Prediction of Interdiffusion Microstructure for High Temperature Coatings and Domain Structures/Piezoelectric Property at Ferroelectric Morphotropic Phase Boundary

DISSERTATION

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Xiaoqin Ke

Graduate Program in Materials Science and Engineering

The Ohio State University

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Dissertation Committee:

Professor Yunzhi Wang, Advisor
Professor Suliman Dregia, Co-advisor
Professor Sheikh Akbar
Abstract

Phase field method is a powerful tool to simulate microstructure evolution and is widely used in nearly all fields of materials science. In this work, we apply the phase field approach coupled with thermodynamic models to simulate microstructural evolution and study the composition-microstructure-property relationship for high temperature coatings and ferroelectric materials at morphotropic phase boundary (MPB).

The study on high temperature coatings in this work focuses on the fundamentals of interdiffusion microstructure maps as well as a special interdiffusion microstructure containing the so called type n boundaries. An interdiffusion microstructure map (IMM) is a two dimensional diagram showing how interdiffusion microstructure varies when one end alloy composition (the base material) is fixed while the other (the coating material) is varied across a region of the phase diagram for dual alloys. It can thus predict the relationship between interdiffusion microstructure and initial alloy compositions and have importance to coating design. The fundamentals for constructing IMMs for dual-alloy systems are established based on the current phase field simulations as well as previous works, which includes the topology of IMM as well as three mechanisms of microstructure type change on an IMM. These fundamentals should be followed when constructing IMMs for a real alloy system. With regards to type n boundaries, which are
defined as interface boundaries at which \( n \) phases changing on crossing them, the characteristics of type \( n \) boundaries and the condition for the formation of type \( n \) boundaries are explored in the current work. For \( n \geq 3 \), type \( n \) boundaries are expected to be infrequent because the diffusion paths of them have to pass through a special feature which is defined as a feature that cannot be intersected by a random line. However, our simulations found that under the right conditions, such boundaries can occur and even if the initial alloy composition varies, it persists to occur. The simulation results are consistent with experimental observations.

The study on ferroelectric MPB in this work focuses on the domain structure and the origin of good piezoelectric property at MPB. MPB of ferroelectric solid solutions is a composition phase boundary between tetragonal and rhombohedral phases and possesses the best piezoelectric property but the phase of the domains at MPB and the origin of good property at MPB are under serious debate. Through advanced phase field simulations, a hierarchical nanodomain structure at the MPB is predicted and agrees well with experimental observations. The phase of nanodomains at MPB is found to be monoclinic. The monoclinic phase is unstable according to the 6\(^{th}\) order Landau free energy of the system but it was found that it is the long range elastic and electrostatic interaction energies in the multi-domain states that stabilize the monoclinic phase. Furthermore, the study on the piezoelectric property of the ferroelectric MPB systems discovered that polarization rotation through the monoclinic phase is responsible for their high \( d_{33} \).
In conclusion, phase field simulation method is employed to understand the relations between composition and interdiffusion microstructure as well as relations among composition, ferroelectric domain structure and piezoelectric property of ferroelectric MPB materials and helps answering some important questions both in the field of interdiffusion microstructure and ferroelectric MPB.
This document is dedicated to my husband Bo and my son Bobby.
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Vita

2007.................................................................B.S., Xi’an Jiaotong University,
Xi’an, Shaanxi, China

2009.................................................................M.S., Xi’an Jiaotong University,
Xi’an, Shaanxi, China

2009 to present ..............................................Graduate Research Associate, The Ohio
State University, Columbus, Ohio, US.

Publications

Dong Wang, Xiaoqin Ke, Yunzhi Wang, Jinghui Gao, Yu Wang, Lixue Zhang, Sen
Yang and Xiaobing Ren, “Phase diagram of polar states in doped ferroelectric systems”.

Xiaoqin Ke, John E. Morral and Yunzhi Wang, “Type n boundaries in n-component

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Chapter 1: Introduction

In Chapter 1, the background of the two issues studied in this thesis, interdiffusion microstructures of high temperature coatings and the morphotropic phase boundary of ferroelectric solid solutions, will be briefly reviewed.

1.1 Interdiffusion microstructure of high temperature coatings

When two alloys of different compositions are in contact with each other at elevated temperatures, atoms in the vicinity of the contact interface will interdiffuse and may react to change the phases present. The affected volume is called “interdiffusion zone” and the new microstructure formed is called “interdiffusion microstructure”.

For coatings utilized at high temperatures, interdiffusion will happen between the coating alloy and the substrate alloy. For example, for turbine blades of aircraft engines, interdiffusion will take place between the $\gamma+\gamma'$ base alloy and $\gamma+\beta$ coating. Different kinds of interdiffusion microstructure can form between the end alloys depending on the initial end alloy compositions as both measured by experiments [1-4] and predicted by simulation [5-8].
To simplify analysis of interdiffusion microstructure, Morral introduced a shorthand notation to represent various layers formed in interdiffusion microstructure and the direction of movement of interface boundaries [9]. For example, the interdiffusion microstructure shown in Fig. 1.1 [10] can be represented by the shorthand notation as \( \gamma + \beta < \gamma > \gamma + \beta > \gamma + \gamma' \). Here four layers within the interdiffusion zone are identified: \( \gamma + \gamma' \), \( \gamma + \beta \), \( \gamma \), and \( \gamma + \beta \). The boundary between two layers moves in a direction given by the caret dividing them. A “<” caret indicates that the boundary between the adjacent layers moves to the left while a “>” caret indicates that it moves to the right. If the boundary is stationary, then a “|” will be inserted between two layers.

Fig 1.1[10] Interdiffusion microstructure of a Ni-Al-Cr \( \gamma + \beta / \gamma + \gamma' \) diffusion couple held at 1200\(^\circ\)C for 100 hours.

Another important concept in the area of interdiffusion is “diffusion path”. Diffusion path
tracks the composition variation in one dimension across the interdiffusion zone [11]. For an infinite diffusion couple, it is a line between the two initial end alloys. The concept of diffusion path is important because diffusion path is easy to visualize and can be used to predict the interdiffusion microstructure. Fig. 1.2 shows the diffusion path of a $\gamma/\gamma$ diffusion couple of Ni-Al-Cr system simulated by DICTRA superimposed on the ternary phase diagram [7]. From the diffusion path, it can be deduced that the interdiffusion microstructure of this diffusion couple is: $\gamma > \gamma + \beta > \gamma$. There are several theorems on diffusion path, which were first reviewed by Kirkaldy and Brown in 1963 [12] and then updated by Morral [11]. These theorems are very helpful in understanding and interpreting diffusion paths and interdiffusion microstructures.
Fig. 1.2 Diffusion path of a $\gamma/\gamma$ diffusion couple of Ni-Al-Cr system simulated by DICTRA superimposed on the ternary phase diagram.

According to Morral [9], the boundaries between two layers in an interdiffusion microstructure can be classified into types based on the number of phases that change on crossing the boundary. For example, a boundary with an $\alpha$ phase region on one side and a $\beta$ phase region on the other would be a type 2 boundary, because two phases change when crossing it. This is the most common type of boundary found in binary diffusion couples, although type 0 and 1 boundaries are possible as well. The different types of boundaries in interdiffusion microstructures have been recently reviewed by Morral [11]. Such a classification of boundaries in interdiffusion microstructures has been proven
useful in analyzing and predicting complicated interdiffusion microstructures in multicomponent and multialloy systems.

