsic diffusion coefficients with the tracer diffusion coefficients of all the components and the thermodynamic factors for a multicomponent system, which are given as:

$$D_{ii} = \frac{2D_i^*}{M_0}\left[\left(\frac{M_0}{2} + P_i\right)\varphi_{ii} + \sum_{s\neq i}^{n} P_s\varphi_{si}\right] \tag{14}$$

$$D_{is} = \frac{2D_i^*}{M_0}\frac{X_i}{X_s}\left[\left(\frac{M_0}{2} + P_i\right)\varphi_{is} + P_s\varphi_{ss} + \sum_{t\neq i,s}^{n} P_t\varphi_{ts}\right] \tag{15}$$

where,

$$P_i = \frac{X_i D_i^*}{\sum_{m=1}^{n} X_m D_m^*} \text{ and} \varphi_{ij} = \frac{X_j}{RT}\frac{\partial \mu_i}{\partial X_j} \tag{16}$$

In Eqs. (14)-(16), D_i^* denotes the tracer diffusion coefficient of component i at the given composition, μ_i is the chemical potential of component i, φ_{ij} are the thermodynamic factors, X_i is the mole fraction of component i and M_0 is the vacancy wind factor, which is equal to 7.15 for FCC solids [65].

In deriving Eqs. (14)-(16) above, the random alloy model was assumed which means that there are no energetically favored sites for a particular atomic species and vacancy, and the jump frequencies do not depend on the identities of the surrounding atomic species.

Furthermore, the intrinsic diffusion coefficient can be related to the experimentally determinable interdiffusion coefficient by the extended Darken equation for the multicomponent systems. Thus, for an assumption of constant molar volume, this expression will be given as [65]:

$$\widetilde{D}_{ij}^{n} = (1 - X_i)D_{ij}^{n} - X_i\sum\nolimits_{p\neq i}^{n} D_{pj}^{n} \tag{17}$$

where the equation:

$$D_{pj}^{n} = D_{pj} - D_{pn} \tag{18}$$

relates the experimentally determinable intrinsic diffusion coefficients to the partial intrinsic diffusion coefficients.

As Manning's model requires the knowledge of tracer diffusivities and thermodynamic factors for the determination of the interdiffusion coefficients, it imposes the limitation to this approach viz. one needs the knowledge of tracer diffusion coefficients of all the diffusing components, i.e., four tracer diffusion coefficients in quaternary and five in case of the quinary system. The tracer experiments are further restricted by the availability of radioactive isotopes for all the components and safety issues that arise while handling these isotopes. Another limitation of the approach of using Manning's theory for getting interdiffusion coefficients is its dependency on the availability of thermodynamic factors. Experimental data for the thermodynamic factors are usually unavailable beyond the binary systems, as the complexity increases in determining these values if we consider ternary and higher-order multicomponent systems. To get the values of the thermodynamic factors, one generally depends on the thermodynamic databases which typically estimate these values by extrapolating the data from binary systems and with certain inherent assumptions. So, for any methodology or model which utilizes these thermodynamic data, the success will strongly depend on the accuracy and reliability of these data. Limitations of the Manning's approach highlight the immediate need for other techniques that can be useful for

determining interdiffusion coefficients in multicomponent systems.

A significant challenge encountered when experimentally determining interdiffusion coefficients in multicomponent systems relates to the intricate process of creating multiple diffusion couples with intersecting diffusion paths. To gain a deeper insight into this matter, it is appropriate to initiate our discussion by exploring the Kirkaldy approach [86], recognized as the most widely accepted method for experimentally ascertaining interdiffusion coefficients within ternary systems.

3.4. Experimental approaches that gives complete set of interdiffusion coefficients

Kirkaldy's approach

Based on Eq. (5), to describe interdiffusion for an n-component system at a particular composition, one requires (n-1) independent fluxes, (n-1) independent concentration gradients, and $(n\text{-}1)^2$ interdiffusion coefficients. Kirkaldy [86] proposed a method for the determination of the composition-dependent interdiffusion coefficients in a ternary system which theoretically can be extended to an n-component system. In this method, for the determination of $(n\text{-}1)^2$ interdiffusion coefficients, one needs to set up (n-1) independent diffusion couples (A diffusion couple is an assembly in which two different alloys or metals are placed in complete contact and annealed at moderate to high temperature to achieve diffusional bonding across a relatively large surface are. The interface of the joined alloys or metals is then analysed to gain insight to the diffusional behavior of the components of the joined metals). A diffusion couple is elucidated through the schematic presented in Fig. 4, comprising two terminal alloys that depict the progression of concentration profiles following diffusion annealing. The left terminal alloy is denoted as Alloy 1, characterized by concentrations *C1, C2,* and *C3*, while the right terminal alloy is designated as Alloy 2, with concentrations $C1'$, $C2'$, and $C3'$ and x_0 denotes the initial contact plane.

A diffusion path is the series of compositions developed in between the two terminal alloys of a diffusion couple as plotted on the compositional space like on a ternary isotherm in case of the ternary system. The basic requirement of this method is that the diffusion paths of these (n-1) independent diffusion couples should intersect at one composition point within the diffusion zone (Diffusion zone is the region developed between the two terminal ends of the diffusion couple which consists of a series of compositions), which means that all the diffusion couples should have at least one common composition within their diffusion zones. Based on Eq. (5) we can write (n-1) independent flux equations for each diffusion couple (i.e., in the case of a ternary system we can write two independent flux equations which means we have a total of four equations) and we can solve simultaneously for $(n\text{-}1)^2$ interdiffusion coefficients (i.e. in the case of a ternary system four independent flux equations can be solved for the four independent interdiffusion coefficients) at the crossover or common composition. The interdiffusion coefficients so evaluated belong to this crossover or common composition. Illustration of Kirkaldy's method is presented in Fig. 5, in which the diffusion paths of two hypothetical diffusion couples I (A/B) and II (C/D) are plotted on a Gibbs triangle and the diffusion paths of the diffusion couples (A/B) and (C/D) intersect at the crossover composition (C1, C2, C3). For this crossover composition, we can have four independent equations, two from each couple, that can be solved for the four-unknown ternary interdiffusion coefficients that belong to the same composition.

Application of Kirkaldy's approach to ternary systems is quite easier and it has been widely used in several ternary systems for the determination of the composition-dependent interdiffusion coefficients. Studies that utilized Kirkaldy's approach in various ternary systems that are essential parts of the two most studied HEA's include: Fe-Ni-Co [87], Fe-Ni-Cr [88], Fe-Ni-Al [89], Fe-Cr-Al [90], Ni-

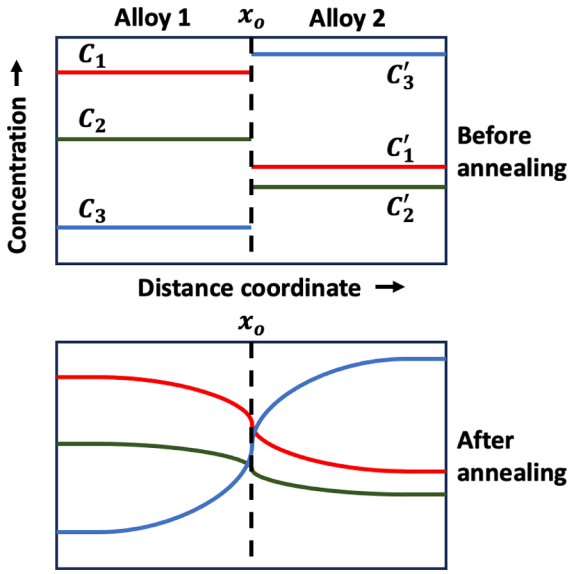

Fig. 4. Schematic illustrating the diffusion couple and concentration profiles that developed following diffusion annealing.

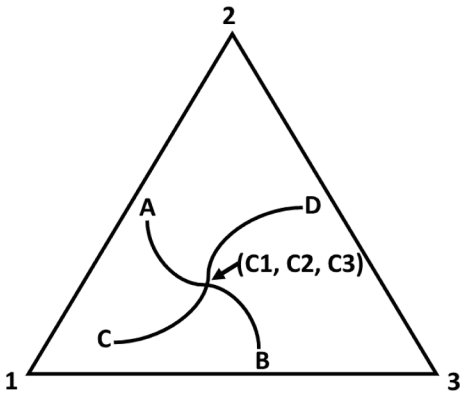

Fig. 5. Schematic concentration profiles illustrating the application of Kirkaldy's approach in which diffusion paths of diffusion couple I (A/B) and couple II (C/D) intersecting at the common composition (C1, C2, C3).

Cr-Al [91], and Co-Al-Cr, Co-Al-Ni and Co-Cr-Ni [92].

However, the applicability of Kirkaldy's approach to quaternary or higher order systems is quite complex because of the requirement of intersecting diffusion paths. As evident from Eq. (5), for describing the interdiffusion behavior in quaternary and quinary systems, requires nine and sixteen interdiffusion coefficients respectively. Determining these interdiffusion coefficients in the quaternary system requires three independent diffusion couples with three independent diffusion paths intersecting at the common composition. At this common composition for all the three diffusion couples, we can write three independent flux equations based on Eq. (5) for each couple which in total gives nine equations. These nine equations can be solved simultaneously using Kirkaldy's approach to determine the nine quaternary interdiffusion coefficients. Similarly, for the quinary system, four independent diffusion couples with four independent diffusion paths intersecting at one common composition are required. For the determination of the sixteen quinary interdiffusion coefficients at the common composition, the sixteen equations can be solved simultaneously from the four independent diffusion couples. The probability of encountering three diffusion paths in quaternary systems and four diffusion paths in quinary systems, all intersecting at a common composition, is extremely low, making quaternary and higher order system diffusion couple experiments challenging to conduct and reproduce.

Body-diagonal diffusion couple approach

To overcome the above-discussed issue in the experimental determination of multicomponent interdiffusion coefficients, a method was needed that was simpler and more practical to apply. Recently, Morral [93] proposed the 'body-diagonal diffusion couple' approach for the experimental determination of interdiffusion coefficients in multicomponent systems. This method is an extension of Kirkaldy's approach [86]. In the body diagonal diffusion couple technique, the terminal alloy compositions of the (n-1) couples are selected as the opposite ends of the body diagonals of a hyper-cube formed in the (n-1) dimensional composition space. The typical feature of such a set of couples, called body-diagonal couples, is that they have the same difference between the terminal end concentrations for the (n-1) independent components and the same average composition. To set up such couples, one needs to first choose two parameters, ΔC and $\overline{C}$, where ΔC is the difference between the terminal concentrations of independent components and $\overline{C}$ is the average terminal concentration, which happens to be the composition of the mid-point of the body diagonal. All the terminal alloy compositions can be obtained by establishing the origin at the average composition. The prerequisites for these diffusion couples are that the diffusion paths must be in a single phase and the sum for all the components in the terminal composition must be 100 at. %. In an 'm' dimensional hypercube, there are 2^m corners and 2^{m-1} body diagonals in which m is the (n-1) independent concentration variable and n is the total number of variables. In the case of m-dimensional compositional space, there are (n-1) independent composition

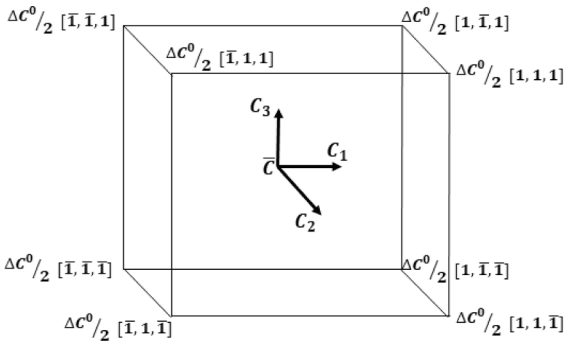

Fig. 6. Schematic of a selection of terminal alloys for body-diagonal diffusion couples in a quaternary system.

vectors. A body diagonal diffusion couple schematic for a quaternary system is shown in Fig. 6.

We can represent the body diagonal diffusion couples in a quaternary compositional space in the form of a cube with four possible independent composition vectors along four body diagonals of the cube. For a particular ΔC and $\overline{C}$ in a quaternary system, we can obtain all the eight compositions at the terminal ends of the cube for the four body diagonals by assigning the origin at $\overline{C}$. Composition for the eight corners of the quaternary system will be given as $\frac{\Delta C}{2}[111]$, $\frac{\Delta C}{2}[\overline{1}\overline{1}\overline{1}]$, $\frac{\Delta C}{2}[11\overline{1}]$, $\frac{\Delta C}{2}[\overline{1}\overline{1}1]$, $\frac{\Delta C}{2}[1\overline{1}1]$, $\frac{\Delta C}{2}[\overline{1}1\overline{1}]$, $\frac{\Delta C}{2}[\overline{1}11]$, $\frac{\Delta C}{2}[1\overline{1}\overline{1}]$. Similarly, for a particular ΔC and $\overline{C}$ in a quinary system, we can obtain all the sixteen terminal end compositions for the eight body diagonals of the diffusion couple.

If the composition difference is small enough, we expect the interdiffusion coefficient to not vary much with composition. Thus, all the diffusion paths should be symmetric (inverted) about the respective Matano plane and all should pass through the mid-point of the body-diagonals. Hence, based on this technique, we could establish a desired number of independent diffusion couples with intersecting diffusion paths in multicomponent compositional space which can be used further for the determination of the interdiffusion coefficients.

Square root diffusivity method

Another sound experimental technique that doesn't require knowledge of tracer diffusivities and investigates the interdiffusion data in quaternary and higher-order systems is the square root diffusivity approach [94]. The square root diffusivity approach is a technique which was often ignored in early literature to study diffusion behavior in quaternary and higher-order systems. The main point to be highlighted here is that the square root diffusivity technique requires constant of interdiffusion coefficients in the diffusion zone which is also the requirement for the body-diagonal diffusion couple approach. Thompson and Morral [94] developed a relation between the square root diffusivity matrix $[r]$ and the interdiffusion coefficients matrix for an n-component system $\left[\widetilde{D}^n\right]$ which is given as Eq. (19) below [94]:

$$\left[\widetilde{D}^n\right] = [r][r] \tag{19}$$

The individual elements of $\left[\widetilde{D}^n\right]$ and $[r]$ can be denoted as $\widetilde{D}^n_{ij}$ and r_{ij} respectively. This square root diffusivity matrix is further related to the two important parameters which can be easily determined form the experimental concentration profiles of individual elements. The first parameter is S_i, which is described as the amount of component i that has crossed the mass balance plane (i.e. $x = 0$ plane) in the diffusion time t and the second parameter is ΔC_i^0, which is the difference in the terminal alloy concentrations of the independent component i. The expression for the square root diffusivity that linked these two parameters that has been described in [94,95,96] is given as Eq. (20):

$$[S] = -\sqrt{\frac{t}{\pi}}[r][\Delta C^0] \tag{20}$$

where the matrices $[S]$ and $[\Delta C^0]$ are defined as:

$$[S] = \begin{bmatrix} S_1 \\ S_2 \\ \vdots \\ S_{n-1} \end{bmatrix} \text{ and } \left[\Delta C^0\right] = \begin{bmatrix} \Delta C_1^0 \\ \Delta C_2^0 \\ \vdots \\ \Delta C_{n-1}^0 \end{bmatrix} \tag{21}$$

Thus, for a quaternary system, the parameter S_i can be written as [95]:

$$S_i = -\sqrt{\frac{t}{\pi}}\left(r_{i1}\Delta C_1^0 + r_{i2}\Delta C_2^0 + r_{i3}\Delta C_3^0\right) \quad i = 1 \text{ to } 3 \tag{22}$$

The quantities S_i can be evaluated from the experimental concentration profiles as [95]:

$$S_i = \int_{x=0}^{\infty}\left(C_{i,x} - C_i^+\right)dx \tag{23}$$

As mentioned above, the applicability of the square root diffusivity approach required a constraint of constant interdiffusivities in the diffusion zone. This indicates that at the mass balance plane (i.e., $x = 0$ plane), the concentration of any diffusing component i represents the average concentration of the two-terminal concentrations. Thus, for the determination of the parameter S_i, the reference plane or the mass balance plane is taken at the average concentration of the two terminal alloys. If the molar volume does not vary with the composition, then this plane should be the same for all diffusing components.

