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Development of a Finite Element Model for Calculating Concentration
Dependent Interdiffusion Coefficient

By

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Abstract

Understanding the mechanism of microstructural changes caused by isothermal phase transformation reactions in materials plays a vital role in driving the development and effective performance of materials in elevated temperature applications. The kinetics of the phase changes in the microstructure of materials which affect their properties, are often diffusion controlled and a key parameter that is used in the prediction and analysis of diffusion effects is concentration-dependent interdiffusion coefficient, $D(C)$. Existing standard analytical methods of extracting $D(C)$ from experimental concentration profiles such as the Boltzmann-Matano, Sauer-Freise, Wagner, and Hall methods have some flaws, which is a major concern for accuracy and reliability. One of the limitations common to these traditional analytical methods is the assumption on which they are formulated which states that the initial composition profile is a step-function in space. In this study, a new numerical diffusion model, which eliminates non-trivial common assumptions in the literature that degrade accuracy, including the assumption of initial composition profile being a step-function in space, is developed. The new model uses finite element and Galerkin weighted residual methods combined with the Dufort Frankel/Leap Frog explicit scheme and one-dimensional Murray-Landau transformation. The model is successfully validated with previously reported experimental data in the literature and the results obtained show excellent agreement between the model predicted results and experimental data, which confirms the reliability of the new model. The model, which incorporates variable diffusion coefficients and coupled with a recently reported forward simulation technique, can be used to extract the $D(C)$ operative between any two isothermal diffusion times, which is crucial for studying the effect of time on $D(C)$. This is an achievement that is not possible by conventional analytical methods such as the Boltzmann-Matano, Sauer-Freise, Wagner, and Hall methods.

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Finally, all glory, honor and adoration belong to the Almighty God for His sustaining mercy, supporting strength, wealth of wisdom, knowledge, and inspiration that give me the understanding and grace to successfully complete this program.

Dedication

I dedicate this dissertation to Christ Jesus, the Crucified and Resurrected, the Savior of my soul and the giver of all knowledge.

List of Abbreviation and Symbols

$C(r, t)$: Concentration profile in natural coordinate system

$p = p(u, t)$: Concentration profile in Murray Landau coordinate system

D : Diffusion coefficient

$D(C)$: Concentration dependent interdiffusion coefficient

$F(C)$: function of concentration

$D_A = D_A(c(r, t))$: Diffusion coefficient in the model

r : radial position

R : Total length of the diffusion system

t : Time

$s = s(t)$: Interfacial position

FEM : Finite element method

FSM : Forward simulation method

FSA : Forward simulation analysis

i : Node number of distance

j : Node number of time

Subscripts and superscripts in the model are used to denote discretization of space and time respectively.

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Chapter 1: Introduction

1.1 Background

The need for a proper understanding and accurate analysis of the mechanism of the microstructural changes caused by isothermal phase transformation reactions in materials cannot be overemphasized as there is a great need to further develop and optimize the performance of effective materials for elevated temperature applications. The kinetics of the phase changes in the microstructure of materials which affects their properties are controlled and influenced through atomic diffusion. Diffusion is the shifting of atoms and molecules from an initial position to a new position in a material based on the vibrational energy of the atoms. This process is known to play a key role in a number of materials and metallurgical processing methods such as diffusion coating, bonding, sintering, solidification, casting, homogenization, precipitation, welding, joining, surface modification and creep deformation [1]. In room temperature, diffusion occurs at a much slower rate of little or no significance in most solids but as the temperature of the system increases, this process occurs at a more rapid rate in most metallurgical processes [2]. In this regard, diffusion-controlled processes become very important when materials are exposed to elevated temperatures [3]. A well-known application of the atomic mechanism of diffusion in crystalline materials is diffusion bonding, a method used to join materials together.

It has been reported in the literature that the difference in atomic size of the solute and solvent has a significant effect on the microstructure and mechanical properties of alloys [4]. The relative difference between the atomic size of the solute and solvent brings about changes in the lattice parameters [3]. Studies have experimentally observed that the diffusion coefficient depends on the concentration of the diffusing substance, especially in the interdiffusion behaviour in metals [1]. Experimental studies

in the existing literatures have established that $D(C)$ is very crucial in the modelling, simulation, and analysis of the effects of diffusion processes.

Ghanbar et al. [5] and Ghanbar [6] developed a numerical diffusion model to analyze the transient liquid phase diffusion bonding process and used the model to study the influence of variable interdiffusion coefficients on the kinetics of isothermal solidification in both planar and non-planar geometric systems. The results of their work showed that when the interdiffusion coefficient varies with solute concentration, there is a significant change in the isothermal solidification kinetics of the diffusion process.

Jin et al. [7] investigated the effect of concentration on the kinetics of thermal diffusion in concentrated solid-solution alloys. Their results also show that concentration has a strong influence on diffusion behaviour which is described by a crucial parameter; namely, the $D(C)$.

Furthermore, non-uniform solute concentration gradients induced by the interdiffusion between atoms of the host material cause variability in the lattice parameters, thereby leading to atomic strain within the crystal framework of the material [3, 8-9]. Residual atomic strain within the crystal framework of the material has been found to influence the interdiffusion coefficient, an important kinetic parameter that is indispensable in simulations, metallurgical based designs, and development of material processes [10-11]. It has also been recognized that diffusion induced stress/strain (DIS) evolves during atomic diffusion [3, 8-10]. Experiments performed and reported by a number of studies have established the presence and influence of DIS on host materials during diffusion heat treatment and that, the generation and relaxation of stress can take place at the same time [3, 8-11]. One important factor that is known to control DIS is the solute concentration gradient [12] which can change with diffusion time. Recently, Olaye and Ojo [13] found that the time variation of a solute concentration

gradient is an essential parameter that can significantly change the $D(C)$. However, the possible and prevailing effects of DIS on $D(C)$ s extracted in binary alloy systems have been largely ignored in the existing literature.

1.2 Research Motivation

It is known that existing analytical methods such as the Boltzmann Matano (BM), Sauer-Freise (SF), Hall, and Wagner methods, which use a single experimental concentration profile cannot be used to extract $D(C)$ when the effect of the diffusion time is being considered. When the diffusion time effect occurs, two experimental concentration profiles (initial and final concentration profiles) are required to calculate the $D(C)$. Unfortunately, existing analytical methods which use a single concentration profile for calculating $D(C)$ are not suitable for this context. These conventional analytical methods are developed based on the assumption that the initial concentration profile is a step function in space. A numerical inverse method needs to be applied to overcome the limitations of these conventional methods. To use the numerical inverse approach, an appropriate and a reliable numerical diffusion model for simulating the diffusion process is required. A large number of the existing numerical methods applied such as finite difference spatial discretization, use implicit schemes to solve partial differential equations in these diffusion models. However, it is well known that explicit schemes are more accurate and more reliable than implicit schemes.

A review of the literature shows finite element method (FEM) are more robust in terms of application although more mathematically involved in terms of model formulation and they can be used with an appropriate scheme to overcome the stability issues of explicit approach. In a bid to employ the

numerical inverse method to accurately extract $D(C)$, it may be a good idea to explore the advantages of finite element based numerical diffusion models that utilize the advantages of explicit schemes over existing finite difference-based models although explicit schemes are unstable at small time steps. Fortunately, although more mathematically involved, Dufort Frankel/Leap Frog schemes can be used to enhance the stability of explicit schemes.

Therefore, the purpose of this study is to develop a finite element-based diffusion model with variable diffusion coefficients and demonstrate its application in the extraction of $D(C)$ that is operative between two isothermal diffusion times, which is crucial to studying the effect of time on $D(C)$. The target is to use the model in the forward simulation method (FSM), an efficient numerical inverse technique that overcomes the limitations of existing conventional analytical methods such as the BM, SF, Hall, and Wagner methods.

1.3 Objective of the Research

The key objective of this thesis is to develop a new numerical diffusion model by combining a FEM with Dufort Frankel/Leap Frog explicit schemes and couple the model with the FSM to extract the $D(C)$ that is operative in between two isothermal diffusion times, which is crucial to studying the effect of time on $D(C)$.

1.4 Major Work done and key findings

A newly developed numerical diffusion model which is formulated by using finite element and Galerkin weighted residual methods in which a Dufort Frankel/Leap Frog explicit scheme combined

with a one - dimensional Murray-Landau transformation that uses flexible spatial discretization is developed. This new model effectively eliminates non- trivial common assumptions in the existing literature that inhibit accurate results. The numerical diffusion model in this study, which incorporates various diffusion parameters is coupled with a recently published FSM, to evaluate the concentration dependency of interdiffusion coefficients between two experimental concentration profiles in a binary alloy system with a planar geometry. The new model is successfully validated with previously reported experimental data in the literature. The results obtained from the implementation of data of previous studies show that the final simulated concentration profile predicted using the $D(C)$ calculated with the new numerical diffusion model matches the experimental final concentration profile. The model results show the reliability of the developed numerical diffusion model. The key achievements in this research are as follows:

- Existing numerical diffusion models in the literature include finite difference discretization which is mostly based on implicit schemes. The scientific innovations of both finite element and Galerkin weighted residual methods are thoughtfully explored. The weighted residual obtained from the Landau transformed diffusion equation is analytically integrated over the functional domains of interest. The first and second element equations are obtained and assembled to develop the new model.
- The result of the von Neumann stability analysis carried out provides justification for the use of the Dufort Frankel/Leap Frog explicit schemes over the common/classical Euler scheme. The Dufort Frankel/Leap Frog explicit schemes show good stability when compared with the classical explicit scheme at a high diffusion factor in stationary boundary conditions.

-
- The results from the newly developed finite element model when combined with a forward simulation analysis show accurate and reliable extraction of the $D(C)$ that is operative between any two isothermal diffusion times, which is crucial for studying the effect of time on $D(C)$.
 - The validity and reliability of the new model is confirmed by the fact that the simulated concentration profile from the calculated $D(C)$ agrees with the experimental final concentration profile. Therefore, the new finite element model which is not yet published in the literature can be reliably used to calculate the $D(C)$ operative between any two experimental isothermal diffusion times. This is an achievement that is not possible by conventional analytical methods such as the Boltzmann-Matano, Sauer-Freise, Wagner, and Hall methods.

1.5 Structure of the Thesis

This thesis contains six chapters. They are organized as follows:

- Chapter 1 provides comprehensive background information, objectives of the research study, research purpose, and significance of this research work.
- Chapter 2 is a literature review with studies that focus on the importance of diffusion in material engineering, influence of $D(C)$ in modelling diffusion problems, analysis of diffusion effects, analytical methods for extraction of interdiffusion coefficients from experimental profiles, and their limitations, existing time schemes and FSM.
- Chapter 3 discusses the mathematical formulations, model development of the newly developed finite element based Dufort Frankel/Leap Frog explicit scheme numerical diffusion model used with forward simulation techniques in the extraction of $D(C)$ from the experimental concentration profiles of diffusion coupled plates.

-
- Chapter 4 describes the validation of the model, presentation, and discussion of the results of the numerical simulations on extraction of $D(C)$ of binary alloy systems.
 - Chapter 5 contains the summary and conclusions of the study.
 - Chapter 6 provides the recommendations for future work.

Chapter 2: Literature Review

2.1. Conventional analytical methods of extracting concentration dependent interdiffusion coefficients

The overall accuracy and reliability of the effects from the analyses and models of diffusion depend on how the diffusion coefficient (constant or variable) is modeled. A review of studies in the existing literature shows that generally, the diffusion coefficient, an essential parameter, greatly varies with solute concentration [5, 14]. The concentration dependency of the diffusion coefficient takes different forms. They include linear, quadratic, polynomial or even an exponential function [2].

A number of existing standard analytical methods for extracting $D(C)$ from experimental concentration profiles can be found in the literature. These methods have some shortcomings which are major concerns for reliable evaluations and determination of accurate diffusivities. A major limitation common to these traditional analytical methods is the assumption that there is no initial distribution of solute in the host material before the beginning of diffusion heat treatment. This limitation implies that these methods are error bound when applied to binary alloy systems with the significant presence of initial non uniform distribution of the solute, most especially in diffusion material processes that involves multiple steps of diffusion-controlled heat treatments.

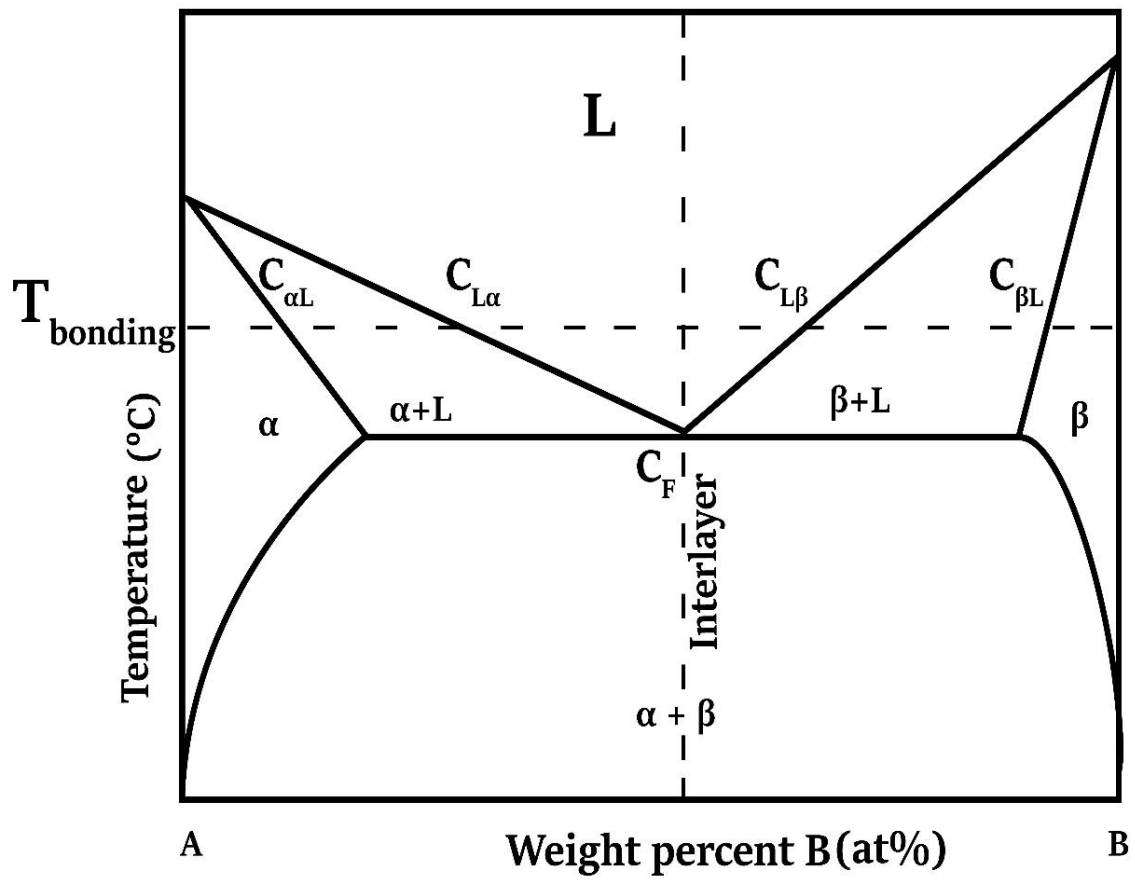


Figure 2.1: Schematic diagram of eutectic phase in binary alloy system [6]

2.1.1 Boltzmann – Matano analysis

The BM method is a widely known method used to extract concentration dependent inter-diffusivity from experimental concentration profiles acquired from diffusion couples [15]. The mathematical techniques of this method are formulated based on Fick's second law of diffusion that governs planar geometric systems.

Figure 2.1 describes the phase relationship of a typical binary eutectic alloy.

The governing equation describing Fick's second law of diffusion is:

$$\frac{\partial C(r,t)}{\partial t} = \frac{\partial}{\partial r} \left[D(C) \frac{\partial C(r,t)}{\partial r} \right] \quad \text{Equation 1}$$

where C denotes the concentration at an arbitrary distance coordinate (r), t is the diffusion time and D is the material diffusion coefficient. The mathematical analysis of this method is outlined below.

The Boltzmann transformation is used to convert Equation 1 (Fick's second law of diffusion) into a solvable ordinary differential equation. The equation comprises the introduction of a variable η which is a function of position r and time t , i.e., $\eta = \eta(r, t)$.

$$\eta = \frac{r}{2\sqrt{t}} \quad \text{Equation 2}$$

The partial derivative functions of η are:

$$\frac{\partial \eta}{\partial t} = -\frac{\eta}{2t} \quad \text{Equation 3}$$

$$\frac{\partial \eta}{\partial r} = -\frac{1}{2\sqrt{t}} \quad \text{Equation 4}$$

Deriving expressions for $\frac{\partial C}{\partial t}$ and $\frac{\partial C}{\partial r}$ in terms of η yields the followings:

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial \eta} \frac{\partial \eta}{\partial t} = -\frac{\eta}{2t} \frac{\partial C}{\partial \eta} \quad \text{Equation 5}$$

$$\frac{\partial C}{\partial r} = \frac{\partial C}{\partial \eta} \frac{\partial \eta}{\partial r} = -\frac{1}{2\sqrt{t}} \frac{\partial C}{\partial \eta} \quad \text{Equation 6}$$

Substituting these expressions into Equation 1 gives the following ordinary differential equation:

$$-\eta \frac{dC}{d\eta} = \frac{1}{2} \frac{d}{d\eta} \left[D(C) \frac{dC}{d\eta} \right] \quad \text{Equation 7}$$

$D(C)$ can be evaluated by integrating both sides of Equation 6. The diffusion coefficient at a known concentration (C^*) is derived as follows:

$$D(C^*) = -2\eta \frac{d\eta}{dC} \int_{C_L}^{C^*} \eta dC = -\frac{1}{2t} \frac{dr}{dC} \int_{C_L}^{C^*} (r - r_m) dC \quad \text{Equation 8}$$

The position of the Matano interface is calculated as:

$$r_m = \frac{1}{C_R - C_L} \int_{C_L}^{C_R} r dC \quad \text{Equation 9}$$

where C_L and C_R are the concentration values at the utmost boundaries of the diffusion couple.

The two major sources of errors when applying the BM method are:

- (i) The numerical calculation of the position of the Matano interface. An inaccurate value of the position of the Matano interface can lead to significant variation from the expected accurate interdiffusion coefficient [15].

-
- (ii) An unreliable interdiffusion coefficient is due to unpredictability in concentration gradient values close to the boundary regions [16]. The concentration gradient is an important parameter in the evaluation of interdiffusion coefficients.

2.1.2 Sauer– Freise method

In a bid to address the inherent error associated with calculating the position of the Matano interface by using the BM method, the SF method was introduced which does not require calculating the position of the Matano interface [17]. Thus, the SF method is a better way of evaluating interdiffusion coefficients. Sauer and Freise [17] established a concentration ratio y which is given below:

$$y = \frac{C - C_L}{C_R - C_L} \quad \text{Equation 10}$$

Where C is the concentration profile at radial position r , C_R and C_L are the concentration value at the right and left end of the boundary respectively.

$$D(C^*) = -\frac{1}{2t} \frac{1}{\left(\frac{dC}{dr}\right)} \left[(1 - y^*) \int_{-\infty}^{r^*} y dr + y^* \int_{r^*}^{+\infty} (1 - y) dr \right] \quad \text{Equation 11}$$

2.1.3 Wagner method

Even though the SF method addresses the error from numerically calculating the position of the Matano interface, the error of uncertainty of the interdiffusion coefficients close to the boundary

regions still persists. There is a significant error in the evaluation of interdiffusion coefficients because the values of the concentration gradient and the integral area are very small and unpredictable.

The Wagner method is thus used in the evaluation of interdiffusion coefficients with various changes in the molar volume varies. [18]:

$$C_m = \frac{c}{v_m} \quad \text{Equation 12}$$

$$D(C^*) = -\frac{v_m(C^*)}{2t} \frac{1}{\left(\frac{dc}{dr}\right)_{N_m^*}} \left[(1 - y_m^*) \int_{-\infty}^{r^*} \frac{y_m}{v_m(C^*)} dr + y_m^* \int_{r^*}^{+\infty} \frac{(1-y_m)}{v_m(C^*)} dr \right] \quad \text{Equation 13}$$

where y_m^* is the concentration ratio expressed as:

$$y_m^* = \frac{C_m - C_{mL}}{C_{mR} - C_{mL}} \quad \text{Equation 14}$$

where C_{mL} and C_{mR} are the concentration values at the left and right boundaries respectively.

Even though the Wagner method [16] takes into consideration the influence of change in molar volume, the error of uncertainty and relatively large error in diffusivity at locations close to the boundaries still exist. This is the result of difficulty in evaluating the integral area and predicting the concentration gradient at regions close to the extreme ends of the diffusion couple.

2.1.4 Hall method

The Hall methods expresses the concentration gradient in terms of a Gaussian probability distribution [19] which facilitates its applicability for an accurate evaluation of impurity diffusion coefficients at regions close to the extreme ends of the diffusion couple. A major requirement of the application of

the Hall method is that a side of the diffusion couple must have a zero-composition value [16, 19]. The concentration gradients are very difficult to evaluate because the concentrations are nearly constant at the terminal ends of the diffusion profiles, thus making the results from the BM, SF methods unreliable. Errors associated with low concentration ends of the diffusion couple are however minimized by using the Hall method [16, 19].

The analysis for the Hall method is outlined below:

$$\frac{C-C_L}{C_R-C_L} = \frac{1}{2} (1 + \operatorname{erf}(V)) \quad \text{Equation 15}$$

In Equation 15, V represents the concentration dependency parameter.

From the analysis of the probability plots of V against $\emptyset$ which is used to calculate the constants G and L , it is commonly assumed that the low concentration end of the profile behaves like a linear function.

$$V = G\emptyset + L \quad \text{Equation 16}$$

$$\emptyset = \frac{r-r_m}{\sqrt{t}} \quad \text{Equation 17}$$

where G is the gradient of the piece-wise linear fit, L , which represents the intercept on the V axis, r is the arbitrary distance coordinate, and r_m is the position of the Matano interface.

For the left extreme boundary of the diffusion couple,

$$D(C^*) = \frac{1}{4G_1} \left(1 + \frac{2L_1\sqrt{\pi}}{G_1^2} \exp(V^2) \times y^* \right) \quad \text{Equation 18}$$

For the right extreme boundary of the diffusion couple,

$$D(c^*) = \frac{1}{4G_2} \left(1 + \frac{2L_2\sqrt{\pi}}{G_2^2} \exp(V^2) \times (1 - y^*) \right) \quad \text{Equation 19}$$

A major limitation of the Hall method is that high strength of concentration dependency of interdiffusion coefficient degrades the accuracy of the result. This is because the numerical constants G and L depend strongly on the range of concentration in the linear fit [19].