It was found that sometimes the interdiffusion microstructure can be drastically different from the initial ones after interdiffusion. For example, several new layers can form between the two end alloys ($\gamma + \gamma'$ and $\gamma + \beta$) as shown in Fig. 1.3 [2]. In Fig. 1.3(a), a new $\gamma + \beta$ and $\gamma'$ layer forms between initial alloys while in Fig. 1.3(b) a new $\gamma$, $\gamma + \beta$ and $\gamma'$ layer forms. The single intermetallic $\gamma'$ layer formed in the interdiffusion zone will be detrimental to the mechanical properties of the turbine blades because they are very brittle. Therefore it is important to know how to choose appropriate initial compositions for the coatings so that such an intermetallic layer can be avoided. Also, if checking the boundary types formed in the two interdiffusion microstructures shown in Fig. 1.2, it can be seen that the boundary between the $\gamma + \beta$ and $\gamma'$ layers in both microstructures is a type 3 boundary. Such a boundary is rare in experiments and has not been predicted by simulation yet. Also, as analyzed in Chapter 4, such type 3 boundaries are unexpected in nature.
Fig. 1.3 Interdiffusion microstructures formed in Ni-Al-Cr $\gamma+\beta/\gamma+\gamma'$ diffusion couples held at 1200°C for 100 hours. (a) a $\gamma+\beta/\gamma+\gamma'>\gamma+\gamma'$ microstructure; (b) a $\gamma+\beta<\gamma+\beta'>\gamma+\gamma'$ microstructure. The dark areas in the $\gamma$ single phase layer are kirkendal porosity. O.I. denotes the original interface.

Two questions thus might arise, first, how does interdiffusion microstructure varies with initial end alloy compositions; second, why type 3 boundary forms and what will affect its formation? To explore the first question, the fundamentals of interdiffusion microstructure map are given in chapter 3. To answer the second question, a simulation study of type 3 boundaries as well as type 4 boundaries are given in chapter 4 by phase field methods. A general introduction of phase field methods is given in Chapter 2.
1.2 Morphotropic phase boundaries of ferroelectric solid solutions

Ferroelectric material is a functional material which has spontaneous polarization and the direction of the spontaneous polarization can be reversed by external electric field. The temperature below which spontaneous polarization appears is called Curie temperature (T_C) and the transition from zero polarization state to spontaneous polarization state at T_C is called paraelectric to ferroelectric phase transition.

Ferroelectric materials are characterized by domain structure. Within each domain, the direction of the polarization vector is the same and the boundary between two adjacent domains with different polarization directions are called domain walls. The polarization direction within domains can be changed by external electric fields. Because of this change of polarization direction under field, like magnetic materials, ferroelectric materials are characterized by hysteresis loops.

Due to its unique structure and properties, ferroelectric materials have a variety of applications in industry. For example, relaxor ferroelectric materials have high dielectric permittivity at broad temperature range and thus are used as capacitors. Another example is that some ferroelectric materials have good piezoelectricity and thus are used as actuators and transducers.
Morphotropic phase boundary (MPB) of ferroelectric solid solutions was first found in PbZrO3-xPbTiO3 system and it is a composition phase boundary between tetragonal (T) and rhombohedral (R) phases [13]. Fig. 1.4 shows the conventional diffusionless phase diagram for PbZrO3-xPbTiO3. It is seen that there is a nearly temperature-independent phase boundary between T and R phase and such boundary is called morphotropic phase boundary. It was found that near MPB the piezoelectric coefficients such as $d_{33}$ are the largest.

Fig. 1.4 The conventional diffusionless phase diagram of PbZrO3-xPbTiO3 solid solutions. C, R and T denotes cubic, rhombohedral and tetragonal phases, respectively.
Due to the superior piezoelectric property at MPB, extensive research has been focused on the ferroelectric MPB in the past decades both from direct experimental measurement and from theoretical calculations.

Experimentally, several main discoveries are listed below: (1) MPB was not only limited to PbZrO$_3$-xPbTiO$_3$ system, but also exist in PbMg$_{1/3}$Nb$_{2/3}$O$_3$-xPbTiO$_3$ [14], PbZn$_{1/3}$Nb$_{2/3}$-x PbTiO$_3$ [15], and even was found in lead free BaZr$_x$Ti$_{1-x}$O$_3$-zBa$_y$Ca$_{1-y}$TiO$_3$ system [16]; (2) It was found that single crystals of some PbMg$_{1/3}$Nb$_{2/3}$O$_3$-xPbTiO$_3$ and PbZn$_{1/3}$Nb$_{2/3}$-x PbTiO$_3$ MPB compositions have extremely large $d_{33}$ coefficients, as high as 2000-3000 pC/V [17]; (3) The ferroelectric domain structure at MPB was found to be hierarchical domain-within-domain structure and the domain size is nanoscale [18-21]; (4) A new phase, monoclinic phase was found at MPB by high resolution XRD and new phase diagrams containing monoclinic phase has been built based on the experimental results[22-24]. There are three kinds of monoclinic phases observed in experiments: $M_A$, $M_B$ and $M_C$. Different from tetragonal, rhombohedral and orthorhombic phases, the polarization vector of these monoclinic phases is not confined to a single direction, rather they can rotate within the mirror plane as shown in Fig. 1.5. A new phase diagram of PZT system containing the newly discovered monoclinic phase is shown in Fig. 1.6 [23].
Fig. 1.5 The three monoclinic phases at MPB of different systems found in experiments.

The shaded planes indicate the mirror planes of these monoclinic phases.
Fig. 1.6 A new diffusionless phase diagram of PbZrO3-xPbTiO3 solid solutions containing the monoclinic phase. FC, FR, FT and FM represent the cubic, rhombohedral, tetragonal and monoclinic phases, respectively.

Theoretically, there are two prevailing models on the origin of high piezoelectricity at MPB based on experimental observations. The first one can be called “polarization rotation model” [25] and is based on the newly discovered monoclinic phase. The polarization rotation model insists that at MPB the polarization vector can rotate in a plane upon application of the external field for monoclinic phase but polarization vector can only be in a single direction for T or R phase. As a result, polarization rotation in the monoclinic phase is the main origin of high piezoelectric coefficients at MPB. The second model can be called “adaptive phase model” [26] and is based on the adaptive
phase theory in martensite [27]. The adaptive phase model insists that at MPB there are still T or R phase but due to the small polarization anisotropy and therefore the small domain wall energy, the domain size at MPB is nanoscale and the piezoelectricity is high at MPB because it is easy for the domain wall to move for the nanodomain structure at MPB because of the small polarization anisotropy. Both models gain many supports from both experiments and theories [28-37] and the real origin of good piezoelectric property at MPB is still under serious debate.

Therefore, despite the extensive research, there are still many issues unclear about the domain structure and piezoelectric property at ferroelectric MPB.