Based on Eq. (22), since there are (n-1) independent interdiffusion fluxes in a n-component system, a single diffusion couple yields (n-1) independent equations. If (n-1) independent diffusion couples were set up with the same average composition and Eq. (22) is applied to all (n-1) couples, it would yield $(n\text{-}1)^2$ number of independent equations that can be solved for the $(n\text{-}1)^2$ interdiffusion coefficients at the average composition. Morral and co-workers have applied the square root diffusivity method to study the interdiffusion behavior in ternary [95] and quaternary [96] systems. Similarly, in the case of a quinary system, a single diffusion couple

yields four independent equations based on Eq. (22). If four independent diffusion couples are designed with the same average composition and Eq. (22) is applied to all four couples, it would yield sixteen independent equations that can be solved for sixteen quaternary interdiffusion coefficients at the average compositions.

Combined body diagonal diffusion couple with pseudo-binary or pseudo-ternary diffusion couple

Dash et al. [50] have recently proposed a novel approach for comprehensively estimating various diffusion coefficients within multicomponent systems by strategically intersecting only two distinct types of diffusion paths. This innovative method overcomes the limitations of conventional techniques like pseudo-binary, pseudo-ternary, and body diagonal methods when applied individually. It allows for the estimation of diffusivities for all elements, in contrast to the restricted estimation of diffusivities for only two or three elements, as seen in pseudo-binary and pseudo-ternary approaches. Additionally, this method simplifies the task of precisely aligning serpentine body diagonal diffusion paths, reducing the challenges associated with estimating diffusivities with unknown uncertainties when exact intersections are not achieved. Instead, as proposed in this study, a serpentine conventional (or body diagonal) diffusion path can be effectively intersected by a straight-line pseudo-binary diffusion path at a specific composition. To understand this methodology, we must understand the correlations among various types of diffusion coefficients in a body-diagonal or traditional diffusion couple.

Based on Manning's theoretical work, the intrinsic diffusion coefficients are linked to the tracer diffusion coefficients when the vacancy wind effect is ignored can be described as:

$$D_{ij}^{n} = \frac{X_i}{X_j} D_i^{*} \varphi_{ij}^{n} \tag{24}$$

where $\varphi_{ij}^{n} = \frac{X_j}{RT}\left(\frac{\partial \mu_i}{\partial X_j} - \frac{\partial \mu_i}{\partial X_n}\right)$ when the vacancy wind effect is considered, the intrinsic diffusion coefficients are linked to the tracer diffusion coefficients as:

$$D_{ij}^{n} = \frac{X_i}{X_j} D_i^{*} \varphi_{ij}^{n}\left(1 + W_{ij}^{n}\right) \tag{25}$$

where $W_{ij}^{n} = \frac{2}{S_o \varphi_{ij}^{n}} \frac{\sum_{p=1}^{n} X_p D_p^{*} \varphi_{pj}^{n}}{\sum_{p=1}^{n} X_p D_p^{*}}$ and S_o is the structure factor

These intrinsic diffusivities are further related to the interdiffusion coefficients by the Darkens relation for multicomponent system described in Eq. (17).

When the molar volume is considered, it is possible to establish a direct relationship between interdiffusion fluxes and the n-tracer diffusion coefficients in an *n*-component system. This relationship can be established without accounting for the vacancy wind effect, utilizing the Eqs. (17), (24), and (5) which is described as:

$$V_m \widetilde{J}_i = -\sum_{j=1}^{n-1}\left[\frac{X_i}{X_j} D_i^{*} \varphi_{ij}^{n} - X_i \sum_{k=1}^{n} \frac{X_k}{X_j} D_k^{*} \varphi_{kj}^{n}\right] \frac{\partial X_j}{\partial x} \tag{26}$$

Likewise, by employing Eqs. (17), (25), and (5) and taking molar volumes into account, it is possible to establish a relationship between interdiffusion fluxes and the n tracer diffusion coefficients in an *n*-component system while considering the vacancy wind effect. This relationship can be described as follows:

$$V_m \widetilde{J}_i = -\sum_{j=1}^{n-1}\left[\frac{X_i}{X_j} D_i^{*} \varphi_{ij}^{n}\left(1 + W_{ij}^{n}\right) - X_i \sum_{k=1}^{n} \frac{X_k}{X_j} D_k^{*} \varphi_{kj}^{n}\left(1 + W_{kj}^{n}\right)\right] \frac{\partial X_j}{\partial x} \tag{27}$$

Similarly, as described in Eqs. (26) and (27), flux equations can be formulated for pseudo-binary and pseudo-ternary diffusion couples, either accounting for or neglecting the vacancy wind effect (for more comprehensive details, please refer to [50]. To obtain the diverse diffusion coefficients in a quaternary system, three distinct, independent flux equations can be established within a binary-diffusion (BD) couple, using Eqs. (26) or (27), while designating one component as the dependent variable. Similarly, two equations can be formulated in a pseudo-ternary (PT) diffusion couple, with one component designated as the dependent variable. Consequently, we have a total of five equations for the determination of tracer diffusion coefficients for the four elements. Based on Eqs. (26), (27), and (17) intrinsic and interdiffusion can also be determined.

The pseudo-binary (PB) and pseudo-ternary (PT) concept introduced by Paul establish direct correlations with tracer diffusion coefficients, enabling their application for comprehensive assessments and independent result cross-verification. This benefit of the PB and PT schemes becomes especially pronounced when an 'ideal' PB or PT profile is meticulously developed. Although, this method offers significant advantages in estimating diverse diffusion coefficients within multicomponent systems, its effectiveness is contingent upon the availability of accurate thermodynamic factors. Notably as discussed earlier, obtaining experimental thermodynamic factor data becomes increasingly challenging as the complexity of the system rises beyond binary configurations. In the case of ternary and higher-order multicomponent systems, determining these values becomes considerably intricate. Typically, researchers rely on thermodynamic databases, which employ extrapolation techniques from binary systems and certain inherent assumptions to estimate thermodynamic factors. Consequently, the success and precision of any methodology or model utilizing these thermodynamic data hinge heavily on the accuracy and reliability of these values.

Table 2
Summary of diffusion studies in HEAs.

Alloy systems	Methodology	Diffusivities	Comments	Reference
Experimental Investigations				
Fe-Ni-Co-Cr-Mn	Pseudo-binary diffusion couple approach	Tracer diffusivities	Ignored cross-terms and sluggish diffusion kinetics was observed on a normalized temperature scale with a melting point of the alloys	Tsai et al. [29]
Fe-Ni-Co-Cr	Diffusion couple technique / Dayananda and Sohn analysis	Average interdiffusivities	Diffusional interactions were found consistent with the relative binary thermodynamic interactions	Kulkarni et al. [30]
Al-Co-Cr-Fe-Ni	Diffusion couple technique / Dayananda and Sohn analysis	Average effective interdiffusivities	Higher configurational entropy of mixing does not always imply greater thermodynamic stability. Sluggish diffusion kinetics was found absent.	Mehta et al. [31]
Al–Co–Cr–Fe–Ni–Mn	Diffusion couple technique / Dayananda and Sohn analysis	Average effective interdiffusivities	Sluggish diffusion effect was observed in the BCC alloy but not in the FCC alloy	Mehta et al. [32]
AlCoCrFeNi	Diffusion couple technique / analytical method	Average interdiffusivities and tracer diffusivities	Sluggish diffusion effect was found absent	Mehta et al. [33]
Ni-Co-Fe-Mo, Al-Mn-Ni-Co-Fe and its subsystems	Pseudo-binary and pseudo-ternary diffusion couple approach	Inter, intrinsic, and tracers diffusivities	Cross-terms are considered partially, and sluggish diffusion behavior not clearly observed	Esakkiraja et al. [34]
Ni-Co-Fe-Cr	Pseudo-binary and pseudo-ternary diffusion couple approach	Inter, intrinsic, and tracers diffusivities	Cross-terms are considered partially	Dash et al. [35]
Ni-Co-Fe-Cr	Pseudo-binary and pseudo-ternary diffusion couple approach	Inter, intrinsic, and tracers diffusivities	Cross-terms are considered partially	Esakkiraja et al. [36]
Fe-Ni-Co-Cr and Fe-Ni-Co-Cr-Mn	Radioactive tracer method	Tracer diffusivities	Sluggish diffusion kinetics was found absent on an absolute temperature scale and consistent on a normalized temperature scale	Vaidya et al. [37]
Fe-Ni-Co-Cr and Fe-Ni-Co-Cr-Mn	Radioactive tracer method	Tracer diffusivities	Sluggish diffusion kinetics was found absent on an absolute temperature scale and consistent on a normalized temperature scale	Vaidya et al. [38]
CoCrFeNi and CoCrFeMnNi	Radioactive tracer method	Tracer diffusivities	Sluggish diffusion kinetics was found absent on an absolute temperature scale	Vaidya et al. [39]
Co-Cr-Fe-Ni and Co-Cr-Fe-Ni-Mn	Diffusion couple technique / numerical inverse method	Inter diffusivities	Ignored cross-terms and sluggish diffusion kinetics was found absent on an absolute temperature scale	Vaidya et al. [40]
Fe-Ni-Co-Cr and Fe-Ni-Co-Cr-Mn	Radioactive tracer method	Tracer diffusivities	Sluggish diffusion kinetics was found absent on an absolute temperature scale	Gaertner et al. [41]
Fe-Ni-Co-Cr-Mn	Radioactive tracer method	Tracer diffusivities	Sluggish diffusion behavior not clearly observed	Kotte et al. [42]
Fe-Ni-Co-Cr-Mn	Diffusion couple technique / Radioactive tracer method	Tracer diffusivities	Sluggish diffusion behavior not clearly observed	Gaertner et al. [43]
Co-Cr-Fe-Ni-Mn	Diffusion couple technique / analytical method	Interdiffusivities	Cross-terms are considered and sluggish diffusion effect was found absent	Li et al. [44]
Co-Cr-Fe-Ni-Mn	Radioactive tracer method	Tracer diffusivities	Accelerated diffusion was observed at homologous temperature and found absent on absolute temperature scale	Zhang et al. [45]
HfTiZrNbTa and HfTiZrNbV	Radioactive tracer method	Tracer diffusivities	Sluggish diffusion kinetics was found absent on both absolute temperature scale and normalized temperature scale	Zhang et al. [46]
HfTiZr and AlScHfTiZr	Radioactive tracer method	Tracer diffusivities	Sluggish diffusion kinetics was found absent on both absolute temperature scale and normalized temperature scale	Sen et al. [47]
CoCrFeMnNi–C	Radioactive tracer method	Tracer diffusivities	An increase in the diffusion rates was observed at lower temperatures and/or greater C concentrations.	Lukianova et al. [48]
Ni-Co-Fe-Cr And Ni-Co-Fe-Cr-Mn	Body diagonal diffusion couple approach	Interdiffusion	Cross-terms are considered	Verma et al. [49]
Ni-Co-Fe-Cr	Combined pseudo-binary, pseudo-ternary and body diagonal diffusion couple approach	Intrinsic, tracer and interdiffusivities	Cross-terms are considered	Dash et al. [50]
Ni-Co-Fe-Cr And Ni-Co-Fe-Cr-Mn	Square root diffusivity approach	Interdiffusion	Cross-terms are considered	Verma et al. [51]
Numerical or computational investigations				
Al-Co-Cr-Fe-Ni and Fe-Ni-Co-Cr-Mn	Diffusion couple technique / Inverse simulation method	Tracer diffusivities	Sluggish diffusion kinetics was observed on an absolute temperature scale	Dabrowa et al. [52]
Fe-Ni-Co-Cr-Mn	Diffusion couple technique / CAHPHAD approach	Tracer diffusivities	Ni tracer diffusion was not found sluggish with an increase in the number of	Zhang et al. [53]

(*continued on next page*)

Table 2 (*continued*)

Alloy systems	Methodology	Diffusivities	Comments	Reference
			components at both absolute and normalized temperature scale	
Fe-Ni-Co-Cr-Mn	Diffusion multiple technique / numerical inverse method	Tracer diffusivities and Inter diffusivities	Considered cross-terms and sluggish diffusion behavior mainly observed for the interdiffusivities on the absolute temperature scale	Chen et al. [54]
Al-Co-Cr-Fe-Ni	Diffusion multiple technique / numerical inverse method	Tracer diffusivities and Inter diffusivities	Considered cross-terms and sluggish diffusion behavior mainly observed for the interdiffusivities on the absolute temperature scale	Li et al. [55]
Co-Cr-Cu-Fe-Ni	Diffusion multiple technique / numerical inverse method	Tracer diffusivities and Inter diffusivities	Ignored cross-terms and sluggish diffusion behavior mainly observed for the interdiffusivities at absolute temperature scale	Wang et al. [56]
Co-Cr-Fe-Mn-Ni, Co-Cr-Fe-Ni and Co-Fe-Mn-Ni	Diffusion couple technique / Inverse simulation method	Tracer diffusivities	Sluggish diffusion kinetics was found absent on an absolute temperature scale	Kucza et al. [57]
Al-Co-Cr-Fe-Ni-Ti	Diffusion multiple technique / numerical inverse method	Tracer diffusivities and Inter diffusivities	Ignored cross-terms and sluggish diffusion behavior mainly observed for the interdiffusivities on the absolute temperature scale	Chen et al. [58]
Co-Cr-Fe-Mn-Ni, Co-Fe-Mn-Ni, Co-Cr-Mn-Ni, Co-Cr-Fe-Ni, and Al-Co-Cr-Fe-Ni	Diffusion couple technique / Inverse simulation method	Tracer diffusivities	Sluggish diffusion behavior was observed on the normalized temperature scale only for the systems that contain Mn.	Dabrowa et al. [59]
NiCoFeCr	Pseudo-binary diffusion couple approach and Physics-informed machine learning based numerical inverse method	Inter diffusivities and Intrinsic diffusivities	Considered cross-terms and Kirkendall plane	Kumar et al. [80]
Theoretical Investigations				
Fe-Ni-Co-Cr-Mn	Semi-empirical approach	Tracer diffusivities	Sluggish diffusion kinetics was observed on a normalized temperature scale	Beke et al. [60]
Fe-Ni-Co-Cr-Mn	Analytical approach	Tracer diffusivities and Inter diffusivities	Considered cross-terms	Paul et al. [61]
Ni-Co-Fe-Cr And Ni-Co-Fe-Cr-Mn	Manning's Model	Interdiffusivities	Considered cross-terms	Verma et al. [62]

4. Diffusion in high entropy alloys

Diffusion behavior in metals and alloys can be described by various types of diffusion coefficients, including tracer diffusion coefficients, which quantify the movement of a specific species under a minimal concentration gradient; intrinsic diffusion coefficients, which delineate the inherent mobility of an element within the lattice structure, driven solely by concentration gradients; and interdiffusion coefficients, which capture the intricate interactions and inter mixing of multiple elements within concentrated alloy systems. Table 2 summarizes the current state of diffusion studies in HEAs, including tracer, intrinsic, and interdiffusion coefficients, as reported through various experimental, theoretical, and numerical approaches.

