Phase Field Modeling Of Thermotransport In Multicomponent Systems

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PHASE-FIELD MODELING OF THERMOTRANSFER IN MULTICOMPONENT SYSTEMS

by

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B.S. University of Central Florida, 2009

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ABSTRACT

Nuclear and gas turbine power plants, computer chips, and other devices and industries are running hotter than ever for longer than ever. With no apparent end to the trend, the potential arises for a phenomenon known as thermotransport to cause undesirable changes in these high temperature materials. The diffuse-interface method known as the phase-field model is a useful tool in the simulation and prediction of thermotransport driven microstructure evolution in materials. The objective of this work is to develop a phase-field model using practical and empirical properties of thermodynamics and kinetics for simulating the interdiffusion behavior and microstructural evolution of single and multiphase binary alloy system under composition and/or temperature gradients. Simulations are carried out using thermodynamics and kinetics of real systems, such as the U-Zr solid metallic fuel, with emphasis on the temperature dependencies of the kinetics governing diffusional interactions in single-phase systems and microstructural evolution in the presence of multiple driving forces in multi-phase systems.

A phase field model is developed describing thermotransport in the γ phase of the U-Zr alloy, a candidate for advanced metallic nuclear fuels. The model is derived using thermodynamics extracted from the CALPHAD database and temperature dependent kinetic parameters associated with thermotransport from the literature. Emphasis is placed upon the importance of the heat of transport, \( Q^* \), and atomic mobility, \( \beta \). Temperature dependencies of each term are estimated from empirical data obtained directly from the literature, coupled with the textbook phenomenological formulae of each parameter. A solution is obtained via a finite volume approach with the aid of the FiPy® partial differential equation solver. Results of the simulations are described based on individual flux contributions from the gradients of both composition and temperature, and are found to be remarkably similar to experimental results from the literature.
In an additional effort the thermotransport behavior of a binary two-phase alloy is modeled, for
the first time, via the phase-field method for a two-phase (γ + β) U-Zr system. The model is similarly built
upon CALPHAD thermodynamics describing the γ and β phases of the U-Zr system and thermotransport
parameters for the γ phase from literature. A parametric investigation of how the heats of transport for
U and Zr in the β phase affect the redistribution is performed, and the interplay between system kinetics
and thermodynamics are examined. Importantly, a strict control over the microstructure that is placed
into the temperature gradient (at t = 0) is used to eliminate the randomness associated with
microstructural evolution from an initially unstable state, allowing an examination of exactly how the β
phase thermotransport parameters affect the redistribution behavior of the system. Results are
compared to a control scenario in which the system evolves only in the presence of thermodynamic
driving forces, and the kinetic parameters that are associated with thermotransport are negligible. In
contrast to the single-phase simulations, in the presence of a large thermodynamic drive for phase
transformation and stability, the constituent redistribution caused by the thermotransport effect is
comparatively smaller.
ACKNOWLEDGMENTS

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CHAPTER ONE: INTRODUCTION

The advances in consumer and industrial technologies seen over the last several decades have been accompanied by an industry-wide demand to minimize the volume of materials used while still improving efficiencies. This trend has inevitably resulted in a continuous decrease in the scale of materials used, with an increase in operating temperatures and durations. Nuclear and gas turbine power plants, computer chips, and other devices and industries are running hotter than ever for longer than ever. With no apparent end to the trend, the potential arises for an increase in the temperature gradient materials used in such applications must endure. As such, a phenomenon known as thermotransport, which can cause undesirable changes in high temperature materials, has gathered interest within the materials science community.

When a homogeneous multicomponent system is subjected to a temperature gradient, a concentration gradient that is characteristic of the system can develop and build in magnitude until it eventually reaches a steady state. Such a redistribution of an alloy’s constituents may cause undesirable effects on the material properties of the system. As modern industry continually increases the demand for materials that operate at higher temperatures for longer durations, thermotransport becomes of increasing interest. Additionally, from the viewpoint of pure materials science, thermotransport is a quantifiable indication of certain details of the diffusion process that are otherwise ambiguous, making it of particular importance in theoretical pursuits.

Traditionally, phase field studies found in the literature are primarily concerned with the microstructural evolution of materials in the presence of a chemical potential gradient under isothermal conditions. However, there are few publications utilizing the phase field model to describe materials subjected to less common driving forces, such as thermotransport [1, 2]. The primary objective of this
research is to utilize phase field modeling to simulate and predict the interdiffusion behavior and microstructural evolution of real materials, primarily U-Zr nuclear fuels, in the presence of driving forces caused by gradients in chemical potential and temperature.
CHAPTER TWO: LITERATURE REVIEW

Thermotransport has been known to the scientific community for more than a century. The first documented observations were made in 1856 by Ludwig [3], while studying aqueous sodium sulfate solutions. Soon after, Soret began to extensively examine the phenomenon in other electrolyte liquid solutions [4, 5, 6]. On account of their exhaustive research, thermotransport in liquids is primarily called the Ludwig-Soret effect today. The first observation of the phenomenon in a solid metallic alloy was made by Ballay [7], who noticed a 0.06 mole fraction difference in Pb content between the 200°C and 300°C zones of a bar of Pb-51.2Tl alloy maintained at 360°C at one end and in open air at the other. This observation led Ballay to expand the field through experiments on Pt-Rb and Pb-Th [8].

The next significant mention of thermotransport was made by Darken and Oriani [9], who published measurements of the effects in binary alloys. However, in the same year, Shockley [10, 11] called into question the true importance of thermotransport in determining atomistic mechanisms of diffusion, suggesting instead that at least part, if not all, of the driving force for diffusion arises directly from the vacancy concentration gradient that develops due to the temperature gradient.

The debate following Shockley’s claims demonstrated a need for a better phenomenological understanding of thermotransport. Several studies ensued to accurately quantify a parameter Shockley did not account for, the heat of transport, $Q^*$, which is associated with the amount of heat carried per atom and is thought to be the factor that dictates the magnitude and direction of a constituent’s migration [12, 13, 14, 15, 16]. In an experiment observing the thermal diffusion of vacancies in pure Zinc [14], Shewmon devised a method to predict the heat of transport term. In a subsequent study [15], Shewmon successfully measured the heat of transport of carbon in two-phase interstitial Fe-C alloys. From his findings, Shewmon developed a model using the heat of transport of the solute that
successfully described the observed migration direction of the interstitial solute atoms in two-phase alloys [16]. Jaffe and Shewmon made further progress while examining thermal diffusion of substitutional impurities in copper, gold, and silver [17]. They demonstrated that, in contrast to thermal diffusion in interstitial alloys, both the atomic mobility and the heat of transport associated with each constituent element were necessary to accurately describe the phenomenon in substitutional alloys. This conclusion was ascribed to the relative rates of motion of the solute and solvent atoms in each alloy system. In an interstitial alloy, the solute atoms move very quickly in comparison to the solvent, therefore, it is easy to see whether the solute approaches hot or cold temperatures in the specimen. However, when a solute and solvent move at roughly the same speed, there is a potential for both of the constituents to move toward the hot end of the system, yet appear to be moving in different directions. For example, if the movement of solvent atoms is faster than that of solute atoms, even if both the solute and solvent are moving toward the hot side relative to the lattice, the solute will tend to fall behind and accumulate in the cooler region of the sample. Thus, it appears to be migrating toward the cold end, even though it moves toward the hotter part of the lattice. Through Shewmon’s discovery, scientific efforts to form a fundamental understanding of the mechanisms behind thermotransport have become more accurate and practical.

The advent of nuclear reactor technologies in the 1960s garnered industrial-sector interest in thermotransport, as understanding the phenomenon had become of paramount importance in reactors using solid metallic fuels. The solid metallic fuel rods used in some nuclear reactors can be subjected to large temperature gradients for potentially months at a time, and any unwarranted effects on the material properties of the fuel could result in catastrophe.
During nuclear reactor operations, there is typically a radial temperature gradient that exists between the core and the surface of the nuclear fuel. The temperature gradient, coupled with the long period of time a fuel rod spends inside a reactor produces favorable conditions for significant redistribution of constituents and fission products in the fuel pin. Evidence of such redistribution has been observed in post-irradiated fuel pins and in controlled experiments [18, 19, 20, 21, 22] undertaken to determine the thermotransport behavior and parameters of nuclear fuel systems.

Notable advancement in understanding the U-based nuclear fuels under a temperature gradient was made by Kim et al. [22], who, in a series of studies examining the migration flux of a U-Pu-Zr fuel after irradiation in the Experimental Breeder Reactor II (EBR-II), calculated flux values that were then used to determine diffusion coefficients and heats of transport for the γ, γ+ζ, and δ+ζ phases of an irradiated U-Pu-Zr pin. In a laboratory controlled experiment, Sohn annealed U-Pu-Zr homogeneous fuel rods under a 220°C/cm axial temperature gradient for a period of 41 days [21]. Subsequent analysis of the interdiffusion fluxes in the diffusion zone yielded kinetic parameters related to thermotransport and the interdiffusion flux contributions attributed to gradients of temperature and concentration.