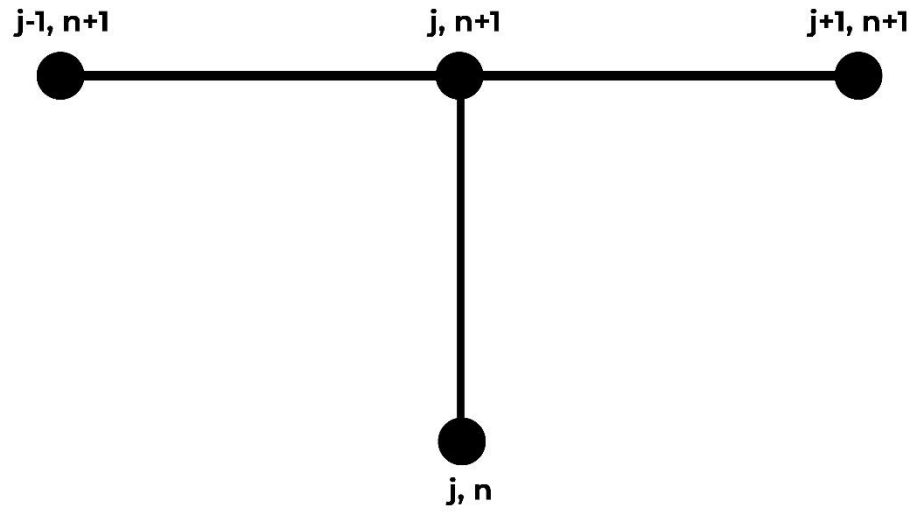


Figure 2.2: Discretization stencil for implicit time

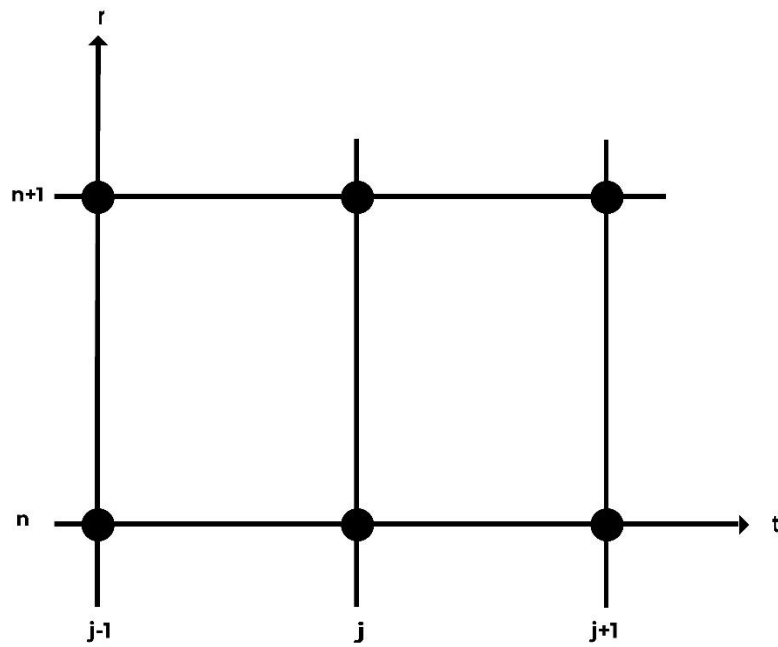


Figure 2.3: 2-level stencil of classical explicit Euler time discretization

2.2 Implicit and classical explicit schemes

Implicit schemes are numerical time discretization schemes whereby the dependent variables are defined by a set of equations that require the application of iterative techniques (such as tridiagonal matrix algorithms) to obtain the solution. Implicit solution methods are very complex to program because they require more computational effort and skill. One of the major advantages however is the use of large time step sizes and unconditional stability [20]. Most parabolic problems with moving boundaries require unconditionally stable schemes to develop their numerical solution. Considering the high computational time as a result of the number of iterations involved, determining the solution of diffusion equations by using implicit schemes is quite demanding due to the number of iterations involved to obtain an accurate solution. For diffusion situations that involve modelling of variable diffusion coefficients, the use of an implicit scheme as described in figure 2.2, some non-trivial assumptions and convergence of the solution depends greatly on the initial conditions used.

Explicit schemes calculate the state of a system at a future time from that described at the current time. Unlike the implicit scheme, iteratives are not necessary since there are no sets of resulting algebraic equations. When the diffusion coefficient is modelled as a function of the concentration parameter, accuracy issues arise with implicit based models [20], while the advantage of large time steps in implicit schemes becomes a major disadvantage in classical (two-level or Euler-type schemes) explicit schemes (as illustrated in figure 2.3) aside from high diffusion coefficient problem. The need for a small space grid size of classical explicit schemes is another disadvantage in terms of the high cost of computation and lower computational efficiency. A fully explicit based solid-solid diffusion model developed by Pabi [21] considers $D(C)$. However, this model does not conserve solute, a major criterion for determining the accuracy of a numerical solution to diffusion problems.

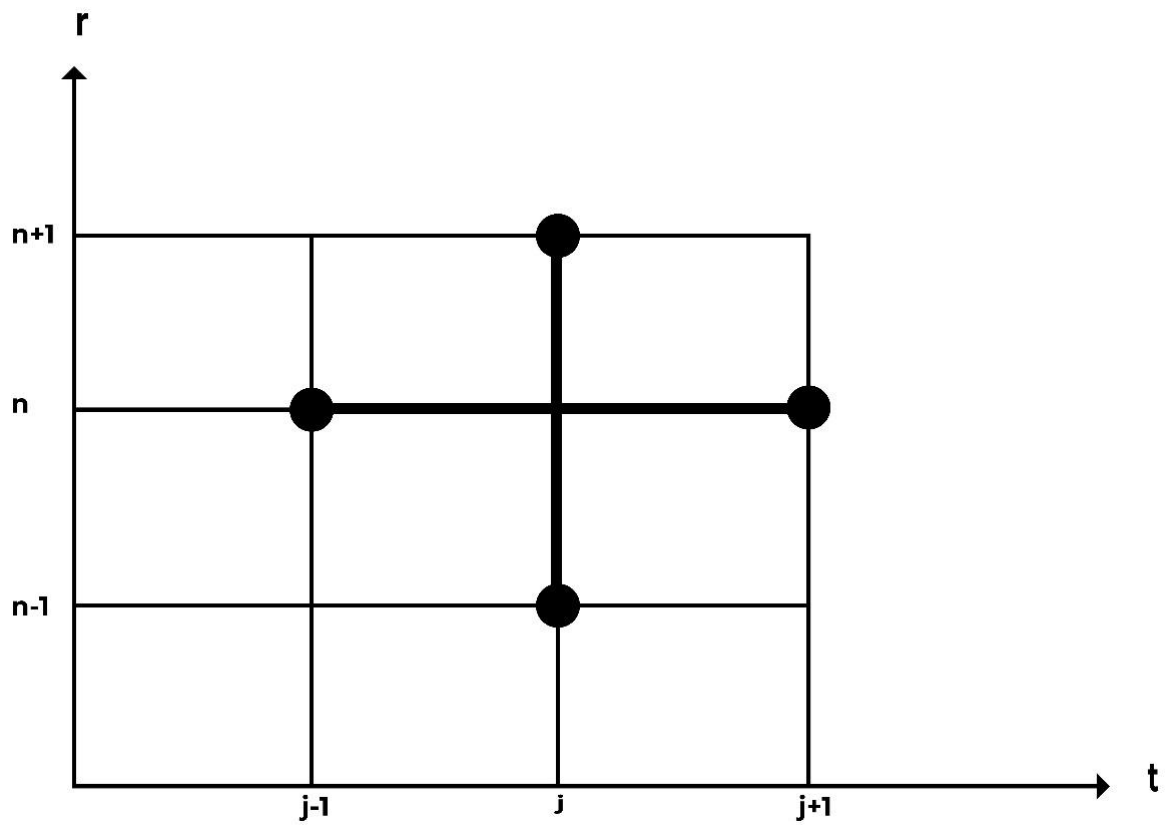


Figure 2.4: 3-level stencil of explicit time discretization in Dufort Frankel

2.3 Dufort Frankel/Leap Frog explicit schemes

Finite difference time discretization can be classified into two categories. They include the Crank-Nicolson scheme and Euler schemes [22]. The conservation laws play a crucial role in finite difference approximations. The Crank-Nicolson scheme is an implicit scheme and can satisfy these laws but is computationally costly [22-24]. They are not accurate when the diffusion coefficient is dependent on concentration. The classical Euler's scheme as described in figure 2.3, is conditionally stable and unlike the Crank-Nicolson scheme, it does not satisfy the law of conservation. Dufort and Frankel [22] developed an explicit scheme that combines the strength of the Crank-Nicolson implicit and Euler's explicit schemes. This unique explicit scheme emerged after a slight adjustment of the unstable Leap-Frog explicit scheme. Figure 2.4 describes the 3-level stencil of explicit time discretization developed by Dufort and Frankel. The Dufort Frankel explicit scheme satisfies the law of conservation, an important criterion for obtaining a reliable numerical solution and can be applied to partial differential equations that involve variable diffusion coefficients [22].

It has been reported that the requirement for consistency for a Dufort Frankel scheme is that the ratio of time step to space step approaches zero [22, 25]. This condition is required for the numerical solution of partial differential equations that govern the physical phenomena of heat or solute diffusion, regardless of existing spatial discretization such as the finite difference and finite element methods. A review of the existing literature also shows that the Dufort Frankel scheme can be applied to both fixed boundary and advective-diffusive equations [26]. Olaye et al. [27] conducted a stability and consistency analysis on the Dufort Frankel/Leap Frog explicit scheme for a diffusion-controlled interphase boundary problem by using a finite difference scheme. They showed that the resulting solution is more stable.

High computational accuracy is also attained in comparison to the classical explicit model [27]. The authors avoid non-trivial assumptions of existing implicit models.

2.4. Existing numerical methods for modelling diffusion problems

The Diffusion equations are major examples of second order parabolic partial differential equations which describe the macroscopic behaviour of microparticles. Analytical solutions to these equations are only obtainable under the same specific conditions and imposed assumptions [28]. These assumptions tend to degrade the accuracy of the expected solutions. An important parameter in these types of equations is the diffusion coefficient which is said to vary with some material factors. To investigate the influence of variable diffusion coefficients, numerical solutions are more dependable, most especially when accuracy is highly essential [29 - 31]. A number of different numerical models and several modelling approaches have been developed for diffusion problems. There is the awareness that numerical solutions require more careful calculations for dependable and accurate results when compared to analytical solutions which are obtained under certain non-trivial assumptions made. They provide the best techniques to evaluate the concentration values for each spatial position at every time specified [2]. Some of the diffusion problems where numerical approaches have been employed include transient liquid phase, temperature gradient transient liquid phase bonding systems and solid-state transformations [20, 32 - 38].

Different numerical techniques are used in the spatial discretization of a partial differential equation model. They include the finite difference method (FDM), different variants of the FEM, and the boundary element method (BEM) [29 - 31]. Diffusion problems have also been solved with models

based on fixed-grid spatial discretization which is coupled with the sharp tracking of interface migration. Furthermore, in recent times, literature reviews on numerical model development show that some researchers [36, 38] have developed unique efficient models which are not based on non-trivial simplification and assumptions considered by previous researchers, but by finite difference schemes.

Fick's law of diffusion provides a fundamental understanding of diffusion in solid, liquid, and gaseous matter. Fick's first law of diffusion describes the relationship between diffusion flux and concentration gradient.

$$J = -D \frac{dC}{dr} \quad \text{Equation 20}$$

where J is the diffusion flux, D is the diffusion coefficient, C is the concentration and r is the position.

Fick's second law of diffusion offers an elucidative explanation on how diffusion induces change in concentration with time.

$$\frac{\partial C}{\partial t} + \frac{\partial J}{\partial r} = 0 \quad \text{Equation 21}$$

Substituting the expression for J in Fick's first law,

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial r} \left(D \frac{\partial C}{\partial r} \right) \quad \text{Equation 22}$$

In materials science and diffusion processes, mathematical models that represent the underlying mechanism are governed by a system of partial differential equations with moving boundary conditions. They are known as the moving boundary problems or Stefan problems.

2.4.1 Solid-solid diffusion analysis

The concept of variable spatial discretization of the interface position which coincides with a discretization point without imposing some kind of restriction on its motion was first proposed in by Tanzilli and Heckel [37] in modelling solid-state phase transformation.

Kajihara and Kikuchi [38] investigated the behaviour of solid $\gamma/\alpha/\gamma$ diffusion couples in an $Fe - Cr - Ni$ system. They utilized a numerical technique, that is, a finite difference method, to calculate the position of a moving interface in a two-phase ternary system. Kajihara and Kikuchi [38] used the Crank Nicolson implicit scheme to solve finite difference equations. The model is used to analyze the dissolution of the α phase in $\gamma/\alpha/\gamma$ diffusion couples of an $Fe - Cr - Ni$ system. The result of their model is compared with experimentally obtained interdiffusion coefficients from the Duh and Dayananda [39] who had established the concentration dependency of interdiffusion coefficients. However, in the course of their numerical computations, Duh and Dayananda [39] assumed that the interdiffusion coefficients in α and γ phases are independent of concentration. This is contrary to the well-established finding that interdiffusion coefficients are concentration dependent.

Pabi [21] developed a fully explicit finite difference numerical scheme for diffusion-controlled dissolution in planar finite multilayer couples by using iso-concentration contour migration (ICCM) in a natural space coordinate system. In this technique, the numerical model modifies the governing equations to express the independence of concentration and time variable parameters. The model uses fully explicit time discretization thereby restricting the number of time steps that can be used to a certain limit. This restriction is on account of the stability challenge that is generally identified with fully explicit schemes. However, Pabi [21] stated that a comprehensive analysis on the stability criteria has not been carried out. Pabi [21] also stated that the aim of the model development is to effectively

handle the situation of concentration dependent diffusion parameters in a bid to extend the work of Tanzili and Heckel [37] which only considers constant diffusion coefficients. The model is applied to an Ag/Cu alloy system and $\alpha - \beta$ brass couple system. The work of Pabi [21] shows that the technique tends to track down the position of known iso-concentration lines after different time intervals. The result of the ICCM-based model shows good agreement between the experimental work and the modelled results. The result of the modelling compares well with the proposed model of Tanzili and Heckel [37].

In the course of extracting interdiffusion coefficient, Olaye and Ojo [40] developed a fully explicit finite difference scheme which incorporates the Leap Frog/Dufort Frankel stability tool. They combined this model with FSM to investigate the time variation of $D(C)$ in a Cu-Ni solid-solid binary system. The result of their study shows that time variation of concentration dependence of interdiffusion coefficient cannot be attributed to grain growth and residual stress. It was also demonstrated that when $D(C)$ changes with diffusion time, conventional analytical methods of extracting interdiffusion coefficient are unreliable.

2.4.2 Solid-liquid diffusion analysis

TLP bonding is a new process developed to address the problems and complexities of joining difficult-to-weld materials that arise from commonly used brazing techniques. In modelling TLP bonding systems, the tracking, and modelling of the migration of solid/liquid moving boundary interface have proven to be very challenging as the difficulties are associated with coordinate transformation and adjusting to the new positions of the moving interface tends to reduce the accuracy of the solutions

[20]. In other words, calculations that involve interface migration are the major source of inherent errors and inaccuracies in TLP bonding systems. However, several approaches have been recommended and developed by different researchers [20, 36 - 38] in the bid to provide numerical solutions to moving boundary problems.

Crank [2] classified these approaches into three major categories. They include: the front tracking method, front fixing method, and fixed domain method. In the front- tracking method, the position of the front of the moving boundary is calculated for each time step. The spatial discretization uses either a fixed or moving grid method. In the fixed grid method, the movement of the moving boundary is tracked while in the moving grid method, a mesh which changes in a way influenced by the movement of the interface is used [2].

A TLP bonding numerical diffusion model developed by Shinmura et al. [32], showed that the interface position is tracked in a classical explicit approach to forecast and evaluate the migration. Their model employed a classical explicit scheme in the discretization of the diffusion equations.

In another review on existing models, Zhou and North [33] formulated a model that employs a semi-implicit method. In their model, the general governing diffusion equations are solved with an implicit scheme while the equation that describes the moving interface is solved explicitly. In addition to this, they also applied a front tracking technique because it is capable of tracking the movement of the interface between successive grid points [33]. However, their method is limited by the size of the time step. In a bid to solve this problem, the attempt to reduce the time steps tends to increase the computational effort and time.

Illingworth and Golosnoy [20] succeeded in developing a more accurate numerical diffusion model for TLP bonding system. They applied specially formulated finite difference schemes (based on

control volume approach) which used a finite volume technique and integration approach on the divergent configuration of the governing equations that describe the concentration functions in both phases for one-dimensional geometric systems. The specially devised numerical scheme is quite different from the widely known direct finite difference schemes with first and second derivatives functions derived based on Taylor's theorem. Furthermore, Murray-Landau spatial transformation was employed to change the coordinate system in the bid to ensure that solute conservation criterion is met, thereby boosting the efficiency, accuracy, and reliability of the model. This transformation technique helps to reproduce the model problem into divergent formulations thereby enabling effective utilization of the strength of finite difference discretization based on control volume concept as employed by these authors. The fully implicit scheme is coupled with up/down wind approximations for intermediate concentration profiles instead of second order center difference schemes which generate oscillating solutions [20]. However, the interdiffusion coefficient parameter was assumed to be constant throughout the application of their model. Though, the result of this modelling method approximates the experimental findings but does not fully replicate an experimental proven diffusion process where the interdiffusion coefficient is said to vary with factors such as solute concentration, time, and temperature, which makes the interdiffusion coefficient a material varying parameter.

Similar to the model in Illingworth and Golosnoy [20], Ghanbar et al. [5] and Ghanbar [6] developed a model by using finite difference numerical schemes that apply a finite volume technique to integrate the differential equations over one spacestep and one timestep. This model incorporates the variable diffusion coefficient and conservation of solute by using an explicit-fully implicit hybrid discretization scheme in both the planar and non-planar geometric systems. This model is used to study TLP bonding

kinetics and the influence of geometry on the deviation of isothermal solidification kinetics from parabolic behaviour.

In modelling the effect and influence of grain boundaries on the execution time required for complete diffusion-induced isothermal solidification, Ghoneim et al. [41] developed a fully implicit two-dimensional moving-mesh finite element model with solute conservation considered as a criterion. This model also avoids assumptions of non-trivial symmetry which are found in numerical models in the existing literature. This model is used by Ghoneim et al. [41] to track diffusion-controlled liquid-solid interfacial displacement for polycrystalline solids in a TLP bonding system. To improve the accuracy of existing moving boundary models, Ghoneim et al. [41] used variable spatial discretization, however, their model assumed that there is constant diffusivity.

It has also been found that one of the deficiencies associated with conventional TLP bonding is the prolonged holding time needed to achieve complete isothermal solidification of the liquid material. Micro-constituents that are detrimental to the properties of the bonded materials could form at the bonded region from the remaining liquid material during the process of cooling. This initiated the emergence and application of a new technique called temperature gradient transient liquid phase diffusion bonding which primarily depends on the use of a temperature gradient across a bond line. A number of numerical diffusion models have been developed that involve this type of diffusion problem. For instance, Bigvand [35] used a fully implicit one-dimensional finite element model to simulate the dissolution and isothermal solidification kinetics to study the underlying mechanisms of partial unidirectional solidification in TG-TLP bonding. Bigvand [35] developed a numerical model for this kind of diffusion problem by employing one of the variants of the conventional finite element model, the Galerkin weighted residual method. This method is used to study and understand the

governing mechanism of isothermal solidification kinetics under an imposed temperature gradient condition in the TG-TLP bonding process. This finite element model assumes a constant diffusivity in the process of bonding. However, evidence from computational and experimental research studies show that diffusion coefficient parameters are not constant as they are significantly dependent on the solute concentration in real situations and the solute concentration dependency on the diffusion coefficient changes with time [5, 6].

Bamidele and Ojo [36] developed a new first order implicit-explicit finite difference numerical model which incorporates a Landau coordinate transformation with evolving spatial discretization and $D(C)$. Bamidele and Ojo [36] used a planar geometric system to study and acquire a concise understanding of the TG-TLP bonding behavior under the influence of various processing parameters which includes gap size, holding time, and temperature range. This model is the most reliable numerical diffusion model for TG-TLP diffusion systems to date.

2.5 An overview on finite element and Galerkin weighted residual methods

The FEM first appeared in Hrennikoff [42] and Courant [43] in the early 1940s to address the need to solve complex elasticity and structural analysis problems in the fields of civil and aeronautical engineering, and aircraft structure systems.

FEM is a semi-analytical method. There are different types of FEMs which include the collocation method, Rayleigh-Ritz approach, and the Galerkin weighted residual method (G-FEM) [43, 44]. These methods are based on approximating the exact solution by using an approximate solution, which is usually a linear combination of specific trial functions, that is, polynomial functions to be precise.

FEM is characterized by the mesh discretization of a continuous domain into a set of distinct, non-overlapping sub-domains which are usually called finite elements. Over these finite elements, function spaces are approximated by using local functions (polynomials).

2.6. Forward simulation analysis

It is generally known that diffusion coefficients are one of the major fundamental data for materials. The development of reliable diffusion databases to design and optimize innovative materials for wide applications at both low and high temperatures is dependent on the accurate determination of self-diffusion and impurity diffusion coefficients [45, 46]. Both are experimentally measured through radioactive isotope tracer diffusion known to generate trustworthy datasets, albeit at the expense of the high cost of operation, time consumed, and difficulties associated with the experiments [45 - 47]. To date, only a few tracer measurements have been performed in the past years. Tracer experiments are however not dependable because thousands of impurity diffusion coefficients have yet to be determined [45 - 47].

FSA is an innovative inverse numerical approach recently developed and implemented by Zhang and Zhao [45]. The FSM incorporates an iterative scheme that is solely dependent on the inverse relationship between diffusivity and solute concentration gradient in the evaluation of interdiffusion coefficient irrespective of a strong or weak dependence on the solute concentration. Zhang and Zhao [45] reported that the FSM is capable of addressing the shortcomings and limitations of existing conventional analytical methods in extracting $D(C)$ from any region of experimental concentration profiles. Different authors have used the FSM. This novel and robust technique has been found to have great advantages and reliability in the sense that its applicability comprises the evaluation of impurity

and interdiffusion coefficients in both single phase and multi-phase binary planar systems [20, 38, 41, 45 - 49]. It is well known that there are other diffusion couple techniques for evaluating the concentration dependence of interdiffusion coefficients when combined with existing analytical methods. Wie and Zhang [14] used distribution functions with the well-known BM method. The quality of the result is said to depend robustly on the degree of fit of the continuous function applied to the discrete concentration profile. Xu et al. [50] determined the interdiffusion coefficient in FCC Ag-In and Ag-Cu-In alloys. They carried out a comparative analysis on the BM method with distribution functions and a numerical inverse method with high-throughput determination of the interdiffusion coefficients. They reported that both methods showed a consistent result but as the number of elements in the alloy system increases, the BM method becomes unsuitable while the numerical inverse method exhibit no limitation as it can be reliably used in alloys with varying number of components [50].

Olaye and Ojo [40] used well-known and robust forward simulation techniques with a newly developed finite difference diffusion model in Cu – Ni and Ag – Cu binary alloy systems to study the effect of time variation by extracting and evaluating $D(C)$. The first mode was developed based on the assumption that there is no pre-existing non uniform solute distribution prior to diffusion in the evaluation of $D(C)$. This assumption is similar to that of the existing conventional analytical methods of determining the interdiffusion coefficients. The first mode is implemented on the basis that the initial concentration profile set is a step function in space which rules out the presence of an initial solute in the system. The second mode is used in the case of the presence of pre-existing non uniform solute concentrations which implies the need for two experimental concentration profiles. The first profile is utilized as the compulsory initial condition while the second profile is used as the main

experimental concentration profile for the calculation of the concentration gradient and interdiffusion coefficient under the influence of pre-existing solute distribution.

A review of the literature also shows that a comparison between the diffusion coefficients extracted from systems with pre-existing non-equilibrium solute concentrations and those obtained from existing standard analytical methods to investigate the validity of the general assumption of existing conventional analytical approaches has been reported [51]. This is done with the application of FSM.

The steps involved in the application of the FSM are outlined below:

1. The experimental concentration profiles obtained are first smoothened. Commonly used data smoothing algorithms are the moving average smoothing and Savitzky-Golay smoothing method. The moving average smoothing is employed in this study.
2. A $D(C)$ function obtained from either the BM or SF method is initially guessed and applied by using a linear function, quadratic (parabolic) behaviour or higher order polynomial trend.
3. The concentration dependent diffusivity function obtained, is used with a numerical diffusion model that solves the Fick's second law of diffusion to execute the simulation of the final concentration profile. In this step, the FSM is applied in two different modes as initially described.
4. The least square errors between the final experimental and simulated concentration profiles are calculated and compared with a pre-set tolerance value in the calculation.
5. The interdiffusion coefficient function which depends on the concentration is evaluated and the values are adjusted if the sum of the squared difference between the simulated and experimental composition profiles calculated in Step 3 is higher than the tolerance range set. This adjustment is achieved based on the inverse relation between the interdiffusion coefficient

and solute concentration gradient calculated for both the experimental and simulated concentration profiles. The equation that describes the inverse relationship is expressed as follows:

$$[D(C)]_{final} = [D(C)]_{initial} \frac{\frac{dx}{dC} \text{ experiment}}{\frac{dx}{dC} \text{ simulated}} \quad \text{Equation 23}$$

6. Steps 3 to 5 are repeated until a satisfactory minimal calculated error is obtained.

Chapter 3: Development of a new numerical diffusion model

3.1 Development of Finite Element Model

The governing equation for the process of diffusion in a single-phase planar system is described as Fick's second law of diffusion by using a one-dimensional planar geometric system:

$$\frac{\partial C(r,t)}{\partial t} = \frac{\partial}{\partial r} \left(D_A [C(r,t)] \frac{\partial C(r,t)}{\partial r} \right) \quad 0 < r < R \quad \text{Equation 24}$$

Equation 24 describes the diffusion of solute in a system, where R is the length of an entire system.