4.1. Experimental investigations

Although researchers commonly employ the concept of sluggish diffusion in HEAs to elucidate their qualitative observations, it wasn't until Tsai et al. [29] conducted a quantitative exploration of interdiffusion in HEAs that one of the fundamental effects was systematically investigated. It took approximately nine years for this experimental study to be conducted after introducing the term HEAs and the concept of sluggish diffusion. Tsai et al. [29] studied the interdiffusion in the Fe-Ni-Co-Cr-Mn system by using the 'quasi-binary' diffusion couple approach. In the quasi-binary, which has similar experimental requirements as the pseudo-binary diffusion couple approach but is different in analysis procedure, only two components are allowed to form diffusion profiles, and the other components remain constant in the diffusion zone. For ease, let's indicate a Quasi-binary diffusion couple as QB_*i-j* in which only *i* and *j* have the concentration gradients and the rest of the concentrations are the same in the two-terminal alloys. With this terminology, the three distinct diffusion couples investigated by Tsai et al. [29] comprised of QB_Cr-Mn, QB_Fe-Co, and QB_Fe-Ni. The studied diffusion couples were annealed at four distinct temperatures in the range from 900 to 1050 °C. It ought to be noted here that they have used Energy Dispersive Spectroscopy (EDS) for concentration measurements instead of a more precise procedure of Wavelength Dispersive Spectroscopy (WDS), which has been a standard technique for the analysis of concentration profiles in diffusion couple experiments. Since they observed negligible marker movement in their study, they assumed that the vacancies are in equilibrium, and neglected the contribution of vacancy wind effect and correlation factor, and also assumed that the Fe-Ni-Co-Cr-Mn system follows the ideal solution behavior. They have estimated the main interdiffusion coefficients from the concentration profiles that are developed in the diffusion zone of the three different couples.

They [29] assumed that these main interdiffusion coefficients are equivalent to the intrinsic diffusion coefficients at the marker plane composition based on the negligible marker movement. Based on the negligible contribution of vacancy wind effect and correlation factor assumption they have ignored the cross-terms i.e., the off-diagonal terms of the diffusion coefficients matrix which comes in Eq. (5). Further, based on the assumption that the system follows the ideal solution behavior they have taken the activity coefficient to be equivalent to unity and ignored the contribution of thermodynamic factor, and assumed that the intrinsic diffusion coefficients are equivalent to the tracer diffusion coefficients at the marker plane composition. The sequence of the diffusion rate for the components as observed in their study is given as: $D^*_{Mn} > D^*_{Cr} > D^*_{Fe} > D^*_{Co} > D^*_{Ni}$, see Fig. 7. Based on the estimated tracer diffusivities, the authors of the study also evaluated the activation energies and frequency factors. They compared the tracer diffusivities of HEAs with those of unary, binary, ternary, and quaternary systems presented in Fig. 8, and concluded that HEAs exhibit sluggish diffusion kinetics. One important point requiring attention is that, according to Eq. (1) or (5), there is typically only one interdiffusion coefficient in the binary system. This arises from the presence of just a single independent concentration gradient, assuming a constant partial molar volume, which also holds true for pseudo-binary couples. But according to Tsai et al. [29], it is feasible to get two interdiffusion coefficients because of a separate investigation of profiles for both components which are having the concentration gradients. This is a very contradictory statement regarding the two different interdiffusion coefficients. Nonetheless, the examination introduced by Tsai et al. [29] needs to be evaluated cautiously prior to reaching any significant conclusions.

Paul [97] has criticized the analysis of interdiffusion coefficients in HEAs using the quasi-binary approach reported by Tsai et al. [29]. He argued that the statement made by Tsai et al. [29] regarding the existence of two distinctive interdiffusion coefficients from the two concentration profiles having the gradient in a quasi-binary diffusion couple does not align with the foundation of the pseudo-binary approach, as the sum of interdiffusion fluxes of the two components having the gradient should be zero; otherwise, the entire formalism becomes invalid. Furthermore, Tsai et al. [29] claimed that the interdiffusion coefficients are equal to the intrinsic diffusion coefficients based on the observation of negligible marker movement, i.e., the marker or Kirkendall plane coinciding with the Matano plane. Although the assumption is correct based on the negligible marker movement, Paul pointed out that it does not align with their first statement. Paul also questioned the treatment of concentration-dependent interdiffusivities as tracer ones based on ideal solution behavior, which, although correct, does not align with the first two statements. Paul recommended re-evaluating these interdiffusivity values with the correct methodology; otherwise, these values have no significance. While Tsai et al. [98] responded to Paul's comments and supported their methodology, it is difficult to ignore the valid points brought up by Paul in [97]. In addition, the present author wishes to highlight a few more points, which will be discussed briefly below.

Upon examination of the QB_Mn-Cr couple, Tsai et al. [29] assumed that the tracer diffusivities of Mn and Cr would be equivalent at the marker plane composition. However, Paul [97] rightfully pointed out that they reported different values for the two components, which is inconsistent. Additionally, the tracer diffusivity data for Mn and Cr in the quinary Co-Cr-Fe-Mn-Ni system reported by Vaidya et al. [38] suggests that there is an order of magnitude difference in tracer diffusivity between Mn and Cr at 1000 °C. This large difference indicates that vacancy wind effects can play a significant role in diffusion couples assembled with these quinary HEA systems, leading to significant cross-terms in the interdiffusivity matrix. Although Vaidya et al.'s data is for the equimolar composition of Co-Cr-Fe-Mn-Ni HEA, it is unlikely that the tracer diffusivities will vary enough to reduce the difference to zero at the composition of $CoCrFeMn_{0.5}Ni$, the marker composition of the quasi-binary couple employed by Tsai et al. [29]. Therefore, this discrepancy in tracer diffusivities raises concerns about the validity of Tsai et al.'s methodology.

Finally, while the quasi-binary couple approach chosen by Tsai et al. [29] for diffusion studies is appropriate, caution must be exercised when adopting any methodology or making assumptions. Oversimplification can lead to erroneous results that hold no significance.

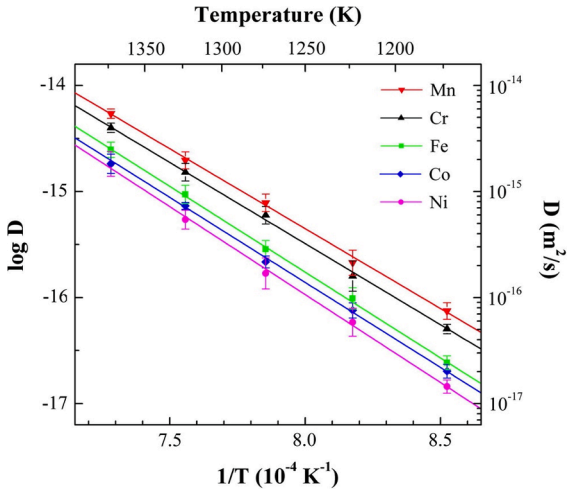

Fig. 7. Temperature dependency of tracer diffusion coefficients of all constituent elements in Fe-Ni-Co-Cr-Mn system, reprinted with permission from Tsai et al. [29].

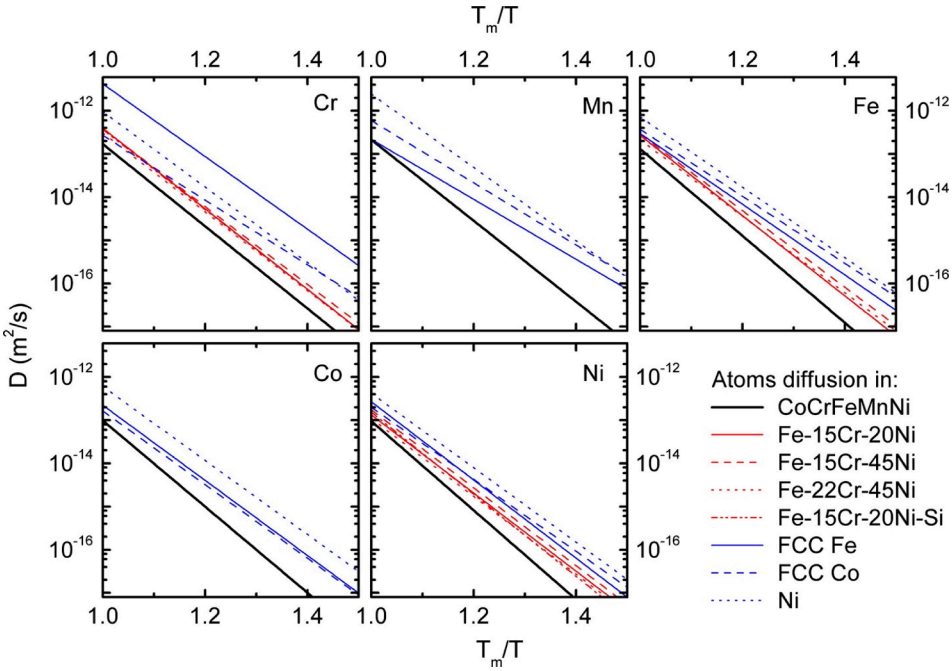

Fig. 8. Temperature dependency of tracer diffusion coefficients for Fe, Ni, Co, Cr and Mn in various systems, reprinted with permission from Tsai et al. [29].

In light of the above discussion, given that HEAs predominantly comprise substitutional elements, it is reasonable to expect that vacancies play a pivotal role in influencing the diffusion kinetics within these materials. The precise determination of vacancy formation energies holds significant relevance for comprehending HEAs' intricate diffusion and creep behavior. However, it is noteworthy that there exists a conspicuous dearth of comprehensive data pertaining to the energetics associated with lattice defects in HEAs, with only a limited number of studies offering insights in this domain within the existing literature.

Huang et al. [99] have studied the evaluation of vacancies in HEAs, specifically CoCrFeNi and CoCrFeMnNi. The study was conducted using a combination of analytical methods including Simmons–Balluffi techniques, positron measurements, and neutron diffraction, with Cu serving as a reference material. The formation enthalpies and associated entropies for both HEAs and Cu were computed, revealing that HEAs exhibit larger vacancy-dependent effective free volumes than Cu. This suggests that HEAs have a greater propensity for vacancy formation due to lattice structure relaxation at elevated temperatures. Spatially resolved synchrotron X-ray measurements unveiled distinct characteristics in the two HEAs under quasi-equilibrium conditions at high temperatures, with element-dependent behavior indicating the influence of Mn in the Cantor Alloy.

Sugita et al. [100] study focuses on ascertaining the vacancy formation enthalpy (ΔH_f) within a HEA comprised of CoCrFeMnNi, employing positron lifetime spectroscopy. By examining the temperature-dependent mean positron lifetime, the temperature at which positrons are captured by thermal vacancies (T_t) was determined to be 1181 K. Subsequently, the calculation of ΔH_f yielded a value in line with the range typically observed for the constituent pure metals found in the alloy. Additionally, the investigation led to the determination of a vacancy diffusion activation energy, closely mirroring the activation energies for self-diffusion reported for the individual face-centered cubic metals constituting the alloy. These outcomes provide significant insights into the vacancy-related characteristics of CoCrFeMnNi HEAs, particularly pertaining to atomic and vacancy diffusion phenomena.

In another study by Nayak et al. [101] have addresses the contentious issue of "sluggish diffusion" in HEAs and the noticeable gap in data concerning the energetics of lattice defects, particularly vacancies, in these alloys. Enthalpies of vacancy formation were experimentally determined using the residual resistivity technique for a range of alloys, from binary Fe-Ni to quinary equimolar Fe–Ni–Cr–Co–Mn. The resistivity of the alloys was measured using the four-probe method. The findings reveal a consistent increase in enthalpies of vacancy formation as the complexity of the alloy composition increases. A qualitative analysis indicates that the nature of the constituent elements has a more pronounced impact on enthalpies of vacancy formation than the sheer number of components. Such studies are very important for understanding the diffusion and creep behavior of materials.

In 2015, Kulkarni and Chauhan [30] reported an experimental investigation concerning the estimation of interdiffusion in HEAs. Their study examined interdiffusion behavior within the quaternary Fe-Ni-Co-Cr system, specifically at an elevated temperature of 1000 °C. This particular system is a subset of numerous HEAs, and their findings were based on the determination of average quaternary interdiffusion coefficients utilizing the analysis method proposed by Dayananda and Sohn [70]. Their findings concluded that Fe is the fastest diffuser and Ni is the slowest diffuser in the Fe-Ni-Co-Cr system, based on the main coefficients. Interestingly, they found that the magnitude of the cross coefficients was more prominent than the main coefficients. This indicates the existence of strong

diffusional interaction in the Fe-Ni-Co-Cr system, which casts doubt on the assumption of ideal solution behavior adopted by Tsai et al. [29] in their study. They also qualitatively demonstrated that the diffusional interactions are consistent with the relative binary thermodynamic interactions. The prominence of the cross terms suggests that diffusional interactions are crucial when studying diffusion in multicomponent alloys, and their understanding in HEA systems is critical. They assumed constant interdiffusion coefficients over the studied composition range, but this method will not be applicable if there is a large dependence on composition.

Similarly, Sohn's group conducted a study investigating the "core" effects of high entropy and sluggish diffusion in an FCC Al-Co-Cr-Fe-Ni alloy [31]. The researchers employed a high throughput combinatorial diffusion couple approach to explore this phenomenon. This involved diffusing Al and Ni into an equiatomic CoCrFeNi alloy within a temperature range of 900 to 1200 °C, resulting in the formation of non-equiatomic compositions.

The investigation unveiled that the average effective interdiffusion coefficients of the individual components within the Al-Co-Cr-Fe-Ni alloy did not exhibit a decrease when compared to those observed in lower-order CoCrFeNi and FeCrNi systems. Furthermore, the study determined the maximum solubility limit of Al in the non-equiatomic Al-Co-Cr-Fe-Ni alloys as a function of temperature, and this limit was compared with the solubility limit in the equiatomic Al-Co-Cr-Fe-Ni alloy. Notably, at temperatures of 1100 °C and higher, the non-equiatomic Al-Co-Cr-Fe-Ni alloy demonstrated a higher solubility limit of Al and exhibited greater thermodynamic stability compared to the equiatomic Al-Co-Cr-Fe-Ni alloy.

Additionally, the study found that the enthalpy of mixing played a significant role in stabilizing the single phase within the non-equiatomic Al-Co-Cr-Fe-Ni alloy compared to the equiatomic counterpart. Although entropy contributes significantly to the overall thermodynamic stability of a given HEA composition, the impact of the enthalpy of mixing cannot be disregarded when comparing the thermodynamic stabilities of different compositions. Consequently, equiatomic compositions, which possess the highest mixing entropy, may only sometimes exhibit the lowest free energy (i.e., thermodynamic stability) at high temperatures.