A proper description of the thermotransport effect is associated with the complex interplay between the thermodynamic and kinetic factors such as diffusivity and/or atomic mobility and the heat of transport terms [23]. The fact that the same constituent can move either up or down the temperature gradient in different systems, as empirical data reports, demonstrates the complexities involved in defining the mechanisms behind the thermotransport phenomenon. These factors often make quantitative experimental studies of thermotransport challenging, and can account for the uncertainties in available data for key parameters. Therefore, in recent years, computational modeling of this complex phenomenon has become the most promising avenue toward examining its effects on materials.
There are many works that serve as a theoretical basis for modeling atomic transport under a temperature gradient [24, 25, 26, 27, 28, 29]. Scientists have also endeavored to develop numerical models for thermotransport with varying degrees of success [18-29]. Ogawa and Iwai first modeled thermotransport in a U-Zr alloy [20], treating the redistribution as a thermal diffusion process utilizing carefully selected combinations of thermodynamic and kinetic parameters. Concentration profiles were compared for different heats of transport and temperature ranges, with a conclusion that the migration was due to thermodynamic properties of the alloy. In another early study [18], Hofman utilized a model based upon interdiffusion flux and partial molar enthalpy of constituents, noting the importance of the magnitude and sign of the heat of transport values upon migration direction of constituents. An effective heat of transport for each phase was first estimated from microprobe data taken from a fuel irradiated to 10% peak burn up. These estimates were fit into the model, and through a parametric study, results comparable to the microprobe data from fuels irradiated to different levels of burn-up were obtained.

While each of these proposed models advanced the understanding of U-based fuel behavior under thermotransport significantly, some of the critical assumptions inherent to each model can result in impractical computational complexities, such as a continuous tracking of moving boundaries in the system, making it difficult to obtain numerical solutions, especially in two and three dimensions. It is well known that the phase-field model, which is based on a diffuse interface description [30], provides a very efficient technique to avoid explicit boundary-tracking and inherently accommodates for Gibbs-Thompson effects [30]. Unlike other numerical models, the phase-field model describes the microstructure with a set of continuous field variables, treating interfaces as being diffused over a finite width, thus eliminating numerical difficulties caused by sharp-interface singularities. In addition, the phase field model provides the framework to use material specific parameters linked to interface
properties such as the interface width and the interface mobility, allowing the model to be derived on a more fundamental basis. Moreover, the unique ability to incorporate thermodynamic and kinetic information directly from existing databases yields flexibility and versatility when modeling the complex material behaviors of real alloy systems. Originally, the phase field model was developed for solidification modeling [31, 32, 33, 34, 35, 36]. However, over the last few decades, the versatility of the phase field model in describing meso-scale materials processes has been demonstrated in various studies modeling order-disorder transformations [37, 38, 39, 40], spinodal decomposition [41, 42, 43, 44, 45, 46, 47, 48], grain growth [49, 50, 51, 52, 53, 54, 55, 56], and allotropic transformations [57, 58, 59, 60, 61, 62].
CHAPTER THREE: THE PHASE FIELD METHOD

Computational methods in materials science and engineering have seen an incredible rate of improvement and growth, due in part to advancements in computational methods and computer processing power over the past few decades. At the meso-scale, the phase field model stands out as a powerful computational tool to simulate and predict the morphological and microstructural evolution of materials. The term phase-field is indicative of the model’s approach to describe the dependent variables of the system; the phase field model uses a set of conserved and non-conserved field variables, or order parameter fields, that are continuous throughout the system, and whose spatial distribution describes the microstructure of the material. One key characteristic that makes the phase field model versatile is its ability to directly implement real material parameters from existing databases, making it possible to predict the evolution of the complex microstructures and morphologies of real material systems and processes. A material’s microstructure plays a critical role in determining the physical and mechanical properties of the material. A microstructure may change or evolve to reduce the total free energy of a system. Similarly, the foundation of the phase-field model description is the minimization of free energy.

Conventional approaches, known as sharp interface models, attempt to capture the nonlinear nature of microstructural evolution by treating the boundary between two compositional or structural domains as a discontinuity of the field variable. This treatment requires explicit tracking of the interface position in time, which is practical only in 1-D systems. In contrast, the phase field model is based upon a diffuse-interface approach developed by Cahn and Hilliard [30, 63] five decades ago, and does not require the explicit tracking of the positions of a moving interface. The corresponding sharp interface descriptions are treated, instead, as a particular limit. The evolution of the field variables is governed by
a Cahn-Hilliard type nonlinear diffusion equation [30], and/or a time-dependent Ginzburg-Landau (Allen-Cahn) equation [64]. Typically, phase-field models are used for isothermal processes driven by a gradient in chemical potential, such as solidification modeling, in which the phase-field method is used simply to avoid interface tracking, and phase separation or order-disorder transformation modeling, in which the field variables correspond to well-defined physical order parameters, such as concentration or crystal structure. In this chapter, a brief overview of the phase-field method is provided, and a model is derived from irreversible thermodynamics describing therмотransport in binary substitutional alloys. The model produced herein is used as the foundation for the phase-field models seen in future chapters.

3.1 Overview of Phase Field Modeling

A general procedure for phase-field modeling first involves a determination of the number and type of field variables that are necessary to fully characterize the material or process. Next, a description of the system free energy is necessary, because, as stated before, the phase-field model is based upon the minimization of system free energy. For any combination of non-conserved and conserved field variables, the total free energy can be defined as the sum of the chemical free energy density, the gradient energy, the elastic strain energy, and any contributions to the free energy from external factors. This total free energy equation can be written as a function of conserved field variables, $c_i$, and non-conserved field variables, $\eta_i$:

$$G[c_i(r,t),\eta(r,t)] = \int [f_c(c_i,\eta_i) + f_{\text{grad}}(c_i,\eta_i) + f_{\text{el}}(c_i,\eta_i) + f_{\text{ex}}(c_i,\eta_i)] \, dr^3$$  \hspace{1cm} (1)

The order parameters of the conserved and non-conserved fields are functions of position, $r$, and time, $t$, and the subscripts $i$, and $j$, are used to distinguish between species, phases, or domains. The chemical and gradient energy terms are the contributions to the system energy from short-range
chemical interactions. The gradient energy term defines the interfacial free energy contribution which, by nature, is zero in bulk regions, and nonzero at and around interfaces. The elastic strain energy and external energy terms stem from long range interactions such as elastic interactions, dipole-dipole interactions, electrostatic interactions, etc. The characteristic that distinguishes one phase-field model from the next is exactly how each of these free energy parameters is treated in the description. The final step in the phase-field procedure generally involves the application of a modified Cahn-Hilliard diffusion equation and a time dependent Allen-Cahn or Ginzburg-Landau equation to describe the temporal evolution of the field variables, then, using the available material parameters as input, solutions to the governing equations are obtained via numerical methods.

3.2 Free Energy Description

The chemical free energy or local free energy density is a parameter that any phase field model hinges upon. The exact description may vary depending upon the requirements of the system, however, the majority of free energy descriptions fall into two categories: a Landau-type expansion, or another type of description in which well-defined chemical free energy densities of different phases are made continuous via interconnected field variables. A Landau expansion is typically used in solid-state phase transformations such as order-disorder transformations, in which field variables are well-defined physical order parameters. Such an expansion describes the free energy density as a polynomial function of order parameters, where all the terms are assumed invariant with respect to the symmetry operations in the higher-temperature phase. If the free energy descriptions of the phases being considered in a model are well defined, they can be combined via ordering parameters to form one continuous chemical free energy density function. Originally, this type of description was utilized in solidification modeling; however, it also provides ample description of solid-solid transformations.
If a hypothetical, two-phase, A-B alloy is considered, in which the phases α and β are of different crystal structure and the free energy functions \( f^\alpha(c,T) \) and \( f^\beta(c,T) \) are known, the chemical free energy density of the system can be expressed as a function of \( c \), the chemical composition in terms of element B, and a phase-field variable \( \phi(r,t) \), which corresponds to the probability of finding the β phase at a position \( r \), and time \( t \). Such an expression may look like:

\[
\begin{align*}
  f(c, \phi, t) &= p(\phi)f^\alpha(c, t) + [1 - p(\phi)]f^\beta(c, t) + w^{\alpha\beta}g(\phi)
\end{align*}
\]

in which \( g(\phi) \) is a double-well function, the parameter \( w^{\alpha\beta} \) is the height of the energy barrier for the double well function, and \( p(\phi) \) is an interpolation function. Common choices for these functions are:

\[
\begin{align*}
  g(\phi) &= \phi^2(1 - \phi)^2 \\
  p(\phi) &= \phi^3(6\phi^2 - 15\phi + 10)
\end{align*}
\]

The interpolation function, \( p(\phi) \), can vary, so long as \( p(\phi) \) and \( g(\phi) \) are 0 and 1 when \( \phi = 0 \) or 1 respectively. They also ensure that \( \frac{\partial f}{\partial \phi} = 0 \) when \( \phi = 0 \) and 1. A notable characteristic of this free energy description is that it has no definite physical meaning. I.e., the atomic arrangement at a specific state (e.g., \( \phi = 0.2 \)) is not defined, nor is it necessary, due to the continuous nature of the phase-field model.