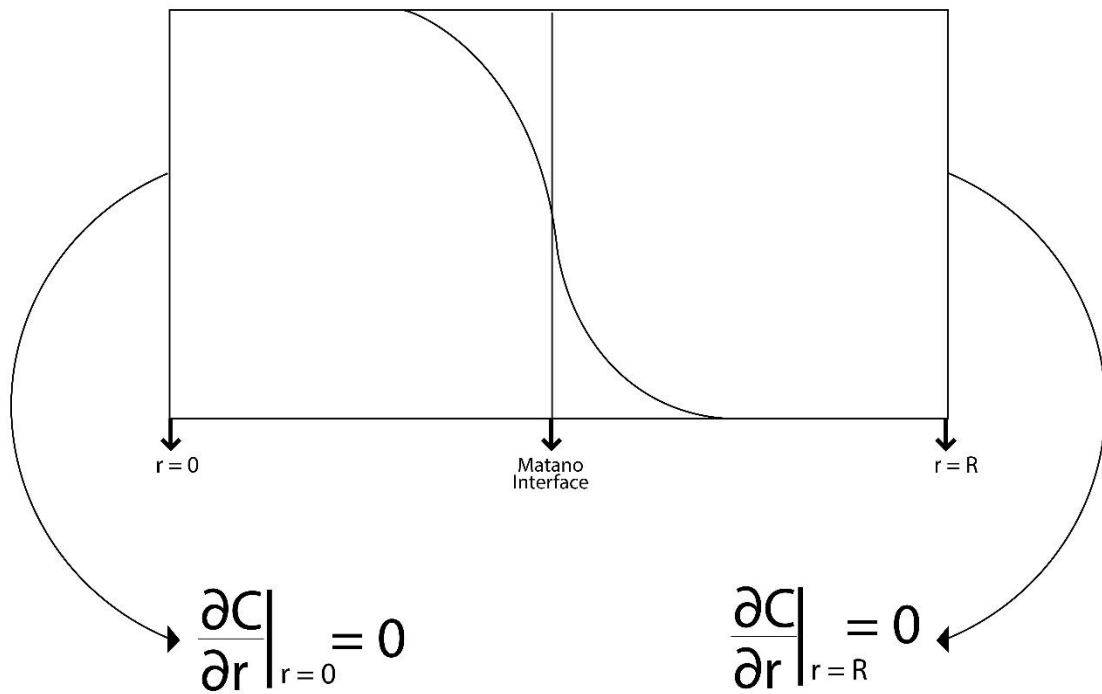


Figure 3.1: Schematic diagram of numerical diffusion modelling in a single-phase planar system

3.1.1 Application of Galerkin weighted residual method in development of the new model

The Galerkin weighted approach belongs to a family of residual methods. Residual methods are described as the integral of the residual in the functional domain of interest. The Galerkin weighted method is based on an approximation of the exact solution of a boundary-value partial differential equation. The approximate solution is a linear combination of distinct trial polynomial functions. These trial polynomial functions exhibit linear independency and tend to satisfy the boundary conditions imposed. The accuracy of the solution depends on the number, size of the elements and type of function (linear or quadratic) that are considered within the elements.

The FEMs such as the Galerkin weighted residual approach which will be used in this study, offer values in-between nodes via shape functions, coupled with the advantage of choice of the degree of function (linear or higher order polynomials). The degree of the shape function defines the level of precision that could be achieved in an analysis.

A major advantage of the Galerkin weighted residual FEM used in this study lies in the non-uniformity of the element size unlike the case with the finite difference method. Small elements can be positioned in regions with large concentration gradients while large elements can be placed in regions with small concentration gradients. In this study, the Galerkin weighted approach is applied to governing diffusion equations when the governing partial differential equations (natural coordinates system/irregular boundary form) are transformed to a variable space coordinates system (fixed boundary form). Nevertheless, it is noted that the transformed formulations become more complicated for smoothly executing the integration of the residual functions. In the finite difference method, the domain is discretized as a set of specified nodes (points) at which the results are determined, whereas in the finite

element approach, the results are known at every point of the domain because the approximation is done with shape (elements) functions (linear or higher polynomials) defined on smaller regions.

The steps involved in implementing the FEM in this study are as follows:

1. Formulation of the problem: In the case of applying Galerkin weighted residual approach, the partial differential equations to be solved are the governing diffusion equations. In a bid to achieve a variable space grid system, the governing equation is modified by applying the one-dimensional Murray- Landau spatial coordinate transformation. It is very logical to use the Galerkin weighted residual method over the Rayleigh Ritz approach since the differential equation that governs the diffusion system is known.
2. Discretization of the problem: The global solution domain $D(u)$ is discretized into subdomains (smaller elements) $D_i(u)$ ($i = 1, 2, \dots, I$). The type of element (i.e., linear, quadratic or polynomials, etc.) to be used is specified.
3. The functional form of the approximate solution $p^i(u)$ (for the model) within each element is assumed and the interpolating function for the elements is selected.
4. The finite element Galerkin weighted residual method is applied. The approximate solution $p(u)$ (for the model) is substituted into the modified governing partial differential equation to determine and define the residual $R(u)$. The residual is then weighted with the weighting functions $W_j(u)$ ($j = 1, 2, 3, \dots$) which results into the weighted residual integral $I(C_i)$.
5. The integrals of the weighted residuals $W_j(u)R(u)$ is set equal to zero.

$$\int_{u_1}^{u_2} W_j(u)R(u)du = 0$$

Equation 25

The equation is integrated and the system of weighed residual integrals for the coefficients C_i ($i = 1, 2, 3, \dots, I$) are solved.

-
6. The first and second element equations of the Galerkin weighted residual approach are determined. The partial derivatives of the weighted residual integral $I(C_i)$ with respect to the nodal values C_i are evaluated and equated to zero. The element equations obtained in Step 5 are combined to form the system equation of the model.
 7. The complete system equations that govern the model are adjusted to account for the implementation of the boundary conditions imposed on the diffusion system.
 8. The adjusted system equations are solved for the nodal values C_i . The diffusion equation can be expressed in the global matrix form described below.

$$[K]\{C\} + [P]\{\dot{C}\} = \{F\} \quad \text{Equation 26}$$

The $[K]$ term is the global stiffness matrix, $[P]$ is the global capacitance matrix, $\{F\}$ is the global force matrix and $\{\dot{C}\}$ is the partial time derivative for the nodal concentration. There are different finite difference approximations that can be applied to derive the time discretization schemes. This selection depends on the stability to be attained.

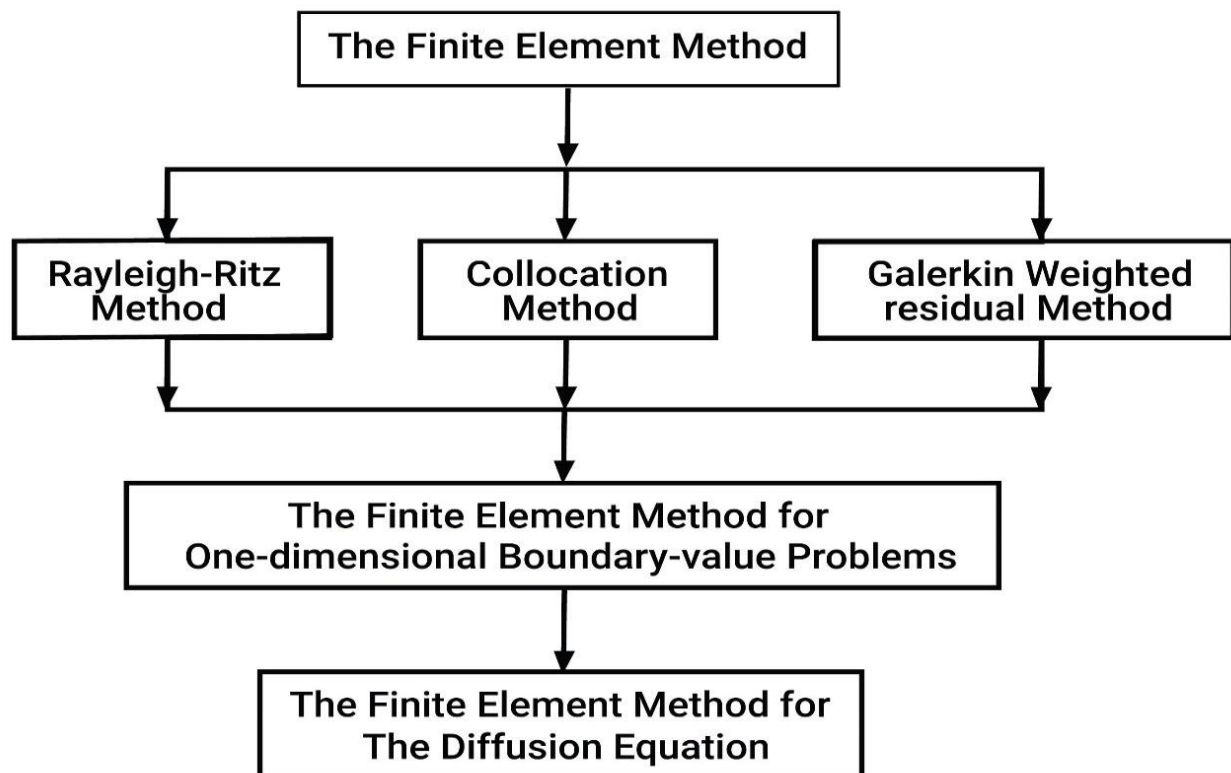


Figure 3.2: General features of variants of FEM as defined by Hoffman [44]

3.1.2 Spatial discretization of governing equations of the model

In this study, a variable space meshing system with a fixed grid is attained by the introduction and implementation of a widely known coordinate transformation process in binary diffusion systems called one dimensional Murray-Landau spatial coordinate transformation [52]. The spatial transformation proposed by Murray and Landau entails a coordinate system in which all of the spatial boundaries are fixed.

The new position variable used is given below.

$$u = \frac{r}{s(t)} \quad \text{Equation 27}$$

Equation 27 is introduced such that, for any time, the space coordinate intervals $0 < r < s(t)$ correspond to $0 < u < 1$.

A change in the spatial coordinate system brings about complete modification of the governing partial differential equation that describes the concentration profile. The transformed equations require partial differentiation and calculation of the material derivatives. The spatial and time derivatives of the concentration profile in a natural spatial coordinates system, $C(r, t)$ are expressed in Equations 29 and 31 respectively. Also note that in the new spatial coordinate system, the interface is immobile at $u = 1$ for all time, t . This shows the possibility of the automatic adjustment of the space meshing which allows the interface movement to be easily tracked. The well-simplified form of the transformed expression of the mathematical model is expressed in Equation 33.

$$\frac{dC(r,t)}{dt} = \frac{dr(t)}{dt} \frac{\partial C(r,t)}{\partial r} + \frac{\partial C(r,t)}{\partial t} \quad \text{Equation 28}$$

Equation 28 relates the concentration profile in the natural spatial coordinates, $C(r, t)$ to the new coordinate concentration profile, $p(u, t)$ of the model. Substituting Equations 29 and 30 into 28 gets Equation 31.

$$\frac{dr(t)}{dt} = u \frac{ds(t)}{dt} \quad \text{Equation 29}$$

$$\frac{\partial C(r, t)}{\partial r} = \frac{1}{s(t)} \frac{\partial p(u, t)}{\partial u} \quad \text{Equation 30}$$

The concept of the chain rule is applied to the material differential of $s(t)p(u, t)$ with respect to time, t . This leads to Equation 32 and substituting the expression for $s(t) \frac{\partial p(u, t)}{\partial t}$ on the left side of Equation 32 with the right-side expression of Equation 31 yields Equation 33.

$$s(t) \frac{\partial p(u, t)}{\partial t} = u \frac{ds(t)}{dt} \frac{\partial p(u, t)}{\partial u} + s(t) \frac{\partial C(r, t)}{\partial t} \quad \text{Equation 31}$$

$$s(t) \frac{\partial p(u, t)}{\partial t} = \frac{1}{s(t)} \frac{\partial}{\partial u} \left[D_A(p(u, t)) \frac{\partial p(u, t)}{\partial u} \right] \quad \text{Equation 32}$$

The transformed governing model is expressed in the simplified form below:

$$\frac{\partial [p(u, t)s(t)]}{\partial t} = \frac{ds(t)}{dt} \frac{\partial [p(u, t)u]}{\partial u} + \frac{1}{s(t)} \frac{\partial}{\partial u} \left(D_A(p(u, t)) \frac{\partial p(u, t)}{\partial u} \right) \quad \text{Equation 33}$$

Illingworth and Golosnoy [20] used a novel approach which consisted of finite volume integral discretization to integrate both the advective and diffusive terms. The applicability and strength of the method is based on the divergent form of the equations.

In this study, it was found that integrating on an element does not require the divergent form of the transformed equation to describe the model in the course of formulating the equations.

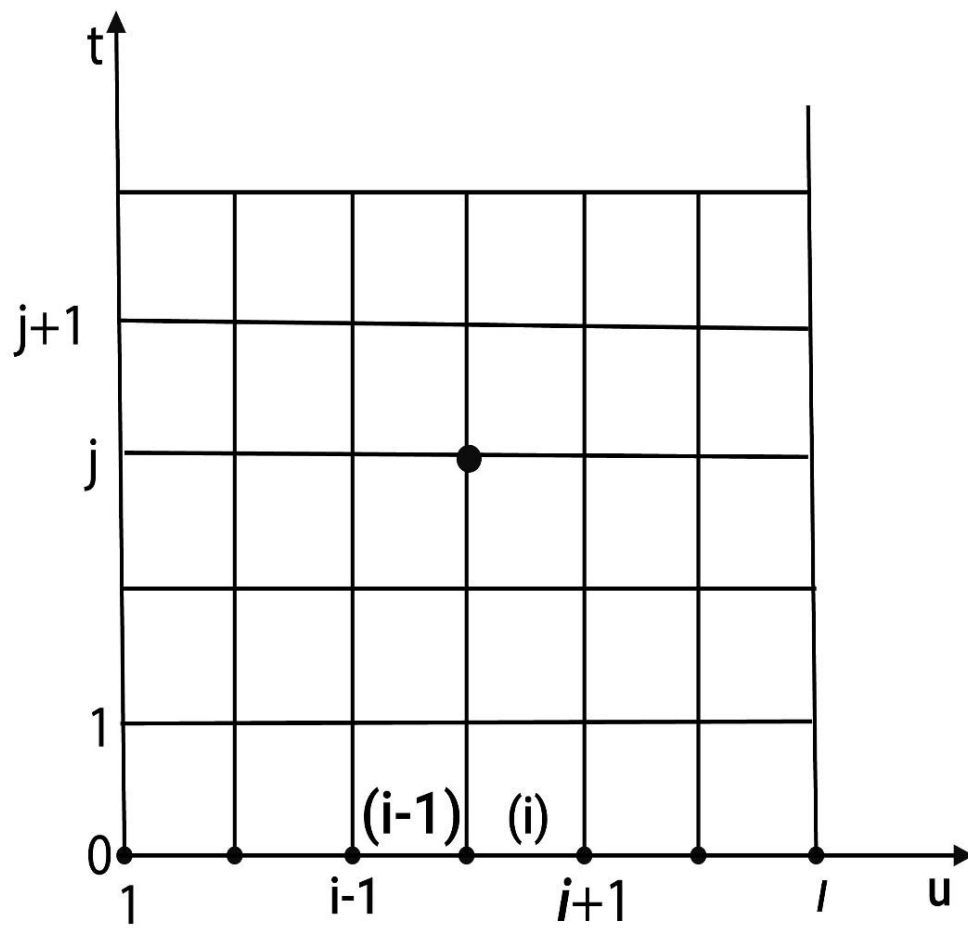


Figure 3.3: Finite element discretization [44]

In the finite element formulations developed for the work in this study, this extra effort is not needed as the direct integration of the resulting weighted residual function, $R_{res}(u)W_j(u)$ over the global solution domain eliminates the need, both in the first and second element analyses.

From the variant of the finite element analysis applied (as illustrated in figure 3.3), that is, the Galerkin weighted residual method, the resulting weighted residual, R_{res} is expressed as:

$$R_{res}(u, t) = \frac{ds(t)}{dt} \frac{\partial[p(u, t)u]}{\partial u} + \frac{1}{s(t)} \frac{\partial}{\partial u} \left(D_A(p(u, t)) \frac{\partial p(u, t)}{\partial u} \right) - \frac{\partial[p(u, t)s(t)]}{\partial t}$$

Equation 34

Expanding the partial derivative functions in Equation 36, we have:

$$\frac{ds(t)}{dt} \left[p(u, t) + u \frac{\partial p(u, t)}{\partial u} \right] + \frac{D_A(p(u, t))}{s(t)} \frac{\partial^2 p(u, t)}{\partial u^2} - \left[s(t) \frac{\partial p(u, t)}{\partial t} + p(u, t) \frac{ds(t)}{dt} \right]$$

Equation 35

The well simplified expression for the resulting weighted residual, R_{res} is given as:

$$R_{res}(u, t) = u \frac{ds(t)}{dt} \frac{\partial p(u, t)}{\partial u} + \frac{D_A(p(u, t))}{s(t)} \frac{\partial^2 p(u, t)}{\partial u^2} - s(t) \frac{\partial p(u, t)}{\partial t}$$

Equation 36

To obtain the weighted residual integral $I(p(u, t))$, we integrate $R_{res}(u, t)W_j(u, t)$ over the global solution domain $D(u, t)$. $W_j(u)$ represents a set of weighting factors ($j = 1, 2, 3, \dots$).

$$I(p(u, t)) = \int_a^b W_j(u, t) R_{res}(u, t) du = 0$$

Equation 37

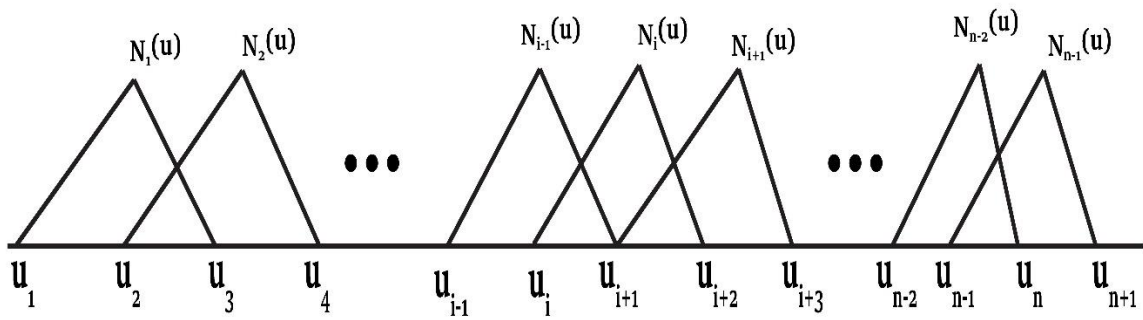


Figure 3.4: Linear function

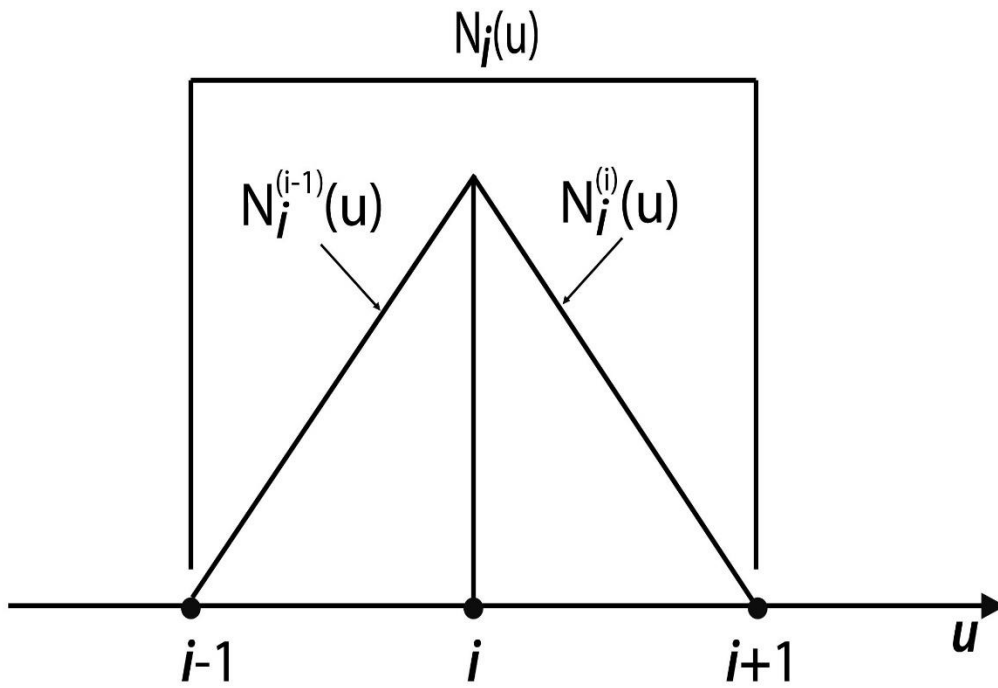


Figure 3.5: Shape function for node i

The weighted residual integral is further expressed as:

$$I(p(u, t)) = \int_a^b W_j(u, t) \left(s(t) \frac{\partial p(u, t)}{\partial t} - u \frac{ds(t)}{dt} \frac{\partial p(u, t)}{\partial u} - \frac{D_A(p(u, t))}{s(t)} \frac{\partial^2 p(u, t)}{\partial u^2} \right) du = 0$$

Equation 38

Let the global exact solution $\bar{p}(u, p)$ be approximated by using the global approximate solution $p(u, t)$, which is the sum of a series of local interpolating polynomials, $p^i(u, t)$ [$i = 1, 2, 3, \dots, I - 1$] that are valid within each element.

$$p(u) = p^1(u) + p^2(u) + \dots + p^i(u) + \dots + p^{I-1}(u) = \sum_{i=1}^{I-1} p^i(u) \quad \text{Equation 39}$$

Figures 3.4 and 3.5 describe the linear subdomain in the interval $[u_i, u_{i+1}]$ and linear shape functions for node i while Figure 3.6 illustrates the strong and weak forms in a finite element domain.

The local interpolating polynomials, $p^i(u, t)$ are defined as follows:

$$p^i(u, t) = p_i(u, t)N_i^{(i)}(u) + p_{i+1}(u, t)N_{i+1}^{(i)}(u) \quad \text{Equation 40}$$

where p_i and p_{i+1} are the values of $p(u)$ at nodes i and $i + 1$ respectively, and $N_i^{(i)}(u)$ and $N_{i+1}^{(i)}(u)$ are linear interpolating polynomials within element (i). The superscript i denotes the grid point where $N_i^{(i)}(u) = 1.0$ and the subscript denotes the element within which $N_i^{(i)}(u)$ applies. The interpolating polynomials are called shape functions.