Another study reported by Sohn's group explores the impact of high entropy and sluggish diffusion on the properties of senary FCC Al–Co–Cr–Fe–Ni–Mn alloys [32]. The research was conducted using solid–solid diffusion couples between β-Al48Ni52 (B2) and Co20Cr20Fe20Ni20Mn20 (FCC) alloys, which allowed the generation of off-equiatomic compositions of senary FCC Al-Co-Cr-Fe-Ni-Mn alloys.

The findings of the study demonstrate that the solubility limit of Al in off-equiatomic Al-Co-Cr-Fe-Ni-Mn alloys exhibits an increase with temperature and surpasses that of equiatomic Al-Co-Cr-Fe-Ni-Mn alloys. Thermodynamic analysis revealed that the off-equiatomic composition of Al-Co-Cr-Fe-Ni-Mn alloy with the highest solubility for Al also displayed greater thermodynamic stability compared to the equiatomic Al-Co-Cr-Fe-Ni-Mn alloy. This can be attributed to the lower enthalpy of mixing observed in off-equiatomic alloys, resulting in a larger magnitude of the enthalpy of mixing, $|\Delta H_{mix}|$, and consequently higher thermodynamic

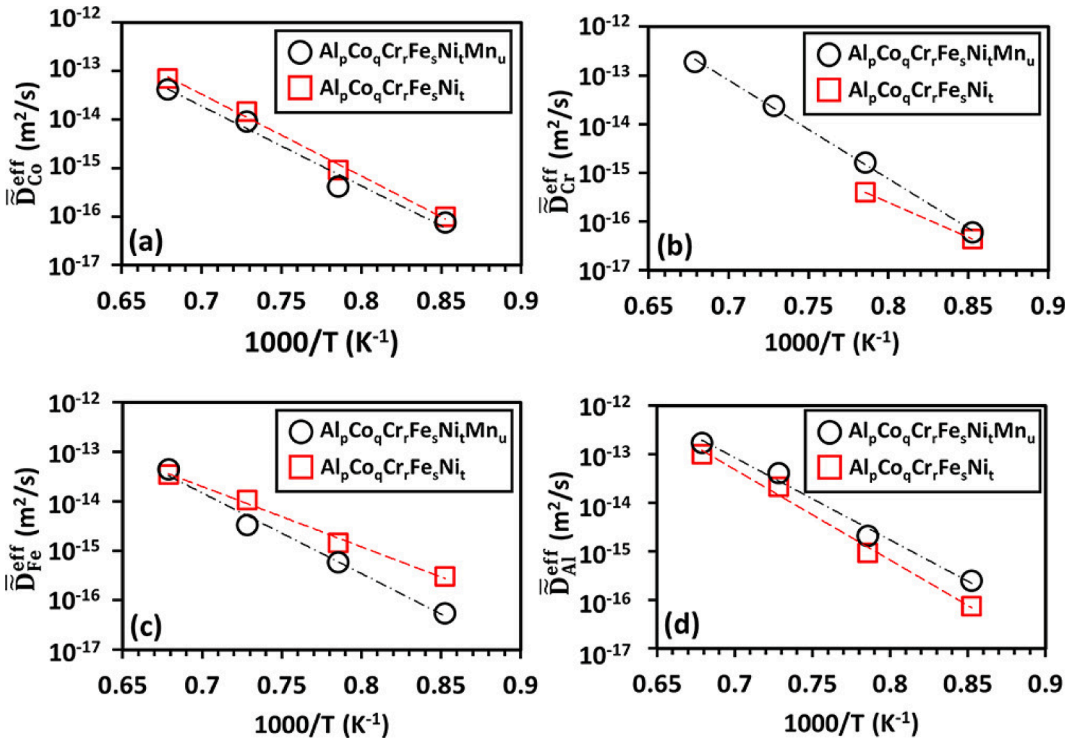

Fig. 9. Average effective interdiffusion coefficients for (a) Cobalt (Co), (b) Chromium (Cr), (c) Iron (Fe), and (d) Aluminum (Al) within the FCC structures of senary Al–Co–Cr–Fe–Ni–Mn and quinary Al–Co–Cr–Fe–Ni alloys, reprinted with permission from Mehta et al. [32]. Copyright (2020), American Chemical Society.

stability. It is noteworthy that this holds true despite the fact that the entropy of mixing is always greater for the equiatomic Al-Co-Cr-Fe-Ni-Mn alloy composition.

This study also investigated the diffusivity of the alloys by determining the average effective interdiffusion coefficients on both sides of the terminal alloys of the diffusion couples. The results showed that the interdiffusion coefficients for constituent elements in the Al–Co–Cr–Fe–Ni–Mn system varied, with some elements showing a "sluggish diffusion" effect, mainly observed in the BCC alloy but not in the FCC alloy see Figs. 9 and 10. This suggests that the potential energy fluctuations cannot always be correlated to the diffusivity in an alloy system. Therefore, a component in HEA with higher potential energy fluctuations may not always have a lower interdiffusion coefficient.

In another study [33], the authors used a traditional diffusion couple approach to determine interdiffusion coefficients for individual elements in the temperature range from 900 °C to 1200 °C. They also determined the tracer diffusion coefficient of Ni in $Al_{0.25}CoCrFeNi$ alloy using a sandwich diffusion couple experiment. They used a novel analytical method proposed by Belova et al. [102], which combines linear response theory with the Boltzmann-Matano approach and Gaussian distribution function [102,103]. The results showed sluggish diffusion kinetics were not observed in alloys with higher configuration entropy than those with lower entropy. This suggests potential energy fluctuations in alloys with higher configuration entropy may not always result in anomalously slow diffusion kinetics.

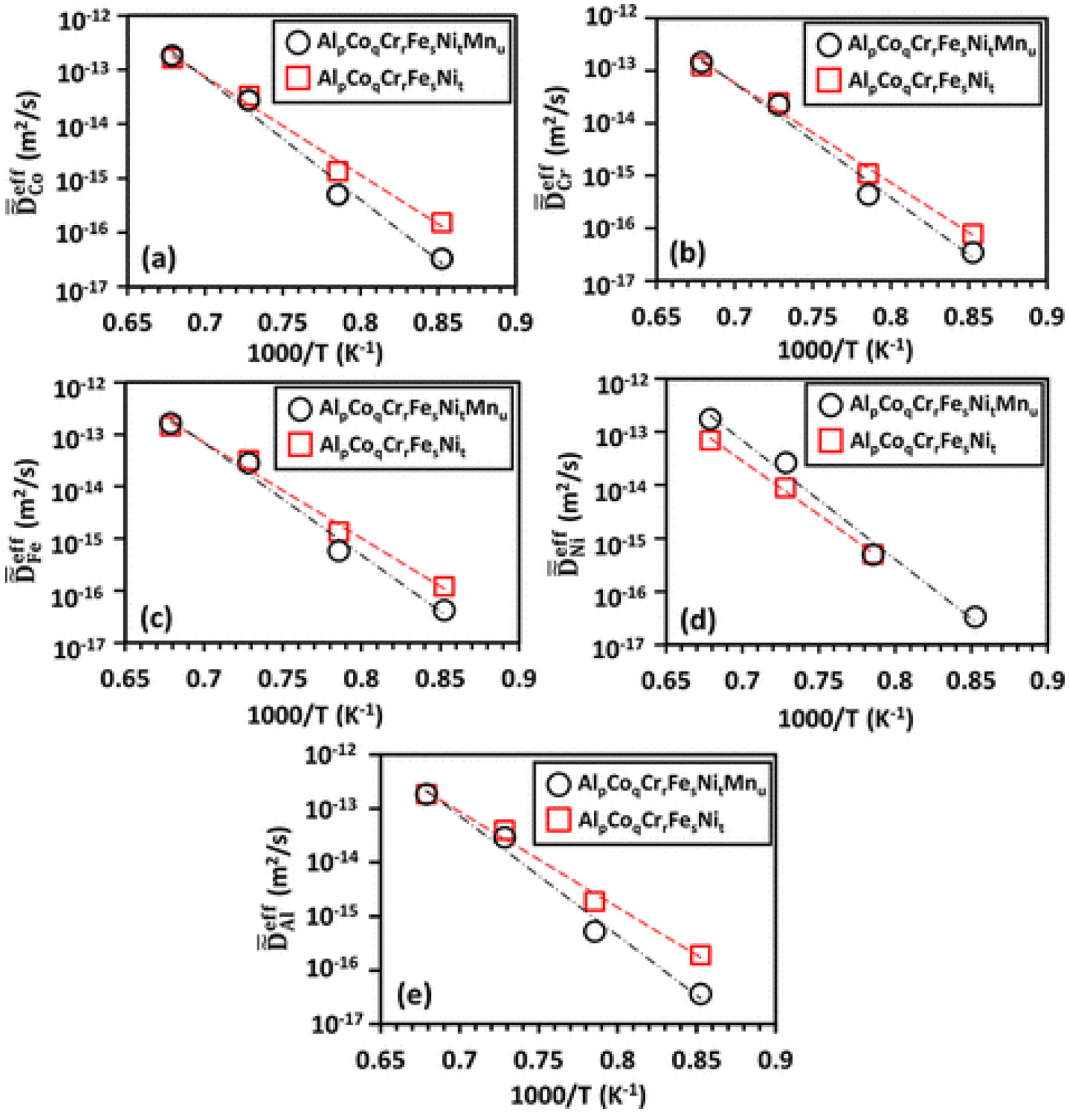

Fig. 10. Average effective interdiffusion coefficients for (a) Cobalt (Co), (b) Chromium (Cr), (c) Iron (Fe), (d) Nickel (Ni), and (e) Aluminum (Al) within the BCC (Body centered cubic) structures of senary Al–Co–Cr–Fe–Ni–Mn and quinary Al–Co–Cr–Fe–Ni alloys, reprinted with permission from Mehta et al. [32]. Copyright (2020), American Chemical Society.

Paul's group introduced the concept of pseudo ternary diffusion couples to gain a deeper understanding of diffusion behavior in multicomponent systems. Unlike the limited information provided by the pseudo binary approach, which yields only one out of nine interdiffusion coefficients in the case of a quaternary system, the Dayananda Sohn analysis offers average interdiffusion coefficients that only offer a qualitative understanding of diffusion behavior. In contrast, the pseudo ternary approach enables insights into the diffusional interactions between components. It allows for the development of diffusion profiles for three components while keeping the others constant. This approach provides a more comprehensive understanding of diffusion behavior by showcasing the diffusional interactions among the components. Nevertheless, pseudo binary approach may not directly provide cross terms for all elements individually. As suggested by Paul et al. [104], one must use several PB couples to address all tracer diffusion coefficients, which can be determined if one trusts thermodynamic description. These tracer diffusivities are fundamental input for any inverse numerical method as discussed previously. Additionally, the combination of pseudo binary and pseudo ternary couples provides a valuable strategy to obtain the complete diffusion matrix and all mobilities. Application of combination of pseudo binary and pseudo ternary couples are discussed in the later literature.

To demonstrate the practicality of this approach, Esakkiraja et al. [34] conducted a study on diffusion in the Ni-Co-Fe-Mo system. They utilized both the pseudo-binary and pseudo-ternary diffusion couple approaches to estimate several composition-dependent diffusion coefficients.

In their study [34], they have systematically studied several sub systems including binary, ternary, and quaternary systems in the Ni-Co-Fe-Mo alloy system. Intrinsic diffusion coefficients of both Ni and Fe were found to be reduced in the pseudo-binary couple PB NiFe (concentration of Co and Mo was taken constant in Ni-Fe-Co-Mo system) as compared to PB NiFe (concentration of Co was taken constant in Ni-Fe-Co system) which is also found consistent with the reduced Fe tracer diffusivity in the studied couples. Similarly, both Ni and Co intrinsic diffusivities were found to be reduced in the pseudo-binary couple PB NiCo (Fe and Mo fixed) as compared to PB NiCo (Fe fixed) which is also found consistent with the reduced Co tracer diffusivity in the studied couples. They have also estimated the composition-dependent main interdiffusion coefficients in ternary Al-Mn-Ni and quinary Al-Mn-Ni-Co-Fe system using the pseudo-binary PB Al-Mn (Ni fixed) and PB Al-Mn (Ni, Co and Fe fixed) couples and found that interdiffusion coefficients have very similar magnitudes in both the cases. Similar trend was also observed in case of the intrinsic diffusivities of Al and Mn. Based upon these observations, they have suggested that increasing the number of components (i.e., adding Co and Fe) does not necessarily reduce the diffusion rate. Further they have also estimated the interdiffusion coefficients in Ni-Co-Fe-Mo system by utilizing pseudo-ternary diffusion couple in which Mo concentration was taken constant. In their study, cross coefficients found to have significant magnitudes as compared to the main coefficients (see Table 7. [34] $\widetilde{D}^{Co}_{NiFe}$ vs $\widetilde{D}^{Co}_{NiNi}$).

Another report was published from the Paul's group [35] in 2020, in which they have studied the diffusion in quaternary Ni-Co-Fe-Cr system at 1200 °C by utilizing the pseudo-binary and pseudo-ternary diffusion couple approach. From the pseudo-binary couples, they have evaluated the composition-dependent main interdiffusion coefficients. In their pseudo-binary couples, they have added the markers to study the intrinsic diffusion in this system and also observed that the marker plane has a composition close to the equimolar composition. Further, they have reported the main interdiffusion, intrinsic, and tracer diffusion coefficients at the marker composition. In their study, vacancy wind factor and thermodynamic factors were also considered. For the evaluation of the thermodynamic factors required for the tracer coefficients, they have utilized Thermocalc software. From the estimated tracer diffusion coefficients and the tracer diffusivities reported by Vaidya et al. [38], they have also evaluated the interdiffusion coefficients at the equimolar composition and compared both the tracer diffusivities and interdiffusivities. A good match with the small difference in the data was found. In the author's opinion the small difference may be due to the uncertainty involved in the two different approaches and value of the thermodynamic factors. Further, they have reported four out of nine interdiffusion coefficients by utilizing the pseudo-ternary diffusion couple approach in the same system. Cross coefficients were found to have the same order of magnitude as the main coefficients. Further, uphill diffusion and the zero-flux planes were also observed, which suggest strong diffusional interactions in this system.

Esakkiraja et al. [36] have recently proposed a methodology by which the estimation of the tracer diffusion coefficients at the crossover composition of diffusion paths of the pseudo-ternary diffusion couples is possible. This newly developed approach does not require radioactive tracers for the diffusion study. This proposed methodology is the extension of the approach proposed by Lane and Kirkaldy in a ternary system. Based on the proposed approach, even part of the main and cross intrinsic diffusion coefficients can be estimated, which was earlier not possible in the ternary system using the Kirkendall marker experiments. Further, they have utilized this proposed approach to estimate the intrinsic and tracer diffusion coefficients. The magnitudes of the intrinsic diffusion coefficients were found similar in both the cases when the contribution of the vacancy wind effect was considered or neglected but in a few intrinsic coefficients, contribution of the vacancy wind effect was found prominent. Tracer diffusion coefficients were estimated based on the interdiffusion coefficients evaluated from the pseudo ternary couples and by utilizing the thermodynamic factors calculated from the Thermocalc software using the TCHEA2 database. Evaluated tracer diffusivities were also found consistent with the data evaluated using different approaches reported by Dash et al. [35], Gaertner et al. [41], and Vaidya et al. [38]. Although the proposed approach has several benefits, but the success of this approach strongly depends on the quality of the thermodynamic factors data available from the thermodynamic databases.