First of all, as experimentally observed, the domain structure at MPB is hierarchical domain-within-domain structure and the domain size is found to be nanoscale. But what is the phase of these nanodomains? Is it monoclinic phase as the polarization rotation model believes, or is it T or R phase as the adaptive phase model thinks? CBED experiments can study the symmetry of domains at nanoscale, however, it is difficult to differentiate T (R) with M phase and different authors give different results [18,21,36-38]. Also, the CBED experiments use the thin foil samples and thus the CBED results might not reflect bulk samples. To resolve this issue, the domain structure of unpoled samples at ferroelectric MPB compositions is studied by phase field methods in Chapter 5.
Secondly, does the good piezoelectric property at MPB originate from the polarization rotation through monoclinic phase as expected by polarization rotation model or the domain wall movement of T or R nanodomains as predicted by the adaptive phase model? To answer this question, the domain structure and piezoelectric property of poled samples at MPB compositions are explored by phase field methods in Chapter 6.
Chapter 2: Phase field methods

Phase field method is a simulation method good at predicting microstructure evolution at mesoscale. Since its advent, it has been widely used in all fields of materials science such as solidification [39], spinodal decomposition [40], multicomponent interdiffusion[41], martensitic phase transformation [42], ferroelectric phase transition [43], ferromagnetic phase transition [44] and many other fields. The phase field method describes any arbitrary microstructure in terms of order parameters and writes the total free energy of a system in terms of the order parameters. The evolution of microstructure can thus be obtained by minimizing the total free energy. In this chapter we will give a brief introduction on these elements of phase field methods. For more detailed reviews of phase field method, see references [45-47].

2.1 Order parameters

An order parameter is a parameter which can characterize a phase transition. For example, for a liquid to solid phase transition, the order parameter can be density; for a paraelectric to ferroelectric transition, the order parameter can be the average polarization; for spinodal decomposition, the order parameter can be composition. The order parameters can be classified into two kinds, conserved and nonconserved. An example of conserved
order parameter is composition and an example of nonconserved order parameter is polarization.

The microstructure of a system, both structural/compositional domains and interfaces, can then be described by these order parameters. The order parameter is homogeneous in the compositional/structural domain but continuous across the interface. In another word, phase field methods adopt the so called diffused interface approach as a contrast to the sharp interface approach used in conventional approaches to simulate microstructural evolutions. Any arbitrary microstructure of a material can be characterized by appropriate order parameters in phase field methods.

2.2 Energy formulation

After choosing appropriate order parameters, the total free energy of a system can then be written in terms of the order parameters. The total free energy can include several terms, two of which are common to almost all systems: the chemical free energy and the gradient energy. In addition to these two terms, other energies such as elastic energy, electrostatic energy and magnetostatic energy can also take effect in some solid state phase transitions.
2.2.1 Chemical free energy

The chemical free energy describes the local contribution to the free energy from the small volume unit within which the chemical property can be considered homogeneous. The chemical free energy can have many forms depending on the order parameter field and the phase transition studied.

For phase separation, for example, the chemical free energy of a system can be modeled by ideal solution model, regular solution model, or subregular solution model. In these models, the chemical free energy can be written as a function of composition with parameters such as interaction parameters and temperature in it. These parameters can be measured directly from experiments.

For many solid-state phase transformations, the chemical free energy of a system can be modeled by Landau theory. The chemical free energy is expressed as a polynomial of order parameters. All the terms in the expansion must be invariant with respect to the symmetry operations of the high-symmetry phase. Usually the terms after the 4th or 6th order will be truncated. For example, for a cubic to tetragonal ferroelectric phase transition, the order parameter can be the polarization vector \((P_1, P_2, P_3)\) and the chemical free energy of the system can be written as Landau polynomial shown below:

\[
\begin{align*}
 f_{\text{chemical}} (P_1, P_2, P_3) &= \alpha_1 (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} (P_1^4 + P_2^4 + P_3^4) \\
 &+ \alpha_{12} (P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) + \alpha_{111} (P_1^6 + P_2^6 + P_3^6) + \\
 &+ \alpha_{112} (P_1^4 (P_2^2 + P_3^2) + P_2^4 (P_1^2 + P_3^2) + P_3^4 (P_1^2 + P_2^2)) + \alpha_{113} (P_1^2 P_2^2 P_3^2)
\end{align*}
\]  

(1)
2.2.2 Gradient energy

The gradient energy describes the local contribution to the free energy from the inhomogeneity among neighboring units. The gradient energy is nonzero only at the interface and is the origin of the interfacial energy.

The gradient energy can contain many terms but high order terms are usually neglected and the most common type of the form of gradient energy is as follows:

\[ f_{\text{gradient}} = \frac{1}{2} \kappa (\nabla \eta)^2 \]  

(2)

in which \( \kappa \) is the gradient coefficient and \( \eta \) is the order parameter of the system.

For more complicated case, for example, when two kinds of order parameter, both conserved and nonconserved, exist for a system, the gradient energy may have more complicated forms.

2.2.3 Elastic, electrostatic and magnetostatic energy

The elastic, electrostatic and magnetostatic energies are all free energy terms coming from long range interaction.

In a coherent microstructure, in order to form a coherent interface, the two lattices must be adjusted to each other along the interface through elastic displacements of atoms from
their regular positions. Therefore elastic energy is generated. Khachaturyan and coauthors developed a field approach formulation of the elastic energy for an arbitrary two-phase system [48]. Under the assumption that the difference between the elastic modulus of different phases is negligible, i.e., homogeneous elasticity, the elastic energy can be written as a close form shown below:

$$ f_{\text{elastic}} = \frac{1}{2} \int \frac{d^3 k}{(2\pi)^3} K_{ijkl} \tilde{\epsilon}_{ij}^0 \tilde{\epsilon}_{ij}^{*} $$

(3)

in which \( \int \) is an integral over \( k \) space, \( K_{ijkl} = C_{ijkl} - n_m C_{ijmn} \Omega_{np} C_{klpq} n_q \), \( \Omega_{ik} = (C_{ijkl} n_j n_i)^{-1} \), \( n = k / k_0 \), \( \epsilon_{ij}^0 \) is the stress-free transformation strain.

Similarly, electrostatic energy and magnetostatic energy can also be written in a close form as shown below [40,44]:

$$ f_{\text{electro}} = \frac{1}{2} \int \frac{d^3 k}{(2\pi)^3} \frac{n_i n_j}{\epsilon_0} \tilde{P}_i \tilde{P}_j^* $$

(4)

$$ f_{\text{magnet}} = \frac{1}{2} \int \frac{d^3 k}{(2\pi)^3} \frac{n_i n_j}{\mu_0} \tilde{M}_i \tilde{M}_j^* $$

(5)

in which \( \epsilon_0 \) and \( \mu_0 \) are the permittivity and permeability of vacuum, respectively, \( P \) and \( M \) are polarization and magnetization, respectively.
2.3 Evolution equations

Microstructure evolution is a process that minimizes the total free energy. Thus after the total free energy has been written in terms of order parameters, the evolution of microstructure can be obtained by solving the following two equations, for conserved and nonconserved order parameters, respectively.

\[
\frac{\partial c_i(r,t)}{\partial t} = \nabla M_{ij} \nabla \frac{\delta F}{\delta c_j(r,t)} \\
\frac{\partial \eta_p(r,t)}{\partial t} = -L_{pq} \frac{\delta F}{\delta \eta_q(r,t)}
\]

in which \(c\) and \(\eta\) is the order parameter, \(F\) is the total free energy, \(r\) is the space coordinate, \(t\) is time, \(M_{ij}\) and \(L_{pq}\) are kinetic coefficients.