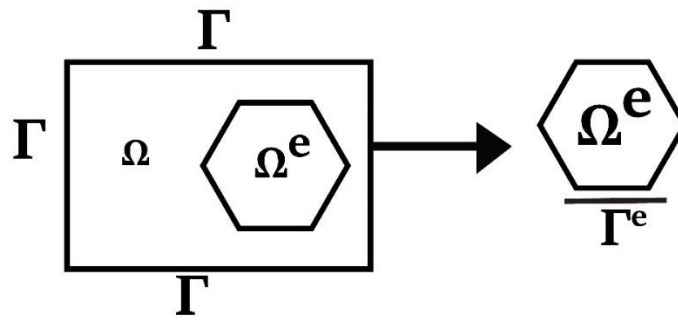


Figure 3.6: Strong and weak forms in finite element domain

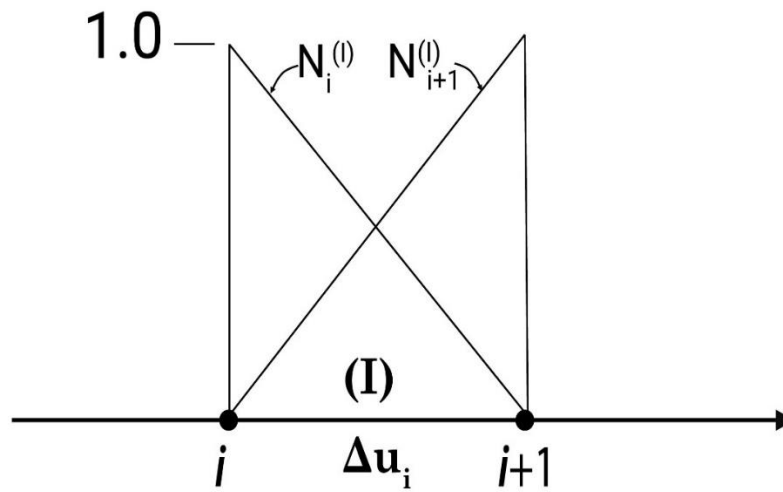


Figure 3.7: Linear shape function for element (i)

The shape functions (as illustrated in figure 3.7) are defined to be unity at their respective nodes, zero at the other nodes, and zero everywhere outside of their element. Thus, $p^i(u) = p_i$, *i.e.* the coefficients p_i evaluated represent the solution at the nodes.

$$N_i^{(i)}(u) = -\frac{u-u_{i+1}}{u_{i+1}-u_i} \quad \text{Equation 41}$$

$$N_{i+1}^{(i)}(u) = \frac{u-u_i}{u_{i+1}-u_i} \quad \text{Equation 42}$$

$$\text{Where } N_i^{(i)}(u) + N_{i+1}^{(i)}(u) = 1 \quad \text{Equation 43}$$

Equation 42 becomes

$$p^i(u, t) = p_i(u, t) \left(-\frac{u-u_{i+1}}{u_{i+1}-u_i} \right) + p_{i+1}(u, t) \left(\frac{u-u_i}{u_{i+1}-u_i} \right) \quad \text{Equation 44}$$

This is a linear Lagrange polynomial applied to element (i).

Higher-order interpolating polynomials can be developed by placing extra nodes within each element by using quadratic or cubic functions.

The weighted residual integral from the transformed diffusion equation is set up as below:

$$\begin{aligned} I(p(u, t)) = & \underbrace{s(t) \int_a^b W_j(u, t) \left(\frac{\partial p(u, t)}{\partial t} \right) du}_{1st \text{ term}} - \underbrace{\frac{ds(t)}{dt} \int_a^b W_j(u, t) \left(u \frac{\partial p(u, t)}{\partial u} \right) du}_{2nd \text{ term}} - \\ & \underbrace{\int_a^b W_j(u, t) \left(\frac{D_A(p(u, t))}{s(t)} \frac{\partial^2 p(u, t)}{\partial u^2} \right) du}_{3rd \text{ term}} = 0 \end{aligned} \quad \text{Equation 45}$$

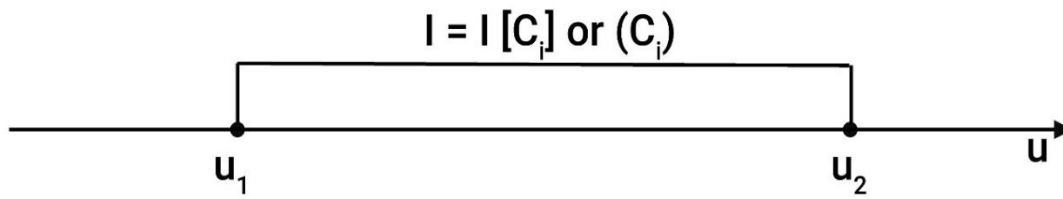


Figure 3.8: Global integral, I

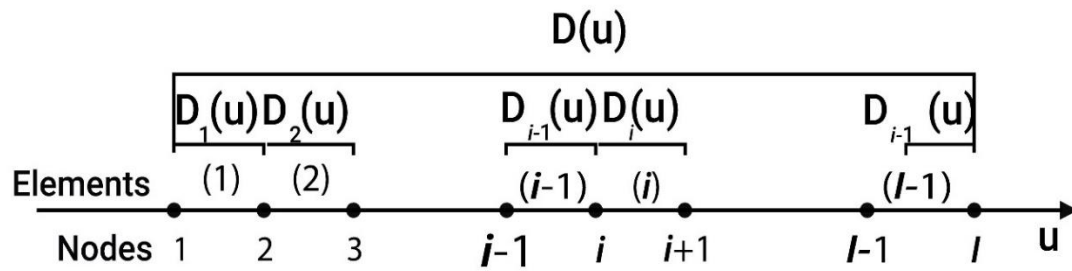


Figure 3.9: Discretized global solution domain, $D(u)$

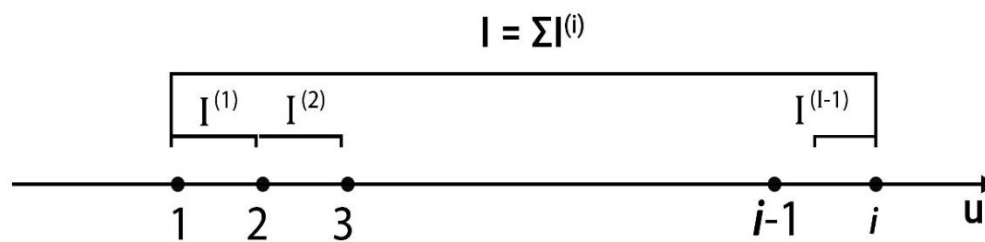


Figure 3.10: Discretized integral, I

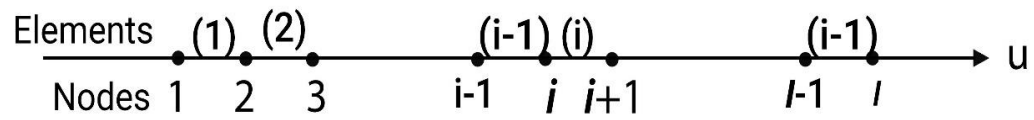


Figure 3.11: Discretized global solution domain

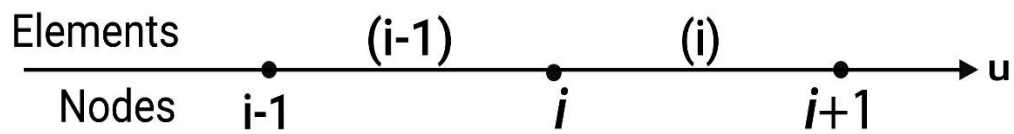


Figure 3.12: Portion of global grid that surrounds node i

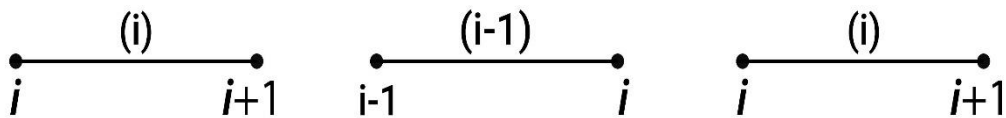


Figure 3.13: Element correspondence

Figure 3.6 describes the strong and weak forms of finite element domain. Figures 3.8 and 3.9 illustrate the underlying concept of the Galerkin weighted residual approach and the global solution domain $D(u)$ respectively. The weight residual integral $I(C_i)$ applies over the entire global solution domain $D(u)$. Let symbol I denote $I(C_i)$.

Figure 3.10 to 3.13 illustrate the discretized global solution domain $D(u)$ which is discretized into I nodes and $I-1$ elements. Note that the symbol I is used for the functional $I(C_i)$, weighted residual integral $I(C_i)$, and number of nodes.

The subscript i denotes the grid points, or nodes, and superscript (i) denotes the elements. Element (i) starts the node i and terminates at nodes $i + 1$. The element lengths (i.e., grid increments) are $\Delta u_i = u_{i+1} - u_i$.

Figure 3.8 illustrates the exact evaluation of the global integral I . This process yields a set of equations that relate the nodal values within each element, which are called nodal equations.

The finite element models from the governing diffusion equation are obtained as shown below.

The first element equation obtained for the models is:

$$I^{(i)}(p(u, t)) = s(2\dot{p}_i + \dot{p}_{i+1}) - \frac{ds}{dt} \left(\frac{p_{i+1}^{j+\sigma} - p_i^{j+\sigma}}{\Delta u_i} \right) (u_{i+1} + 2u_i) - \frac{6D_A}{s} \frac{p_{i+1}^{j+\sigma} - p_i^{j+\sigma}}{(\Delta u_i)^2} = 0$$

Equation 46

The second element equation obtained for the models is:

$$I^{(i-1)}(p(u, t)) = s(\dot{p}_{i-1} + 2\dot{p}_i) - \frac{ds}{dt} \left(\frac{p_i^{j+\sigma} - p_{i-1}^{j+\sigma}}{\Delta u_{i-1}} \right) (u_{i-1} + 2u_i) + \frac{6D_A}{s} \frac{p_i^{j+\sigma} - p_{i-1}^{j+\sigma}}{(\Delta u_{i-1})^2} = 0$$

Equation 47

Combining the first and second element equations together and using the concentration dependent diffusion coefficients, we have:

$$\begin{aligned} & s(\dot{p}_{i-1} + 4\dot{p}_i + \dot{p}_{i+1}) \\ &= \frac{ds}{dt} \left[\left(\frac{p_{i+1}^{j+\sigma} - p_i^{j+\sigma}}{\Delta u_i} \right) (u_{i+1} + 2u_i) + \left(\frac{p_i^{j+\sigma} - p_{i-1}^{j+\sigma}}{\Delta u_{i-1}} \right) (u_{i-1} + 2u_i) \right] \\ &+ \frac{6}{s^{j+\sigma}} \left[(D_A[p])_{i,i+1}^{j+\sigma} \frac{p_{i+1}^{j+\sigma} - p_i^{j+\sigma}}{(\Delta u_i)^2} - (D_A[p])_{i-1,i}^{j+\sigma} \frac{p_i^{j+\sigma} - p_{i-1}^{j+\sigma}}{(\Delta u_{i-1})^2} \right] \end{aligned}$$

Equation 48

Using Leap Frog explicit approximations and substituting the fully explicit scheme parameter, $\sigma = 0$, we have:

$$\begin{aligned}
& s^{j+1}(p_{i-1}^{j+1} + 4p_i^{j+1} + p_{i+1}^{j+1}) - s^{j-1}(p_{i-1}^{j-1} + 4p_i^{j-1} + p_{i+1}^{j-1}) \\
&= (s^{j+1} - s^{j-1}) \left[\frac{(p_{i+1}^j - p_i^j)(u_{i+1} + 2u_i)}{\Delta u_i} + \frac{(p_i^j - p_{i-1}^j)(u_{i-1} + 2u_i)}{\Delta u_{i-1}} \right] \\
&+ \frac{6\delta t}{s^j} \left[(D_A[p])_{i,i+1}^j \frac{p_{i+1}^j - p_i^j}{(\Delta u_i)^2} - (D_A[p])_{i-1,i}^j \frac{p_i^j - p_{i-1}^j}{(\Delta u_{i-1})^2} \right]
\end{aligned}$$

Equation 49

The FEM diffusion model developed is used to analyze single phase binary systems as zero flux conditions for the two ends of the diffusion system. The Dufort Frankel/Leap Frog finite element explicit scheme works efficiently for single phase planar system when coupled with forward simulation techniques. The depth of analytical integration schemes required to formulate finite element equations for a transformed coordinate system of partial differential equations is a major challenge. However, the use of computational programming makes the process easier when compared to the Dufort Frankel based finite difference method which involves up/down winding schemes for the concentration profiles as more computational effort and skills are required in this scheme. The first and second element equations obtained from direct Dufort Frankel/Leap Frog explicit scheme based on finite element models do not accommodate up/down winding schemes since the element equations obtained do not contain intermediate concentrations profiles as employed in the finite difference method in the bid to apply up/down winding approximations that enhance the stability of the models. The Dufort Frankel/Leap Frog explicit schemes with zero flux conditions imposed at the extreme ends are outlined below.

The averaging for the concentration parameter is expressed as:

$$p_{i-1}^{j+1} + p_{i+1}^{j+1} = 2p_i^{j+1} \quad \text{Equation 50}$$

$$p_{i-1}^{j-1} + p_{i+1}^{j-1} = 2p_i^{j-1} \quad \text{Equation 51}$$

For simplification of the model, a uniform space grid is considered in the FEM nodal equation throughout the calculations in the model as expressed below:

$$\Delta u_i = u_{i+1} - u_i = \Delta u_{i-1} = u_i - u_{i-1} \quad \text{Equation 52}$$

For enhanced stability, the Dufort Frankel approximations applied for the time step in the model are:

$$p_i^j = \frac{1}{2}(p_i^{j-1} + p_i^{j+1}) \quad \text{Equation 53}$$

The Murray-Landau transformed FEM governing equation as expressed in Equation 48 is solved by applying the Dufort Frankel/Leap Frog explicit time discretization to obtain the discretized governing model. They are expressed below:

$$\begin{aligned} s^{j+1}p_i^{j+1} - s^{j-1}p_i^{j-1} \\ = \left(\frac{t^{j+1} - t^{j-1}}{s^j} \right) \left((D_A[p])_{i,i+1}^{j+1} \frac{p_{i+1}^j - p_i^j}{(u_{i+1} - u_i)^2} - (D_A[p])_{i-1,i}^{j+1} \frac{p_i^j - p_{i-1}^j}{(u_i - u_{i-1})^2} \right) \\ + (s^{j+1} - s^{j-1}) \left(\frac{(p_{i+1}^j - p_i^j)(u_{i+1} + 2u_i)}{u_{i+1} - u_i} + \frac{(p_i^j - p_{i-1}^j)(u_{i-1} + 2u_i)}{u_i - u_{i-1}} \right) \end{aligned} \quad \text{Equation 54}$$

After implementing the Dufort Frankel approximation, the coefficients terms are carefully sorted, rearranged, and expressed as follows:

$$\delta P_A * p_i^{j+1} = \delta P_B * p_i^{j-1} + \delta P_C * p_{i+1}^j + \delta P_D * p_{i-1}^j \quad \text{Equation 55}$$

where

$$\begin{aligned}\delta P_A = & s^{j+1} + \left(\frac{t^{j+1} - t^{j-1}}{2s^j} \right) \left(\frac{(D_A[p])_{i,i+1}^j}{(u_{i+1} - u_i)^2} + \frac{(D_A[p])_{i-1,i}^j}{(u_i - u_{i-1})^2} \right) \\ & + \left(\frac{s^{j+1} - s^{j-1}}{12} \right) \left(\frac{(u_{i+1} + 2u_i)}{(u_{i+1} - u_i)} - \frac{(u_{i-1} + 2u_i)}{(u_i - u_{i-1})} \right)\end{aligned}$$

Equation 56

$$\begin{aligned}\delta P_B = & s^{j-1} - \left(\frac{t^{j+1} - t^{j-1}}{2s^j} \right) \left(\frac{(D_A[p])_{i,i+1}^j}{(u_{i+1} - u_i)^2} + \frac{(D_A[p])_{i-1,i}^j}{(u_i - u_{i-1})^2} \right) \\ & - \left(\frac{s^{j+1} - s^{j-1}}{12} \right) \left(\frac{(u_{i+1} + 2u_i)}{(u_{i+1} - u_i)} - \frac{(u_{i-1} + 2u_i)}{(u_i - u_{i-1})} \right)\end{aligned}$$

Equation 57

$$\delta P_C = \left(\frac{t^{j+1} - t^{j-1}}{s^j} \right) \left(\frac{(D_A[p])_{i,i+1}^j}{(u_{i+1} - u_i)^2} \right) + \left(\frac{s^{j+1} - s^{j-1}}{6} \right) \left(\frac{u_{i+1} + 2u_i}{u_{i+1} - u_i} \right)$$

Equation 58

$$\delta P_D = \left(\frac{t^{j+1} - t^{j-1}}{s^j} \right) \left(\frac{(D_A[p])_{i-1,i}^j}{(u_i - u_{i-1})^2} \right) + \left(\frac{s^{j+1} - s^{j-1}}{6} \right) \left(\frac{u_{i-1} + 2u_i}{u_i - u_{i-1}} \right)$$

Equation 59

In the single-phase diffusion of binary alloys, a fixed concentration condition imposed at the boundaries implies that there is no possibility of the build-up of solute at the extreme boundaries of the host material, but this cannot be ascertained. A zero-flux boundary condition is however a confirmed boundary condition that can be applied to the ends of the host material to ensure that the total amount of diffusing solute in the sample is being conserved during the simulation of the single-phase diffusion of the binary alloy. By this reason, it is very certain that the extreme boundaries of the

material functions as a no solute flux boundary. The most accurate and reliable imposed zero flux conditions at both extreme ends of the single-phase diffusion system are expressed as:

$$\left. \frac{\partial p}{\partial u} \right|_1^{k-1} = \left. \frac{\partial p}{\partial u} \right|_1^k = \left. \frac{\partial p}{\partial u} \right|_1^{k+1} = 0 \quad \text{Equation 60}$$

$$\left. \frac{\partial p}{\partial u} \right|_{M+1}^{k-1} = \left. \frac{\partial p}{\partial u} \right|_{M+1}^k = \left. \frac{\partial p}{\partial u} \right|_{M+1}^{k+1} = 0 \quad \text{Equation 61}$$

By implementing zero flux conditions at the first node ($i = 1$) in Equation 62 and simplifying the Dufort Frankel/Leap Frog discretization expressed from Equations 57 to 61, the actual equation that determines that there is no solute migration at the left boundary for the single-phase diffusion in a binary alloy system is:

$$\delta P_{AA} * p_1^{j+1} = \delta P_{BB} * p_1^{j-1} + \delta P_{CC} * p_2^j \quad \text{Equation 62}$$

where

$$\delta P_{AA} = s^{j+1} + \left(\frac{t^{j+1} - t^{j-1}}{2s^j} \right) \left(\frac{(D_A[p])_{1,2}^j}{(u_2 - u_1)^2} \right) + \left(\frac{s^{j+1} - s^{j-1}}{12} \right) \left(\frac{u_2 + 2u_1}{u_2 - u_1} \right) \quad \text{Equation 63}$$

$$\delta P_{BB} = s^{j-1} - \left(\frac{t^{j+1} - t^{j-1}}{2s^j} \right) \left(\frac{(D_A[p])_{1,2}^j}{(u_2 - u_1)^2} \right) - \left(\frac{s^{j+1} - s^{j-1}}{12} \right) \left(\frac{u_2 + 2u_1}{u_2 - u_1} \right) \quad \text{Equation 64}$$

$$\delta P_{CC} = \left(\frac{t^{j+1} - t^{j-1}}{s^j} \right) \left(\frac{(D_A[p])_{1,2}^j}{(u_2 - u_1)^2} \right) + \left(\frac{s^{j+1} - s^{j-1}}{6} \right) \left(\frac{u_2 + 2u_1}{u_2 - u_1} \right) \quad \text{Equation 65}$$

Zero flux conditions are implemented at the last node, $i = M + 1$ by using:

$$\delta P_A * p_{M+1}^{j+1} = \delta P_B * p_{M+1}^{j-1} + \delta P_D * p_M^j \quad \text{Equation 66}$$

where

$$\delta P_A = s^{j+1} + \left(\frac{t^{j+1}-t^{j-1}}{2s^j} \right) \left(\frac{(D_A[p])_{M,M+1}^j}{(u_{M+1}-u_M)^2} \right) - \left(\frac{s^{j+1}-s^{j-1}}{12} \right) \left(\frac{4u_{M+1}-u_M}{(u_{M+1}-u_M)} \right) \quad \text{Equation 67}$$

$$\delta P_B = s^{j-1} - \left(\frac{t^{j+1}-t^{j-1}}{2s^j} \right) \left(\frac{(D_A[p])_{M,M+1}^j}{(u_{M+1}-u_M)^2} \right) + \left(\frac{s^{j+1}-s^{j-1}}{12} \right) \left(\frac{4u_{M+1}-u_M}{(u_{M+1}-u_M)} \right) \quad \text{Equation 68}$$

$$\delta P_D = \left(\frac{t^{j+1}-t^{j-1}}{s^j} \right) \left(\frac{(D_A[p])_{M,M+1}^j}{(u_{M+1}-u_M)^2} \right) + \left(\frac{s^{j+1}-s^{j-1}}{6} \right) \left(\frac{u_M+2u_{M+1}}{u_{M+1}-u_M} \right) \quad \text{Equation 69}$$

For a single-phase diffusion system, it is very clear that there is no moving interface. By using the governing numerical diffusion models, the implication is expressed as:

$$s^{j-1} = s^j = s^{j+1} \quad \text{Equation 70}$$

First order Differential Equation	Time Discretization	Discretized Equation
$\frac{d\varphi}{dt} = F(\varphi)$	Fully Implicit scheme	$\frac{\varphi^{j+1} - \varphi^j}{t^{j+1} - t^j} = F(\varphi^{j+1})$
	Fully Explicit Scheme	$\frac{\varphi^{j+1} - \varphi^j}{t^{j+1} - t^j} = F(\varphi^j)$
	Crank-Nicolson scheme	$\frac{\varphi^{j+1} - \varphi^j}{t^{j+1} - t^j} = F\left(\varphi^{j+\frac{1}{2}}\right)$
	Leap Frog Explicit scheme	$\frac{\varphi^{j+1} - \varphi^{j-1}}{t^{j+1} - t^{j-1}} = F(\varphi^j)$

Figure 3.14: Finite difference time discretization schemes in numerical analysis

3.2 Consistency analysis of the model

The consistency analysis of the new numerical diffusion model is presented in this section. The error associated with the numerical scheme applied is analyzed.

A constant diffusion coefficient in a planar geometric system that uses the FEM governing model formulated, is considered.

$$\begin{aligned} \frac{s^{j+1}p_i^{j+1} - s^{j-1}p_i^{j-1}}{t^{j+1} - t^{j-1}} &= \frac{D_A}{s^j(t)\Delta u^2} [p_{i+1}^j - 2p_i^j + p_{i-1}^j] \\ &+ \frac{s^{j+1} - s^{j-1}}{6(t^{j+1} - t^{j-1})} \left[\frac{(p_{i+1}^j - p_i^j)(u_{i+1} + 2u_i) + (p_i^j - p_{i-1}^j)(u_{i-1} + 2u_i)}{\Delta u} \right] \end{aligned}$$

Equation 71

Equation 71 is obtained by the discretization of the general finite element model by using the Dufort Frankel/Leap Frog explicit scheme. Also, by using a uniform space grid in the numerical model stated above and applying a Taylor series expansion to the dependent variable (p) in time and space about (t_j, u_i) , the equations obtained are as follows:

$$p_{i\pm 1}^j = p_i^j \pm \frac{\partial p}{\partial u} \Delta u + \frac{1}{2} \frac{\partial^2 p}{\partial u^2} \Delta u^2 + O(\Delta u^3) \quad \text{Equation 72}$$

$$p_i^{j\pm 1} = p_i^j \pm \frac{\partial p}{\partial t} \Delta t + \frac{1}{2} \frac{\partial^2 p}{\partial t^2} \Delta t^2 + O(\Delta t^3) \quad \text{Equation 73}$$

The Taylor's series is also applied to the expansion of the interface displacement which is a function of time about (t_j) . The equation is:

$$s^{j\pm 1} = s^j \pm \frac{\partial s}{\partial t} \Delta t + \frac{1}{2} \frac{\partial^2 s}{\partial t^2} \Delta t^2 + O(\Delta t^3) \quad \text{Equation 74}$$

Also, $u_{i\pm 1} = u_i \pm \Delta u$

Equation 75

Substituting Equation 74 to 77 into Equation 73, the revised equation obtained, which describes the actual transformed partial differential equation, and the truncation error is given below:

$$T_E^n = \underbrace{\frac{\partial(ps)}{\partial t} - \frac{D_A}{s} \frac{\partial^2 p}{\partial u^2} - \frac{ds}{dt} \frac{\partial(pu)}{\partial u}}_{\text{Actual transformed PDE}} + \underbrace{\frac{1}{2} \frac{\partial^2(ps)}{\partial t^2} (\Delta t)^2 - \frac{ds}{dt} \left[\left(u \frac{\partial^2 p}{\partial u^2} + \frac{\partial p}{\partial u} \right) \Delta u + \frac{1}{4} \frac{\partial^2 p}{\partial u^2} \Delta u^2 + \frac{1}{4} \frac{\partial^2 p}{\partial t^2} \Delta t^2 \right]}_{\text{Truncation Error from the leapfrog-Dufort Frankel FEM model}} + O(\Delta t^3, \Delta u^3)$$

Equation 76

$O(\Delta u^3)$ represents the terms from the third-degree function in the above Taylor series expansion which is removed in the computational analysis of the numerical model.