Tracer diffusivities are important material property that provide fundamental information on the diffusion behavior of constituent elements in alloys under negligible concentration gradient. The first study on tracer diffusion in HEAs using radioactive tracers was conducted by Vaidya et al. [37]. They investigated the tracer diffusion of Ni in equimolar Co-Cr-Fe-Mn-Ni and Co-Cr-Fe-Ni HEAs. In a subsequent report [38], they extended their investigation to include the bulk tracer diffusion of the remaining components in the same alloys at temperatures ranging from 800 to 1100 °C.

In their first report [37], they found that at the absolute temperature scale, the magnitude of Ni tracer diffusivity was higher in the quinary Co-Cr-Fe-Mn-Ni system compared to the quaternary one for equimolar compositions. They explained this observation by the addition of Mn, which reduces the melting temperature of the alloy and results in a higher concentration of equilibrium vacancy at a particular temperature. At the normalized temperature, they observed a higher Ni tracer diffusivity in the quaternary Co-Cr-Fe-Ni system than the quinary one up to a crossover temperature, beyond which the trend reversed. This was attributed to the different diffusion behavior in the two systems due to the presence of Mn in one and its absence in the other. Ni tracer diffusion coefficient in various systems on an absolute and normalized temperature scale are presented in Fig. 11 for comparison.

In their second report [38], they determined the tracer diffusivities of the remaining components and found that the overall diffusivity trend for the fastest to slowest diffusing species was $D^*_{Cr} > D^*_{Fe} > D^*_{Co} > D^*_{Ni}$ in case of the quaternary and $D^*_{Mn} > D^*_{Cr} > D^*_{Fe} > D^*_{Ni} > D^*_{Co}$ in the quinary system over most of the temperature range studied see Fig. 12. This trend was consistent with conventional alloys see Fig. 13. They compared their results with those of conventional FCC alloys and concluded that an increasing number of components does not always guarantee sluggish diffusion behavior, as it is only observed at the normalized temperature scale and is absent at the absolute temperature scale.

In a separate investigation, Vadiya et al. [39] conducted a study on grain boundary diffusion in CoCrFeNi and CoCrFeMnNi alloy systems. The researchers employed radiotracer analysis using the 63Ni isotope to quantify the grain boundary diffusion of Ni in these alloys. The study confirmed the absence of elemental segregation at grain boundaries, allowing for a reliable estimation of the grain boundary width at approximately 0.5 nm.

The classification of grain boundary diffusion kinetics by the authors involved three distinct types: A-, B-, or C-type. The measurements conducted in this study were found to belong to either the B- or C-type kinetic regimes, which depended on the temperature and duration of diffusion. The C-type regime, commonly associated with lower temperatures and shorter annealing times, indicated that atomic transport predominantly occurred along the grain boundaries. On the other hand, the B-type regime was characterized by a significant contribution of bulk diffusion, particularly at higher temperatures.

Remarkably, the study demonstrated that an increase in the number of constituent elements in HEAs did not automatically lead to a reduction in grain boundary diffusion rates. Instead, the specific nature of the added constituents played a more influential role. Additionally, the authors made an interesting observation that grain boundary diffusion in a quinary HEA was higher than that in the quaternary alloy at temperatures around 800 K, but the relationship reversed at lower temperatures. In comparison, the diffusivity of grain boundary diffusion in CoCrFeNi was approximately one order of magnitude slower than in pure Ni and the binary alloy. Meanwhile, CoCrFeMnNi exhibited decelerated diffusivities only above a specific temperature threshold.

In another study, Vaidya et al. [40] estimated the thermodynamic factors for diffusion in the Co-Cr-Fe-Ni and Co-Cr-Fe-Ni-Mn systems at 1150 °C using pseudo-binary couples. Initially, they evaluated the main interdiffusion coefficients and found that interdiffusion was faster in the quinary system compared to the quaternary system. The authors attributed this to the lower melting point of the quinary alloy, which resulted in higher equilibrium vacancies at a given temperature, leading to faster diffusion. Furthermore, they assessed the thermodynamic factors using the Darken-Manning relation, utilizing the calculated interdiffusion coefficients and tracer diffusivities from their own previous study [38]. Although they reported a significant difference in the Mn and Cr tracer diffusion coefficients in their previous study [38], they did not consider the contribution of vacancy wind factors in this report. These vacancy wind factors could have a substantial impact based on the difference in tracer diffusivities.

Based on their findings, they noted that the thermodynamic factor values were close to unity for the quaternary system but exhibited significant deviations for the quinary system. This raised questions regarding the assumption of ideal solution behavior adopted by Tsai et al. [29] in their report. However, in a recent publication, Belova and Murch [105] considered the vacancy wind factor and reported thermodynamic factors for the same system studied by Vaidya et al. [40]. They discovered that the thermodynamic factors ranged from 0.43 to 0.77 for the quaternary system and from 0.84 to 2.34 for the quinary system.

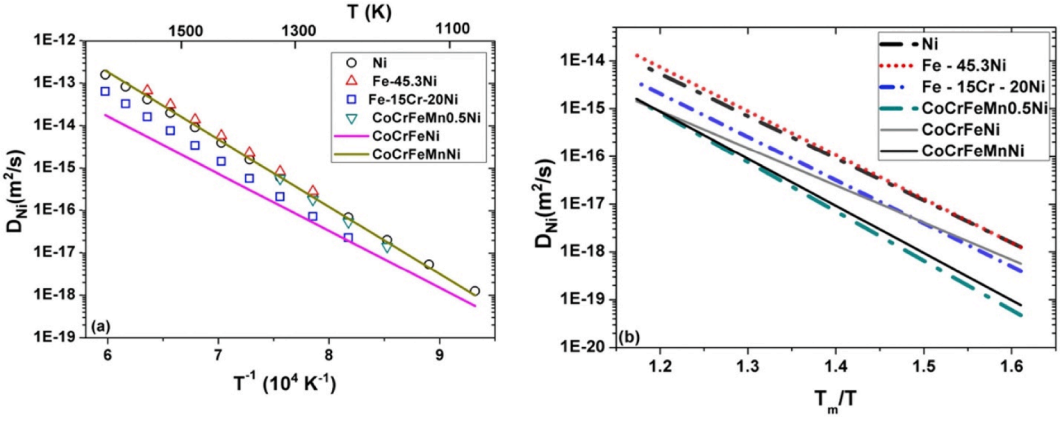

Fig. 11. Comparison of Ni tracer diffusion coefficient on an absolute (left) and normalized (right) temperature scale in various systems, reprinted with permission from Vaidya et al. [37].

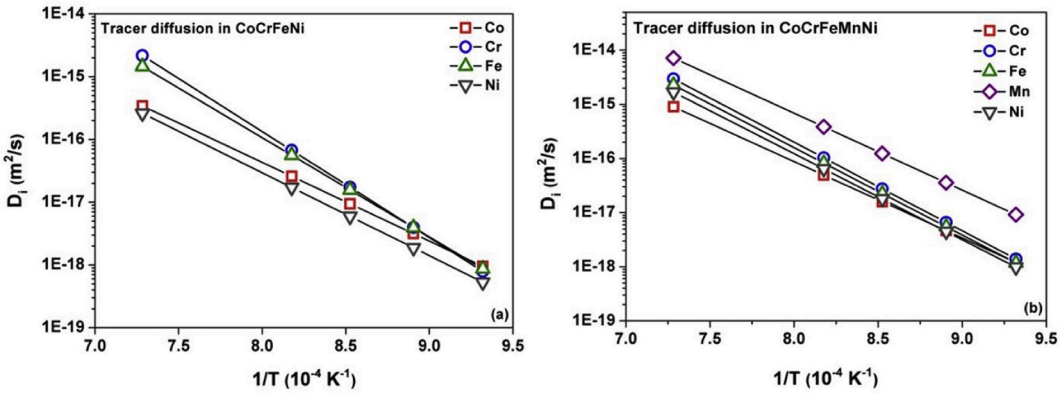

Fig. 12. Temperature dependent tracer diffusion coefficients of all constituent elements in quaternary Fe-Ni-Co-Cr (left) and quinary Fe-Ni-Co-Cr-Mn (right) systems, reprinted with permission from Vaidya et al. [38].

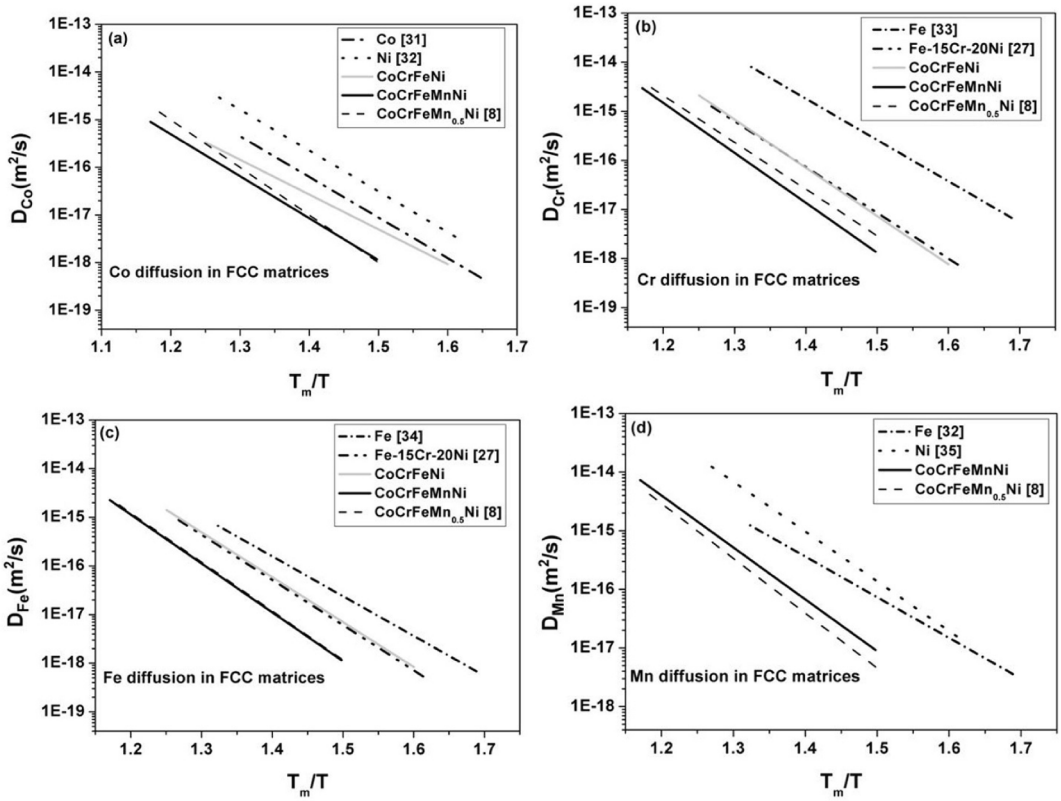

Fig. 13. Comparison of tracer diffusion coefficients on a normalized temperature scale for (a) Co, (b) Cr, (c)Fe and (d) Mn in various systems, reprinted with permission from Vaidya et al. [38].

Gaertner et al. [41] have studied the tracer diffusion in the same system as studied by Vaidya et al. [38] i.e., Co-Cr-Fe-Ni and Co-Cr-Fe-Ni-Mn systems but on the single crystalline alloys at 1100 °C. They have also studied Cu tracer diffusion in Co-Cr-Fe-Ni system in the temperature range of 700 to 900 °C. They have adopted a similar methodology to study tracer diffusion, followed by Vaidya et al. in [38]. They have observed good agreement with the evaluated tracers reported by Vaidya et al. [38], based upon which they have disregarded the theory of sluggish diffusion in HEAs. They further observed that Cu is the fastest diffuser and has the lowest activation energy as compared to the other components in the CoCrFeNi system. In the author's opinion, this may be because of the existence of strong solute–vacancy pair interactions, which may cause the formation of the clusters that are rich in Cu in the CoCrFeNi system.

On the similar lines of Vaidya et al. [38], Kottke et al. [42] have studied tracer diffusion in Co-Cr-Fe-Ni-Mn system using three different alloys in which one alloy has the equimolar composition i.e., Co20Cr20Fe20Mn20Ni20 and the other two alloys are Ni-rich

alloys i.e. Co10Cr10Fe10Mn10Ni60, and Co2Cr2Fe2Mn2Ni92 at 1100 °C. They have adopted a similar methodology to study tracer diffusion, followed by Vaidya et al. in [38]. They have observed that the tracer diffusion kinetics was slower for Cr, Co, and Mn components in the case of the equimolar composition compared to the Ni-rich alloys or dilute solid solutions at absolute temperature. However, on comparing the diffusion coefficients of HEA with pure Ni, they have observed that coefficients are in a similar range within 50 %. But in the case of the normalized temperature, magnitudes of the diffusion coefficients were found higher for Ni by a factor of 3 and for Co by a factor of 8 in the case of the Co10Cr10Fe10Mn10Ni60 alloy system as compared to the equimolar composition. Furthermore, it was observed that the diffusion coefficients exhibited notably higher values in the Co2Cr2Fe2Mn2Ni92 alloy system when compared to the equimolar composition. Specifically, for Ni, the diffusion coefficients were higher by a factor of 10, while for Fe, they were higher by a factor of 30. Notably, despite this substantial deviation in data, these magnitudes remain within the typical range observed for most FCC conventional alloys. Consequently, based on these findings, the authors did not lend support to the theory of sluggish diffusion in HEAs.

Gaertner et al. [43] conducted a study using a combined approach of diffusion couple and tracer methods to investigate the composition-dependent tracer diffusion coefficients in Co-Cr-Fe-Mn-Ni at 1100 °C. Their experiment employed pseudo-binary couples and placed radioisotopes (57Co, 51Cr, 59Fe, and 54Mn) between the two terminal alloys. Additionally, these isotopes were applied to the terminal end members of the couple to estimate the composition-dependent tracer diffusivities. Although the initial concentrations of Mn, Cr, and Fe were kept constant, the researchers observed an uphill diffusion phenomenon after performing diffusion annealing. This observation was evident from the concentration profiles in Fig. 14 (a). It suggests the presence of strong diffusional interactions within this system. To evaluate the composition-dependent tracer coefficients, the researchers employed the formalism proposed by Belova et al. [102], specifically designed for the thin-film isotope sandwich configuration. This choice was made because the Gaussian solution is invalid in the presence of significant diffusional interactions.

Based on the experimentally determined tracer diffusivities, they have verified different commercially available and newly developed thermodynamic and mobility databases by simulating the diffusion profiles. Commercially available databases TCFE9/MOBFE4, TCNI8/MOBNI4, and HEA-DB/MOBNI4 failed to predict the correct experimental profiles. They were unsuccessful in predicting the direction of the uphill diffusion in the case of the Cr and Fe see Fig. 15. Simulations utilizing the HEA-DB database combined with the composition-dependent atomic mobility data from two different sources i.e., MTIC-Lin and MTIC-BM show that it predicts directions for the uphill diffusion for Cr and Fe correctly and also very successful in predicting the concentration profiles and composition-dependent tracer profiles.

