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A novel concept of pseudo ternary diffusion couple for the estimation of diffusion coefficients in multicomponent systems

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ABSTRACT

A pseudo ternary diffusion couple technique in a multicomponent system by simplifying the mathematical complications of Onsager formalism is proposed for the estimation of composition dependent values of the interdiffusion coefficients. This is otherwise impossible following the conventional method in a system with more than three components. Other alternative methods estimate the average diffusion coefficients over a composition range of random choice and lack physical significance. This method can be followed in a multicomponent system with any number of components on the condition that only three components develop diffusion profiles keeping others as constant.

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Diffusion studies in inhomogeneous multicomponent systems represent an unsolved challenge. Mathematical complexities based on Onsager's formalism [1–3] makes it impossible to estimate meaningful diffusion coefficients [4,5]. Due to relative ease, most of the experimental studies in the academic world are conducted in binary systems for an understanding of the basic atomic and phenomenological diffusion mechanisms. The studies in ternary systems are much smaller in number because of increase in complexities; however, these are used to understand diffusional interactions among components. No experimental studies are available estimating the composition dependent values of the diffusion coefficients following the conventional method in a system with a higher number of components. This is simply not possible because of mathematical complexities [4,5]. On the other hand, to achieve a property balance, most of the material systems in applications are multicomponent. Diffusion coefficients are important to understand microstructural evolution and many physicomechanical properties of a material. Therefore, this difficulty brings an unbridgeable gap between academics studying basics of diffusion mechanisms in simple systems and industries developing complicated material systems for various applications.

To counter the mathematical and experimental complications in ternary and multicomponent systems [4], few alternative experimental methods were developed with mixed success [5]. Thompson and Morral [6] developed the concept of square root diffusivity for the estimation of constant diffusion coefficient, which could not be used for composition range more than 5 at.% [7]. Dayananda and Sohn [8] developed a method for the estimation of average interdiffusion coefficients. However, these are not material constants but depend on the composition range of the diffusion couple and the composition range over which these average values are estimated. Therefore, these data lack physical significance compared to the composition dependent values of the diffusion coefficients estimated following the conventional method [5]. At present few other numerical methods are being proposed in multicomponent systems [9,10]; however, further refinement and rigorous analyses in many systems with different situations might be required before adopting them with a certain degree of confidence. Most importantly, there is a need for a purely experimental method with straightforward and easy to follow steps such that the research students and engineers can adopt in their studies without much difficulty for the estimation of meaningful composition dependent (not average) diffusion coefficients.

Fulfilling this requirement, Paul and co-workers recently proposed a pseudo binary approach [11,12]. This needs only a single diffusion couple in a multicomponent system with an added advantage of estimation of composition-dependent (not average) values of the interdiffusion coefficients and even the intrinsic diffusion coefficients [12], which was not possible by the conventional or any other alternative methods even in a ternary system [5]. This method is established based on the concept that only two components develop diffusion profiles in a ternary or multicomponent system countering the mathematical complications of the Onsager formalism. This is already used successfully in few systems [12,13,14,15]. It should be noted here that this is named differently by different groups as pseudo binary or quasi binary although the basic concept is the same irrespective of the name used. Most importantly, it gives a unique opportunity to relate diffusion rates of components with defects and thermodynamic driving forces for understanding the growth kinetics and microstructural evolution in a multicomponent system of practical importance [16,17]. However, this approach has a drawback that the contribution of cross diffusivity

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terms towards the interdiffusion flux i.e. diffusional interactions among different components cannot be determined, which sometimes play a major role on phenomenological diffusion process.

Therefore, in this manuscript, we propose an experimental pseudo ternary approach simplifying the mathematical complications of the Onsager formalism such that only three components develop diffusion profiles keeping the composition of all other components as constant in a multicomponent system. This can be considered as an extension of the pseudo binary apparoch [11,12]. As explained, we can now estimate the composition dependent (not average) values of the main and cross interdiffusion coefficients in a system with more than three components, which is not possible following the conventional or any other available alternative methods.