From Equation 76, it is clear that the Dufort Frankel/Leap Frog explicit scheme yields consistency when $\Delta t^2 \rightarrow 0$ and $\Delta u \rightarrow 0$ since all of the error terms tend toward zero.

3.3. Stability analysis of the model

Stability in numerical analyses is defined as numerical schemes that produce bounded errors for numerical solutions which usually depend on the approximation scheme applied. It is well recognized that errors are unavoidable in any numerical computation. A stability analysis is therefore necessary to examine the values of approximation variables that would lead to increased errors in the required solutions which needs to be bounded [53]. The nature of partial differential equation that govern a diffusion problem, the step size and type of numerical scheme employed collectively determine the

stability of a numerical scheme: for example, a particular method can be stable for a problem but not stable when applied to another problem [53]. There are many available tools that are reliable and can be used to investigate and determine the stability of a numerical scheme. They include the von Neumann and Lax equivalence theorems.

The von Neumann stability analysis is a very useful tool for investigating the generation of numerical errors which in turn provides information about the stability of a numerical scheme. Potential for the amplification of errors can be thoroughly examined for any numerical discretization scheme applied [54]. The stability of a numerical scheme is ascertained when the truncation error from the numerical scheme decays with time [55]. When the maximum absolute amplification factor (G) between the time interval is less than or equal to one ($|G^\pm| \leq 1$), stability is attained [24, 55].

In this work, the stability analysis of the developed finite element model is carried out by using the von Neumann analysis. This is applied to the governing model with consideration of a constant diffusion coefficient. A nodal point which describes the concentration parameter (dependent variable) in the model discretization can be described by using a harmonic plane wave equation which is expressed as:

$$p_i^k = G p_o e^{ij\phi\Delta u} \quad \text{Equation 77}$$

where G is the amplification factor between the given time interval, p_o is the initial amplitude of the harmonic plane wave, and $\phi\Delta u$ describes the wavenumber.

The discretized dependent variable in the von Neumann analysis can be described as:

$$p_i^{k+1} = G p_i^k \quad \text{Equation 78}$$

$$p_i^{k-1} = \frac{p_i^k}{G} \quad \text{Equation 79}$$

$$p_{i\pm 1}^k = e^{\pm ij\phi\Delta u} p_i^k \quad \text{Equation 80}$$

The general situation considered when the interface displacement is of equal rate of change is:

$$w = \frac{s^{k+1}}{s^k} = \frac{s^k}{s^{k-1}} \quad \text{Equation 81}$$

For the case of a stationary boundary interface, $s^{k+1} = s^k = s^{k-1}$ which implies that $w = 1$ from Equation 81. The expression that describes the combination of time step, diffusion coefficient, current interface position and space step is known as the diffusion factor as follows:

$$\mu = \frac{\Delta t D_A}{(s^k \Delta u)^2} \quad \text{Equation 82}$$

The ratio of the applied space step to the current transformed position variable in the model is expressed below:

$$\varphi = \frac{\Delta u}{u_i} \quad \text{Equation 83}$$

In the von Neumann stability analysis, the combination of numerical constants, w , μ and φ forms the determining factor for the Courant-Friedrichs-Lewy (CFL) convergence criteria which usually arises in numerical analysis for explicit time discretization schemes.

Equation 86 is obtained by applying the classical explicit time discretization scheme to a general finite element model.

$$\begin{aligned}
s^{j+1}p_i^{j+1} - s^j p_i^j &= \frac{D_A(t^{j+1} - t^j)}{s^j(t)\Delta u^2} [p_{i+1}^j - 2p_i^j + p_{i-1}^j] \\
&+ \left(\frac{s^{j+1} - s^j}{6} \right) \left[\frac{(p_{i+1}^j - p_i^j)(u_{i+1} + 2u_i)}{\Delta u} + \frac{(p_i^j - p_{i-1}^j)(u_{i-1} + 2u_i)}{\Delta u} \right]
\end{aligned}$$

Equation 84

Considering a planar geometric system and the case of a constant diffusion coefficient, the overall substitution of Equations 73 – 80 into Equation 81 yields the required modified equation that describes the maximum amplification factor required to analyze and study the convergence and the stability condition. The modified equation obtained is:

$$G = \frac{1}{w} \left[1 - 4\mu \sin^2 \left(\frac{\phi \Delta u}{2} \right) + \left(\frac{w-1}{6} \right) \left(\frac{6j \sin(\phi \Delta u)}{\phi} - 4 \sin^2 \left(\frac{\phi \Delta u}{2} \right) \right) \right]$$

Equation 85

Equation 85 describes the common and classical Euler explicit time discretization scheme of a general finite element model. Substituting Equations 73 – 80 into Equation 68 yields the modified equation that describes the maximum amplification factor for the Dufort Frankel/Leap Frog explicit scheme. The modified equation is:

$$\begin{aligned}
G \left[w + \mu + \frac{1}{6} \left(w - \frac{1}{w} \right) \right] &= \frac{1}{G} \left[w - \mu - \frac{1}{6} \left(w - \frac{1}{w} \right) \right] + e^{j\phi \Delta u} \left[\mu + \frac{1}{6} \left(w - \frac{1}{w} \right) \left(\frac{3}{\phi} + 1 \right) \right] \\
&+ e^{-j\phi \Delta u} \left[\mu - \frac{1}{6} \left(w - \frac{1}{w} \right) \left(\frac{3}{\phi} - 1 \right) \right]
\end{aligned}$$

Equation 86

Equation 82 and 83 are solved to compare the level of stability for both the classical explicit and Dufort Frankel/Leap Frog schemes. Figures 3.15 and 3.16 and 3.17 plot the graphical plots of amplification factor for stationary boundaries.

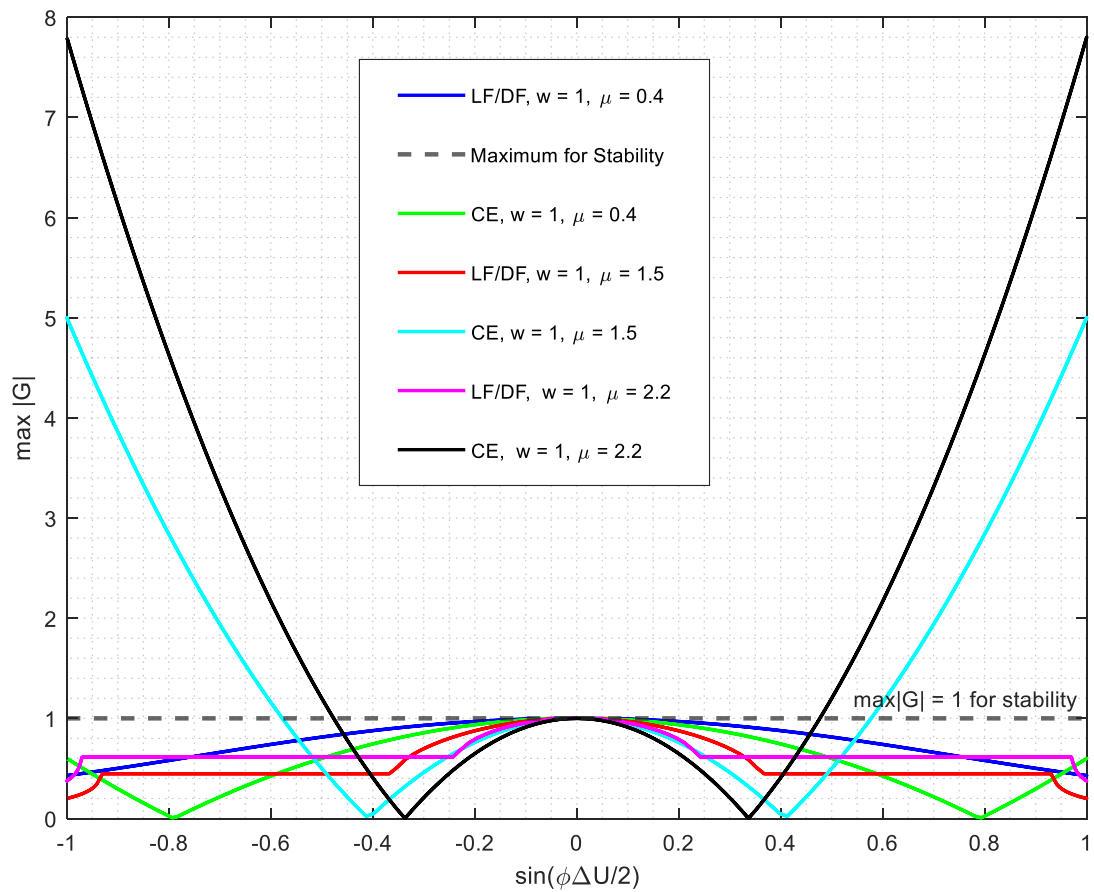


Figure 3.15 Amplification factor for a stationary boundary case in finite element model

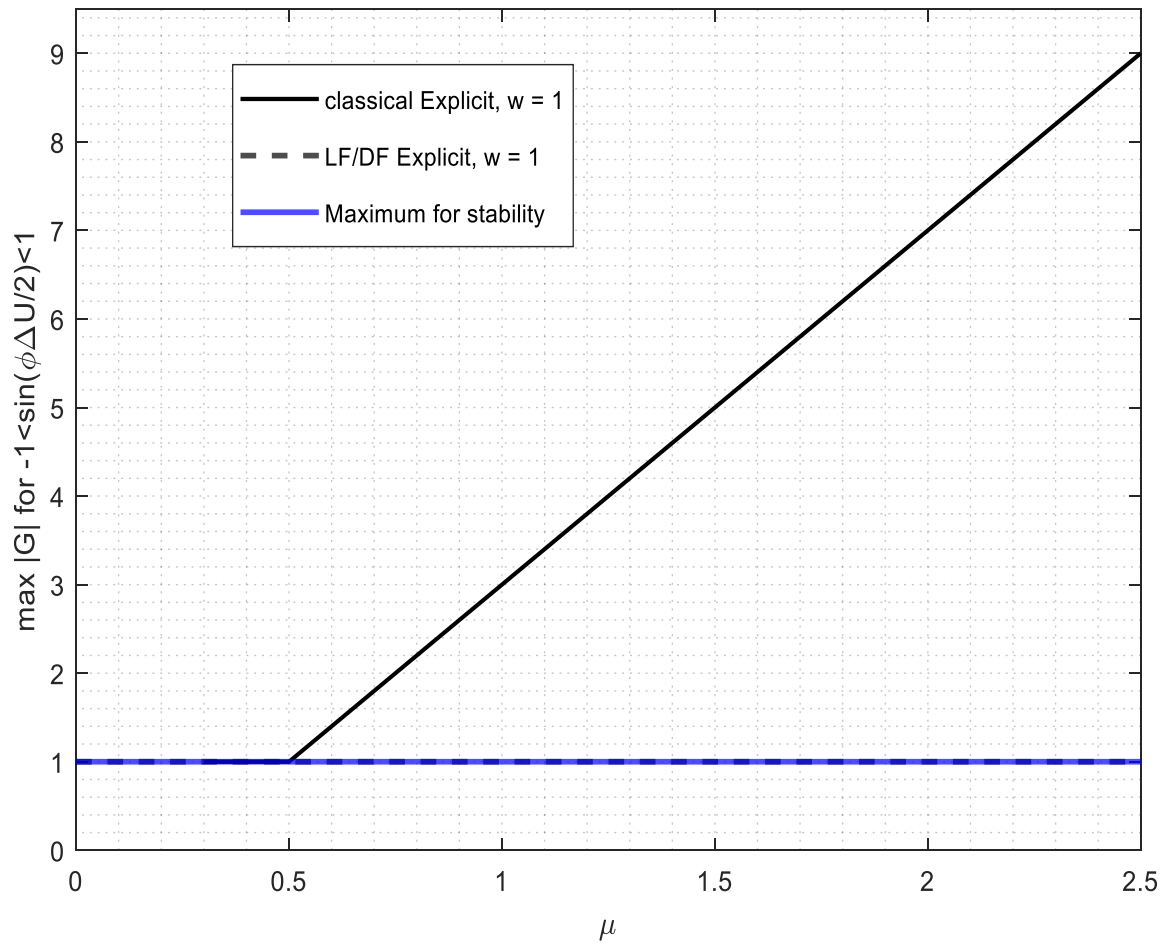


Figure 3.16 Amplification factor vs μ for stationary boundary using classical explicit finite element model

3.4 Implementation of the newly developed numerical model

Up/down winding schemes are very common schemes in the solution of diffusion problems when control volume approaches are used because they overcome the generation of oscillating (non-monotonic) solutions. These schemes are very applicable to numerical discretization with intermediate profiles.

In the application of the newly developed numerical diffusion model, the interdiffusion coefficient, which is a function of concentration, is evaluated at the average centered concentration values between two nodal points since the model does not contain intermediate concentration profiles. From the implementation of the new models, there are no issues of non-monotonic (oscillating) solutions. The $D(C)$ employed in this model are given below:

$$(D)_{i,i+1}^{j+\sigma} = \frac{1}{2} [(D)_i^{j+\sigma} + (D)_{i+1}^{j+\sigma}] \quad \text{Equation 87}$$

$$(D)_{i-1,i}^{j+\sigma} = \frac{1}{2} [(D)_{i-1}^{j+\sigma} + (D)_i^{j+\sigma}] \quad \text{Equation 88}$$

The time step chosen in the numerical simulation is based on Zhou and North [33]. A time step in a logarithm scale was selected for the even distribution of points. The whole diffusion system is then more optimized.

$$time_{log} = \log(t_{initial}) : \left(\frac{1}{M}\right) \log\left(\frac{t_{final}}{t_{initial}}\right) : \log(t_{final}) \quad \text{Equation 89}$$

where M denotes the number of discretization points in the whole diffusion system.

Hence, the algorithm and procedures for solving the boundary-valued problem are outlined as follows:

-
1. The initial and final experimental concentration profiles are first extracted and smoothened. Data smoothening is carried out through moving average smoothening.
 2. The BM or SF method is used to provide an initial estimate of the $D(C)$ function (linear or quadratic behaviour).

$$D = \exp[F(C)]$$

Equation 90

$F(C)$ is a functional behaviour that gives the behavioral trends of the composition dependent interdiffusion coefficient from the analytical method given above.

3. The newly developed numerical model is used to simulate the concentration profile by solving Fick's second law of diffusion. The newly developed Dufort Frankel/Leap Frog scheme which is a three-level explicit method requires the use of $p_i^2 = p_i^1$. This is because at $k = 1$, the two-step classical explicit method gives the same result. When $k > 1$, the future concentration profile, p_i^{k+1} is calculated by using the newly developed Dufort Frankel/Leap Frog finite element model. The above method outlined requires no assumption or any sort of iteration as commonly used in implicit schemes.
4. A threshold value is set to compare the experimental and simulated concentration profiles. The difference between the two profiles is calculated. When the value of the difference is lower than the pre-set threshold, the evaluated interdiffusion coefficient obtained is taken as the best result.
5. The forward simulation technique is used to adjust the interdiffusion coefficient. If the sum of the squared difference obtained in Step 4 is higher than the threshold value set, the interdiffusion coefficient is adjusted. This is achieved through the inverse proportionality between the interdiffusion coefficient and concentration gradient at any given concentration value.

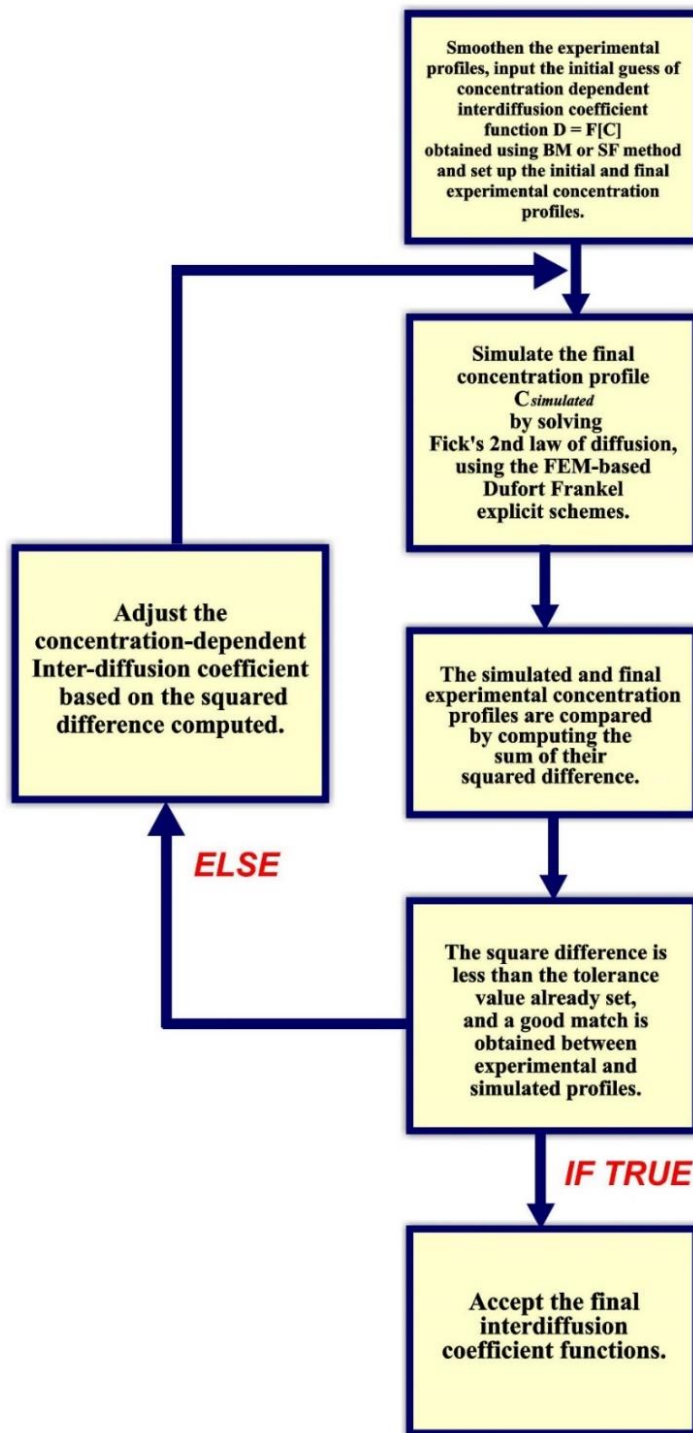


Figure 3.17 Flow chart diagram of forward simulation analysis

Chapter 4

Validation and result of the newly developed numerical model

4.1 Validation of numerical model

A numerical diffusion model is developed for a two-profile system which requires two experimental concentration profiles for the extraction of $D(C)$. It is noted that the newly developed numerical diffusion model is combined with forward simulation techniques in two different modes, which both consider two profiles. The first mode (FEM–FSM I) is the case where the initial concentration profile is a step function profile, and the final concentration profile is experimentally obtained. The first mode assumes that there is no initial non-uniform solute distribution in the material prior to the diffusion process, which is the main reason why the initial profile is a step-function. This assumption is reasonable as long as the actual initial profile is infinitesimally small compared to the final experimental concentration profile. The second mode (FEM–FSM II) is the case where both the initial and final concentration profiles are experimentally obtained which is the main focus of this research study. For this reason, the validation of the new model is executed in the two modes.

In this section, the numerical diffusion model developed in this research work is validated by using the experimental data in the existing literature [see 45 -48]. The results of numerical inverse simulation study in [45-48], for cases where the assumption of step-function initial concentration profile is valid, are compared to those of the present model to determine the reliability of the new model developed in this research. However, in the second phase of the model validation, experimental concentration profiles reported in the literature [56-57] are used. The $D(C)$ extracted from the experimental profiles

by the new model are used to predict the final concentration profiles and the predicted profiles by the model are compared to the actual final experimental profiles.

The authors of [45-48] developed a numerical inverse method called forward simulation techniques in the bid to overcome the limitations and major flaws associated with existing analytical methods. Their work are cases where the initial profile (significantly small relative to the final experimental concentration profile) is assumed to be a step function while the final profile is experimentally obtained. They developed a MATLAB program for effective extraction and evaluation of both interdiffusion and impurity coefficients from the concentration profiles of binary diffusion couples. They reported the experimental results and data for a number of different binary alloy systems. Three of their binary systems are examined by extracting $D(C)$ with the new diffusion model. They include iron - nickel (Fe - Ni), cobalt - nickel (Co - Ni), and niobium - tungsten (Nb - W) binary systems [45 - 47]. The experimental diffusion profiles were heat treated at 1100°C for a diffusion time of 1000 hours. The experimental concentration profiles from different binary alloy systems were investigated. The result from the numerical simulations carried out with the new model was compared with the existing numerical results in [45-47].

The $D(C)$ calculated from the present model accurately reproduces the experimental concentration profiles in [45-47].