Li et al. [44] have investigated the inter-diffusion behavior in a series of alloys ranging from the binary CoNi alloy to the quinary FeCrMnCoNi HEA. The findings of the study reveal important insights into inter-diffusion in these alloys. Firstly, it was observed that the sluggish diffusion effect, often associated with high entropy alloys, was not evident in the FeCrMnCoNi HEA in both absolute and homologous temperature scales. This suggests that the exceptional high-temperature properties of HEAs may not solely rely on sluggish diffusion.

The study further demonstrates that the addition of specific elements has a significant impact on inter-diffusion behavior. The presence of Mn increases inter-diffusion in the absolute temperature scale but decreases it in the homologous temperature scale. Conversely, the addition of Cr decreases inter-diffusion in both temperature scales. The effects of Fe are more complex, with its influence on inter-diffusion depending on the presence of other elements. The interactions between Fe and other elements also play a crucial role in diffusion behavior. The study also revealed that the atomic diffusion process may not change qualitatively from binary to multiple principal alloys. The pre-exponential factor and activation energy were analyzed, showing a correlation between them. The analysis suggested that the higher activation energy alone does not lead to slower diffusion, indicating that other factors, such as the effects of specific elements, play a crucial role. While significant findings have been reported, the present author has serious concerns

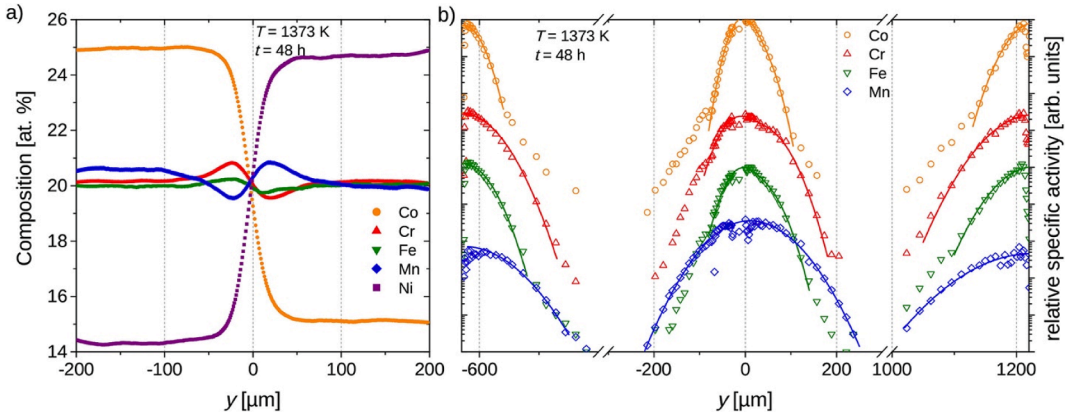

Fig. 14. A) concentration profile developed in the diffusion zone obtained by epma-analysis and b) penetration profiles obtained for the diffusion of tracers 57co, 51cr, 59fe, and 54mn (indicated by open symbols) from both the external surfaces and the internal source positioned at the initial interface between the two alloys (the gaussian fits for these profiles are depicted by the straight lines.), reprinted with permission from Gaertner et al. [43].

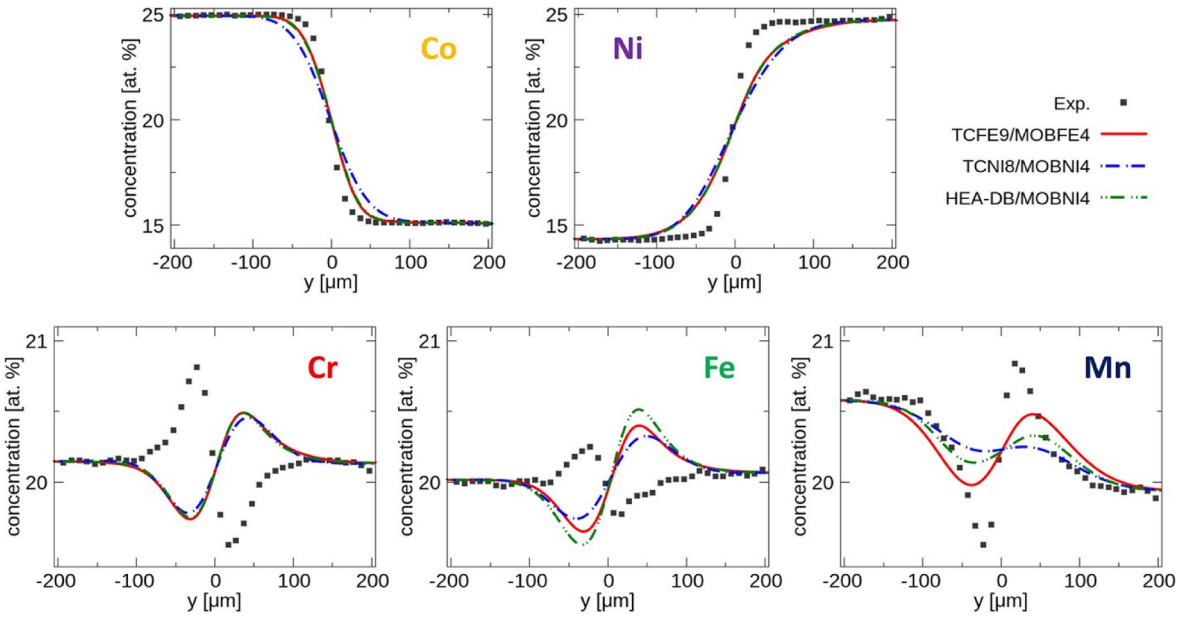

Fig. 15. Comparison between the interdiffusion profiles obtained through experimental measurements and those simulated with the utilization of three distinct thermodynamic/kinetic databases for the five elements (Co, Cr, Fe, Mn, and Ni) following exposure to 1373 K for a duration of 48 h, reprinted with permission from Gaertner et al. [43].

regarding the concentration profiles. The use of Energy Dispersive Spectroscopy (EDS) for measuring the concentration profile has resulted in notable scatter in the concentration data. The presence of significant scatter in the data raises concerns about the potential oversight of uphill diffusion (especially see Fig. 16, d and f). Neglecting to consider uphill diffusion in the profile analysis of the pseudo binary diffusion couple can result in erroneous interpretation of the results.

The majority of diffusion studies reported in the literature concerning HEAs have primarily focused on the FCC alloys. These FCC alloys are known for their relatively low lattice strain compared to the body-centered cubic (BCC) alloys. However, a few recent publications by Divinski's group specifically address diffusion in other systems like BCC, hexagonal close-packed (HCP), and tetragonal alloys. These studies contribute to expanding our understanding of diffusion behavior in a broader range of alloy structures beyond the commonly studied FCC HEAs.

In their 2021 publication, Zhang et al. [45] conducted a study on the diffusion behavior of nickel (Ni) and iron (Fe) in the CoCrFeMnNi sigma-phase alloy, utilizing the radioactive tracer technique. The researchers measured the tracer diffusion coefficients of Ni and Fe in the sigma-phase alloy to be within the range of 10^{-21} to 10^{-17} m^2/s, across temperatures ranging from 928 K to 1173 K. Interestingly, the diffusion rates of Ni and Fe were found to be similar. Remarkably, the study revealed an accelerated bulk diffusion in the compositionally complex sigma-phase alloy compared to the equiatomic CoCrFeMnNi alloy when comparing them on the homologous temperature scale. However, when examined on the absolute temperature scale, diffusion occurred at approximately the same rate in both the quinary sigma-phase and the equiatomic CoCrFeMnNi alloy within the investigated temperature range. This observation challenges the conventional notion of sluggish diffusion in HEAs. Notably, the similarity in the diffusion rates of Ni and Fe within the sigma-phase alloy further challenges this traditional understanding. These findings underscore the necessity for direct measurements of diffusion rates in complex alloys to accurately predict their long-term phase stability.

In another report by Zhang et al. [46], they have studied the diffusion behavior of Zr in BCC refractory HEAs. The authors used a radioactive tracer technique to measure the diffusion coefficients of Zr in two BCC HEAs, HfTiZrNbTa and HfTiZrNbV. The results showed that the diffusion coefficients of Zr in both alloys are significantly higher than those in traditional BCC alloys, considering both the absolute and homologous temperature scales refer to Fig. 17. Their findings also suggest that the diffusion of Zr in the refractory HEAs is not sluggish and does not show a significant correlation with the factors like chemical complexity, mixing entropy, potential energy fluctuation, and lattice mismatch. Interestingly, Zr diffusion in the TiZrHfNbTa alloy appears to be enhanced rather than retarded, while diffusion in the TiZrHfNbV alloy found slower due to its higher melting point. These findings indicates that the diffusion behavior in refractory HEAs is complex and not solely influenced by chemical complexity or lattice characteristics.

Sen et al. [47] have studied diffusion of Ti in the HCP alloys using the radiotracer technique and ^{44}Ti isotope. This study investigates the diffusion behavior of titanium (Ti) in HCP HEAs containing a combination of Hf, Ti, Zr, Al, and Sc. The experimental results show that the Ti diffusion rates in the multi-principal element alloys are significantly higher than those predicted by a simple geometric mean of the pure metals diffusion coefficients (see Fig. 18). This unexpected behavior is referred to as "anti-sluggish" diffusion. This study focuses on the impact of chemical complexity and lattice distortions on the diffusion of Ti in HCP HEAs. Alloying HfTiZr alloy with Al and Sc enhances the Ti diffusion rates, with the effect becoming more pronounced as the Al content increases. Furthermore, the analysis of lattice distortions reveals that the HCP alloys exhibit higher mean squared atomic displacements (MSAD) for Ti atoms

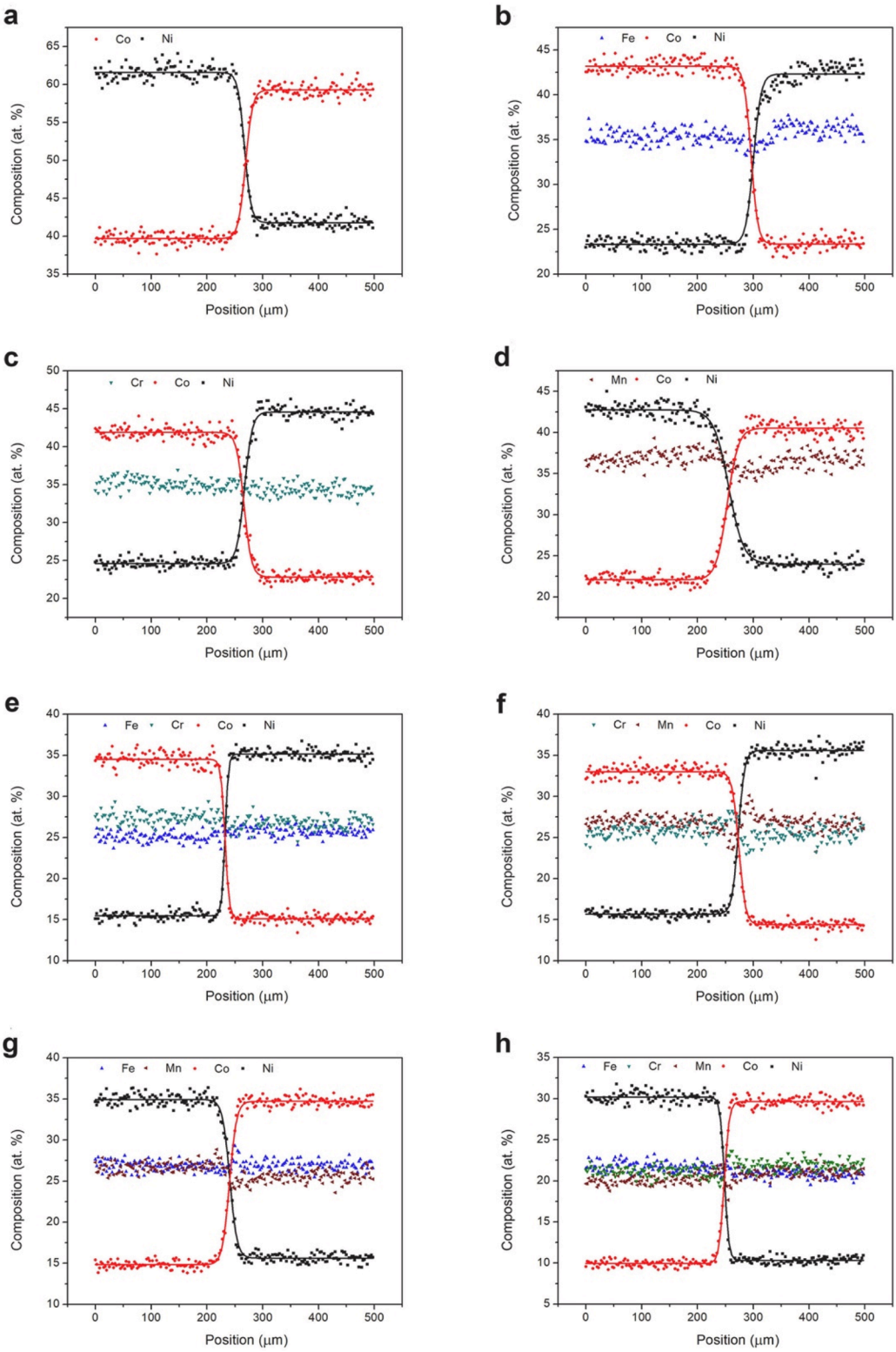

Fig. 16. Profiles depicting the composition variations of CoNi (a), FeCoNi (b), CrCoNi (c), MnCoNi (d), FeCrCoNi (e), CrMnCoNi (f), FeMnCoNi (g), and FeCrMnCoNi (h) in diffusion couples subjected to annealing at 1250 K. The markers illustrate the experimental outcomes, while the lines correspond to the fitted results, reprinted with permission from Li et al. [44].

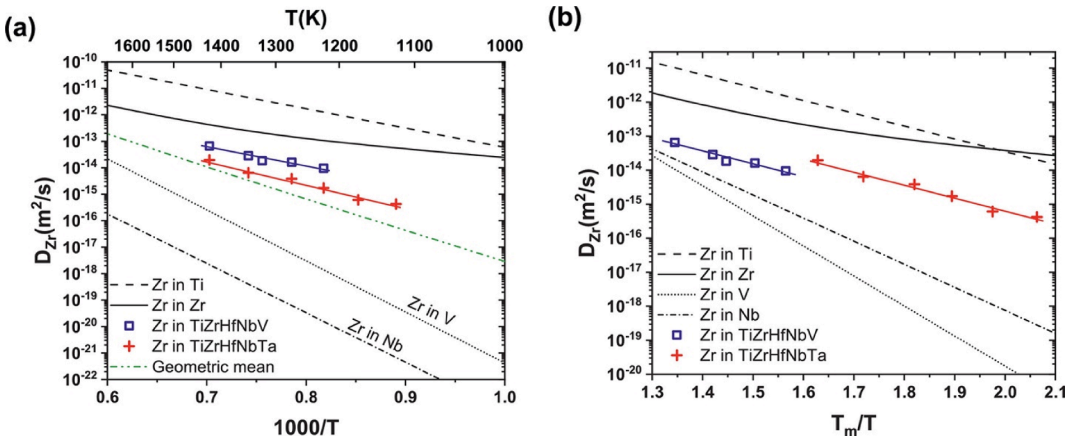

Fig. 17. Comparison of Zr tracer diffusion coefficient on an (a) absolute (left) and (b) normalized (right) temperature scale in various BCC systems, reprinted with permission from Zhang et al. [46].