If this free energy description is extended to define the multicomponent, multiphase system, the resultant free energy density function takes the form:
\[ f(c_i \ldots c_n, \phi_i \ldots \phi_m, T) = \sum_{i=1}^{m} f^\alpha_i (c_1 \ldots c_n, T) p(\phi_i) + \frac{1}{2} \sum_{i=1}^{m} \sum_{j=1}^{m} w^{\alpha \beta}(T) g(\phi_i, \phi_j) \]  

where \( n \) and \( m \) are the number of components or the number of phases, respectively, and the function \( f^\alpha \) is the free energy of a phase, \( \alpha \). For a binary system, the last term in (5) is equated to \( g(\phi_i, \phi_j) \equiv (1 - \delta_{ij}) \phi_i^2 \phi_j^2 \), and for multicomponent systems, \( g(\phi_i, \phi_j) \equiv (1 - \delta_{ij}) \phi_i \phi_j \), where \( \delta \) is the Kronecker delta.

The second contribution to the system free energy is the gradient or interfacial energy, a parameter associated with compositional or structural inhomogeneity of a microstructure. In a phase-field model, the interfacial regions are expressed as a combination of gradient energy terms, which are generally derived by the method proposed by Cahn and Hilliard [30]. The gradient energy term is expressed:

\[ f_{grad} = \int \left[ \frac{1}{2} \sum_{i=1}^{n} \kappa_c (\nabla c_i)^2 + \frac{1}{2} \sum_{i=1}^{m} \kappa_\phi |\nabla \phi_i|^2 \right] dr \]  

where \( \kappa_c \) and \( \kappa_\phi \) are gradient energy coefficients. For composition fields, or fields describing long-range ordering, \( \kappa_c \) and \( \kappa_\phi \) can be described in terms of pair-wise interactions, and the total interfacial energy is a combination of \( f_{chem} \) and \( f_{grad} \).

For the purpose of the system descriptions used in this study, the elastic strain energy and external energy contributions are assumed negligible. For a phenomenological description of these parameters, please refer to [65].

12
3.3 Governing Equations and Numerical Solutions

The third step in a generalized phase-field model approach is to use the aforementioned field variables, defined by the free energy description pertaining to the system under examination, as inputs for a Cahn-Hilliard and/or Allen-Cahn type equations governing the evolution of the microstructure. The modified Cahn-Hilliard diffusion equation typically governs the conserved field variables, such as a concentration field, and is given by the equation:

\[
\frac{\partial c_{i(r,t)}}{\partial t} = \nabla \cdot \left[ M_{ij} \left( \nabla \left( \frac{\delta G}{\delta c_j(r,t)} \right) \right) \right]
\]  

(7)

While the Allen-Cahn, (time dependent Ginzburg-Landau, TDGL) is expressed:

\[
\frac{\partial \phi_p(r,t)}{\partial t} = -L_{pq} \frac{\delta G}{\delta \phi_q} = L_{pq} \left[ \kappa_p \nabla^2 \phi_p - \frac{\partial f}{\partial \phi_q} \right]
\]  

(8)

and governs the non-conserved field variables, such as \( \phi(r,t) \). The mobility parameters in each function, \( M_{ij} \) and \( L_{pq} \), are the atom or interface mobility associated with the conserved and non-conserved field variables, respectively [64]. The microstructural evolution of an alloy system is obtained by finding numerical solutions to these equations, given the material parameters input for the chemical free energy and gradient energy of the different constituents and phases. Due to the non-linear nature of the equations, typically, such numerical solutions are obtained via finite differencing techniques using a uniform spatial grid and explicit time stepping. Other appropriate numerical methods include fast Fourier transformations with periodic boundary conditions, or semi-implicit Fourier-spectral methods.
3.4 Summary

This work describes a general approach to the development and implementation of a phase-field model for multicomponent, multiphase systems. Such an approach can predict the complex arbitrary microstructures produced by diffusional processes in real materials without any a-priori assumptions. The governing equations accept real material parameters for conserved and non-conserved field variables and are solved via finite differencing techniques. However, the phase-field model is not without its downfalls. One potential issue arises in the length scale of the model. Due to the continuum diffuse-interface nature of the model and techniques used to obtain numerical solutions to the governing equations, a requirement is that interfacial regions be resolved to at least a few matrix spaces. This requirement is most significant when interfaces are very sharp, or times are very short. Thus, in such a scenario within a phase-field model, the interface width is artificially enlarged, increasing the system size and computational time. Nonetheless, in spite of its disadvantages, the advantages and sheer potential of the phase-field method make it a very powerful tool to model meso-scale material processes.
CHAPTER FOUR: PHASE FIELD MODELING OF γ U-Zr

Shortly after the advent of nuclear reactor technologies in the 1960s, the first reports of constituent redistribution in irradiated fuel rods were published. This phenomenon, known as thermotransport or thermomigration, is induced by large radial temperature gradients that affect a fuel rod during irradiation, and can cause undesirable changes to the material properties of the fuel. In an environment as volatile as a nuclear reactor, unwarranted changes that can be caused by thermotransport such as changes to localized melting temperatures, and changes in material properties and fission product generation rates, can result in catastrophe. Naturally, a fundamental understanding of thermotransport, and further knowledge of common fuel behaviors in the presence of this phenomenon is of prime importance to the industry. There are many works that serve as a theoretical basis for describing atomic transport under a temperature gradient [24, 25, 26, 27, 28, 29]. Scientists have also attempted to develop numerical models for thermotransport with varying degrees of success [18-29]. Notably, Ogawa and Iwai [20] developed a model of thermotransport in a U-Zr alloy in which constituent redistribution was considered a thermal diffusion process. Solutions to the model were obtained utilizing carefully selected combinations of thermodynamic and kinetic parameters. Their conclusion was that the migration was driven by the thermodynamics of the system. In another study, [18] Hofman et al. created a model based upon the interdiffusion fluxes and partial molar enthalpies of constituents. Hofman noted the importance of the magnitude and sign of the heat of transport values in describing the direction of constituent migration. An effective heat of transport term for each phase in the system was first estimated from microprobe trace results of an irradiated U-Pu-Zr fuel rod, these estimates were fit parametrically into the model. Results from the model were compared to microprobe data from several irradiated fuels.
Over the last several years, as numerical methods have improved and personal computers have become more commonplace and vastly more powerful, increased interest has been placed in computational modeling of diffusional phase transformations and microstructural evolution like that caused by thermotransport. Among the computational methods to emerge over the last few decades, the phase-field model stands out as a powerful tool for modeling mesoscopic scale microstructural evolution in materials. The phase-field model is founded upon a diffuse interface approach originally developed to describe solidification [31, 32, 33, 34, 35, 36]. However, the versatile phase field has found its use in describing multiphase systems with complicated interface conditions, including a wide range of materials processes such as order-disorder transformations [37, 38, 39, 40], allotropic phase transformations [57, 58, 59, 60, 61, 62], grain coarsening [49, 50, 51, 52, 53, 54, 55, 56], and spinodal decomposition [41, 42, 43, 44, 45, 46, 47, 48].

In this work, a phase field model developed by R.R. Mohanty describing therмотransport in a hypothetical binary alloy was adapted to model the γ phase of the U-Zr alloy, a candidate for advanced metallic nuclear fuels. The model is derived using thermodynamics extracted from the CALPHAD database and temperature dependent kinetic parameters associated with therмотransport from the literature. A new model is produced with emphasis placed upon the heat of transport, Q*, and atomic mobility, β. Temperature dependencies of each term are estimated from empirical data obtained directly from the literature, coupled with the textbook phenomenological formulae of each parameter. A solution is obtained via a finite volume approach with the aid of the FiPy® partial differential equation solver [66]. Results of the simulations are presented and discussed with a focus on individual flux contributions from the gradients of both composition and temperature.
4.1 Method

To characterize the substitutional U-Zr alloy, the phase-field model requires only a conserved concentration field variable, describing compositionally distinct, structurally similar phases in the system. In this model the molar fraction of Zr was chosen as the concentration field variable, \( c(x,t) \). The chemical free energy for the alloy was calculated based on the CALPHAD approach [67, 68] using the commercial database available with the ThermoCalc® software. The composition-temperature domain of the \( \gamma \)-phase is shown in the phase diagram in Figure 1.