Equation (6) is called Cahn-Hillard equation and is for conserved order parameters like concentration while equation (7) is called time dependent Ginsberg-Landau equation and is for nonconserved order parameters like strain, polarization, etc.
Chapter 3: Interdiffusion microstructure maps (IMMs) for high temperature coatings

As stated in Chapter 1, how the interdiffusion microstructure varies with initial end alloy compositions has importance to the design of high temperature coatings. Interdiffusion microstructure maps can help answer this equation and will be explored in this chapter.

3.1 Introduction of IMMs

An Interdiffusion Microstructure Map, or IMM, is a graphical representation drawn on a two-dimensional isothermal phase diagram. It shows how the interdiffusion microstructure changes when one dual-alloy composition varies while the other dual-alloy composition is fixed. As such it has relevance to a number of obvious applications such as high temperature coatings and metal joining.

Previous work [5, 49] has shown that a particular type of interdiffusion microstructure can be found over an area of compositions on a two-dimensional phase diagram section. The areas for different types are contiguous, meeting along a line. The lines can be straight or curved and form nodes where three or more lines meet. Special microstructures are associated with both the lines and the nodes.
Meisenkothen and Morral [49] found five interdiffusion microstructures on their experimental IMM for Ni-Cr-Al dual-alloys in which the fixed alloy contained $\gamma + \gamma'$ phases and the varied alloy contained $\gamma + \beta$ phases. The five microstructures occurred in five areas of the $\beta + \gamma$ region of an isothermal section of the phase diagram. The areas were separated by five lines that met at a node. It was shown that the lines had to meet at the node in order to satisfy the fundamentals of IMMs.

Boettinger and coauthors [5] found three interdiffusion microstructures on a model 3-component IMM in which the fixed alloy contained $\alpha + \beta$ phases and the varied alloy contained just the $\alpha$ phase. The IMM was derived using a simplified phase diagram and ternary kinetic equations for velocities between layers. The three areas were separated by three lines that met at a node.

How one interdiffusion microstructure changes to another was analyzed in both papers. Both found that there are two mechanisms for microstructures changing from one type to another. In one mechanism a boundary velocity changes from positive to negative. In the other, velocities of interfaces on either side of a layer become equal [5, 49]. In this case, the thickness of the layer will be zero due to the equal velocities of the two interfaces (remember that at the initial state, the thickness of all layers except the two end layers is zero.) and thus the microstructure will change to a new type which does not form such a
layer. Note that the above findings on model systems as well as the conclusions made in this paper are based on the assumption of local equilibrium.

Following reference [49], the line separating two areas, for example, area x and y, on the IMM will be referred to as line x/y in accord with the areas on either side of the line. And the boundary velocity will be denoted by $v$ with the boundary type indicated on the superscripts. For example, the velocity of boundary $\alpha>\beta$ will be denoted by $v^{\alpha>\beta}$.

### 3.2 Models and simulations

In the current work, four model systems with different thermodynamic and kinetic parameters are simulated.

In all the four systems, element A, B and C form regular solutions with each other. The free energy functions of the systems are:

$$G_m = RT(X_A \ln X_A + X_B \ln X_B + X_C \ln X_C) + I_{AB} X_A X_B + I_{BC} X_B X_C + I_{AC} X_A X_C + I_{ABC} X_A X_B X_C$$  \hspace{1cm} (8)$$

where $G_m$ is the molar free energy, $R$ the gas constant, $T$ the temperature, $I_{AB}$, $I_{AC}$, $I_{BC}$ and $I_{ABC}$ are the regular solution interaction parameters and $X_A$, $X_B$ and $X_C$ are the mole fractions of A, B and C.

In the phase field approach, any microstructure in a ternary system can be characterized by two composition fields $X_B$ and $X_C$, which are spatially continuous and time dependent.
The temporal evolutions of the concentration of element B and C are obtained by solving the generalized Cahn-Hilliard diffusion equations under the assumption of constant molar volume, $V_m$ [8, 41, 50-51]:

\[
\frac{1}{V_m} \frac{\partial X_B}{\partial t} = \nabla \left[ M_{BB} \nabla \left( \mu_B - \mu_A - 2\kappa_{BB} \nabla^2 X_B - 2\kappa_{BC} \nabla^2 X_C \right) \right] + \nabla \left[ M_{BC} \nabla \left( \mu_C - \mu_A - 2\kappa_{BC} \nabla^2 X_B - 2\kappa_{CC} \nabla^2 X_C \right) \right] \tag{9}
\]

\[
\frac{1}{V_m} \frac{\partial X_C}{\partial t} = \nabla \left[ M_{CB} \nabla \left( \mu_B - \mu_A - 2\kappa_{BB} \nabla^2 X_B - 2\kappa_{BC} \nabla^2 X_C \right) \right] + \nabla \left[ M_{CC} \nabla \left( \mu_C - \mu_A - 2\kappa_{BC} \nabla^2 X_B - 2\kappa_{CC} \nabla^2 X_C \right) \right] \tag{10}
\]

in which $t$ is time, $\mu_A$, $\mu_B$, and $\mu_C$ are the chemical potential of element A, B, and C, respectively [obtained from equation (8)], $\kappa_{BB}$, $\kappa_{CC}$, and $\kappa_{BC}$ are the gradient energy coefficients, $M_{BB}$, $M_{BC}$, $M_{CB}$, and $M_{CC}$ are the chemical mobilities defined in the laboratory reference frame, which are related to the atomic mobilities $\beta_j$ by the following equations [52, 53]:

\[
M_{ij} = \frac{1}{V_m} \sum_{k=1}^{n} (\delta_{ik} - X_i)(\delta_{jk} - X_j)X_i \beta_k \tag{11}
\]

in which $\delta$ represents the Kronecker delta and therefore $\delta_{ik} = 1$ when $i=k$ and $\delta_{ik} = 0$ when $i \neq k$.

Thermodynamic and kinetic parameters used in the four systems S1-S4 are listed in Table 3.1. There both the gradient energy coefficients and atomic mobility are given in dimensionless forms: $\tilde{\beta}_i = \frac{\beta_i}{\beta}$ and $\tilde{\kappa}_{jk} = \frac{\kappa_{jk}}{\Delta f^{2}}$, in which $\tilde{\beta}_i$ and $\tilde{\kappa}_{jk}$ are the reduced form of $\beta_i$ and $\kappa_{jk}$, respectively, while $\beta = 1.0 \text{ m/s/N}$, $\Delta f = 10.0 \text{ kJ/mol}$, and $L$, the length
scale, was adjusted so that the diffuse interface width was a length of three to five grid points. How these parameters are chosen is explained below.