For the sake of explanation of the experimental method and subsequent analysis, we consider a quaternary Ni-Co-Fe-Mo system although this can be used in a system with even higher number of components without any further modification of the concept. Following the Onsager's formalism, the interdiffusion fluxes ($\tilde{J}_i$) of different components (i) with respect to the interdiffusion coefficients are related by [1,4,5]

$$\tilde{J}_i = -\sum_{j=1}^{n-1} \tilde{D}_{ij}^{n} \frac{dC_j}{dx} = -\sum_{j=1}^{n-1} \tilde{D}_{ij}^{n} \frac{1}{V_m} \frac{dN_j}{dx}, \tag{1}$$

$\frac{dC}{dx} = \frac{1}{V_m}\frac{dN}{dx}$ is the concentration gradient considering a constant molar volume since the composition dependent lattice parameter variations are not known in a multicomponent system. In such a situation, the interdiffusion fluxes estimated with respect to different components are related by [4]

$$\sum_{i=1}^{n} \tilde{J}_i = 0 \tag{2}$$

n^{th} component is considered as the dependent variable. Considering the major component Ni as the dependent variable, the interdiffusion fluxes in the Ni-Co-Fe-Mo system can be written as

$$\tilde{J}_{Co} = -\tilde{D}_{CoCo}^{Ni} \frac{1}{V_m}\frac{dN_{Co}}{dx} - \tilde{D}_{CoFe}^{Ni} \frac{1}{V_m}\frac{dN_{Fe}}{dx} - \tilde{D}_{CoMo}^{Ni} \frac{1}{V_m}\frac{dN_{Mo}}{dx} \tag{3a}$$

$$\tilde{J}_{Fe} = -\tilde{D}_{FeFe}^{Ni} \frac{1}{V_m}\frac{dN_{Fe}}{dx} - \tilde{D}_{FeCo}^{Ni} \frac{1}{V_m}\frac{dN_{Co}}{dx} - \tilde{D}_{FeMo}^{Ni} \frac{1}{V_m}\frac{dN_{Mo}}{dx} \tag{3b}$$

$$\tilde{J}_{Mo} = -\tilde{D}_{MoMo}^{Ni} \frac{1}{V_m}\frac{dN_{Mo}}{dx} - \tilde{D}_{MoCo}^{Ni} \frac{1}{V_m}\frac{dN_{Co}}{dx} - \tilde{D}_{MoFe}^{Ni} \frac{1}{V_m}\frac{dN_{Fe}}{dx} \tag{3c}$$

$$\tilde{J}_{Ni} + \tilde{J}_{Co} + \tilde{J}_{Fe} + \tilde{J}_{Mo} = 0 \tag{3d}$$

$\tilde{D}_{ii}^{n}$ and $\tilde{D}_{ij}^{n}$ are the main and cross interdiffusion coefficients and n (Ni in this set of equations) is the dependent variable [4]. Therefore, $(n-1)^2$ interdiffusion coefficients are required to determine in n component system. The interdiffusion flux of the component considered as the dependent variable is related to the interdiffusion fluxes of other components following Eq. (3d) [1,5]. Interdiffusion fluxes can be calculated utilizing the Wagner or den Broeder's relation for constant molar volume as [4,5]

$$\tilde{J}_i = -\frac{N_i^{+} - N_i^{-}}{2tV_m}\left[(1-Y_i^{*})\int_{x^{-\infty}}^{x^{*}} Y_i dx + Y_i^{*}\int_{x^{*}}^{x^{+\infty}} (1-Y_i)\,dx\right] \tag{4}$$