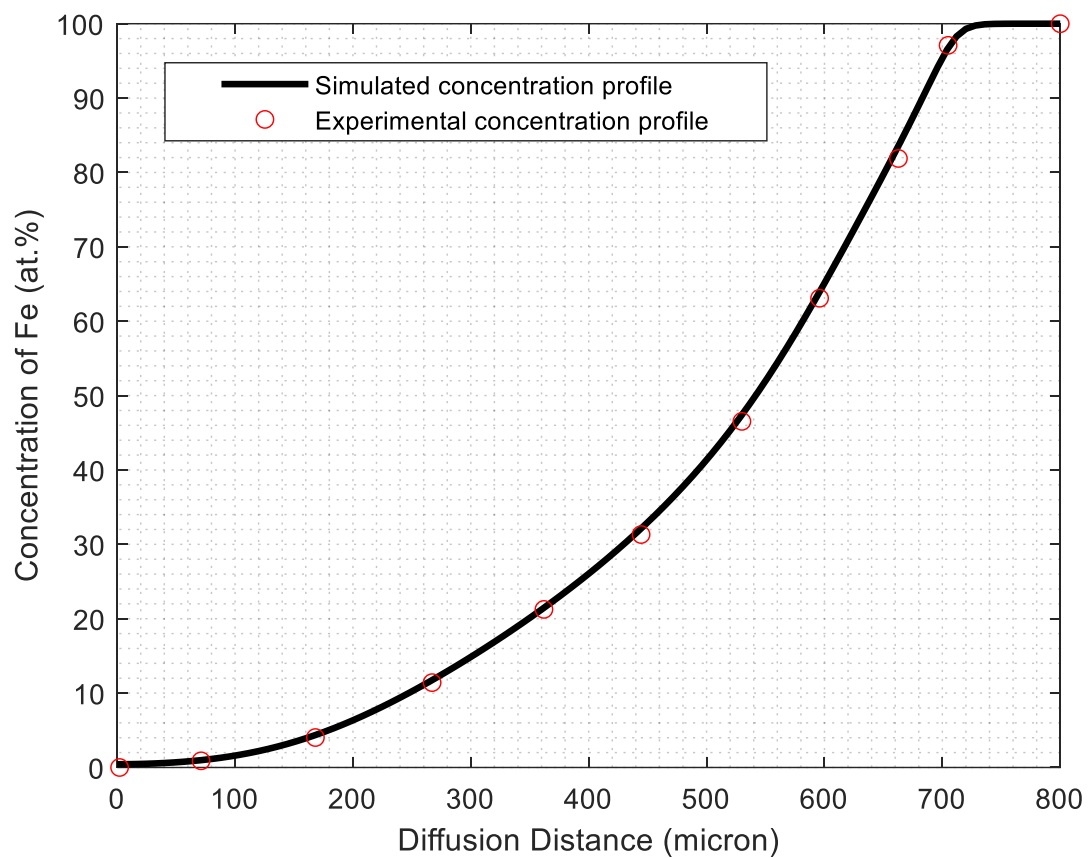


Figure 4.1 Relative comparison between simulated and experimental concentration profiles [45-47] in an Fe- Ni diffusion couple at 1100°C

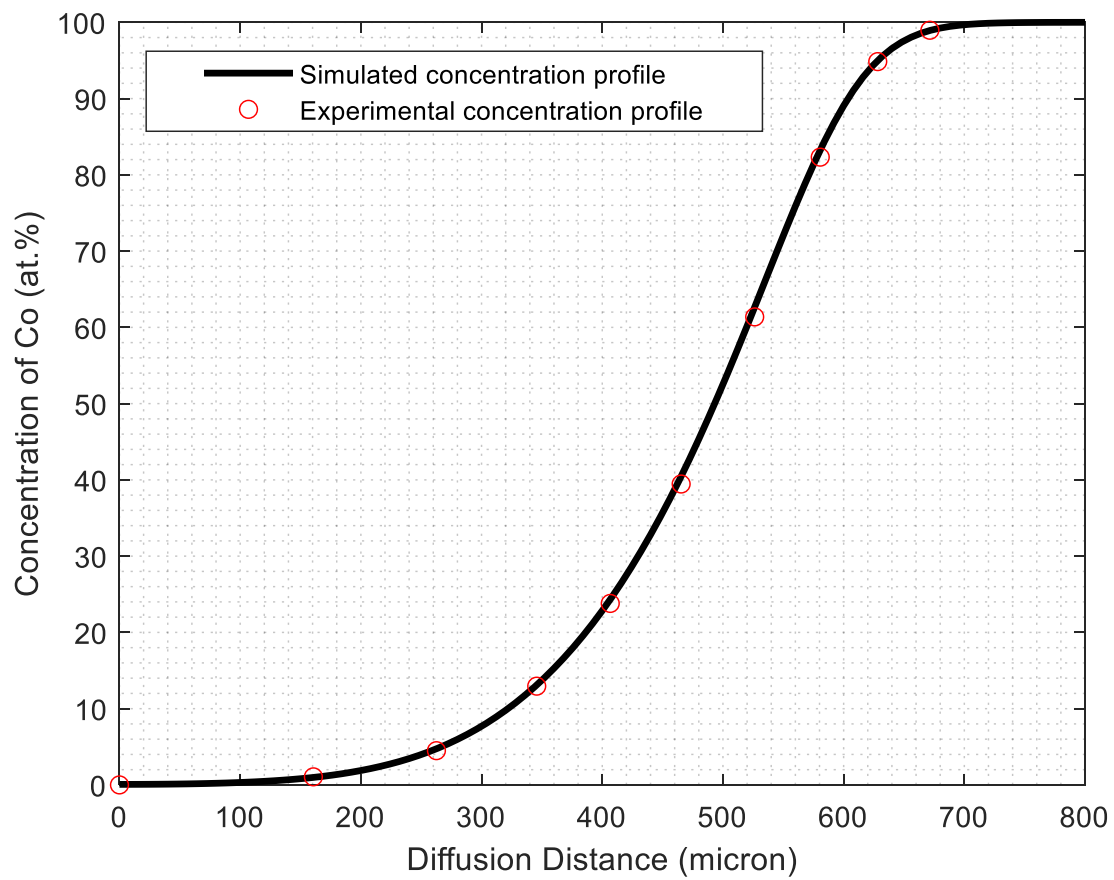


Figure 4.2 Relative comparison between simulated and experimental concentration profiles [45-47] in an Ni - Co diffusion couple at 1100°C

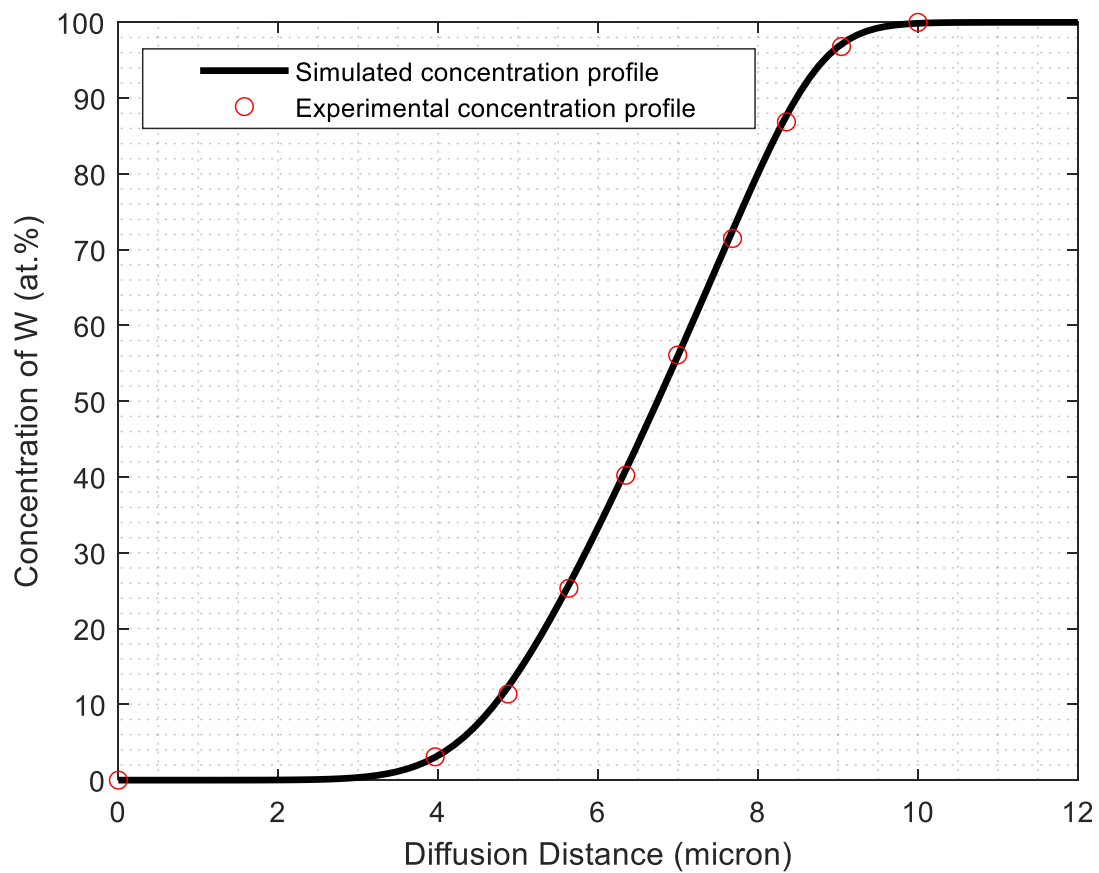


Figure 4.3 Relative comparison between simulated and experimental concentration profiles [45-47] in an Nb - W diffusion couple at 1100°C

In the Fe-Ni diffusion couple system illustrated in Figure 4.1, the $D(C)$ evaluated with forward simulation techniques and the newly proposed model shows a polynomial behaviour of degree five, which is a quintic function of Fe concentration.

Another binary alloy system investigated with the newly developed model is the Co-Ni alloy system. In the system, the $D(C)$ obtained from the implementation of the FSM and current model applied to simulate the concentration profile shows a linear trend with Co composition. The data from the extracted interdiffusion coefficient versus concentration of Co show that as the concentration of Co increases, the interdiffusion coefficient decreases. This is supported in [46].

The Nb-W system (as illustrated in Figure 4.3) is also investigated with the present model. It has a small diffusion zone that is about $5\mu m$ compared to Fe-Ni system (as illustrated in Figure 4.1) which is about $700\mu m$ and approximately a $500\mu m$ diffusion zone in the Co-Ni system (as illustrated in Figure 4.2). However, even if the diffusion zone is small, the combination of FSM and the present model effectively extracts the $D(C)$.

The above diffusion couple systems investigated are all found to have excellent qualitative agreement with their result and quantitative approximation with the experimental data at both few and large discretization points. This demonstrates the accuracy, efficiency, and reliability of the new model.

As discussed earlier, the main purpose of this study is to test and investigate if the newly developed finite element model can be used to successfully extract a $D(C)$ from experimental concentration profiles. For this reason, two experimental concentration profiles are required unlike the first mode of validation where one final experimental concentration profile is necessary. This is the second mode of the validation. These provide further validation of the newly developed finite element diffusion model.

Two binary alloy systems, the Ni - Cu and Cu - Si with available experimental concentration profiles are carefully selected from the literature for this purpose. The numerical diffusion model developed in this work is effectively used to simulate non steady state diffusion in a single-phase binary alloy system and extract the $D(C)$ that operates between two experimental concentration profiles.

The simulated final concentration profiles produced by using the calculated $D(C)$ obtained by the new model shows an excellent agreement with the final experimental concentration profile, which validates the reliability of the new numerical diffusion model.

The results of the modelling and a series of numerical simulations under different conditions implemented are hereby presented and discussed. The analyses of the results are outlined based on the binary alloy systems investigated.

4.2 Extraction of $D(C)$ s in nickel - copper diffusion couple system

The experimental concentration profiles for the Ni – Cu binary alloy system at a diffusion temperature of 1025°C are extracted from [56]. The diffusion times for the experimental concentration profiles extracted are 40, 72, and 120 hours. Different analyses were carried out for the three different time intervals and plotted in Figures 4.4 to 4.8.

In the Ni – Cu system, electrodeposition of Cu on substrate samples of Ni – Cu diffusion couple was carried out by [56] and diffusion heat treatment was done at a sufficiently elevated temperature of 1025°C . The experimental concentration profiles collected at two different diffusion times are used to calculate the $D(C)$ which is plotted against the simulated concentration profile in Figure 4.4.

For an Ni – Cu binary alloy system, the existing literature indicates that the standard error calculated from several samples of experimental concentration profiles is found to range from 10% – 15% [15]. A standard error of 15% is used in plots of $D(C)$ against concentration profile.

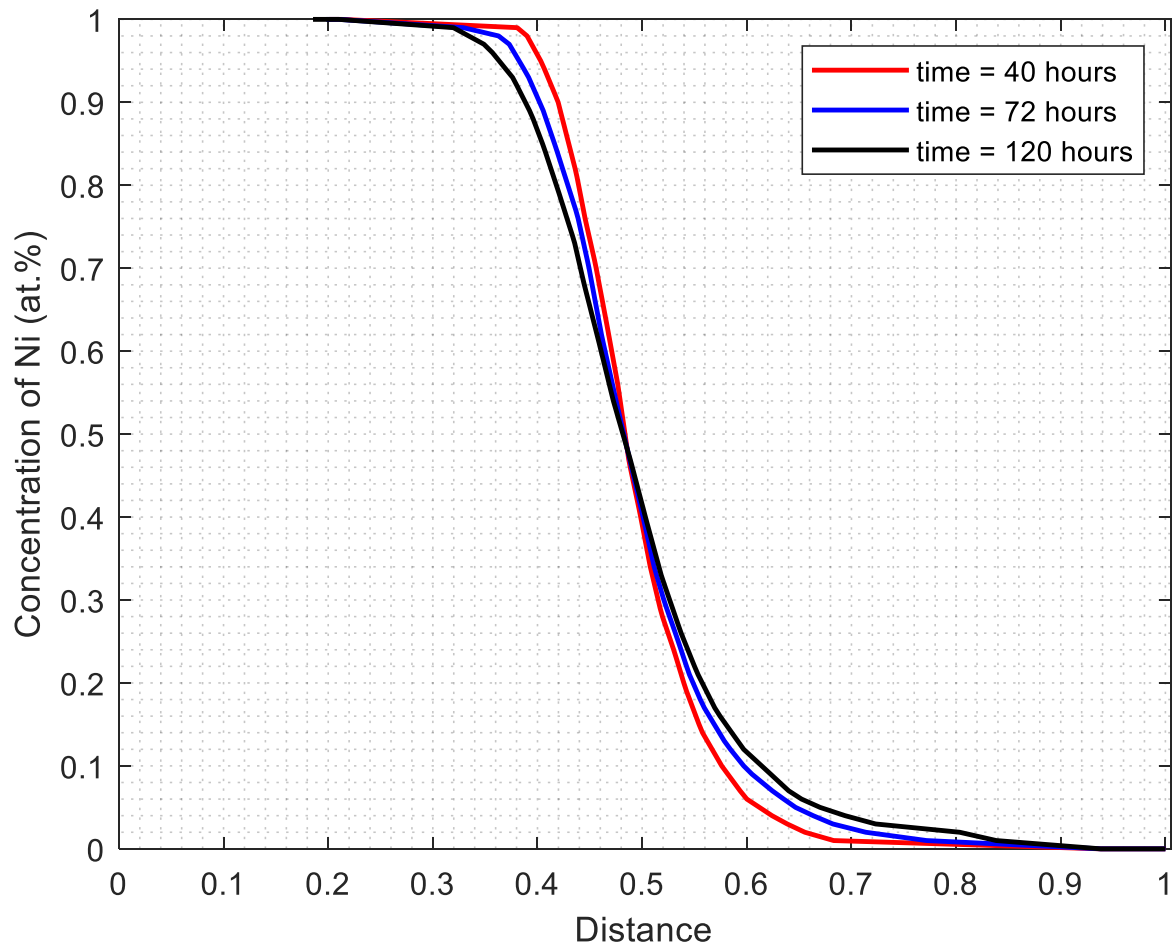


Figure 4.4: Extracted experimental concentration profiles [56] in Ni - Cu binary alloy system at 1025°C for 40, 72 and 120 hours

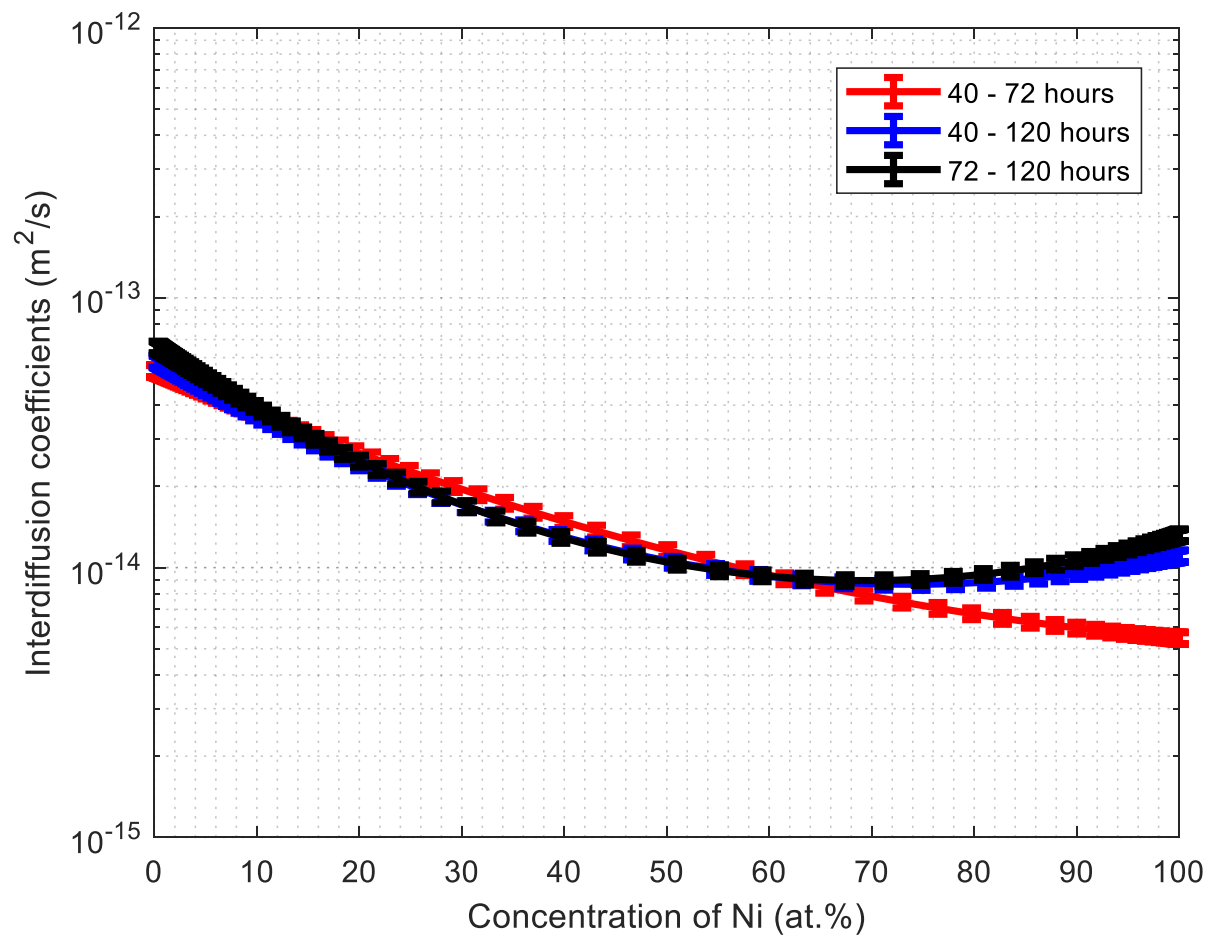


Figure 4.5: Time variation of $D(C)$ with concentration of Ni at different time intervals for Ni – Cu diffusion couple system at 1025°C

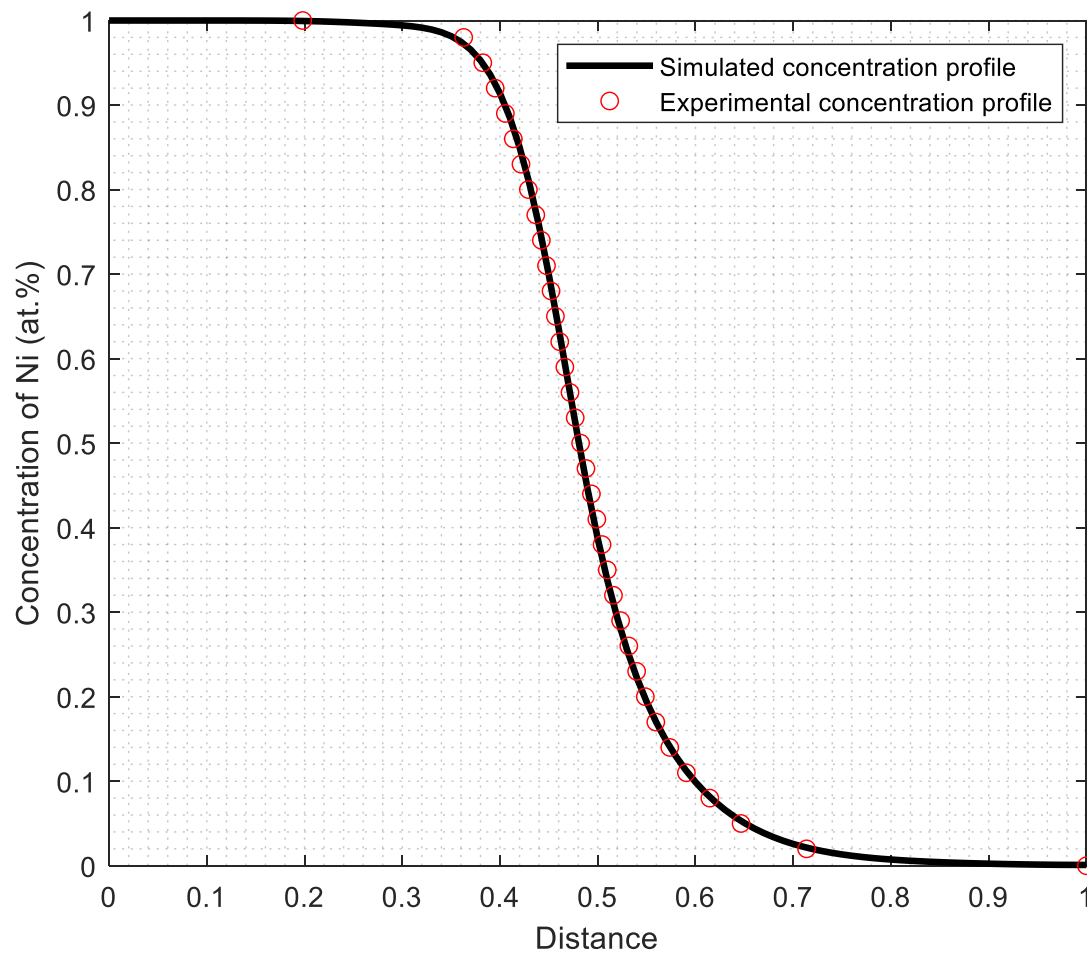


Figure 4.6: Comparison between extracted experimental [56] and simulated concentration profiles in Ni - Cu binary alloy system at 1025°C for 40 – 72 hours

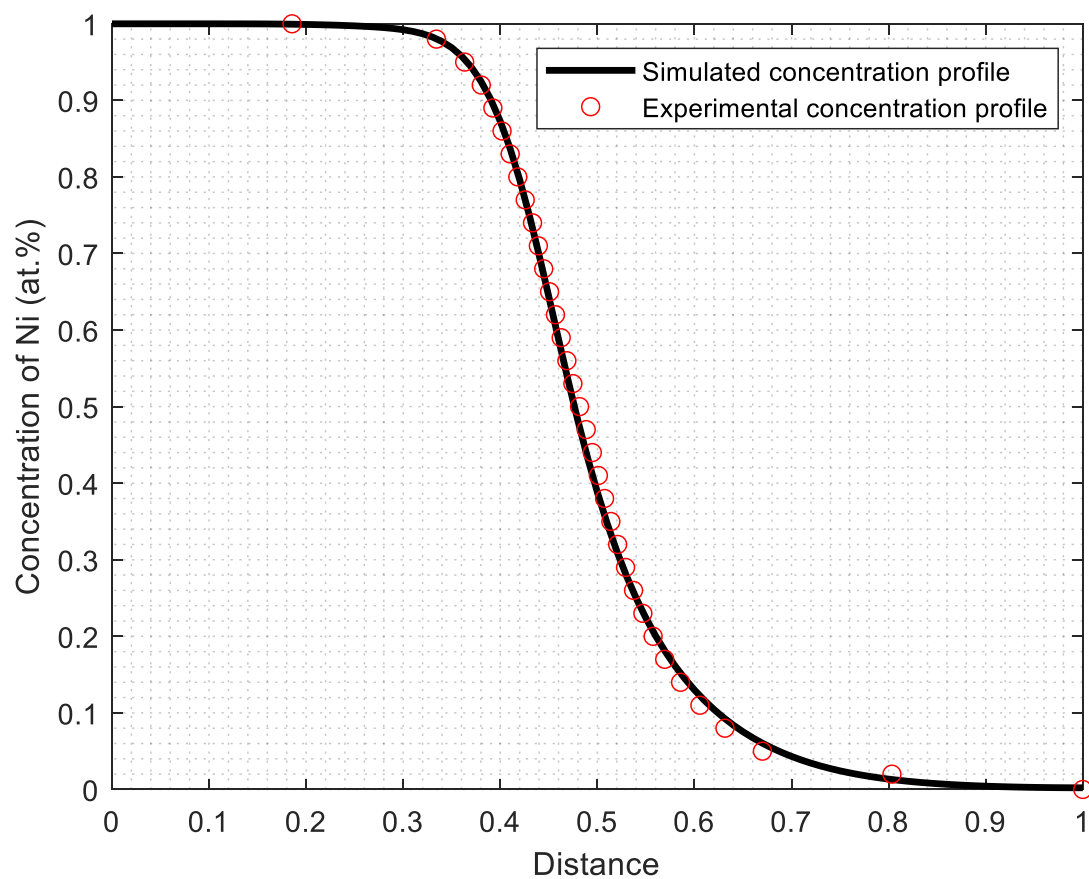


Figure 4.7: Comparison between extracted experimental [56] and simulated concentration profiles in Ni - Cu binary alloy system at 1025°C for 72 – 120 hours