![U-Zr Phase Diagram obtained from from the CALPHAD database via ThermoCalc software.](image)

The \( \gamma \)-phase of the U-Zr system was chosen as a focus for its importance in nuclear fission reactions, and its presence at high temperatures. Under isothermal conditions the spatio-temporal evolution of the composition field in phase-field models is governed by a non-linear Cahn–Hilliard equation [30], which is obtained from the variation of the free energy functional with respect to the composition field. In situations where a temperature gradient exists in addition to the gradients in the
composition or chemical potential, the Cahn–Hilliard equation requires modification to properly account for the contribution of the temperature gradient to the total flux of atoms. When describing therмотransport in a binary alloy, the modified version of the non-linear Cahn–Hilliard equation takes the form:

$$\frac{1}{V_m} \frac{\partial c(c, t)}{\partial t} = -\nabla \cdot \bar{j}_{Zr} = \nabla \cdot \left[ V_m \left( M_c \nabla \left( \frac{\partial f}{\partial c} - 2 \kappa_c \nabla^2 c \right) - M_Q \frac{\nabla T}{T} \right) \right]$$

(9)

In (9), \( \bar{j}_{Zr} \) is the interdiffusion flux of Zr, \( V_m \) is the molar volume assumed to be independent of composition and temperature, \( \nabla c \) is the gradient energy coefficient that vanishes in a single-phase alloy, and \( f \) is the bulk chemical free energy function derived directly from the thermodynamic database. The free energy curves extracted from the CALPHAD description of the U-Zr system [68] are shown in Figure 2.

![Free energy as a function of composition at 700°C](image)

Figure 2 Free energy as a function of composition at 700°C, obtained from the CALPHAD database via ThermoCalc.
$M_{c}$ and $M_{Q}$ are the chemical mobility and the mobility of thermotransport, respectively, which are functions of composition, atomic mobility, and/or heat of transport terms of the individual atoms, as expressed by:

$$M_{c} = \frac{1}{V_m}c(1-c)[c\beta_U + (1-c)\beta_{Zr}]$$  \hspace{1cm} (10)

And

$$M_{Q} = \frac{1}{V_m}c(1-c)[\beta_U \tilde{Q}_U + \beta_{Zr} \tilde{Q}_{Zr}]$$  \hspace{1cm} (11)

In (10) and (11), $\beta_i$ and $\tilde{Q}_i^*$ represent the atomic mobility and effective heat of transport of a species, $i$, respectively. The heat of transport is related to the amount of heat carried per atom [69]. It is quantified as the contribution of the flux of atoms to the heat flux of a species up or down the temperature gradient. For the U–Zr alloy system, the atomic mobility and heat of transport terms were extracted from literature [18, 19, 20, 21, 22, 70, 71, 72]. Empirical data available in the literature for mobility terms $\beta_U$ and $\beta_{Zr}$, though limited, exhibited an Arrhenius behavior. Following this Arrhenius relationship, the temperature dependence of atomic mobility is expressed:

$$\beta_i = \beta_0 \exp \left( -\frac{H_i}{RT} \right)$$  \hspace{1cm} (12)

The activation energy in (12) is taken as that of self-diffusion of each element [18]:

$$H_{U} = 128000 \text{ (J/Mol)}$$

$$H_{Zr} = 195000 \text{ (J/Mol)}$$
The pre-exponential factor, $\theta_0$, was considered a constant. For each constituent, an average $\theta_0$ was calculated from reported values of $\theta$ by solving (12). The calculated atomic mobility for each constituent, $\beta_i$, plotted versus the temperature can be found in Figure 3.

Traditionally, the Heat of transport $\bar{Q}_i^*$, has been described as varying linearly with temperature. However, Figure 4 shows an insignificant variance in the magnitude and sign of $\bar{Q}_i^*$ in the temperature and composition ranges considered. It is worth noting, however, that all the reviewed literature data reports a positive $\bar{Q}_{U*}$, and a negative $\bar{Q}_{Zr*}$ within the $\gamma$-phase. Therefore, for the scope of this study, $\bar{Q}_i^*$ was considered a constant that is characteristic of each species. The values $\bar{Q}_{U*} = 2.5 \cdot 10^{-20} \text{J}$ and $\bar{Q}_{Zr*} = -17.5 \cdot 10^{-20} \text{J}$ were used for all simulations. In spite of the difference in magnitude of $\bar{Q}_{U*}$ and $\bar{Q}_{Zr*}$, the so-called mobility of theromtransport, $\beta_i\bar{Q}_i^*$, of each constituent remains nearly equal in magnitude and opposite in sign for the temperature domain considered.
Figure 4 Heat of transport, $Q^*$, extracted from the literature and plotted as a function of temperature. Dashed lines represent constant values assumed for simulation.

4.2 Model Parameters

The objective of the study is to model and simulate thermotransport in a γ-phase U-Zr alloy. The U-Zr alloy is examined because of its candidacy as a solid metallic fuel for use in nuclear reactors. The γ-phase of a U-Zr alloy is necessary for fission reactions. Therefore, the chosen composition-temperature domain lies within this single phase region on the phase diagram. This work examines two simulation sets involving γ-phase U-Zr alloys. First, simulations are carried out on an initially homogeneous, γ-phase alloy: is U-39at.%Zr (U-20wt.%Zr). Next, simulations are carried out on a diffusion couple of two U-Zr alloys of different initial compositions, a U-22.5at%Zr alloy and U-39at%Zr.

A linear temperature gradient was applied in all simulations such that one end of the spatial domain was maintained at 1050 K, referred to herein as the cold end; and the other side of the spatial domain, the hot end, was maintained at 1405K. This temperature domain corresponds to the γ-phase
region of the phase diagram over the entire range of compositions considered. The applied temperature field obeys Laplace’s equation:

\[ \nabla^2 T = 0 \]  

With fixed value boundaries governed by:

\[ J_q \cdot \hat{n} = 0, \quad T|_{x=0} = T_{min} \quad \text{and} \quad T|_{x=L} = T_{max} \]

With thermal conductivity assumed to be independent of composition and temperature.

The composition field was governed by a fixed flux boundary condition:

\[ \frac{\partial \tilde{c}}{\partial \bar{x}} = 0 \quad \text{and} \quad \frac{\partial^3 \tilde{c}}{\partial \bar{x}^3} = 0 \quad \text{at} \quad \bar{x} = 0, L \]

The governing equation (9) was rewritten in a dimensionless form for numerical convenience:

\[ \frac{\partial \tilde{c}(x, t)}{\partial t} = \nabla \cdot \left[ \tilde{M}_c(\tilde{c}) \nabla \left( \frac{\partial \tilde{f}}{\partial \tilde{c}(x, \tau)} - \kappa_c \nabla^2 \tilde{c}(x, \tau) \right) - \tilde{M}_q \frac{\nabla T}{T} \right] \]  

by introducing the reduced quantities: \( \nabla = \left( \frac{\partial}{\partial (x/l)}, \frac{\partial}{\partial (y/l)} \right), \tilde{M}_c = \frac{v_m M_c}{\beta}, \tilde{f} = \frac{v_m}{\Delta f}, \tilde{\kappa} = \frac{\kappa v_m}{\Delta f l^2}, \tilde{M}_q = \frac{v_m M_Q}{\Delta f \beta} \)

and \( \tau = \frac{\beta \Delta f}{l^2} t \) where \( x \) and \( \tau \) are the reduced length and time, \( l \) is the actual length scale of the system, \( \Delta f \) is a normalization factor for the free energy, and \( \beta \) is a constant in the units of atomic mobility. (14) was solved numerically using a finite volume method on a 1D domain of length of \( L = 300 \mu m \).
4.3 Results and Discussion

It must be understood that the scope of results presented in this work represents the behavior of U-Zr in the presence of thermotransport based upon the CALPHAD thermodynamics and empirical kinetic parameters available at the time of the study. Figure 3, Figure 4, and the U-Zr phase diagram found in Figure 1 present a visual representation of these parameters. Ergo, the magnitude and direction of constituent migration is dictated by the interplay of the parameters assessed from literature. Furthermore, the simulation was carried out only within the U-Zr γ-phase. Thermotransport behaviors have been shown to be different among differing phases of an alloy [73], therefore the results can be directly compared only to experimental observations reported in literature [18]. Phase field simulation of thermotransport in the lower temperature phases, (α, β, δ) is not included due to the lack of kinetic parameters available at the time of this study. However, recent advances in computational methods, specifically ab-initio calculations of U-Zr alloys [74, 75] can provide some of the necessary parameters that are difficult to obtain experimentally, for the integrated development of phase field microstructural modeling.

Figure 5 Comparison of redistribution profiles when (a) $\beta_i^T$ and $\tilde{Q}_i^T$ are constant, (b) when $\beta_i^T$ is constant and $\tilde{Q}_i^T$ is temperature dependent, and (c) when $\beta_i^T$ is temperature dependent, and $\tilde{Q}_i^T$ is constant.
Figure 6 illustrates Zr migration due to an applied temperature gradient on an initially homogeneous U - 39 at.% Zr alloy. The results were obtained using a combination of constant and temperature-dependent atomic mobilities and heat of transport terms. A comparison of the composition profiles depicted in Figure 5 (a) and (b) indicates that the use of a constant atomic mobility parameter with either constant or temperature-dependent heat of transport terms produces similar redistribution behavior of Zr, because the heat of transport terms do not vary significantly with temperature as shown in. In contrast, the use of temperature dependent atomic mobilities results in mobility of thermotransport parameters that are orders of magnitude larger, yielding the Zr redistribution presented in Figure 5(c) In all three cases, the flux of Zr atoms was up the temperature gradient, toward the high temperature side, a behavior that is in agreement with published data [22, 71, 72]. The total accumulated concentration of Zr at the hot end (i.e., 40–50 at.%) and the presence of a relative minimum along the Zr concentration profile also correspond quite well to experimental observations [18, 21, 22], despite the difference in the composition-temperature domain.