The composition normalized variable is expressed as $Y_i = \frac{N_i - N_i^{-}}{N_i^{+} - N_i^{-}}$. N_i^{-} and N_i^{+} are the compositions in mole (or atomic) fraction in left ($x^{-\infty}$) and right hand ($x^{+\infty}$) side of the unaffected parts of the diffusion couple. It can be seen in Eqs. (3a), (3b), (3c), and (3d) that in a quaternary system, total nine interdiffusion coefficients should be estimated. On the other hand, only three independent interdiffusion fluxes can be estimated in a particular diffusion couple. Therefore, following this conventional method, we need three diffusion couples such that all of them intersect at one particular composition at which these data can be estimated since the diffusion coefficients are material constants which vary with composition because of change in thermodynamic driving forces and defects assisting the diffusion process. It is practically impossible to predict the end member compositions of three different diffusion couples in a four-component space such that all of them intersect at one particular composition because of different serpentine diffusion (composition) paths followed by individual diffusion couples [4,18]. Therefore, no experiments are available in a quaternary or higher order systems following the conventional method estimating the composition dependent (not average over a composition range) values of the interdiffusion coefficients. Because of this reason only, an alternative method was developed by Dayananda and Sohn [8] for the estimation of average interdiffusion coefficients. The major advantage of this approach is that only one diffusion couple is required in a system with any number of components. However, these are average over a composition range of random choice leading to different values for different composition ranges. Even the values will be different when a common composition range is considered but from diffusion couples with different composition ranges of the end members. This additional complication comes from the fact that it is not easy to control the diffusion paths which depends on the initial end member alloys [19]. Therefore, the estimated data are vague without any physical significance [5]. This is still practiced to get a rough idea of the diffusion coefficients since no other efficient and straightforward experimental method is available in multicomponent systems.

Because of the difficulties explained above, we need an approach for the estimation of composition dependent values of the interdiffusion coefficients. To circumvent the mathematical complications based on Onsager formalisms [2,3], we propose a pseudo ternary approach. Therefore, in the Ni-Co-Fe-Mo quaternary system used to demonstrate this approach, we make one of the components, for example, Mo to remain constant without producing any diffusion profiles. It further means that we keep the content of Mo as same in both the end members of a diffusion couple with the expectation that it remains constant throughout the diffusion couple. Experimental results of two such diffusion couples are shown in Fig. 1(a) (DF1: $Ni_{95}Mo_5/Ni_{75}Co_{10}Fe_{10}Mo_5$) and (b) (DF2: $Ni_{90}Fe_5Mo_5/Ni_{85}Co_{10}Mo_5$) which are used for further analysis. The method of producing diffusion couples can be found in Chapter 3 in ref. [5] in details. Experimental procedure for this study is described in the supplementary file.

In such a situation, $\tilde{J}_{Mo}$ and $\frac{dN_{Mo}}{dx}$ are equal to zero so that series of Eqs. (3a), (3b), (3c), and (3d) reduces to

$$\tilde{J}_{Co} = -\tilde{D}_{CoCo}^{Ni} \frac{1}{V_m}\frac{dN_{Co}}{dx} - \tilde{D}_{CoFe}^{Ni} \frac{1}{V_m}\frac{dN_{Fe}}{dx} \tag{5a}$$

$$\tilde{J}_{Fe} = -\tilde{D}_{FeFe}^{Ni} \frac{1}{V_m}\frac{dN_{Fe}}{dx} - \tilde{D}_{FeCo}^{Ni} \frac{1}{V_m}\frac{dN_{Co}}{dx} \tag{5b}$$

$$\tilde{J}_{Ni} + \tilde{J}_{Co} + \tilde{J}_{Fe} = 0 \tag{5c}$$

Therefore, the relations above reduces similar to a ternary system in which only four interdiffusion coefficients are required to estimate. This can be easily achieved by making only two diffusion couples and by forcing them to intersect at one particular composition for estimation of the diffusion coefficients at that composition. The same concept can be followed in a system with even higher number of components by preparing the diffusion couples such that only three components develop the diffusion profiles keeping all other components constant.

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