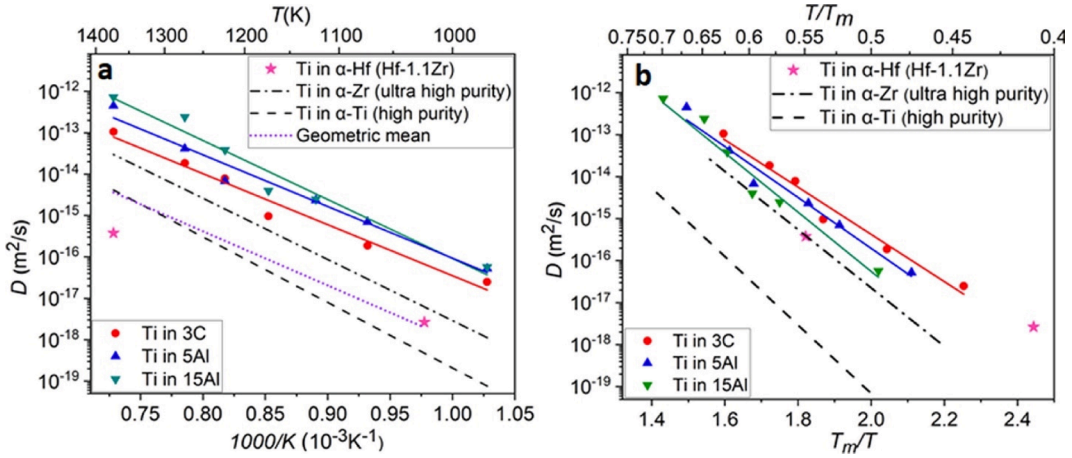

Fig. 18. Comparison of Ti tracer diffusion coefficient on an (a) absolute (left) and (b) normalized (right) temperature scale in various HCP systems where 3c, 5Al and 15Al represents equiatomic ternary HfTiZr, quinary Al5Hf25Sc20Ti25Zr25 and Al15Hf25Sc10Ti25Zr25 alloys respectively, reprinted with permission from Sen et al. [47].

compared to unary HCP metals. This signifies that the alloys possess greater distortions within their lattice structures. The increased lattice distortions play a key role in promoting the increased diffusivity of Ti within the alloys, thus contributing to the observed enhancement in Ti diffusion rates.

These findings challenge the notion of "sluggish diffusion" as a core effect of high-entropy alloys. In contrast to previous observations in FCC and BCC systems, where diffusion rates were lower or similar to the corresponding unary metals, the HCP HEAs demonstrate accelerated Ti diffusion. The results highlight the significance of lattice distortions and suggest they play a more significant role than entropy and potential energy factors in governing diffusion behavior.

Lukianova et al. [48] have studied effects of carbon addition on self-diffusion in CoCrFeMnNi HEAs. The results shows that the carbon alloying affects the self-diffusion behavior of constituent elements in CoCrFeMnNi HEAs. At elevated temperatures, the addition of interstitial carbon leads to complex effects on self-diffusion rates. A small amount of carbon (0 to 0.2 at.%) retards self-diffusion, particularly for slower-diffusing elements such as nickel (Ni). The observed diffusion retardation at high temperatures is attributed to a reduction in anharmonic contributions to the temperature-dependent vacancy formation entropy. In addition, Activation energies of self-diffusion were found to be decreased with increasing carbon content, indicating facilitated atomic movement. The influence of interstitial carbon on self-diffusion found most pronounced for manganese (Mn), which exhibits the largest enhancement in diffusion rates due to the larger size of Mn atoms and associated elastic distortions caused by dissolved carbon. Continuous and linear trend in the diffusion behavior of carbon alloyed HEAs were observed, with diffusion rates increasing with the addition of interstitial carbon. Carbide precipitates, present as a secondary phase in the alloys, have a negligible impact on self-diffusion due to their low volume fraction (<1%). Further studies utilizing density functional theory (DFT) calculations are needed to comprehensively understand the effects of carbon on self-diffusion in HEAs, considering the complexities of chemical environments and thermal excitations.

The author and their fellow researchers conducted a groundbreaking study [49] that represented a pioneering effort in the experimental determination of comprehensive sets of quaternary and quinary interdiffusion coefficients. Their specific focus lay on investigating the Fe-Ni-Co-Cr and Fe-Ni-Co-Cr-Mn systems. To achieve this, they employed the body-diagonal diffusion couple method to select the terminal compositions for the diffusion couples, conducting their investigations at a temperature of 1000 °C. The outcome of their research unveiled cross coefficients of a comparable magnitude to the primary coefficients. Particularly noteworthy were the unique characteristics observed in the diffusion profiles, such as uphill diffusion and the presence of zero flux planes, both indicative of substantial diffusional interactions within the quinary Fe-Ni-Co-Cr-Mn system. Moreover, their study demonstrated the effectiveness of the body diagonal diffusion couple approach in systems characterized by diffusion profiles featuring zero-flux planes, uphill diffusion, and substantial differences in terminal concentrations, all satisfying the requirement of constant interdiffusivities in the diffusion zone. An additional significant finding from their study was that the magnitudes of quinary interdiffusion coefficients were higher when compared to their respective quaternary counterparts at equimolar compositions. This suggests that an increase in the number of components does not necessarily ensure sluggish interdiffusion kinetics.

Another groundbreaking study reported by Dash et al. [50] recently introduced a method to estimate different types of diffusion coefficients in complex systems with multiple components. In their study, they focused on the NiCoFeCr alloy system. Their analysis involved examining intersecting diffusion paths, where diffusion profiles were generated for various types of paths, such as multi-component body diagonal paths with pseudo-binary or pseudo-ternary paths. To modify the flux equations, they incorporated the Lane and Kirkaldy as well as Manning's relations. Using these equations, they determined the tracers, intrinsic, and interdiffusion coefficients by utilizing fluxes and concentration gradients from the body diagonal and pseudo-binary or ternary diffusion paths. Additionally, they utilized the thermodynamic factor, which was calculated using the Thermocalc software with the TCHEA3 database. The analysis considered intersecting diffusion paths and accounted for the vacancy wind effect. One noteworthy finding highlighted in the articles was the impact of the vacancy wind effect on diffusion coefficients. Experimental results indicated that the vacancy wind effect had a minor influence on the primary intrinsic diffusion coefficients, but it significantly affected certain cross intrinsic and interdiffusion coefficients, causing changes in magnitude and even a reversal in sign. Although this approach is efficient and requires fewer diffusion couples compared to the body diagonal diffusion couple approach, the authors emphasized that its success heavily relies on fulfilling the constraints of the pseudo-binary system and the quality of the thermodynamic factor data. Nevertheless, this novel technique is useful for providing all tracer diffusivities/mobilities with arbitrary concentration dependence.

In a recent report, the present author and coauthor [51] determined interdiffusion coefficients within the quaternary Fe-Ni-Co-Cr and quinary Fe-Ni-Co-Cr-Mn systems using the square root diffusivity method. Interestingly, this method was originally proposed by Thompson and Morral in 1986 but remained largely overlooked by the diffusion research community. It's worth noting that this method shares similar prerequisites with the body diagonal diffusion couple approach. For their investigation of the square root diffusivity method in quaternary and quinary systems, the present author employed diffusion couples prepared based on the body diagonal diffusion couple approach, as described in their earlier study.

The agreement observed in the interdiffusivity data derived from the square root diffusivity method was excellent when compared to data determined using the Kirkaldy's approach, with only a few coefficients showing discrepancies. This variation may be attributed to the relatively small magnitudes of these coefficients, which inherently introduce more uncertainty. Additionally, differences in the concentration gradients used by both methods may contribute to these variations. Specifically, the square root diffusivity approach utilizes gradients from the terminal compositions, whereas Kirkaldy's approach employs the actual gradient at the crossover composition.

These findings suggest that both techniques, i.e., Kirkaldy's approach and the square root diffusivity method based on the body diagonal diffusion couple approach, perform effectively in systems featuring diffusion profiles with zero-flux planes and uphill diffusion. They are also suitable for systems characterized by large differences in terminal concentrations, as long as the prerequisite of constant interdiffusivities within the diffusion zone is met.

4.2. Numerical or computational investigations

Dabrowa et al. [52] investigated tracer diffusion in the Al-Co-Cr-Fe-Ni system using the inverse simulation method and they reassessed the tracer diffusivities previously reported by Tsai et al. [29] with the same approach. They employed two methodologies, namely the Levenberg-Marquardt and genetic algorithms coupled with the Darkens-Manning approach for mobility optimization. The authors assumed ideal solution behavior for the system and considered tracer diffusivities to be independent of composition. They first tested their methodology on the results obtained by Tsai et al. [29], then applied it to the Al-Co-Cr-Fe-Ni system. The results were qualitatively consistent with those reported by Tsai et al. [29], but the activation energy was lower quantitatively. Interestingly, the authors observed uphill diffusion in some profiles of diffusion couples in the Co-Cr-Fe-Ni-Co system, indicating the existence of strong diffusional interactions in this system and raising questions about the suitability of the quasi-binary approach adopted by Tsai et al. The sequence of the fastest to the slowest diffuser in both systems was found to be $D^*_{Cr} > D^*_{Fe} > D^*_{Co} > D^*_{Ni}$. The researchers observed that the diffusivities in the Al-Co-Cr-Fe-Ni system were comparable to those in the Co-Cr-Fe-Ni-Co system, suggesting sluggish diffusion behavior [52]. However, they did not account for the normalization of the temperature scale using the alloy melting point, as done by Tsai et al. [29].

Zhang et al. [53] have studied diffusion in quinary Co-Cr-Fe-Ni-Mn system. First, they have used the CALPHAD approach for optimization of mobility parameters and then utilized the diffusion couple experimental approach to validate these obtained parameters. In the CALPHAD approach, properties related to multicomponent systems can be assessed based on the knowledge of the

properties data available for its constituent lower-order or subsystem. So, for the optimization of the mobility parameters, they have utilized the diffusion data available in the literature for Co-Fe, Co-Ni, Cr-Fe, Cr-Ni, Fe-Ni, Fe-Mn, Mn-Ni binary systems, Co-Fe-Ni, Co-Cr-Ni, Cr-Fe-Ni ternary systems, and Ni-based superalloys. For the calculation of the thermodynamic factors, they have used the PAN-HEA database [26,106]. For the validation of the mobility database, they have regenerated both values of the diffusion parameters and also the experimental concentration profiles that are available in the literature. Using the refined mobility database, the authors assessed the tracer diffusivities of Ni within the subsystems of the Co-Cr-Fe-Ni-Mn quinary system. Their analysis revealed no correlation between sluggish diffusion behavior and the number of components, both in terms of absolute temperature and the normalized temperature scale.

Chen et al. [54] have studied diffusion in Fe-Ni-Co-Cr-Mn system using the diffusion multiple techniques by utilizing the inverse simulation method, which they describe as a "pragmatic numerical inverse metho". Authors have simulated the concentration profiles by numerically solving the continuity equation; based on that, they have optimized mobilities parameters from the best fit of experimental and simulated concentration and flux profiles to get reliable data. They have found a good match for the concentration profiles for both the cases (experimental and simulated) for all the components except for Mn. The same sequence for the inter-diffusivities of components that were found on comparing the main interdiffusivities (when Ni treated as the dependent component) was observed as the order reported by Tsai et al. [29] but not for the whole range of studied compositions. These authors then compared the main interdiffusivity of Fe and Co with the interdiffusivities data available in the binary and ternary systems. They found that magnitude of the interdiffusion coefficients becomes smaller with the increasing number of components. They have also compared the main interdiffusivity data of Fe with the data reported by Kulkarni et al. [30] and found that the diffusivities have the same order of magnitude in spite that these values are determined at a difference of 100 K. Based on these outcomes authors concluded that interdiffusion is sluggish in this system. They have also assessed the tracer diffusivity data by utilizing the mobilities data and compared the Ni tracer diffusivity with the data available in the binary, ternary, and quaternary systems, and they did not find similar behavior. Although this method has an edge over the methods which only utilizes concentration profiles (as it utilizes both concentration and flux profiles) but the error involved based on the flux-calculations from the raw concentration data, without rigorous fitting, puts limitations on this approach as the large errors are involved while using the unfitted data as Chen et al. [54] have done.

On similar lines as Chen et al. [54], Li et al. [55] have studied diffusion in FCC phase of Al-Co-Cr-Fe-Ni system by utilizing the inverse simulation technique. Their experimental and computational procedure is similar to Chen et al.'s [54]. Authors have reported the main interdiffusion coefficients as a function of composition. They have observed the following sequence for the interdiffusion and found a large variation, with composition, in the magnitudes of the interdiffusion coefficients for Al and Co but a small variation in the case of Fe and Cr. The sequence of the interdiffusion coefficient magnitudes was consistent with the results reported by Dabarow et al. [52]. Authors have also estimated the tracer diffusion coefficients and compared them with the data available in the literature for the unary, binary, and ternary systems. Based upon that author has concluded that the diffusion in the HEA cannot be considered as sluggish.

As we have already mentioned the methodology adopted by Chen et al. [54] involves large errors in the flux calculations from the raw concentration profiles that are truly reflected in the flux profiles presented by Li et al. [55], which suggests the large error involvement in interdiffusion flux calculations. Thus, large error can also be expected in the reported values of their interdiffusion and tracer diffusion coefficients.

Wang et al. [56], from the same group as Chen, have studied diffusion in FCC phase of Co-Cr-Cu-Fe-Ni system by utilizing the inverse simulation technique. Their experimental and computational procedure is similar to Chen et al.'s [54]. They have assumed the ideal solution behavior ignored the vacancy wind effect and cross-term effects. From their sandwich-type diffusion couples, they have evaluated the composition-dependent interdiffusion coefficients and tracer diffusion coefficients and compared their results with the data available in the literature on unary, binary, ternary, quaternary, and quinary systems. Based upon it, they observed that sluggish diffusion behavior is more prominent in the case of interdiffusion coefficients as compared to the tracer ones. Limitation of this approach has already been discussed earlier.

Kucza et al. [57], on similar lines as Dabrowa et al. [52], have studied tracer diffusion in quinary CoCrFeMnNi and quaternary CoCrFeNi and CoFeMnNi systems. The experimental and computational methods employed by the authors closely resemble those employed by Dabrowa et al. [52]. However, in this study, the authors incorporated thermodynamic interactions and utilized the marker plane position in their optimization procedure. The mobility parameters were optimized as composition-dependent functions to achieve the closest match between simulated profiles and experimental concentration profiles, taking into account all three alloy systems simultaneously. For the best-fitted profiles, diffusion data was assumed to be accurate. Diffusion data determined for the quinary system was used to generate the concertation profiles for all three alloy systems. Authors have found a good match for all the profiles suggesting that the diffusion behavior does not change on increasing the number of components in the system which challenges the theory of sluggish diffusion in HEAs. It should be noted here that authors have only considered the concentration profiles for the optimization but ignored the flux profiles which may also help to support their data. Apart from that, we have already learned the limitation of this approach that it only works with the system having small or negligible concentration gradients and impart large errors to the calculated diffusion data. In their study, two of the quinary couples and four of the quaternary couples have components having negligible concentration gradients, which cast questions on the accuracy of their data.