Figure 6 Composition of Zr at 0, 5, 10, and 30 Days elapsed time under the applied temperature gradient.
The temporal evolution behavior of an initially homogeneous U-39 at.% Zr γ-phase alloy subjected to temperatures of 1405K on the hot bound, and 1105K on the cold end is presented in Figure 6. Composition of Zr at 0, 5, 10, and 30 Days elapsed time under the applied temperature gradient.

Composition profiles reported at 5, 10 and 30 days of annealing under the temperature gradient show the Zr flux up the temperature gradient, resulting in a depletion of Zr (or apparent enrichment of U) at the cold end. The accumulation of Zr at the hot end of the alloy occurs rapidly during an initial period (e.g., 5 days), Figure 7, followed by a gradually diminishing rate of accumulation for the following 25 days.

![Zr composition vs. time at the hot end (x = L) of the system.](image)

The absence of a large concentration gradient at early stages of redistribution results in a rapid flux of Zr up the temperature gradient due to thermotransport. As Zr accumulates on the hot side, a flux caused by the concentration gradient opposes further accumulation. The magnitude of change in Zr fraction from the initial state after 30 days at the hot and cold ends, respectively, was 11 and 7 at.%. 

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Figure 8 Diffusion couples of U-Zr alloys of different composition subjected to temperature gradient for 30 days. Note: Left depicts a couple subjected to a negative temperature gradient, while right depicts a diffusion couple subjected to a positive temperature gradient.

The behavior of U-Zr alloys in the presence of a temperature gradient and a pre-existing composition gradient was examined by means of a U–39 at.% Zr and U–22.5 at.% Zr diffusion couple, subjected to an imposed temperature gradient. Results of the simulations involving a temperature gradient were compared to an isothermal anneal of the diffusion couple shown in Figure 8; an isothermally annealed diffusion couple yields a trend of U and Zr diffusing down their respective composition gradients, Zr moving to the right-hand-side in this case while the U moves toward the left. This resultant composition profile after 30 days of annealing isothermally at 1225 K is shown in Figure 8, as well. Two different simulations were carried out on the diffusion couples, one with a temperature gradient applied in the same direction as the Zr concentration gradient, the other with a temperature gradient in the opposite direction of the Zr concentration gradient. The resultant composition profile when a temperature gradient is applied in the opposite direction as that of the Zr composition gradient is shown in Figure 8 (left). In this case, a simultaneous diffusion of Zr up the temperature gradient and down the composition gradient results in a smoothing effect on the diffusion zone, and an accumulation of Zr at the hot end of the system, producing the linear composition profile shown. Applying a temperature gradient in the same direction of the composition gradient yields a much less linear
redistribution profile, shown in Figure 8 (right). In this case, the composition and temperature gradients drive the Zr atoms in the same direction, up the temperature gradient and down the composition gradient, both toward the right hand side of the system. The early effects of thermotransport in the initially homogeneous regions of the system (away from the diffusion zone) become apparent, resulting in relative maxima and minima of the resultant concentration profile.

Prediction of an alloy’s behavior when subjected to an imposed temperature gradient becomes complex when the system contains a pre-existing composition gradient. The modified Cahn-Hilliard governing equation, \((14)\), describes the flux of a constituent as consisting of a contribution from two different driving forces; one due to the composition gradient, and the other due to the gradient in temperature. Calculations of each independent flux contribution in the U–39 at.% Zr and U–22.5 at.% Zr diffusion couple express a flux driven by the temperature gradient that is initially several orders of magnitude larger than the flux contribution produced by the composition gradient. In the first case, in which both composition and temperature gradients are applied in the same direction, this large drive for Zr atoms to move up the temperature gradient causes the Zr outside the immediate diffusion zone to migrate against the composition gradient. This is due to the fact that the heat of transport terms in combination with the atomic mobilities \((\beta_i \tilde{Q}_i^t)\) dominate the overall directionality of moving atoms; these parameters determine the sign and magnitude of the mobility of thermotransport, \(M_Q\). Given the input data used for the \(\gamma\)-phase U–Zr alloy considered, the interplay of the negative \(\beta_{Zr} \tilde{Q}_{Zr}^*\) value and the positive \(\beta_U \tilde{Q}_U^t\) value makes the thermotransport mobility, \(M_Q\) in \((14)\), positive. Hence, the flux of Zr atoms caused by the temperature gradient is up the temperature gradient, opposing the flux contribution produced by the pre-existing concentration gradient. The same condition is applicable to the diffusion couple described in Figure 8. However, in this scenario, where the composition and temperature gradients are applied in opposite directions, the Zr flux contributions from the temperature
and composition gradients are in the same direction and therefore combine to produce a total flux of Zr down the composition gradient.

![Figure 9](image)

**Figure 9** Temporal evolution of flux contributions from the temperature gradient, and the composition gradient at initial time, at a metastable intermediate time, and near steady state.

### 4.4 Summary

The phase-field model developed in Chapter 3 describing thermodiffusion in hypothetical binary substitutional alloys was extended to investigate thermodiffusion in single-phase (bcc-γ) U-Zr alloys. Alloy thermodynamics from the commercially available CALPHAD database ThermoCalc® were incorporated in the model to describe the free energy of the system. Temperature dependencies of atomic mobility parameters and heat of transport terms within the composition-temperature domain considered were calculated from the available literature at the time of the study using trends in empirical data and text-book phenomenological formulae. Initially homogeneous U–39 at.% Zr alloys and U–39 at.% Zr to U–22.5 at.% Zr diffusion couples were subjected to temperatures of 1150K and 1405K at the spatial boundaries of the system. Simulations subjecting the alloys to up to 30 days under the temperature gradient with constant heat of transport input parameters and temperature dependent atomic mobility parameters were carried out. Resultant composition profiles markedly resembled
empirical data (compare [18], [22]): in the presence of a temperature gradient, Zr appeared to migrate up the temperature gradient, towards the hot end of the system. Conversely, a migration of U down the temperature gradient was apparent. The flux of each constituent was calculated and examined with consideration of individual flux contributions from the gradients of composition and temperature, yielding a better chronological understanding of the thermotransport behavior of γ-phase U-Zr alloys.
CHAPTER FIVE: PHASE FIELD MODELING OF TWO-PHASE U-ZR

When a temperature gradient is applied to an initially homogeneous multicomponent alloy, its constituents may demix or migrate, resulting in a concentration gradient that is characteristic of the system. The earliest observations of this phenomenon are attributed to Ludwig [3] and Soret [4, 5, 6], who observed the phenomenon in liquids in the 1860s. Since their early observations, the thermotransport phenomenon has been seen to produce composition-sensitive changes in solid materials, such as melting, phase transformations, and various changes in physical and mechanical properties [18]. Thermotransport is of particular interest in nuclear reactors using metallic fuels, where considerable radial temperature gradients (~240°C/cm) are characteristic of the irradiation process, and can cause significant redistribution of fuel constituents and fission products in metallic fuel pins. Thermotransport has been attributed to: changes in fuel swelling behaviors, changes in fission product generation, localized changes in thermal conductivity, and changes to local melting temperatures.

Hence, to better understand the behavior of nuclear fuels during the irradiation process, fuel redistribution has been examined in post-irradiated fuel pins, and experimental work has been performed to study the thermotransport phenomenon [18-29].

In early observations of thermotransport in nuclear fuels, G.L. Hofman [18] observed thermotransport in solid metallic fuel pins irradiated to 10% burn up. The study utilized a model based upon interdiffusion flux and partial molar enthalpy to examine how the magnitude and sign of the heat of transport, a parameter associated with the amount of heat carried per atom [12-17], influences the migration of an alloy’s constituents. The heat of transport in each phase was estimated from microprobe traces of a fuel pin irradiated to 10% peak burn up. Then, the heat of transport was varied parametrically to fit microprobe traces from several other irradiated fuels. More recently, Y.S. Kim [22]
examined thermotransport in a U-Pu-Zr fuel pin following its irradiation in the Experimental Breeder Reactor II (EBR-II). Calculated values of the interdiffusion fluxes were used to determine diffusion coefficients and the heats of transport for the $\gamma$, $\gamma+\zeta$, and $\delta+\zeta$ phases, which were found in the irradiated fuel pin. In a study of a similar U-Pu-Zr alloy, Sohn et al. imposed a 220°C/cm temperature gradient on a fuel rod for a period of 41 days [21]. Individual analysis was performed on each of the different driving forces present in the system, yielding kinetic parameters related to the thermotransport and interdiffusion fluxes at several temperatures.