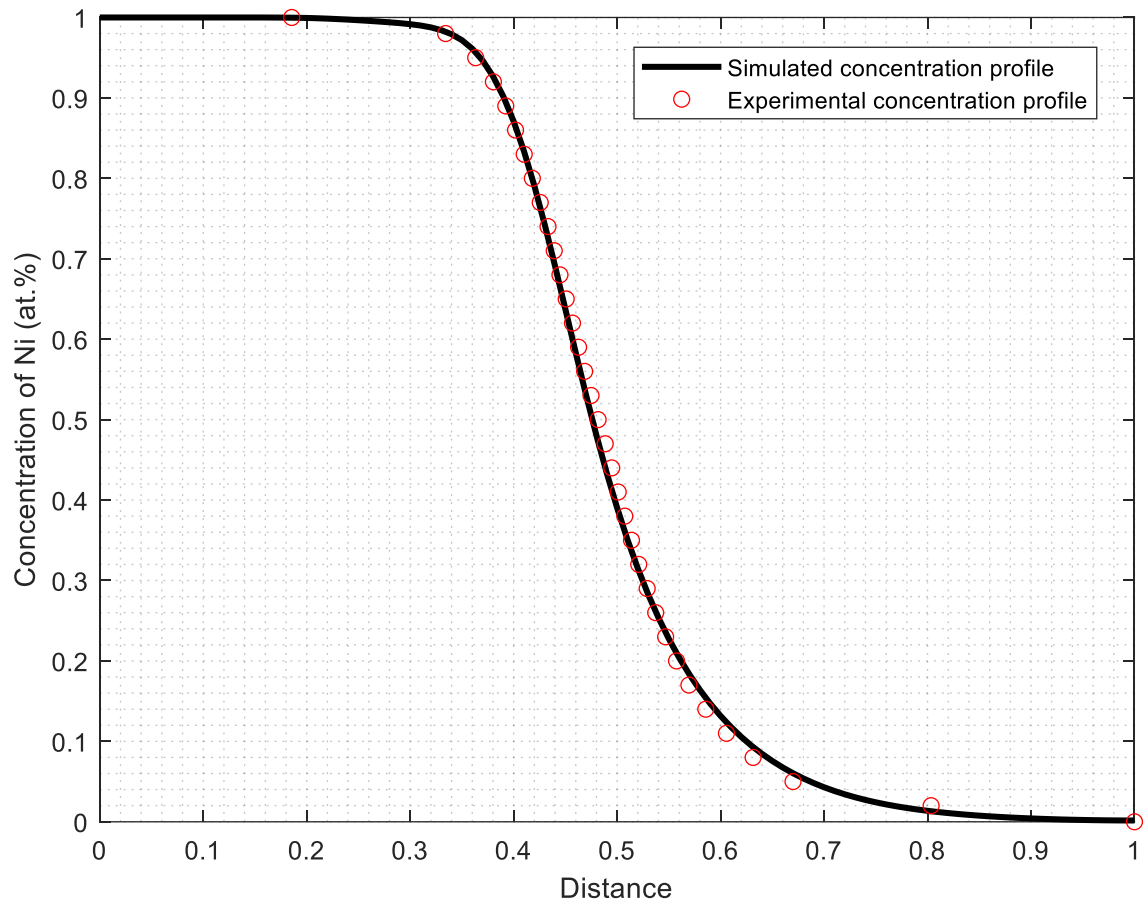


Figure 4.8: Comparison between extracted experimental [56] and simulated concentration profiles in Ni - Cu binary alloy system at 1025°C for 40 – 120 hours

Time is observed to be significant influence in the figures that describe the $D(C)$ with the presence of overlapping regions between the error bars of the samples at different times. The extracted experimental concentration profiles from both binary systems investigated at different diffusion times are also compared with the simulated concentration profiles as shown in Figures 4.6, 4.7, and 4.8 for the Ni – Cu binary alloy system. The $D(C)$ with concentration are calculated and extracted by using the forward simulation technique and the newly developed finite element diffusion model. The extracted results are shown in Figure 4.5. It is evident from the outlined results obtained that the new diffusion model successfully extracts the $D(C)$.

In the case of 40 – 120 hours as illustrated in Figure 4.8, the solute concentration profile at 40 hours is taken as the initial profile while that at 120 hours is taken as the final concentration profile. Unlike the usual conventional analytical method such as the BM method and SF method which assume a step function of space, the 40-hour initial profile shows an accurate and practical situation of existing diffusion treatment in a substrate. Figure 4.5 describes the significant variation of the $D(C)$ as the diffusion time interval changes from 40 and 72 to 72 and 120 and to 40 and 120 hours. Note that [57] experimentally performed the diffusion heat treatment at a very high temperature of 1025°C . It is well-known in the field of atomic diffusion that higher temperatures result in greater depth of penetration of the solute, thereby providing sufficient supporting evidence of the reliability of the new model used in the analysis of the result obtained.

4.3 Extraction of $D(C)$ s in copper - silicon diffusion couple system

The concentration profiles for Cu-Si binary diffusion system were obtained from the experimental work in Rhines and Mehl [57]. Three experimental concentration profiles at 17.92, 37.46, and 66.96 days are available for the calculation and extraction of $D(C)$ between any two experimental concentration profiles.

Similar to the Ni-Cu binary system, the required experimental concentration profiles from the diffusion heat treatment experiments in [57] were used to validate the new model. The results from the numerical simulations conducted are presented in Figures 4.9 and 4.10.

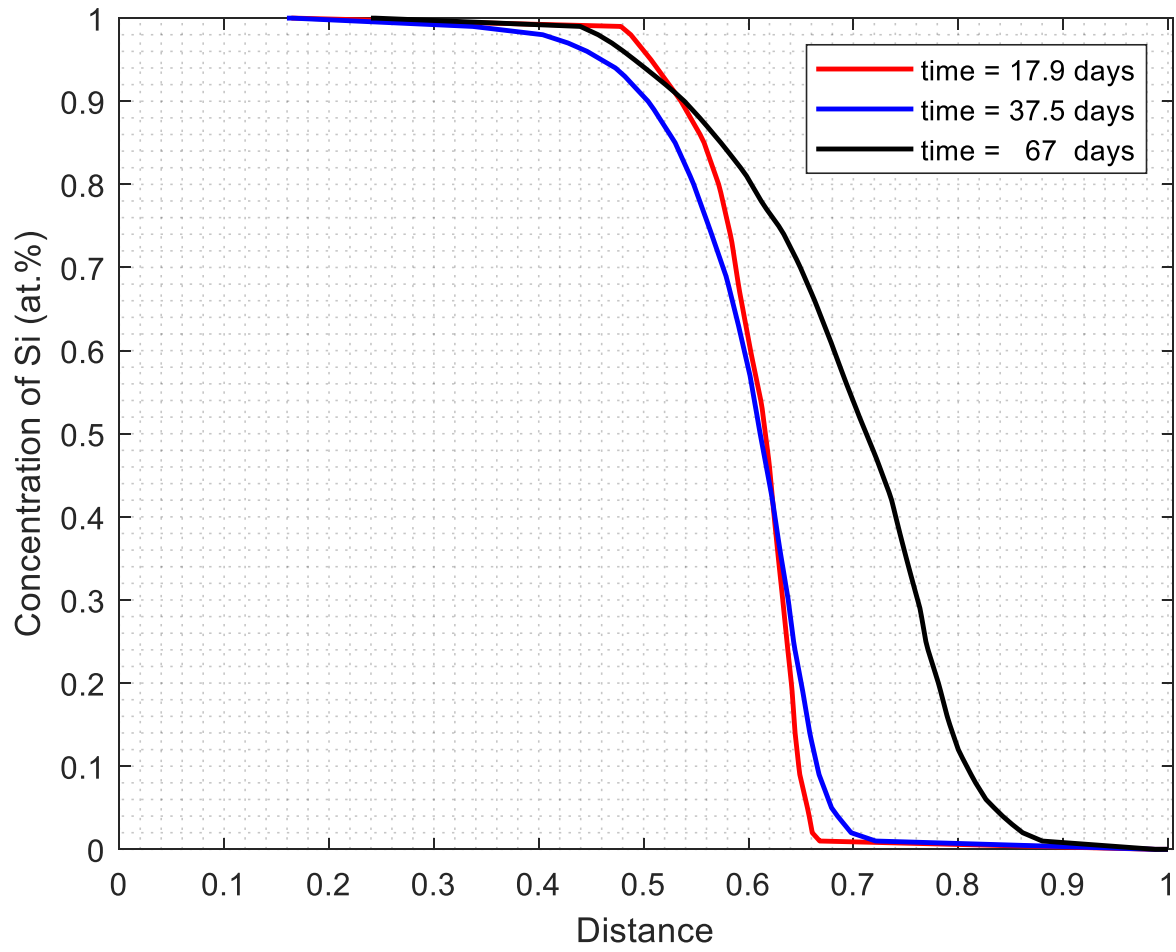


Figure 4.9: Extracted experimental concentration profiles [57] in Cu - Si binary alloy system at 700°C for 17.9, 37.5 and 67 days

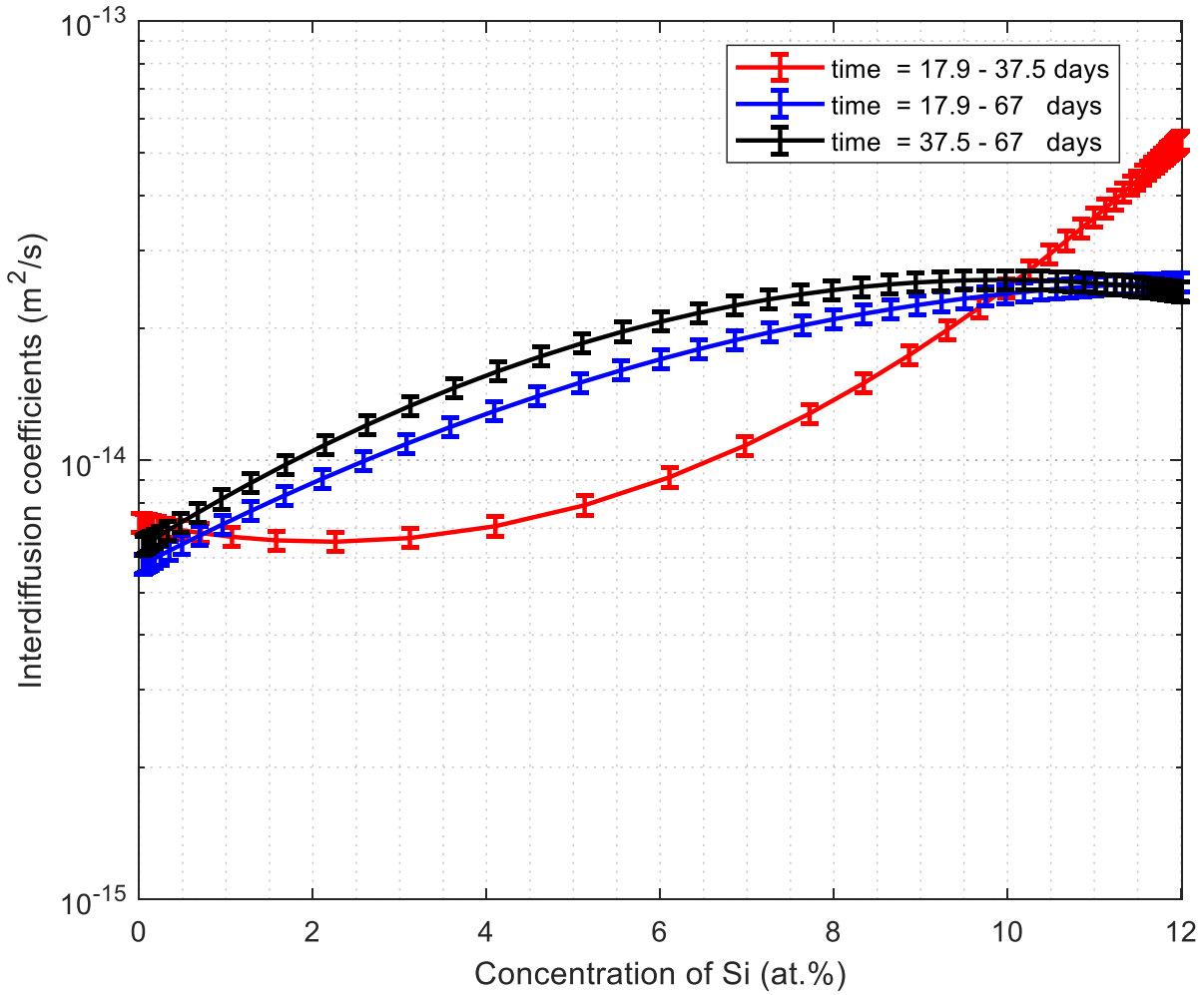


Figure 4.10: Time variation of $D(C)$ with concentration at different time intervals for Cu – Si diffusion couple system at 700°C

A detailed assessment of the method in [58] of the collected data used to prepare the diffusion couple showed that Cu is deposited through electrodeposition on an Si – Cu alloy. These experimental concentration profiles as shown in Figures 4.11, 4.12, and 4.13, are used in the new model developed to extract the $D(C)$. The $D(C)$ calculated by the new model as shown in Figure 4.10 accurately reproduces the extracted experimental concentration profiles. It is worth emphasizing that this is not the objective of [58].

In this study, subsequent to evidence of the successful extraction of $D(C)$ shown in Figure 4.5 and 4.10, mathematical polynomial functions that describe the behavioral trend of the extracted $D(C)$ are also obtained.

The general form of the interdiffusion coefficient (D) as a function of concentration (C) is described by using Equation 94. $F(C)$ illustrates the polynomial function which is:

$$F(C) = \beta_n C^n + \beta_{n-1} C^{n-1} + \beta_{n-2} C^{n-2} + \dots + \beta_2 C^2 + \beta_1 C + \beta_0 \quad \text{Equation 92}$$

The $F(C)$ of the three different time intervals investigated in the $Ni - Cu$ and $Cu - Si$ binary alloy systems are given in Tables 4.1 and 4.2, where β_i (i represents the degree term of the polynomial) are the coefficients of the polynomial that describe the concentration dependent interdiffusion behaviour as shown in Tables 4.1 and 4.2.

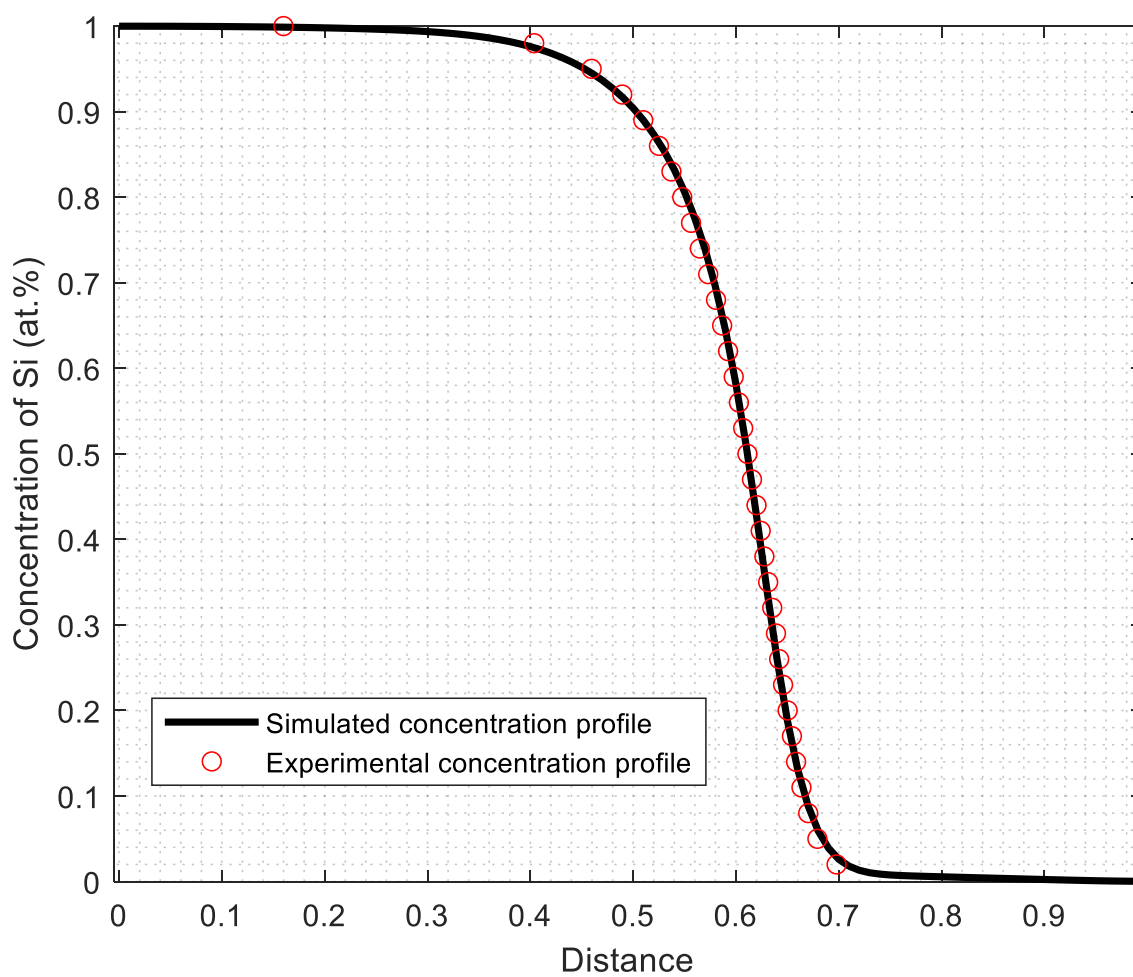


Figure 4.11: Comparison between extracted experimental [57] and simulated concentration profiles in Cu - Si binary alloy system at 700°C for 17.9 – 37.5 days

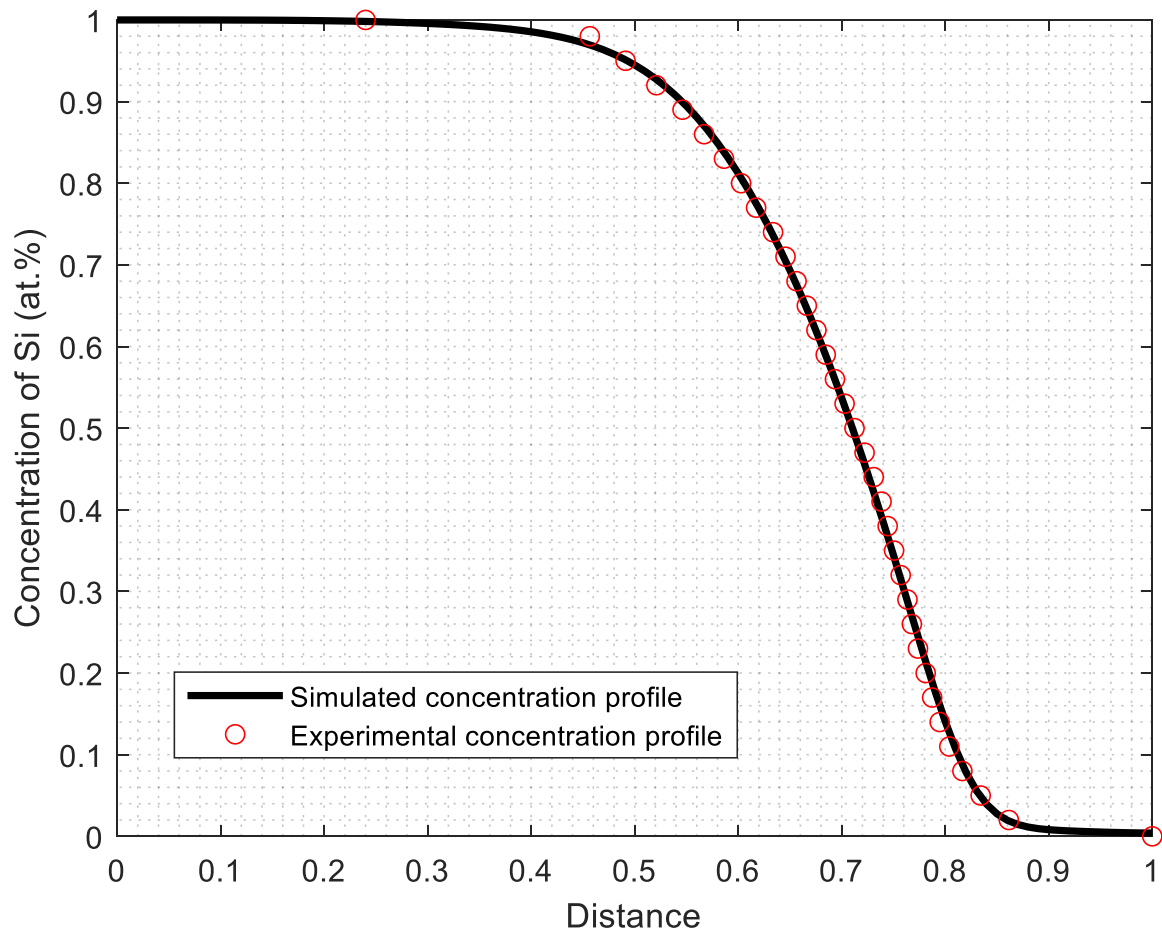


Figure 4.12: Comparison between extracted experimental [57] and simulated concentration profiles in Cu - Si binary alloy system at 700°C for 37.5 – 67 days

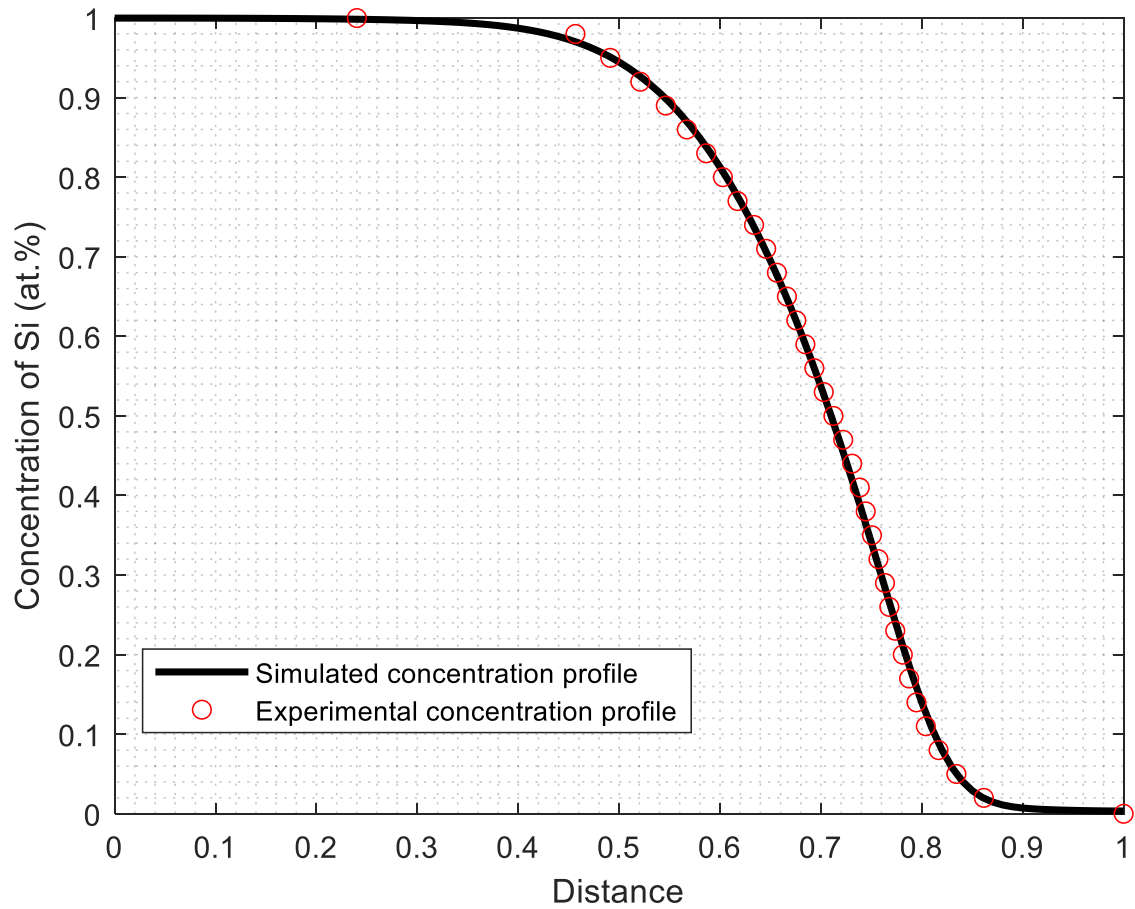


Figure 4.13: Comparison between extracted experimental [57] and simulated concentration profiles in Cu - Si binary alloy system at 700°C for 17.9 – 67 days

Table 4.1

Polynomial function $F(C)$ at different time intervals investigated for Ni - Cu binary system at 1025°C

Time Interval (hours)	Polynomial function $F(C, t)_{\text{Ni-Cu}}$
40 - 72	$1.4267C^2 - 2.8134C - 29.8604$
40 - 120	$2.7588C^2 - 4.1950C - 30.1513$
72 - 120	$2.7589C^2 - 4.198C - 29.6405$

Table 4.2

Polynomial function $F(C)$ at different time intervals investigated for Cu - Si binary system at 700°C

Time Interval (days)	Polynomial function $F(C, t)_{\text{Cu-Si}}$
17.9 - 37.5	$3.4125C^2 - 1.5638C - 31.7373$
17.9 - 67	$-0.4955C^2 - 1.8917C - 32.3349$
37.5 - 67	$-0.4955C^2 - 1.8918C - 32.6956$

The results obtained with the application of the newly developed model in this study are the outcome of a comprehensive review and analysis of two different binary alloy systems in the existing literature that involves three distinct experimental concentration profiles and a sustained diffusion heat treatment temperature.