<table>
<thead>
<tr>
<th>System</th>
<th>( I_{AB} ) kJ/mol</th>
<th>( I_{BC} ) kJ/mol</th>
<th>( I_{AC} ) kJ/mol</th>
<th>( \tilde{\kappa}_{BB} )</th>
<th>( \tilde{\kappa}_{CC} )</th>
<th>( \tilde{\kappa}_{BC} )</th>
<th>( \tilde{\kappa}_{CB} )</th>
<th>( \tilde{\beta}_A )</th>
<th>( \tilde{\beta}_B )</th>
<th>( \tilde{\beta}_C )</th>
<th>( T ) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>0.25</td>
<td>0.25</td>
<td>0.125</td>
<td>0.125</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1083</td>
</tr>
<tr>
<td>S2</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>0.25</td>
<td>0.25</td>
<td>0.125</td>
<td>0.125</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1083</td>
</tr>
<tr>
<td>S3</td>
<td>17</td>
<td>20</td>
<td>23</td>
<td>20</td>
<td>0.51</td>
<td>0.6</td>
<td>0.42</td>
<td>0.42</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>S4</td>
<td>20</td>
<td>20</td>
<td>40</td>
<td>20</td>
<td>0.4</td>
<td>0.4</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.1: Thermodynamic and Kinetic Parameters for the \( \beta/\alpha + \gamma \) Dual-Alloy Systems

The interaction parameters and temperatures given in the table yield the isothermal ternary phase diagrams shown in Fig. 3.1(a)-(d). The phase diagrams for system S1 and S2 in Figs. 3.1(a) and 3.1(b) are identical, but the simulations differ because the atomic mobility of component A in S2 is double that of the other mobilities. In real alloy systems like in Ni-Al-Cr system, the highest atomic mobility can be several times of the lowest atomic mobility, so the change of atomic mobility in system S2 compared to system S1 is reasonable. The phase diagrams for S3 and S4 differ both from each other and from S1 and S2 because their interaction parameters differ as well as their temperatures. The temperatures differ to ensure that each single phase region in the phase diagram is large enough to clearly view the diffusion path. The gradient energy coefficients were calculated using the regular solution model derived by Dregia and
Wynblatt [54]. Their model is a function of the binary interaction parameters, but not the ternary interaction parameter, $I_{ABC}$.

Fig. 3.1(a)-(d) The isothermal phase diagrams for systems S1-S4 considered in the phase field simulations. The parameters used in each system are listed in Table 3.1.

In previous work on IMMs the starting dual-alloy microstructures were of the following type; $\alpha/\alpha+\beta$ and $\alpha+\gamma/\alpha+\beta$, in which the alloy on the left was varied. In the current work, starting dual-alloy microstructures were of the type $\alpha+\gamma/\beta$ in which the
composition of $\alpha+\gamma$ alloys were varied. The fixed $\beta$ alloy compositions for all four systems are given in Table 3.2. The $\alpha+\gamma$ dual-alloy compositions were varied within the $\alpha+\gamma$ region in the phase diagram. Only half of the two-phase region was simulated for system S1, because the phase diagram is symmetrical and the atomic mobilities of the elements are equal. As a result the interdiffusion microstructures on either side of the $\alpha+\gamma$ region must be similar except that the $\alpha$ and $\gamma$ phases will interchange in order that $\alpha$ is the matrix phase on the $\alpha$-rich side of the $\alpha+\gamma$ region and $\gamma$ is the matrix phase on the $\gamma$-rich side of the $\alpha+\gamma$ region. Therefore the microstructures must invert at the mid-line of the two-phase region.

<table>
<thead>
<tr>
<th>System</th>
<th>$X_A$</th>
<th>$X_B$</th>
<th>$X_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.15</td>
<td>0.7</td>
<td>0.15</td>
</tr>
<tr>
<td>S2</td>
<td>0.15</td>
<td>0.7</td>
<td>0.15</td>
</tr>
<tr>
<td>S3</td>
<td>0.25</td>
<td>0.7</td>
<td>0.05</td>
</tr>
<tr>
<td>S4</td>
<td>0.249</td>
<td>0.75</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Table 3.2: Fixed $\beta$ Alloy Compositions for the $\beta/\alpha+\gamma$ Dual-Alloy Systems

The initial microstructure in all the simulations consists of fine secondary phase particles randomly distributed in the matrix phase. The microstructure was produced by letting random fluctuations evolve into precipitates [55-56]. In the simulations, Eqs. (9) and (10) are solved numerically in two-dimension using a system of $2048 \times 128$ grid points. Periodic boundary conditions are applied along both dimensions.
3.3 Metrics and Topology of IMMs

The IMMs for system S1-S4 are shown in Figs. 3.2-3.5. The IMM given in Fig. 3.2 is based on the simulated interdiffusion microstructures for system S1. Fig. 3.2(a) shows the distribution of the seven types of interdiffusion microstructures which are labeled as areas I to VII on the $\alpha+\gamma$ region of the phase diagram. The areas are separated with dotted lines that have been sketched between the data points. In addition the seven microstructures are listed in shorthand notation on the figure key. Fig. 3.2(b) is an enlargement of just the IMM. It shows more clearly how the seven IMM lines meet at a seven-line node. Also, it lists, on the figure key, the limiting microstructures associated with lines. Similarly, Figs 3.3-3.5 give details of IMMs for systems S2-S4.
Fig. 3.2 (a) The IMM for system S1 based on phase field simulation results are sketched on the phase diagram with dashed lines. The microstructure type and shorthand notation is given for each area between the dashed lines. (b) An enlarged $\alpha + \gamma$ area of the IMM shown in (a) is shown along with line designations and the microstructure on the lines.
Fig. 3.3 (a) The IMM for system S2 based on phase field simulation results are sketched on the phase diagram with dashed lines. The microstructure type and shorthand notation are given for each field between the dashed lines. (b) An enlarged $\alpha+\gamma$ area of the IMM shown in (a), along with line designations and microstructures on the lines.
Fig. 3.4 (a) The IMM for system S3 based on phase field simulation results are sketched on the phase diagram with dashed lines. The microstructure type and shorthand notation are given for each field between the dashed lines. (b) An enlarged $\alpha + \gamma$ area of the IMM shown in (a), along with line designations and microstructures on the lines.
Fig. 3.5 (a) The IMM for system S4 based on phase field simulation results are sketched on the phase diagram. The IMM consists of only one field with one type of microstructure. (b) An enlarged $\alpha+\gamma$ area of the IMM shown in (a).

Changing the thermodynamic and kinetic parameters can change both the metrics and the topology of an IMM as shown by the results of the S2-S4 simulations. For example in Fig. 3.3, although the topology of the IMM for system S2 remains the same, i.e., consisting of
seven microstructure types connected by seven lines and a seven-line node, two microstructure types (VIII and IX) are different from those shown in Fig. 3.2 for system S1. In Fig. 3.4, the topology of the IMM for system S3 changes to one consisting of five microstructure types connected by five lines and a five-line node. Four types of interdiffusion microstructure in Fig. 3.2 (type I, II, III, VII) disappear with two new types (type X, XI) appearing. As shown in Fig. 3.5, the IMM for system S4 now contains only one field, a field with the type VI microstructure.

The reasons for why the IMM changes with modifications of the interaction parameter and the atomic mobility are complex, even for a ternary system. Changing the interaction parameters will change the phase diagram, $\kappa_{ij}$, and the thermodynamic term driving diffusion. It was shown in previous work [53] why this changes the IMM. There it was shown qualitatively that the diffusion path depends on the relative location of phase diagram boundaries and the major eigenvector direction of the initial alloys. The eigenvector direction can steer the diffusion path toward or away from a nearby phase boundary. Unfortunately the major eigenvector of a single phase ternary system is a complex function that depends on 12 mixed kinetic and thermodynamic terms that result from the diffusivity being the product of a kinetic mobility matrix and a thermodynamic Hessian. Therefore explicit reasons for how and why the IMM changes with input parameters are elusive.
3.4 Mechanisms of microstructure change from one type to another on an IMM

How the interdiffusion microstructures were analyzed and the mechanisms for how one type of interdiffusion microstructure changes to another are explained in the following using the example of system S1.