A suitable model of thermotransport must account for the complexities associated with thermodynamic and kinetic factors such as the heat of transport, and atomic mobility. The fact that the same constituent may behave differently in different systems [14, 15, 16] demonstrates the difficulty in describing the thermotransport phenomenon. Traditional kinetic models may require explicit tracking of boundaries that continuously move in the system, making it difficult to obtain numerical solutions. Other assumptions inherent in some models, such as the assumption that solute diffusivity is much faster than the solvent or that a local thermodynamic equilibrium exists at the boundary between the two phases, can yield further complications when describing thermotransport. However, the diffuse interface description of the phase-field model, by nature, provides an efficient description of meso-scale microstructures without the need for explicit interface tracking. Additionally, the phase-field model can readily incorporate material properties such as interfacial widths and mobilities, and has the unique ability to utilize practical thermodynamic and kinetic descriptions obtained directly from existing databases. Moreover, the use of realistic material parameters produces a more robust model for observing complex behaviors, such as those associated with thermotransport.
Recently, R.R. Mohanty [2] developed a model describing thermotransport in a hypothetical binary substitutional alloy system based upon the theory of irreversible thermodynamics. The model was adapted to describe the thermotransport of a U-Zr (γ-BCC) solid solution system [1] incorporating real CALPHAD thermodynamics and thermotransport parameters extracted from experimental data reported in the literature. The study examined how temperature dependence of the system kinetics affected the redistribution profile shape of an initially homogeneous, single phase alloy; and, similarly, the effect on diffusion couples of γ phase U-Zr with different terminal compositions. Through the use of temperature dependent thermodynamic and kinetic parameters, the phase-field model yielded results that closely resembled the distinct profile shapes seen in experimental observations. [18-22]

The objective of this study is to examine the thermotransport behavior of a binary two-phase alloy for the first time in a two-phase (γ + β) U-Zr system. The model is built upon CALPHAD thermodynamics describing the γ and β phases of the U-Zr system, and thermotransport parameters for the γ phase from literature [70, 71, 72, 18, 19, 20, 22]. A parametric investigation of how heats of transport for U and Zr in the β phase affect the redistribution is performed, with emphasis on examining the interplay between system kinetics and thermodynamics. Importantly, a strict control over the microstructure that is placed into the temperature gradient (at \(t = 0\)) is used to eliminate the randomness associated with microstructural evolution, allowing an examination of exactly how the β phase thermotransport parameters affect the redistribution behavior of the system.

5.1 The Phase-Field Model

The alloy system described herein is a binary U-Zr alloy consisting of two phases, the solid solution γ (BCC) phase, and the U rich β (Tetragonal) phase. These phases were chosen based upon their presence in post-irradiated U-Zr fuels [18, 68]. The microstructure of the system is fully described by two
field variables: $\phi_i(r, t)$, an ordering parameter representing the current phase $i$ at a position $r$ and time $t$, and a concentration field $c_i(r, t)$, describing the molar concentration of constituent $i$ at position $r$ and time $t$. A linear temperature field $T(r)$ is applied to the system, when appropriate. A volume fixed frame of reference was chosen such that, the field parameters $(c, \phi)$ are normalized, i.e.

for $n$ possible phases:

$$\sum_{i=1}^{n} \phi_i = 1.0 \quad (15)$$

and for all constituents:

$$\sum_{i} c_i = 1.0 \quad (16)$$

The spatio-temporal evolution of the system is described by a modified Cahn-Hilliard equation [30, 63], governing the evolution of the concentration field, and a time dependent Ginzburg-Landau (Allen-Cahn) equation [64], governing the phase-field, respectively described:

$$\frac{\partial c}{\partial t} = V_m^2 \nabla \cdot \left[ M_c \nabla \left( \frac{\partial f}{\partial c} - \kappa_c \nabla^2 c \right) - M_Q \frac{\nabla T}{T} \right] \quad (17)$$

$$\frac{\partial \phi}{\partial t} = M_\phi \left[ \kappa_\phi \nabla^2 \phi - \frac{\partial f}{\partial \phi} \right] \quad (18)$$

In these equations, $V_m$ is the molar volume, $M_c$ and $M_\phi$ are the chemical mobility and structural relaxation mobility, $M_Q$ is the mobility of thermotransport, $f$ is the total free energy of the system, $\kappa$ is a gradient energy coefficient, and $T$ is the temperature.
5.2 Thermodynamic Description

In the phase field method, the microstructural evolution is driven by the minimization of the system free energy. By nature, it is a continuum method; however, within an alloy, the free energy descriptions of phases with crystal structures that are different are not continuous. It is therefore necessary to link the free energy of each phase being considered. In the U-Zr, the free energy of the β and γ phase is governed and made continuous by the relationship:

\[ f(c, \phi, t) = p(\phi)f^\gamma(c, t) + [1 - p(\phi)]f^\beta(c, t) + w^\gamma,\beta g(\phi). \]  

The Gibbs free energy density functional for each phase, \( f^\beta(c, t) \) and \( f^\gamma(c, t) \), respectively, are:

\[ f^\gamma(c, t) = (1 - c)f_U^\gamma(T) + cf_Zr^\gamma(T) + RT[c\ln(c) + (1 - c)\ln(1 - c)] + c(1 - c)l^\gamma_{UZr} \]  

and

\[ f^\beta(c, t) = (1 - c)f_U^\beta(T) + cf_Zr^\beta(T) + RT[c\ln(c) + (1 - c)\ln(1 - c)] + c(1 - c)l^\beta_{UZr} \]

The parameters, \( f_i^\gamma \) and \( f_i^\beta \) are the free energy contributions of the pure elements in each respective phase, and \( l^\gamma_{UZr} \) and \( l^\beta_{UZr} \) are the excess energy associated with each phase. The parameters \( f_{UZr}^\gamma, f_{UZr}^\beta, l_{UZr}^\gamma, \) and \( l_{UZr}^\beta \) were extracted from the ThermoCALC® CALPHAD database, and assessed for consistency with experimental thermodynamic assessments available in the literature [67, 68].

The parameter \( w^\gamma,\beta \) is the magnitude of the energy barrier, and \( g(\phi) \) is a double well potential, given by:

\[ g(\phi) = \phi^2(1 - \phi)^2 \]  

An interpolation function

\[ p(\phi) = \phi^3(6\phi^2 - 15\phi + 10) \]
was chosen such that \( p(\phi) \) and \( g(\phi) \) are 0 and 1 when \( \phi = 0 \) or 1, and \( \frac{\partial f}{\partial \phi} = 0 \) when \( \phi = 0 \) and 1.

### 5.3 Thermodynamic Parameters

Due to the scarcity of experimental data, reasonable estimates for the energy barrier \( w_{\gamma\beta} \) and gradient energy coefficient \( \kappa \), were made from equilibrium states on the phase diagram. The free energy curves of the \( \gamma \) and \( \beta \) phases are linked by (19) in such a way that it can be assumed that the phase transformation is a result of spinodal decomposition, in spite of the difference in crystal structures of the \( \gamma \) and \( \beta \) phases [76]. This assumption provides a means to estimate \( w_{\gamma\beta} \) and \( \kappa \) through spinodal theory [77, 78].

From spinodal theory, the decomposition of a supersaturated solution into a thermodynamically stable \( \beta + \gamma \) two phase mixture under isothermal conditions yields:

\[
4\kappa_{\phi}k_c^2 = \frac{\partial \Delta f_{\gamma\rightarrow\beta}}{\partial \phi^2} = -2w_{\gamma\rightarrow\beta}(1 - 6\phi + 6\phi^2)
\]

The parameter \( k_c \) is a preferential wave number, related to the preferential wavelength of spinodal decomposition, \( \lambda_c \) by

\[
k_c = \frac{2\pi}{\lambda_c}.
\]

At a local equilibrium, when the profile of \( \phi \) across the interface is stable, \( \kappa_{\phi} \) can be obtained:

\[
\kappa_{\phi} = \frac{9\gamma_s^2V_m^2}{w_{\gamma\rightarrow\beta}}
\]

where \( \gamma_s \) is the interfacial energy density, and \( V_m \) is the molar volume.

Substitution of (26) into (24) yields
\[ w_{\gamma \rightarrow \beta} = \frac{6\pi y_s V_m}{\lambda_c} \sqrt{\frac{2}{-(1 - 6\phi + 6\phi^2)}} \quad (27) \]

The values of \( y_s \) and \( \lambda_c \) were estimated, and the equilibrium values necessary for the analysis were extracted from the equilibrium phase diagram Figure 1 which was obtained from ThermoCalc®.