Chapter 5

Summary and Conclusions

The key objective of this study is to develop and validate a new numerical diffusion model for the extraction of $D(C)$ in between two experimental concentration profiles obtained from diffusion couple plates. The new numerical model is developed for the planar geometric systems. The idea is to start first with a simple geometry and affirm the reliability of the model, which can later serve as the basis for studies in higher geometric dimensions. In this study, $D(C)$ s are extracted from Cu - Si and Ni - Cu binary alloys by using the new model in the FSM to address major flaws associated with traditional analytical methods. The key findings from this research are summarized as follows.

1. A new numerical diffusion model which is developed with the use of the Galerkin weighted residual FEM and Dufort-Frankel/Leap Frog explicit scheme has been successfully developed and applied. A weighted residual set up from the Landau transformed diffusion governing model is subjected to rigorous analytical integration over the functional domains of interest. The element equations obtained are assembled together. The model is then used to simulate interdiffusion behavior in binary alloy systems and applied with FSA in the successful extraction of interdiffusion coefficient under the influence of concentration dependency.
2. A consistency analysis of the truncation errors associated with the numerical scheme applied in the new model is carried out. The result of the analysis reveals the consistency criteria for the decay of the truncation errors which come from the governing diffusion model.
3. Also, a stability analysis that uses the von Neumann method is implemented to justify the application of the Dufort Frankel/Leap Frog explicit scheme for time discretization in the newly

developed model. The result of this analysis provides evidence for using the Dufort Frankel/Leap Frog explicit scheme over classical Euler schemes. Observations from comparisons of both schemes show that the Dufort Frankel/Leap Frog explicit scheme is more stable than the classical explicit scheme.

4. The new model which eliminates non-trivial assumptions associated with existing implicit finite difference models, has been successively validated with reliable experimental data in the literature. The final experimental concentration profiles predicted by the model using the $D(C)$ calculated by the model agree with the actual final experimental concentration profiles, thereby proving the accuracy and reliability of the newly developed model.
5. Therefore, the new model can be effectively used to extract the $D(C)$ operative between any two isothermal diffusion times, which is crucial for studying the effect of diffusion time on $D(C)$. This is an achievement that is not possible by conventional analytical methods such as the Boltzmann-Matano, Sauer-Freise, Wagner, and Hall methods.

Chapter 6

Recommendations for future work

The newly developed numerical diffusion model in combination with a FSM is used in the present work to extract the $D(C)$ s in binary alloy systems. However, as future work, the following points are recommended:

1. With the application of this newly developed finite element model, future work can be done on other factors such as the influence of pre-existing non-uniform solute distributions and boundary conditions in different binary alloy systems. A case study where the solute concentration at the surfaces of the material samples changes with time instead of remaining constant throughout the simulation can also be investigated with the new model.
2. The reliability, effectiveness, and accuracy of a numerical model play an important role in the simulation of diffusion processes and evaluation of $D(C)$. The type of shape function applied in the course of formulating the finite element model determines the overall accuracy of the numerical simulations. In place of commonly used linear shape functions, higher ordered shape functions can be used to improve the accuracy of the model.
3. Due to the numerous advantages associated with the FEM over the finite difference method, the method of Dufort Frankel/Leap Frog finite element numerical diffusion model can be used and extended to cases of higher geometric and non-planar systems such as cylindrical and spherical systems.

-
4. Research studies using finite element modelling, simulations, and experimental investigations study isothermal variation of $D(C)$ can also be done for ternary and other multi-component alloy systems.

Appendix: Mathematical Formulations and Algorithms of the Finite Element Models

Section A: 1-D Murray-Landau Coordinate Transformation

A description of the spatial parameters is given as follows:

r = spatial position in the natural coordinate system.

$s(t)$ = displacement

u = new position in a variable space grid system

R = length of the whole system.

$C(r, t)$ = concentration profile in a natural coordinate system.

$p(u, t)$ = concentration profile in a Landau transformed spatial coordinate system.

Proof

Given the interval, $0 < r < s(t) \leftrightarrow 0 < u < 1$ Equation A.1

Divide through by $s(t)$,

we have: $0 < \frac{r}{s(t)} < 1$, we say $u = \frac{r}{s(t)}$ in the spatial coordinate transformation.

$$\begin{array}{ccc} & \text{fixed boundary transformation} & \\ \mathbf{0} < \mathbf{r} < \mathbf{s(t)} & \Leftrightarrow & \mathbf{0} < \mathbf{u} < \mathbf{1} & \text{diffusion model} \end{array}$$

The governing equation of the diffusion model that describes the concentration profile of the system is:

$$\frac{\partial C(r, t)}{\partial t} = \frac{\partial}{\partial r} \left(D_A [C(r, t)] \frac{\partial C(r, t)}{\partial r} \right) \quad 0 < r < s(t) \quad \text{Equation A.2}$$

Equation A.2 describes the diffusion in the binary alloy system. D_A is the diffusion coefficient. $s(t)$ describes the position. R is the length of the entire system.

Targeted transformation: $(r, t) \leftrightarrow (u, t)$

C is a function of (r, t) in the natural coordinate system and p is a function of (u, t) in a Landau transformed spatial coordinate system.

$$\frac{dC(r,t)}{dt} = \frac{dr}{dt} \frac{dC(r,t)}{dr} + \frac{\partial C(r,t)}{\partial t} \quad \text{Equation A.3}$$

Using the chain rule on the differential of spatial coordinates with respect to time in terms of the displacement parameter gives:

$$\frac{dr}{dt} = \frac{r}{s(t)} \frac{ds(t)}{dt} \quad \text{Equation A.4}$$

The expression that describes the relationship between $C(r, t)$ and the new coordinate concentration profile $p(u, t)$ for the system is given by:

$$\frac{\partial C(r,t)}{\partial r} = \frac{1}{s(t)} \frac{\partial p(u,t)}{\partial u} \quad \text{Equation A.5}$$

Substituting Equations A.4 and A.5 into A.2 results in:

$$s(t) \frac{\partial p(u,t)}{\partial t} = \frac{r}{s(t)} \frac{ds(t)}{dt} \frac{\partial p(u,t)}{\partial u} + s(t) \frac{\partial C(r,t)}{\partial t} \quad \text{Equation A.6}$$

The Landau coordinate transformation of the left side of Equation A.2 is:

$$\frac{dC(r,t)}{dt} = \frac{\partial p(u,t)}{\partial t} + \frac{u}{s(t)} \frac{ds(t)}{dt} \frac{\partial p(u,t)}{\partial u} \quad \text{Equation A.7}$$

The Landau transformed expression for the governing diffusion model as expressed in Equation A.2 is stated in Equation A.8. Further simplifications required in the derivation of Equation A.11 are expressed in Equations A.9 to A.11.

$$\frac{\partial p(u,t)}{\partial t} = \frac{1}{[s(t)]^2} \frac{\partial}{\partial u} \left[D_A(p(u,t)) \frac{\partial p(u,t)}{\partial u} \right] \quad \text{Equation A.8}$$

$$s(t) \frac{\partial p(u,t)}{\partial t} = \frac{\partial (s(t)p(u,t))}{\partial t} - p(u,t) \frac{ds(t)}{dt} \quad \text{Equation A.9}$$

$$\frac{\partial (sp(u,t))}{\partial t} = \frac{ds(t)}{dt} \frac{\partial (up(u,t))}{\partial u} + [s(t)]^2 \frac{\partial p(u,t)}{\partial t} \quad \text{Equation A.10}$$

$$\frac{\partial (sp(u,t))}{\partial t} = \frac{ds(t)}{dt} \frac{\partial (up(u,t))}{\partial u} + \frac{1}{s(t)} \frac{\partial}{\partial u} \left[D_A(p(u,t)) \frac{\partial p(u,t)}{\partial u} \right] \quad \text{Equation A.11}$$

Finite Element Analysis

The main idea behind the FEM is changing the partial differential equation (strong form) to a weak form. The solution of the weak formulation of the equation involved approximates the exact or analytical solution of the partial differential equation.

The resulting weighted residual,

$$R_{res}(u,t) = s(t) \frac{\partial p(u,t)}{\partial t} - u \frac{ds(t)}{dt} \frac{\partial p(u,t)}{\partial u} - \frac{D_A(p(u,t))}{s(t)} \frac{\partial^2 p(u,t)}{\partial u^2} \quad \text{Equation A.12}$$

To obtain the weighted residual integral $I(p(u,t))$, we integrate $R_{res}(u,t)W_j(u,t)$ into the global solution domain $D(u,t)$. $W_j(u)$ represents a set of weighting factors ($j = 1, 2, 3, \dots$).

$$I(p(u,t)) = \int_a^b W_j(u,t) R_{res}(u,t) du = 0 \quad \text{Equation A.13}$$

$$I(p(u, t)) = \int_a^b W_j(u, t) \left(s(t) \frac{\partial p(u, t)}{\partial t} - u \frac{ds(t)}{dt} \frac{\partial p(u, t)}{\partial u} - \frac{D_A(p(u, t))}{s(t)} \frac{\partial^2 p(u, t)}{\partial u^2} \right) du = 0$$

Equation A.14

The function to calculate values of the concentrations at locations between the nodes is derived. This interpolation function is termed as the shape function. It is noted that, for linear elements, the polynomial interpolation function is first order.

The concentration varies linearly between the nodal points. The equation is given below:

$$p(u) = A + Bu \quad \text{Equation A.15}$$

The coefficients A and B can be determined by using the nodal conditions stated below

$$p = p_i \text{ at } u = u_i \quad \text{Equation A.16}$$

$$p = p_{i+1} \text{ at } u = u_{i+1} \quad \text{Equation A.17}$$

Solving simultaneously, the expression for A and B are obtained.

$$A = \frac{p_i u_{i+1} - p_{i+1} u_i}{u_{i+1} - u_i} \quad \text{Equation A.18}$$

$$B = \frac{p_{i+1} - p_i}{u_{i+1} - u_i} \quad \text{Equation A.19}$$

Substituting Equation A.18 and Equation A.19 into Equation A.15 yields:

$$p(u) = \left(\frac{p_i u_{i+1} - p_{i+1} u_i}{u_{i+1} - u_i} \right) + \left(\frac{p_{i+1} - p_i}{u_{i+1} - u_i} \right) u \quad \text{Equation A.20}$$

Further simplification of Equation A.20 leads to Equation A.21 expressed below.

$$p(u) = p_i \left(\frac{u_{i+1}-u}{u_{i+1}-u_i} \right) + p_{i+1} \left(\frac{u-u_i}{u_{i+1}-u_i} \right) \quad \text{Equation A.21}$$

The local interpolating polynomials, $p^i(u, t)$ are defined by:

$$p^i(u, t) = p_i(u, t)N_i^{(i)}(u) + p_{i+1}(u, t)N_{i+1}^{(i)}(u) \quad \text{Equation A.22}$$

Let the global exact solution $\bar{p}(u, p)$ be approximated by the global approximate solution $p(u, t)$, which is the sum of a series of local interpolating polynomials, $p^i(u, t)[i = 1, 2, 3, \dots, I - 1]$ that are valid within each element.

$$N_i^{(i)}(u) = -\frac{u-u_{i+1}}{u_{i+1}-u_i} \quad \text{Equation A.23}$$

$$N_{i+1}^{(i)}(u) = \frac{u-u_i}{u_{i+1}-u_i} \quad \text{Equation A.24}$$

$$\text{where } N_i^{(i)}(u) + N_{i+1}^{(i)}(u) = 1 \quad \text{Equation A.25}$$

Equation A.22 leads to

$$p^i(u, t) = p_i(u, t) \left(-\frac{u-u_{i+1}}{u_{i+1}-u_i} \right) + p_{i+1}(u, t) \left(\frac{u-u_i}{u_{i+1}-u_i} \right) \quad \text{Equation A.26}$$

This is a linear Lagrange polynomial applied to the element (i)

Further simplification of Equation A.14 yields

$$\begin{aligned} I(p(u, t)) &= s(t) \int_a^b W_j(u, t) \left(\frac{\partial p(u, t)}{\partial t} \right) du \\ &\quad - \frac{ds(t)}{dt} \int_a^b W_j(u, t) \left(u \frac{\partial p(u, t)}{\partial u} \right) du - \int_a^b W_j(u, t) \left(\frac{D_A(p(u, t))}{s(t)} \frac{\partial^2 p(u, t)}{\partial u^2} \right) du = 0 \end{aligned}$$

Equation A.27

The above equation comprises terms that include the time derivative of the concentration profile residual term which is the first term. The second term is the convective residual term, and the third term is the diffusive residual term as described in equation A.28 below.

$$\begin{aligned} I(p(u, t)) = & \underbrace{s(t) \int_a^b W_j(u, t) \left(\frac{\partial p(u, t)}{\partial t} \right) du}_{1st \text{ term}} - \underbrace{\frac{ds(t)}{dt} \int_a^b W_j(u, t) \left(u \frac{\partial p(u, t)}{\partial u} \right) du}_{2nd \text{ term}} \\ & - \underbrace{\int_a^b W_j(u, t) \left(\frac{D_A(p(u, t))}{s(t)} \frac{\partial^2 p(u, t)}{\partial u^2} \right) du}_{3rd \text{ term}} = 0 \end{aligned}$$

Equation A.28

Section B: Dufort Frankel/Leap Frog Explicit schemes for model with zero flux conditions imposed at the extreme ends of single-phase systems

The averaging for the concentration parameter is:

$$p_{i-1}^{j+1} + p_{i+1}^{j+1} = 2p_i^{j+1} \quad \text{Equation B.1}$$

$$p_{i-1}^{j-1} + p_{i+1}^{j-1} = 2p_i^{j-1} \quad \text{Equation B.2}$$

For simplification of the model, a uniform space grid is considered in the nodal FEM equation throughout the computation of the model as:

$$\Delta u_i = u_{i+1} - u_i = \Delta u_{i-1} = u_i - u_{i-1} \quad \text{Equation B.3}$$

For enhanced stability, the Dufort Frankel approximations applied for the time step in the model is:

$$p_i^j = \frac{1}{2}(p_i^{j-1} + p_i^{j+1}) \quad \text{Equation B.4}$$

The Murray-Landau transformed FEM governing equation as expressed in Equation B.3, is solved by applying the Dufort Frankel/Leap Frog explicit time discretization to obtain the discretized governing numerical models for a single-phase binary alloy system. They are:

For the model, we have:

$$\begin{aligned} & s^{j+1}p_i^{j+1} - s^{j-1}p_i^{j-1} \\ &= \left(\frac{t^{j+1} - t^{j-1}}{s^j} \right) \left((D_A)_{i,i+1}^{j+1} \frac{p_{i+1}^j - p_i^j}{(u_{i+1} - u_i)^2} - (D_A)_{i-1,i}^{j+1} \frac{p_i^j - p_{i-1}^j}{(u_i - u_{i-1})^2} \right) \\ &+ (s^{j+1} - s^{j-1}) \left(\frac{(p_{i+1}^j - p_i^j)(u_{i+1} + 2u_i)}{u_{i+1} - u_i} + \frac{(p_i^j - p_{i-1}^j)(u_{i-1} + 2u_i)}{u_i - u_{i-1}} \right) \end{aligned}$$

Equation B.5

After implementing the Dufort Frankel approximation, the coefficients terms are carefully sorted, rearranged, and expressed as follows:

$$\delta P_A * p_i^{j+1} = \delta P_B * p_i^{j-1} + \delta P_C * p_{i+1}^j + \delta P_D * p_{i-1}^j \quad \text{Equation B.6}$$

where

$$\begin{aligned} \delta P_A = & s^{j+1} + \left(\frac{t^{j+1} - t^{j-1}}{2s^j} \right) \left(\frac{(D_A)_{i,i+1}^j}{(u_{i+1} - u_i)^2} + \frac{(D_A)_{i-1,i}^j}{(u_i - u_{i-1})^2} \right) \\ & + \left(\frac{s^{j+1} - s^{j-1}}{12} \right) \left(\frac{(u_{i+1} + 2u_i)}{(u_{i+1} - u_i)} - \frac{(u_{i-1} + 2u_i)}{(u_i - u_{i-1})} \right) \end{aligned}$$

Equation B.7

$$\begin{aligned} \delta P_B = & s^{j-1} - \left(\frac{t^{j+1} - t^{j-1}}{2s^j} \right) \left(\frac{(D_A)_{i,i+1}^j}{(u_{i+1} - u_i)^2} + \frac{(D_A)_{i-1,i}^j}{(u_i - u_{i-1})^2} \right) \\ & - \left(\frac{s^{j+1} - s^{j-1}}{12} \right) \left(\frac{(u_{i+1} + 2u_i)}{(u_{i+1} - u_i)} - \frac{(u_{i-1} + 2u_i)}{(u_i - u_{i-1})} \right) \end{aligned}$$

Equation B.8

$$\delta P_C = \left(\frac{t^{j+1} - t^{j-1}}{s^j} \right) \left(\frac{(D_A)_{i,i+1}^j}{(u_{i+1} - u_i)^2} \right) + \left(\frac{s^{j+1} - s^{j-1}}{6} \right) \left(\frac{u_{i+1} + 2u_i}{u_{i+1} - u_i} \right)$$

Equation B.9

$$\delta P_D = \left(\frac{t^{j+1} - t^{j-1}}{s^j} \right) \left(\frac{(D_A)_{i-1,i}^j}{(u_i - u_{i-1})^2} \right) + \left(\frac{s^{j+1} - s^{j-1}}{6} \right) \left(\frac{u_{i-1} + 2u_i}{u_i - u_{i-1}} \right)$$

Equation B.10

In a single-phase diffusion system of binary alloys, a fixed concentration condition imposed at the boundaries implies that there is no possibility of build-up of solute at the extreme boundaries of the

host material, but this cannot be ascertained. A zero-flux boundary condition is a confirmed boundary condition that can be applied to the ends of the host material to ensure that the total amount of diffusing solute in the sample is being conserved during the simulation of a single-phase diffusion system of binary alloys. By this reasoning, it is very certain that the extreme boundaries of the material functions as a no solute flux boundary. The most accurate and reliable imposed zero flux conditions at both extreme ends of the single-phase diffusion system are expressed as:

$$\left. \frac{\partial p}{\partial u} \right|_1^{k-1} = \left. \frac{\partial p}{\partial u} \right|_1^k = \left. \frac{\partial p}{\partial u} \right|_1^{k+1} = 0 \quad \text{Equation B.11}$$

$$\left. \frac{\partial p}{\partial u} \right|_{M+1}^{k-1} = \left. \frac{\partial p}{\partial u} \right|_{M+1}^k = \left. \frac{\partial p}{\partial u} \right|_{M+1}^{k+1} = 0 \quad \text{Equation B.12}$$

By implementing zero flux conditions at the first node ($i = 1$) stated in Equation B.11 and simplifying the Dufort Frankel/Leap Frog discretization expressed from Equations B.10 to B.15, the actual equation that shows no solute migration at the left boundary for a single-phase diffusion system of binary alloys is:

$$\delta P_{AA} * p_1^{j+1} = \delta P_{BB} * p_1^{j-1} + \delta P_{CC} * p_2^j \quad \text{Equation B.13}$$

where,

$$\delta P_{AA} = s^{j+1} + \left(\frac{t^{j+1}-t^{j-1}}{2s^j} \right) \left(\frac{(D_A)_{1,2}^j}{(u_2-u_1)^2} \right) + \left(\frac{s^{j+1}-s^{j-1}}{12} \right) \left(\frac{u_2+2u_1}{u_2-u_1} \right) \quad \text{Equation B.14}$$

$$\delta P_{BB} = s^{j-1} - \left(\frac{t^{j+1}-t^{j-1}}{2s^j} \right) \left(\frac{(D_A)_{1,2}^j}{(u_2-u_1)^2} \right) - \left(\frac{s^{j+1}-s^{j-1}}{12} \right) \left(\frac{u_2+2u_1}{u_2-u_1} \right) \quad \text{Equation B.15}$$

$$\delta P_{CC} = \left(\frac{t^{j+1}-t^{j-1}}{s^j} \right) \left(\frac{(D_A)_{1,2}^j}{(u_2-u_1)^2} \right) + \left(\frac{s^{j+1}-s^{j-1}}{6} \right) \left(\frac{u_2+2u_1}{u_2-u_1} \right) \quad \text{Equation B.16}$$

Zero flux conditions are implemented at the last node, $i = M + 1$ by using the equation below:

$$\delta P_A * p_{M+1}^{j+1} = \delta P_B * p_{M+1}^{j-1} + \delta P_D * p_M^j \quad \text{Equation B.17}$$

where

$$\delta P_A = s^{j+1} + \left(\frac{t^{j+1} - t^{j-1}}{2s^j} \right) \left(\frac{(D_A)_{M,M+1}^j}{(u_{M+1} - u_M)^2} \right) - \left(\frac{s^{j+1} - s^{j-1}}{12} \right) \left(\frac{4u_{M+1} - u_M}{(u_{M+1} - u_M)} \right) \quad \text{Equation B.18}$$

$$\delta P_B = s^{j-1} - \left(\frac{t^{j+1} - t^{j-1}}{2s^j} \right) \left(\frac{(D_A)_{M,M+1}^j}{(u_{M+1} - u_M)^2} \right) + \left(\frac{s^{j+1} - s^{j-1}}{12} \right) \left(\frac{4u_{M+1} - u_M}{(u_{M+1} - u_M)} \right) \quad \text{Equation B.19}$$

$$\delta P_D = \left(\frac{t^{j+1} - t^{j-1}}{s^j} \right) \left(\frac{(D_A)_{M,M+1}^j}{(u_{M+1} - u_M)^2} \right) + \left(\frac{s^{j+1} - s^{j-1}}{6} \right) \left(\frac{u_M + 2u_{M+1}}{u_{M+1} - u_M} \right) \quad \text{Equation B.20}$$

For a single-phase diffusion system, it is very clear that there is no moving interface. By using the governing numerical diffusion models, the implication is:

$$s^{j-1} = s^j = s^{j+1} \quad \text{Equation B.21}$$

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