Fig. 3.6 illustrates the mechanism for the interdiffusion microstructure change from type III to IV. It is seen in Figs. 3.6(a)-(e) that as B is added to the initial $\alpha+\gamma$ alloy composition, the velocity of the boundary between $\gamma$ and $\beta$ gradually decreases and changes from being positive in area III, where $v^{\gamma\beta}>0$, to being negative in area IV where $v^{\gamma\beta}<0$. On the III/IV line, $v^{\gamma\beta}=v^{\gamma\beta}=0$ and the microstructure becomes $\alpha+\gamma<\gamma|\beta$. This mechanism of microstructure type change has been reported also in references [5,49,57] and can be found in IMM for systems S2 and S3 as shown in Fig. 3.3 and 3.4.
Fig. 3.6 Change of interdiffusion microstructure from type III to type IV as component B is added to the \( \alpha + \gamma \) composition of the dual-alloys for system S1. At a composition between (d) and (e) a line is crossed on the IMM. On the line the velocity of the \( \gamma / \beta \) interface is zero, yielding a unique microstructure for the line given as \( \alpha + \gamma \leq \gamma / \beta \).
Fig. 3.7 illustrates the mechanism for the interdiffusion microstructure change from type IV to V. It can be seen in Figs 3.7(a)-(e) that when A is added to the initial $\alpha+\gamma$ alloy composition, the velocity of boundaries on either side of the $\gamma$ layer, $v_{\alpha+\gamma}^\gamma$ and $v_{\gamma}^\beta$, gradually become equal to each other. On the IV/V line in Fig. 3.7(e), $v_{\alpha+\gamma}^\gamma$ equals $v_{\gamma}^\beta$, the $\gamma$ layer disappears, and the microstructure becomes $\alpha+\gamma<\beta$. On passing from area IV to V the microstructure inverts from $\alpha+\gamma<\gamma<\beta$ to $\alpha+\gamma<\alpha<\beta$. This change can be deduced from the symmetry of the thermodynamic and kinetic parameters. Accordingly, as the composition moves from line IV/V into area V toward increasing amounts of $\alpha$, the microstructure changes in reverse order from (e) to (a) except that the $\alpha$ and $\gamma$ phases are interchanged. A schematic figure for microstructure type V is shown in Fig. 3.7(f). This mechanism of microstructure type change has apparently not been reported before. The mechanism also appears in the IMMs for systems S2 and S3 as shown in Fig. 3.3 and 3.4.
Fig. 3.7 Change of the interdiffusion microstructure from type IV to type V as the initial \( \alpha + \gamma \) composition of the dual-alloys in area IV approach the line IV/V for system S1. Fig. 3.7(e) is the microstructure on IV/V line, which is \( \alpha + \gamma < \beta \). Due to the symmetry of the thermodynamic and kinetic parameters, the line acts like a mirror plane between areas IV and V. Accordingly, as the composition moves into area V toward increasing amounts of \( \alpha \), the microstructure changes in reverse order from (e) to (a) except that the \( \alpha \) and \( \gamma \) phases are interchanged. Fig. 3.7(f) is a schematic figure showing type V microstructure.
Fig. 3.8 illustrates that the interdiffusion microstructure cannot change directly from type I to III. Therefore an intermediate microstructure, shown in 3.8(e) has been added between the 3.8(d) type I microstructure and the 3.8(f) type III microstructure. The 3.8(e) microstructure is labeled type II and in shorthand notation is $\alpha + \gamma | \alpha + \gamma > \gamma > \beta$. As explained before the type II microstructure could not be clearly simulated because the $\gamma$ layer was too small to be clearly detected, but the intermediate microstructure is necessary to go continuously from I to II and then from II to III with a variation in dual-alloy composition. The mechanism is that Type II changes to type I on line I/II when $v^{\alpha + \gamma > \gamma} = v^{\gamma > \beta}$ and the microstructure becomes $\alpha + \gamma | \alpha + \gamma > \beta$ and type II changes to type III on line II/III when $v^{\alpha + \gamma > \gamma} = 0$ and the microstructure becomes $\alpha + \gamma | \gamma > \beta$. 
Fig. 3.8 Change of the interdiffusion microstructure from type I to type III showing that an intermediate type II area is needed for system S1. Although no simulation was obtained for the type II area, a cartoon of the area microstructure has been sketched in frame (e).

In addition, the need for a type II microstructure is suggested by a diffusion path analysis. Fig. 3.9 gives the diffusion path of the five dual-alloys with initial compositions along the AC edge in Fig. 3.1 (a). The compositions in the $\alpha+\gamma$ layer were calculated from the
simulations by averaging the composition in a window that was 128 grid points wide by 256 grid points high except in the new $\alpha+\gamma$ layer whose composition was calculated by averaging all the compositions in that layer.

Fig. 3.9 Diffusion paths of five dual-alloys along the A-C axes in Fig. 3.1(a) for system S1.
It is shown in Fig. 3.9 that the lowest diffusion path in the figure has a type I microstructure. As component C is added to the initial $\alpha + \gamma$ alloy composition, which raises the diffusion path on the figure, the average composition of the new $\alpha + \gamma$ layer changes gradually from layer with a high volume fraction of $\alpha$ phase (about 50%) to a low volume fraction of $\alpha$ phase. When the alloy composition reaches line II/III, the amount of $\alpha$ becomes zero and the layer contains only $\gamma$ phase.

Fig. 3.10 gives a schematic diagram of three diffusion paths that are similar to diffusion paths in Fig. 3.9. Their initial alloy compositions are labeled x, y and z. The composition of alloy x is on line I/II, alloy y is in area II and z is in area III. It can be seen that a continuous series of diffusion paths could be drawn for initial alloys with compositions that vary between areas I and III via area II.
Fig. 3.10 Diffusion paths showing that there must be an intermediate microstructure II between microstructures I and III for system S1. Alloy x: type I microstructure on line I/II ($\alpha+\gamma|\alpha+\gamma>\beta$); alloy y: type II microstructure ($\alpha+\gamma|\alpha+\gamma>\gamma>\beta$); alloy z: type III microstructure ($\alpha+\gamma<\gamma>\beta$).
3.5 Fundamentals of IMMs

When drawing or interpreting interdiffusion microstructure maps from experimental or simulated microstructural data, several fundamental properties of IMMs deduced from the above and previous work and must be followed. These fundamentals are:

1. Variations in microstructure metrics (e.g. amounts of phases, thickness of layers, etc) can occur over each area in an IMM, but the microstructure as depicted by shorthand notation, which only gives phases present in each layer, remains the same as long as the dual-alloy thicknesses are much longer than the diffusion distance for the heat treatment.