### 5.4 System Kinetics

A phenomenological kinetic description is adapted from the phase field model derived from irreversible thermodynamics by R.R. Mohanty [2]. The chemical mobility, \( M_c \), and the mobility of thermotransport, \( M_Q \), are defined:

\[
M_c = \frac{1}{V_m} c(1 - c)[c \beta_U + (1 - c)\beta_{Zr}] 
\]

\[
M_Q = \frac{1}{V_m} c(1 - c)[\beta_U \tilde{Q}_U - \beta_{Zr} \tilde{Q}_{Zr}] 
\]

In which the atomic mobilities, \( \beta_i \), and heats of transport, \( \tilde{Q}_i \), can be either temperature dependent or constant material parameters. In this study, the heats of transport of U and Zr were considered temperature independent. Additionally, the atomic mobilities of U and Zr were assumed not to vary between phases. The kinetic parameters associated with the Arrhenius definition of atomic mobility are reported in Table 1, and were extracted from available experimental analysis of the U-Zr \( \gamma \)-phase [18, 20, 22, 70, 71, 72]. In interfacial regions, the mobility of thermotransport, \( M_Q \), is assumed to vary linearly with the phase variable, \( \phi \), i.e.,

\[
M_Q^{eff} = \phi M_Q^\gamma + (1 - \phi) M_Q^\beta 
\]
Values for $\tilde{Q}_i^*$ within the $\gamma$-phase are extracted from data available in the literature at the time of this study, and can be found in Table 1. The kinetic data for the U-rich $\beta$ phase is not well reported in the literature; therefore a parametric study is performed to qualitatively examine the effect of these parameters on the redistribution of the system.

### 5.5 Numerical Procedure

For numerical convenience, the governing equations were written in a dimensionless form by introducing the following reduced quantities:

$$
\begin{align*}
\bar{x} &= \frac{x}{l}, \quad \bar{y} = \frac{y}{l}, \quad \bar{M}_c = \frac{V_m M_c}{\beta}, \\
\bar{f} &= \frac{V_m f}{\Delta f l^2}, \quad \bar{R} = \frac{\kappa \gamma_m}{\Delta f l^2}, \quad \bar{M}_Q = \frac{M_0 V_m}{\Delta f \beta l^2}, \quad \text{and} \quad \bar{\tau} = \frac{\beta l^2}{\Delta f t}
\end{align*}
$$

where $l$ is the length scale of the system, $\beta$ is a constant with the units of atomic mobility, $\Delta f$ is a free energy normalization factor, assumed $\Delta f = RT_{avg}$, $T_{avg}$ is the average system wide temperature, and $\bar{x}$ and $\bar{\tau}$ are the scaled length and time.

The simulations involved a volume fixed frame of reference, with zero flux boundary conditions for the phase field and composition field applied to all exterior faces of the microstructure. For all systems being considered, an initially stable system was subjected to an applied temperature gradient following Laplace’s equation and neglecting the Dufour effect:

$$\nabla^2 T = 0,$$

with the applied fixed-value boundary conditions:

$$J_q \cdot \hat{n} = 0, \quad T|_{x=0} = T_{min}, \quad T|_{x=L} = T_{max}.$$
The reduced-quantity governing equations were solved numerically, by an iterative process applying a finite-volume method in the Python programming language through the use of the FiPy® partial differential equation solver library [66].

5.6 Simulation Procedure

The phase field model described herein was utilized to examine the effects of thermotransport on a U-Zr (γ + β) alloy. Simulations were performed in a three step process. First, a metastable supersaturated solution of U-10at.%Zr was annealed at 973 K for 10 days, until an equilibrium microstructure (Figure 10 Temporal evolution from an initially metastable state of a U-Zr alloy isothermally annealed at 973K was obtained. This microstructure was then saved for use as a starting point for all subsequent simulations. Next, a parametric examination was performed of the constituent redistribution behavior when different β-phase $Q_i^*$ inputs were used, requiring multiple simulations for different input parameters. For convenience, simulations involving each set of input parameters were organized into a series of ‘cases’, which are outlined in Table 1. Finally, the results from each case were compared and conclusions were drawn based upon the observed redistribution behavior.

Figure 10 Temporal evolution from an initially metastable state of a U-Zr alloy isothermally annealed at 973K
5.7 Results

The result of annealing an initially metastable supersaturated solid solution of U-10at.%Zr for 24 hours at 973°K is shown in Figure 11. Resultant phase (A) and composition (B)'s distribution, respectively, when the initial microstructure (t₃ from Figure 8) is subjected to the temperature gradient shown for 15, with zero-value thermotransport kinetics. This resultant microstructure, t₃ from Figure 10, was used as the starting microstructure for all U-10Zr thermotransport simulations performed (i.e., Cases 1-5) as described in table 1.

Figure 11 Resultant phase (A) and composition (B)'s distribution, respectively, when the initial microstructure (t₃ from Figure 8) is subjected to the temperature gradient shown for 15, with zero-value thermotransport kinetics.

Figure 11 depicts the result of subjecting the starting microstructure to a linearly distributed temperature gradient starting at 975K at the cold side, to 1075K at the hot end of the system. Figure 11 provides a control scenario, in which the effects from thermotransport are ignored, resulting in a thermodynamic controlled composition distribution. The concentration in either phase is constant, in spite of the linearly increasing temperature.
Figure 12 Resultant phase and composition distribution, respectively, when the initial microstructure is subjected to the shown temperature gradient for 15 days, when the β-phase thermotransport parameters of each element are equivalent to the respective γ-phase values.

The results of Case 2, Figure 12, depict the redistribution of a U-10Zr alloy caused by thermotransport after the microstructure from Case 0 was placed in a temperature gradient for 15 days, heat of transport parameters in β equivalent to those in γ, i.e., $\beta Q_{\text{U}}^* = \gamma Q_{\text{U}}^*$ and $\beta Q_{\text{Zr}}^* = \gamma Q_{\text{Zr}}^*$. The effects of thermotransport are seen primarily near the terminals of the alloy, i.e., $x = 0 \mu m$ and $x = 75 \mu m$, near the hot end, a buildup of Zr is observed near the hot end, and a depletion of Zr, or buildup of U is observed at the cold end of the system.
Figure 13 Resultant phase and composition distribution, respectively, when the initial microstructure is subjected to a temperature gradient for 15 days, when $\beta Q_U^* = 10 \cdot \gamma Q_U^*$, and the $Q_{Zr}$ is equivalent in both phases.

In Figure 13, the microstructure from Figure 10 was again subjected to a temperature gradient for 15 days. However, the heat of transport for U in the β-phase was an order of magnitude larger than that of U in the γ phase, i.e., Case 3. ($\beta Q_U^* = 10 \cdot \gamma Q_U^*$ and $\beta Q_{Zr}^* = \gamma Q_{Zr}^*$). In spite of the change, a Zr buildup is seen near $x = 75 \mu m$, similar to Figure 12. Likewise, a depletion of Zr is seen near $x = 0 \mu m$. It is worth noting that the γ and β phase and composition distribution results of Figure 12 are nearly indistinguishable from those of Figure 13.

The resultant microstructure and composition distribution when the initial microstructure was placed under a temperature gradient for 15 days, assuming the heat of transport of Zr in the β-phase is an order of magnitude larger than it is in the γ-phase, and that the U heat of transport remains equivalent in each phase (i.e., $\beta Q_U^* = \gamma Q_U^*$ and $\beta Q_{Zr}^* = 10 \cdot \gamma Q_{Zr}^*$) is shown in Figure 14. Again, redistribution is
primarily seen only near the terminals, and the magnitude and direction of redistribution are similar to those seen in prior cases.

Figure 15 Resultant microstructure accompanied by the composition distribution, respectively, after 15 days subjected to the temperature gradient. In this scenario, the β-phase thermodtransport parameters are assessed as 3 orders of magnitude larger than their respective γ-phase counterparts.

Because the first 3 examined scenarios yielded similar redistribution behavior, in spite of variation in the heat of transport parameters of each phase, Case 5 was performed as a limiting scenario, in which both the heats of transport of U and Zr are much larger in the β-phase than they are in the γ-phase (i.e. $\beta Q^\circ_U \gg \gamma Q^\circ_U$ and $\beta Q^\circ_{Zr} \gg \gamma Q^\circ_{Zr}$). Constituent redistribution follows the same trend as seen in prior simulations, the resultant microstructure and composition distribution, Figure 13, are similar to those seen in the prior cases.
A more quantitative representation of the redistribution behavior is yielded in Figure 16, in which composition-redistribution profiles are extracted using spatial averages of the composition along the length of each microstructure. When thermotransport is disabled, in the $\beta + \gamma$ region, the Zr composition increases to 11.8% then remains constant in the $\gamma$ phase region. The results from Figure 11, where $\hat{Q}_{U}^* = \dot{\gamma} \dot{Q}_{U}^*$ and $\hat{Q}_{Zr}^* = \dot{\gamma} \dot{Q}_{Zr}^*$, show a maximum Zr composition of 14.6 at.% at $x = 75 \mu m$, which represents a 2.8 at.% enrichment over the case in which thermotransport was not considered, or a deviation of 4.6% from the initial state. At $x = 0 \mu m$, a composition of 4.5 at% Zr is 0.9at.% less than what was seen when thermotransport effects were not considered, a 5.5 at.% change from the isothermal case. Similarly, the resultant redistribution profile from simulations where $\hat{Q}_{U}^* = 10 \cdot \dot{\gamma} \dot{Q}_{U}^*$ and $\hat{Q}_{Zr}^* = \dot{\gamma} \dot{Q}_{Zr}^*$, yields a maximum Zr composition of 14.6 at.% and a minimum at $x = 0 \mu m$ of 4.5 at% Zr. The largest redistribution magnitudes are seen in results from Figure 14. At $x = 75 \mu m$, a Zr buildup to 14.8 at% is evident, while at $x = 0 \mu m$, Zr is 3.9 at% of the alloy composition.
5.8 Discussion