In another study, Chen et al. [58] have studied diffusion in the FCC phase of the Al-Co-Cr-Fe-Ni-Ti system. Their experimental and computational procedure is similar to those followed in their earlier studies [54]. They have evaluated the composition-dependent interdiffusivities and found that they strongly depend on composition. They have observed the following sequence of inter-diffusivities for the main coefficients when Ni is treated as a dependent component: $\widetilde{D}^{Ni}_{FeFe} > \widetilde{D}^{Ni}_{AlAl} > \widetilde{D}^{Ni}_{CoCo} > \widetilde{D}^{Ni}_{CrCr} > \widetilde{D}^{Ni}_{TiTi}$. Authors have

also evaluated the data for tracer diffusivities and compared their results for the main interdiffusion and tracer diffusivities with the data available in the literature for the conventional alloys and observed that the sluggish diffusion behavior exists mainly in case of the interdiffusion but absent in case of the tracer one.

Dabrowa et al. [59] have studied tracer diffusion in quinary CoCrFeMnNi and quaternary CoCrFeNi, CoFeMnNi and CoCrMnNi systems. They have also re-evaluated their own data reported in the AlCoCrFeNi system [52]. Their experimental and computational procedures are similar to those followed in the previous studies [52,57] but this time they have assumed the diffusivities to be composition independent based on the relatively low concentration gradients apparent in their studied couple, i.e., concentration difference is not more than 12 atom %. They also adopted some modifications in the experimental part to reduce errors in their analysis. Tracer diffusivities evaluated for the CoCrFeMnNi system were found to be consistent with the data reported by Tsai et al. [29], Vaidya et al. [38], and Zang et al. [53]. For the quaternary systems, good agreement was found for all the components except for Ni, which is due to the limitation associated with the adopted methodology i.e., component having negligible or very low gradient and component having very low diffusivity value as compared to the other components. Further, they have reevaluated the tracer diffusion data for the AlCoCrFeNi system and compared their results with the data available in the literature for conventional alloys in unary, binary, and ternary systems both at the absolute and normalized temperatures. Authors have observed no sign of sluggish diffusion at absolute temperatures but at a normalized temperature in some systems, they have observed sluggish behavior, and the opposite trend was observed on comparing the diffusion in binary Mn-Ni and ternary Cu-Mn-Ni with the HEAs. Based upon that they have concluded the diffusion in HEAs is not sluggish.

Xia et al. [81] have proposed a novel approach for simulating bulk diffusion in multi-component systems and determining atomic mobilities via a single-phase diffusion couple with Kirkendall markers. They emphasized on the inadequacies of current multi-component diffusion kinetic databases and the challenges in estimating interdiffusion coefficients as the number of components increases. The authors propose a mobility-extraction method that overcomes these limitations and efficiently calculates all types of diffusion coefficients by directly determining atomic mobilities from experimental data. This method is based on an atomistic model and considers the Kirkendall effect, which is the shift of marker planes due to unequal diffusion rates of components.

Authors clearly discusses the importance of using tracer diffusion or intrinsic diffusion coefficients in addition to interdiffusion coefficients for a more accurate and reliable kinetic database. Tracer diffusion coefficients are needed to understand the behavior of individual atoms in a mixture and are particularly important when the system contains a large number of components. The proposed simulation and mobility-extraction methods can accurately predict both the tracer diffusion and Kirkendall effect, demonstrating their applicability and effectiveness.

Another study reported by Kumar et al. [80] focused on enhancing the accuracy of diffusion coefficients in NiCoFeCr alloys through the application of a physics-informed neural network-based numerical inverse method. To address the challenges and limitations associated with traditional methods, particularly in multi-component systems, they proposed alternative approaches for a more precise and comprehensive analysis.

Initially, Kumar et al estimated composition-dependent pseudo-binary (PB) interdiffusion coefficients and primary intrinsic diffusion coefficients near equiatomic compositions of the NiCoFeCr system using the PB diffusion couple method. This method is notable for its ability to estimate these coefficients across the entire composition range from a single diffusion couple, as well as intrinsic diffusion coefficients at the Kirkendall plane (K-plane).

Specifically focusing on tracer diffusion, the study meticulously explores the limitations of the radiotracer method and underscores the advantages of the diffusion couple technique. The authors emphasize the importance of accurately estimating tracer diffusion coefficients, especially when reliable thermodynamic data is available, using the augmented Darken-Manning relation. Additionally, the study underscores the significance of these tracer diffusion coefficients, establishing connections with the intrinsic diffusion coefficients estimated at the K-plane. A thorough analysis based on the radiotracer method reveals specific relationships between tracer diffusion coefficients at or near the equiatomic composition of the alloy. The study further explores the optimization of diffusion parameters without the need for detailed thermodynamic data, suggesting that even without these details, accurate tracer diffusion coefficients can be estimated and used to calculate all main and cross intrinsic diffusion coefficients. This is critical because an exact match with diffusion profiles alone might not yield accurate diffusion parameters if thermodynamic details are inaccurate or unavailable.

4.3. Theoretical investigations

Beke et al. [60] have reanalyzed Tsai et al. [29] data by using the theoretical approach. For that, they have used the modified empirical Arrhenius relation to compare the normalized diffusion parameters in HEA with the other existing structural FCC alloys for Fe and Ni. Normalized activation energy magnitude was found higher in the case of HEA as compared with the other FCC alloys, based upon which the authors [60] claimed sluggish diffusion in HEA.

Paul et al. [61] have studied diffusion in Co-Cr-Fe-Ni-Mn system by utilizing the three different theoretical models including Darken's model [107], Manning and Holdsworth-Elliot (HE) approach [108], and a "light version" of Moleko, Allnatt, and Allnatt (MAA) model [109]. In their study they have assumed that the system follows the ideal solution behavior. Based on these three models, the authors have evaluated the tracer diffusion coefficients by utilizing the experimental interdiffusion data reported by Tsai et al. [29]. They have found a good match for their estimated tracer diffusivities with the experimental ones for all the components except for Ni. The present author believes that the tracer diffusivities so evaluated have better accuracy than assuming the interdiffusion coefficient equal to tracer diffusion coefficients as done by Tsai et al [29]. Further, they have also evaluated the interdiffusivity matrix and observed that off-diagonal coefficients have significant magnitudes, as much as half, as compared to the main or diagonal

coefficients. This indicates that even on considering the ideal solution behavior cross terms have significant magnitudes. Considering the large difference in the tracer diffusivities of the fastest and slowest diffusing species reported by Vaidya et al. [38] we can expect the actual magnitudes of the cross terms even more significant.

Verma et al. [62] have conducted a study in which they reported interdiffusion coefficients within the quinary Fe-Ni-Co-Cr-Mn system, employing Manning's theoretical model [65]. Initially, they tested the applicability of Manning's theoretical model on the ternary Fe-Ni-Cr system to assess its suitability for higher-order systems. Subsequently, they employed this model to evaluate interdiffusion coefficients at the equimolar composition of the Fe-Ni-Co-Cr-Mn system. The interdiffusion coefficients, as determined by Manning's relation, generally exhibited agreement within a factor of three for the majority of coefficients in the Fe-Ni-Cr ternary system. This level of agreement is considered reasonable, given the inherent uncertainties that often accompany experimental determination of interdiffusion coefficients. Such uncertainties can arise during processes such as concentration measurement, fitting concentration profiles, determining the location of the Matano plane, or calculating interdiffusion fluxes. It's worth noting that Manning's theoretical model relies on certain assumptions, including the assumption of random mixing, and utilizes thermodynamic factors derived from Thermocalc software, which, in turn, relies on specific underlying assumptions. Nevertheless, the interdiffusion coefficients obtained were deemed convincing, effectively capturing both the signs and relative magnitudes of diffusional interaction terms. To estimate the interdiffusion coefficients at the equimolar composition in the quinary Fe-Ni-Co-Cr-Mn system, the authors utilized tracer diffusivity data previously reported by Vaidya et al. [38] for Fe, Ni, Co, Cr, and Mn at equimolar composition. Thermodynamic factors essential for estimating interdiffusion coefficients were derived using Thermocalc software at 1000 °C, employing the TCHEA 3 database. Their study underscores the utility of Manning's model in predicting interdiffusion coefficients based on knowledge of tracer diffusivities and thermodynamic factors.

The above literature review of diffusion studies in HEAs suggests that, due to the lack of proper experimental and theoretical techniques, and the constraints on the multicomponent diffusion, at present only a handful of studies on diffusion in HEAs are available in the literature. Among these, some studies support the hypothesis of sluggish diffusion while the others disregard this hypothesis. In some systems, presence of a particular element reduces the diffusion kinetics of others, but that is not the case for some systems which lack clear evidence of sluggishness in HEAs. Sluggish diffusion may exist in some HEAs and not in others, but the diffusion mechanisms in HEAs still depend on the alloy's specific constituent elements, not just the sheer content of constituents. The available literature mainly consists of tracer diffusion studies which describe the diffusion behavior of components in the presence of a negligible concentration gradient in any alloy system, but only a few interdiffusion studies are available that describe the diffusion behavior in the concentrated alloy system. Further descriptions of the interdiffusion of the constituents in an HEA are necessary for industrial applications. In light of this, the next section summarizes our findings and discusses potential future research directions.

5. Summary and future directions

This comprehensive review serves to provide an in-depth depiction of our current understanding of diffusion in HEAs while delving into potential methodologies for the quantitative elucidation of diffusion in these intricate, multicomponent alloy systems. The question of the existence of the sluggish diffusion effect within HEAs is critical within the field, primarily due to its potential to augment their suitability for high-temperature applications. Nevertheless, despite numerous efforts to substantiate its presence, current evidence remains inconclusive. It appears that the observed sluggish behavior in specific HEAs is closely tied to the presence of particular elements, rather than representing a universal attribute tied solely to the number of components in the alloy. According to most studies, the sluggishness of diffusion in HEAs becomes apparent only after normalizing the diffusion data with respect to the alloy's melting temperature. There is no evidence of diffusion sluggishness when considering tracer diffusivities on the absolute temperature scale. However, some studies report sluggish diffusion behavior when interdiffusivities are considered. It is important to note that many of these studies used the ideal system assumption, which is likely to lead to significant errors. For instance, Vadiya et al. [38] observed that the tracer diffusion coefficient of Mn is more than three times larger than that of Cr, and more than two and a half times greater than that of Co at 1000 °C in the equimolar composition of the Co-Cr-Fe-Mn-Ni system. Such substantial differences between tracer diffusivities in the Co-Cr-Fe-Ni-Mn system could result in a significant vacancy wind effect.

For a comprehensive understanding of sluggish interdiffusivities in HEAs, further studies benefiting from detailed thermodynamic descriptions of the systems are necessary. It is also essential to have access to ternary and higher-order interdiffusion data for better optimization of the mobility parameters. Additionally, having thermodynamic descriptions and diffusion data in higher-order systems will enhance the predictive capabilities of techniques which utilizes theoretical models like the CALPHAD approach. In addition, exploring defect concentration measurements in these intricate multicomponent systems constitutes a compelling direction for future research. Accurate quantification of defect concentrations, including vacancies and other lattice imperfections, is paramount to gaining deeper insights into the diffusion behavior and related phenomena within these materials. Additionally, from a theoretical standpoint, there is a significant opportunity to advance the field by developing models that account for vacancy wind factors specifically tailored for non-random alloying scenarios. This area of research holds substantial promise in enhancing our comprehension of diffusional interactions within complex multicomponent systems. By devising models that accurately capture the effects of non-random alloying on vacancy wind factors, we can pave the way for more precise predictions and a comprehensive understanding of diffusion mechanisms in these intricate materials.

Another promising avenue for future research involves a comprehensive investigation into the impact of composition-dependent molar volume variations on the development of concentration profiles and the subsequent generation of diffusion-induced stresses. An inherent challenge in this context is the absence of well-established methodologies capable of accurately incorporating molar volume alterations within the framework of multicomponent diffusion processes [110]. Additionally, the scarcity of reliable molar

volume data specific to multicomponent systems presents a significant hindrance. Addressing this knowledge gap becomes crucial, not only for advancing our understanding of diffusion phenomena but also for accurately characterizing the thermodynamic properties inherent to these complex multicomponent systems. Consequently, future endeavors should prioritize the development of techniques to account for molar volume fluctuations and focus on acquiring essential molar volume data within the realm of multicomponent diffusion studies.

The prevailing focus of diffusion studies within the realm of HEAs predominantly revolves around single-phase systems. However, there exists a notable scarcity of investigations into multiphase diffusion phenomena in the context of HEAs. This research gap underscores the need for a comprehensive exploration of multiphase diffusion within HEAs [111], offering insights into diffusion-controlled processes such as precipitation, dissolution, and the kinetics associated with phase growth. Addressing this knowledge gap is crucial for advancing our understanding of the intricate diffusion mechanisms that govern the evolution of phases and microstructures in high-entropy alloy systems.

Furthermore, the influence of interstitial elements in shaping the microstructure and properties of HEAs is of paramount significance [112]. However, the study of interstitial diffusion within the context of HEAs is lacking, creating a gap in our understanding of the intricate interplay between these elements and the resultant material characteristics. The scarcity of investigations into interstitial diffusion in HEAs underscores the need for comprehensive research in this domain to unravel the nuanced mechanisms and behaviors governing these advanced alloy systems. Such investigations are essential for elucidating the full spectrum of interactions between interstitial elements and the host lattice in HEAs, ultimately contributing to a more thorough comprehension of their microstructural evolution and resultant properties.

The latest advancements in methodologies, such as the body-diagonal diffusion couple approach and the combined body-diagonal diffusion couple with pseudo-binary or pseudo-ternary approaches, have proven effective in determining interdiffusion coefficients in systems beyond ternary configurations. However, more studies are required using such techniques. It is essential to rigorously validate diffusion couples to exhibit diffusional interaction effects, especially for quaternary and quinary systems, rather than restricting the validation to simple quasi-binary type couples. Specifically, the couple should be designed to purposefully exhibit features like uphill diffusion and zero flux planes to account for diffusional interactions.

These developments also help gain a comprehensive understanding of diffusion behavior in vast compositional space in HEAs. As most of the diffusion studies reported in the literature focus on FCC alloys, which have a distinctively low lattice strain compared to BCC alloys. This opens further scope for diffusion studies in BCC and HCP alloys. Additionally, there are only a few studies reported on grain boundary diffusion. Understanding diffusion along grain or phase boundaries is crucial, especially for compositionally complex alloys with single and two-phase microstructures. The interactions between multicomponent elements and element segregation can significantly influence the microstructure and properties of these materials. Through these investigations, we can gain invaluable knowledge that will further our understanding of diffusion phenomena in these cutting-edge materials.

CRediT authorship contribution statement

Vivek Verma: Conceptualization, Formal analysis, Investigation, Resources, Validation, Visualization, Writing – original draft, Writing – review & editing. **Calvin H. Belcher:** Resources, Writing – review & editing. **Diran Apelian:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing, Resources. **Enrique J. Lavernia:** Conceptualization, Funding acquisition, Resources, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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