2. At lines along the edges of an area, the microstructure attains a limiting form which has a shorthand notation that may or may not be different from that of the area as a whole. For example the amount of a phase might go to zero at the line and thus disappear from the microstructure. Variations in microstructure metrics can occur along the line, but the shorthand notation remains the same.

3. Areas on either side of a line must have the same limiting microstructure on the line. In that way the microstructure can vary continuously when traversing from one side of the line to the other.

4. Areas surrounding a node as well as lines contacting the node must have the same limiting microstructure at the node. In that way the microstructure can vary continuously when crossing the node. Currently it has been established that 3, 5, and 7 line nodes are
possible and also that no lines or nodes (only one microstructure type exists in the map) is possible as well.

5. It is possible for the interdiffusion microstructure, as expressed in shorthand notation, to be the same as the initial microstructure. However to date that has only been seen at nodes of an IMM drawn for dual alloys containing two or three phases.

6. Three mechanisms have been identified for how microstructures change when crossing an IMM line. In the following examples the line microstructure is given in {} brackets:

a. The velocity of a boundary changes direction.

(e.g. \( \alpha + \gamma | \alpha + \gamma > \beta \rightarrow \{ \alpha + \gamma | \alpha > \beta \} \rightarrow \alpha + \gamma < \alpha > \beta \))

b. The velocity of two boundaries become equal thereby eliminating a layer.

(e.g. \( \alpha + \gamma | \alpha + \gamma > \beta \rightarrow \{ \alpha + \gamma | \alpha + \gamma > \beta \} \rightarrow \alpha + \gamma | \alpha + \gamma > \beta \))

c. The velocity of two boundaries become equal and an inversion of the microstructure occurs in which two phases (\( \alpha \) and \( \gamma \) in the example) interchange places in the shorthand notation.

(e.g. \( \alpha + \gamma < \gamma < \beta \rightarrow \{ \alpha + \gamma < \beta \} \rightarrow \alpha + \gamma < \alpha < \beta \))
7. It must be possible to rationalize changes in microstructure when crossing an IMM line by a continuous change in the diffusion path as a function of the variable alloy composition.

3.6 Summary

Fundamentals of interdiffusion microstructure maps have been listed based on previous experimental and computational work as well as the current phase field simulations. It has now been established empirically through simulations that IMMs can have 1, 3, 5, or 7 areas. However no reason has been given for why, in principle, that 2, 4, 6, 8 or more areas could not occur. Also, all lines separating the areas have met at a single node, thereby creating 3, 5 and 7 line nodes in the IMMs. In all these examples the node microstructure was that of the initial dual alloy.

Different IMMs ranging from a complicated one containing seven areas and a simple one containing only one area can be obtained when changing the thermodynamic and/or kinetic parameters used in the simulations. Two mechanisms of microstructure change that had previously been reported were found in the current simulations as well as a new mechanism that results in a microstructure inversion. Also, it was found that a seven-line node could occur on an IMM in addition to the three and five-line nodes reported before.
In all examples the nodes were found to have the same microstructure, when expressed in shorthand notation, as the initial dual-alloy before interdiffusion occurs. This work is meant to provide an understanding of interdiffusion microstructure maps and can be a guide for how to organize experimental or simulated interdiffusion data on multicomponent and multiphase dual-alloys.
Chapter 4: Type n boundaries ($n \geq 3$) in interdiffusion microstructures of high temperature coatings

Type n boundaries are interface boundaries that n phases changes on crossing that boundary in diffusion couples of ternary or higher order systems [9]. Type n boundaries ($n \geq 3$) have characteristics that make them unexpected in nature. However, they do occur in experiments. In this chapter, the characteristics of type n boundaries are introduced and also type n boundaries are simulated by phase field methods. Furthermore, the effects of eigenvector direction of effective diffusivity on the formation of type n boundaries are explored.

4.1 Characteristics of type n boundaries ($n \geq 3$)

Type $n$ boundaries ($n \geq 3$) have characteristics that make them unexpected in nature. However there is sufficient experimental evidence that they can form and even be favored over boundaries with a type number less than $n$. 
One characteristic of type \( n \) boundaries is that various equilibria can exist at them. These are listed in Table 4.1. For ternary systems only one equilibrium is possible, but for quaternary and quinary systems there are two possibilities. By inspection of Table I it can be seen that for an \( n \)-component system the number of possible equilibria is given by the floor function \( \lfloor n/2 \rfloor \), which is \( n/2 \) rounded off to the smallest integer.

<table>
<thead>
<tr>
<th>Components</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Possible equilibria at a Type-( n ) boundary</td>
<td>( \alpha = \beta + \gamma )</td>
<td>( \alpha = \beta + \gamma + \delta )</td>
<td>( \alpha = \beta + \gamma + \delta + \epsilon )</td>
<td>( \alpha = \beta + \gamma + \delta + \epsilon + \zeta )</td>
<td>( \alpha = \beta + \gamma + \delta + \epsilon + \zeta + \eta )</td>
<td>( \alpha = \beta + \gamma + \delta + \epsilon + \zeta + \eta )</td>
<td></td>
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<tr>
<td>( \alpha + \beta + \gamma = )</td>
<td>( \alpha + \beta + \gamma + \delta = )</td>
<td>( \alpha + \beta + \gamma + \delta + \epsilon = )</td>
<td>( \alpha + \beta + \gamma + \delta + \epsilon + \zeta = )</td>
<td>( \alpha + \beta + \gamma + \delta + \epsilon + \zeta + \eta = )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total possible equilibria</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>( \left\lfloor \frac{n}{2} \right\rfloor )</td>
</tr>
</tbody>
</table>

Table 4.1 Equilibria at type-\( n \) Boundaries in \( n \)-component systems

Another characteristic of type \( n \) boundaries is that in order for them to form, the diffusion path for a diffusion couple, which is a line when plotted on a phase diagram of any dimensions, must pass through a special feature on the phase diagram. A special feature is defined here as any feature that cannot be intersected by a random line. Although
diffusion path lines are not random, it is less likely that they will intersect a special feature than other features on a phase diagram.

The only features that can be intersected by a line in an $n$-component phase diagram at constant temperature and pressure are $n-1$ or $n-2$ dimensional ($(n-1)D$ or $(n-2)D$). For example in a ternary system, $n$ equals three and only 1D and 2D features can be crossed by a random line, i.e. only single-phase, two-phase and three-phase regions as well as phase boundaries can be crossed on a ternary isotherm. Corners of tie-triangles, however, are points (0D). Therefore they cannot be crossed by a random line.

For $n$ greater than three, the $(n-1)D$ features are volumes and $(n-2)D$ features are planes. These planes define all phase boundaries on the phase diagram and are also known as zero-phase fraction planes (ZPF planes) [54]. Other features on a phase diagram can be viewed as intersections of ZPF planes. For example in a quaternary system the edges of a tie-tetrahedron are the intersection of two ZPF planes and the corners of the tetrahedron are intersections of three ZPF planes. These are special features because they are $(n-3)D$ and $(n-4)D$, respectively. In other words they are lines and points, which cannot be intersected by a random line in 3D space.