By using the same starting microstructure for all simulations, the randomness involved in microstructural evolution was eliminated, providing an opportunity to observe exactly how changes to the heat of transport in one phase of a two phase microstructure affected the redistribution behavior of the U-10Zr alloy. Interestingly, a comparison of the resultant microstructures when the heat of transport of $\beta$ was varied parametrically indicates negligible changes to the phase distribution of the system. Truthfully, the differences in the composition-redistribution profiles for each set of inputs, Figure 16, are only fractions of a percent. The rigidity of the system may be ascribed to the strong thermodynamic inclination to maintain phase equilibrium, governed by the Gibbs free energy, and the large volume fraction of the $\gamma$ phase (for which $\bar{Q}^*$ was fixed) in the system.

Qualitatively, the redistribution profiles from Figure 16 are in agreement with the literature [18-22], and the migration direction of Zr up the temperature gradient follows convention. In this study, the sign of $\bar{Q}^*$ was assumed to be the same in both phases, only the magnitude was changed. The magnitude and direction of redistribution is attributed to the interplay of $\bar{\beta}\bar{Q}^*_U$, $\gamma\bar{Q}^*_U$, $\bar{\beta}\bar{Q}^*_Zr$, and $\gamma\bar{Q}^*_Zr$. For the U-Zr system, because $\bar{Q}^*_U$ is positive, and $\bar{Q}^*_Zr$ is negative, any changes to simply the magnitude of these parameters will yield the same migration directions seen in this model and the literature, only the magnitude of redistribution will change. An examination of (29) confirms this.

5.9 Conclusions

For the first time, a phase field model based on irreversible thermodynamics was developed to describe the microstructural evolution of a two-phase U-Zr ($\beta + \gamma$) system using real material properties such as thermodynamics imported from the CALPHAD database and kinetics from experimental data in
the literature. Constituent redistribution driven by gradients in chemical potential and temperature was observed as a function of a parametrically varied heat of transport in a series of simulations.

The behavior of U-Zr constituents seen near the terminals of the alloy was in qualitative agreement with prior studies. Within the gamma phase, Zr migrated up the temperature gradient, to a maximum relative increase in composition of 3at.% Zr, and near the cold end, $x = 0$, the maximum depletion of Zr was -1.5at%. Both maxima occurred in an alloy for which $\beta \dot{Q}_U = \gamma \dot{Q}_U$ and $\beta \dot{Q}_{Zr} = 10 \cdot \gamma \dot{Q}_{Zr}$.

For the system considered, the interplay of constituent heats of transport within each phase dictates only the magnitude of redistribution. (29) shows that because $\dot{Q}_U$ is positive, and $\dot{Q}_{Zr}$ is negative, in spite of any changes made to the magnitudes, the mobility of thermotransport, $M_a$, will remain positive.

Interestingly, even with large changes to constituent heats of transport in the beta phase, only a minor change is seen in the magnitude of redistribution at the hot and cold ends of the sample. This may be attributed to large thermodynamic driving forces in the two-phase region of the alloy, or to the relatively low solute concentration of the system, or it may be an indication of how minor a role thermotransport can play in constituent redistribution when compared to thermodynamic driving forces.
Table 1: Parameters used in each ‘case’ of the parametric study. For all cases, the γ-phase parameters are unchanged for U and Zr, only changes to the β-phase parameters were considered.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Case 0</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
<th>Case 5</th>
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<tr>
<td>$T_{\text{left}} (K)$</td>
<td>973</td>
<td>973</td>
<td>973</td>
<td>973</td>
<td>973</td>
<td>973</td>
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<td>1073</td>
<td>1073</td>
<td>1073</td>
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<tr>
<td>$\beta_U \times 10^5 \text{ m}^2 \cdot \text{mol} \cdot \text{J} \cdot \text{s}$</td>
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<td>5.80</td>
<td>5.80</td>
<td>5.80</td>
<td>5.80</td>
<td>5.80</td>
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<tr>
<td>$\beta_{Zr} \times 10^5 \text{ m}^2 \cdot \text{mol} \cdot \text{J} \cdot \text{s}$</td>
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<td>2.40</td>
<td>2.40</td>
<td>2.40</td>
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<tr>
<td>$\beta Q_U^* \times 10^{-20} \text{ J}$</td>
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<td>2.50</td>
<td>25.0</td>
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<tr>
<td>$\beta Q_{Zr}^* \times 10^{-20} \text{ J}$</td>
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<td>-17.50</td>
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<tr>
<td>$\gamma Q_U^* \times 10^{-20} \text{ J}$</td>
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<td>-17.50</td>
<td>-17.50</td>
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CHAPTER SIX: CONCLUDING REMARKS AND FUTURE WORK

The primary objective of this research is to understand and predict the interdiffusion behavior and microstructure evolution of real materials, primarily U-Zr nuclear fuels, in the presence of driving forces caused by gradients in chemical potential and temperature. The research focused around the use of the phase-field model to simulate and predict said microstructure evolution in the presence of two distinct driving forces: a gradient in chemical potential, and a thermal gradient. The U-Zr nuclear fuel system was used as an example, and several scenarios were examined, including an isothermal control, thermotransport in a single phase and thermotransport in a multiphase system. The conclusions of the studies performed are as follows:

6.1 Phase Field Model of the U-Zr (γ-phase) System

This investigation had three main objectives: first, to predict the concentration profiles of a single phase U-Zr alloy subjected to driving forces due to a chemical potential gradient and a thermal gradient, second to examine the effects of thermotransport on U-Zr alloys with a pre-existing gradient in composition (i.e., diffusion couples of different terminal compositions), and third to quantify the concentration-flux contributions from each driving force. To satisfy these objectives, a phase field model incorporating thermodynamics directly linked from the CALPHAD database, ThermoCALC®, and temperature dependent kinetic parameters was produced. Simulations were performed on an initially homogeneous U-39at.%Zr γ-phase alloy, bounded by temperatures of 1050K at x=0 and 1405K at x=L. The results showed a migration of Zr up the temperature gradient with a concurrent movement of U down the temperature gradient. Analysis of flux contributions from the gradients of composition and temperature was carried out, providing a quantified chronological understanding of the thermotransport behavior of γ-phase U-Zr alloys.
6.2 Phase Field Model of the U-Zr (β+γ) System

Often, when U-based metallic fuels are subjected to the temperature gradients present in a nuclear reactor, multiple phases are present. The objective of this work was to observe the effects of thermotransport on an alloy system with multiple phases present. Toward this end, and for the first time, a phase field model based was developed to describe the microstructure evolution of a two-phase U-Zr (β + γ) system using CALPHAD thermodynamics and kinetic parameters from published experimental data. The interplay between thermodynamic driving forces and thermotransport was observed for a parametrically varied heat of transport term in a series of simulations. To reduce the degrees of freedom in the system, the same two-phase initial microstructure was used for all simulations. This initial microstructure was then subject to a temperatures of 975K at $x=0$ and 1075K at $x=L$. The temperatures were chosen based upon estimated radial temperatures of a U-Zr fuel pin in a breeder reactor.

The behavior of U-Zr constituents seen near the terminals of the alloy was in qualitative agreement with prior studies. Within the gamma phase, Zr migrated up the temperature gradient, to a maximum relative increase in composition of 3at.% Zr, and near the cold end, $x = 0$, the maximum depletion of Zr was -1.5at%. The simulations demonstrated that the interplay of constituent heats of transport within each phase dictates only the magnitude of redistribution, and within this system, not the direction up or down the temperature gradient each constituent tends to move. This behavior is inherent in (29), which shows that as long as $\tilde{Q}_{U}^{*}$ is positive, and $\tilde{Q}_{Zr}^{*}$ is negative, in spite of any changes made to the magnitude of each individual term, the mobility of thermotransport, $M_{Q}$, will remain positive. Perhaps the most important observation garnered from the results is that, even with large changes to constituent heats of transport in the beta phase, only very minor changes are seen in the magnitudes of redistribution at the hot and cold ends of the sample. This may be attributed to large
thermodynamic driving forces in the two-phase region of the alloy, or to the relatively low solute concentration of the system. It may be an indication of how minor a role thermotransport can play in constituent redistribution when compared to thermodynamic driving forces.
REFERENCES