It is significant that all type $n$ boundaries when $n \geq 3$ are formed by a diffusion path passing through either one or two special features. For example it is shown in Table III that a type 5 boundary is formed when there is an $\alpha+\beta$ region on one side of the boundary
and a $\gamma + \delta + \varepsilon$ region on the other side. The $\alpha + \beta$ equilibrium is represented by a tie-line while the $\gamma + \delta + \varepsilon$ is represented by a tie-triangle. These are 1D and 2D features, respectively. However only 3D and 4D features can be intersected by a random line. In this case a random line would have to intersect two special features to form that type 5 boundary. However with the other type 5 boundary, which has an $\alpha = \beta + \gamma + \delta + \varepsilon$ equilibrium, only the 0D $\alpha$ corner of the 4D tie-simplex is a special feature. Fig. 4.1 shows schematically why type 3 and two kinds of type 4 boundaries have to pass through a special feature. Fig. 4.1(a) shows that for type 3 boundaries, the diffusion path has to pass from one corner of the tie-triangle to the non-intersecting edge of it, in which the corner of the tie-triangle as represented by the red symbol is a special feature. Fig. 4.1(b) and (c) show that for type 4 boundaries, the diffusion path either has to pass from one corner of the tie-tetrahedron to the non-intersecting edge of it, or it has to pass from one edge of the tie-tetrahedron to the non-intersecting edge of it. Both the corner of the tie-tetrahedron and the edge of the tie-tetrahedron are special features as analyzed above.
Fig. 4.1 Special features that the diffusion paths of type 3 boundaries and two kinds type 4 boundaries have to pass through. (a) The diffusion path of type 3 boundaries has to pass from the corner of the tie-triangle to the non-intersecting edge of it, in which the corner of the tie-triangle is a special feature. (b) and (c) The diffusion path of type 4 boundaries either has to pass from the corner of the tie-tetrahedron to the non-intersecting edge of it or it has to pass from one edge to the non-intersecting edge of it. Both the corner and the edge of the tie-tetrahedron are special features.

By inspection of Table III it is apparent that at least one feature associated with each equilibrium is more than \((\lfloor n/2 \rfloor - 1)D\). This dimension will always be smaller than \((n-2)D\) that is required for intersection by a random line, because:

\[
(n-2) - \left(\left\lfloor \frac{n}{2} \right\rfloor - 1\right) > 0 \quad \text{for all } n \geq 3
\]  

(12)
The fact that type $n$ boundaries require that diffusion paths must cross special features is what makes them unexpected and explains why they are rarely seen in practice. However if they do occur they may be difficult to eliminate by small composition variations. The reason is that there must have been a kinetic reason that makes the diffusion path pass through the special features. As a result it might require a substantial change in alloy composition to free it from the special features.

A few type $n$ boundaries can be found in the experimental literature on diffusion couples. They tend to be rare, but can be readily identified on a micrograph by counting the number of phases that change on crossing the boundary. For example, a type 3 boundary can be seen in Fig. 5 of reference [59] where the interdiffusion region of a Zn-Mg-Al diffusion couple contains a boundary with a $\gamma$ region on one side and a $\delta + \lambda$ region on the other side. Another example of a type 3 boundary can be seen in Fig. 10 of reference [60] where the interdiffusion region of a Ni-Cr-Al diffusion couple contains a boundary with a $\alpha + \beta$ region on one side and a $\gamma$ region on the other side. A third example of a type 3 boundary can be seen in Fig. 5 of reference [61] where the interdiffusion region of an Fe-Ni-Al diffusion couple contains a boundary with a $\beta + \beta'$ region on one side of the boundary and a $\gamma$ region on the other side.

Only one other experimental report of type 3 boundaries was found in this investigation. That was in an M.S. thesis [2] that was reprinted as a NASA report [62]. This was the only report found where a number of diffusion couples were prepared that contained type
3 boundaries. The study gives unequivocal evidence via both microstructures and microprobe traces that a series of ternary Ni-Cr-Al diffusion couples with different starting compositions all had diffusion paths that passed through the $\gamma'$ corner of the $\gamma+\beta+\gamma'$ tie-triangle. In some diffusion couples the initial end-alloys contained $\gamma+\beta$ and $\gamma+\gamma'$ phases. In that case the diffusion path left the $\gamma+\gamma'$ region to enter the $\gamma'$ region of the phase diagram before crossing the $\gamma+\beta+\gamma'$ tie-triangle into the $\gamma+\beta$ region.

By all accounts type 3 boundaries, and especially type $n$ boundaries for $n>3$ (which were not found in the existing literature), are uncommon in $n$-component diffusion couples. What is common are type 0 boundaries that form whenever a multiphase region straddles the initial interface of a diffusion couple [63], two kinds of type 1 boundaries that differ from each other depending on their direction of motion, and type 2 boundaries that may be the most common type boundary of all [64]. Type 0, 1, and 2 boundaries have been modeled before by 1D finite difference programs [65], while Type 0 and 1 have been modeled by 2D phase field simulations [8,41,50,51,66]. The simulations had special value because they were responsible for theories that were developed later as to why and when they will occur [5, 67]. Currently, simulations of type 3, 4 or higher order boundaries have not yet been reported by any method. It was the goal of this work to create a phase field model that could simulate type $n$ boundaries in both ternary and quaternary systems, both to show that it could be done and to confirm predictions about type $n$ boundaries.
4.2 Models and Simulations

Regular solution thermodynamics and phase field kinetics were combined to calculate 2D microstructures for model A-B-C and A-B-C-D systems using techniques similar to those described in reference [8]. The thermodynamics of both the ternary and the quaternary systems are given by a single thermodynamic function that has miscibility gaps to create single-phase regions in each corner of the phase diagram. The ternary model free energy:

\[
G_m = RT \sum_{i=1}^{3} X_i \ln X_i + I_1 \sum_{i=1}^{3} \sum_{j>i} X_i X_j + I_2 X_1 X_2 X_3
\]  

(13)

and the quaternary model free energy:

\[
G_m = RT \sum_{i=1}^{4} X_i \ln X_i + I_1 \sum_{i=1}^{4} \sum_{j>i} X_i X_j + I_2 \sum_{i=1}^{4} \sum_{j>i} \sum_{k>j} X_i X_j X_k + I_3 X_1 X_2 X_3 X_4
\]  

(14)

In both equations \( G_m \) is the molar free energy, \( R \) the gas constant, \( T \) the temperature, \( I_1, I_2, \) and \( I_3 \) are regular solution interaction parameters, and \( X_i \) are mole fractions of components A, B, C, and D.

Evolution of 2D microstructures was obtained by solving the Cahn-Hilliard generalized diffusion equations under the assumption of constant molar volume \( V_m \):

\[
\frac{1}{V_m} \frac{\partial X_i}{\partial t} = \nabla \sum_{j=1}^{n-1} \left[ M_{ij} \nabla (\mu_j - \mu_n - 2 \sum_{k=1}^{n-1} \kappa_{jk} \nabla^2 X_k) \right] \quad (i = 1, 2, ..., n - 1)
\]  

(15)
where $V_m$ is the molar volume, $t$ the time, $\mu$ the chemical potential, $\kappa_{jk}$ are gradient energy coefficients that are related to the interfacial energy between different phases, and $M_{ij}$ are chemical mobilities defined in the laboratory reference frame by

$$M_{ij} = \sum_{k=1}^{n} (\delta_{jk} - X_i)(\delta_{jk} - X_j)X_k \beta_k$$  \hspace{1cm} (16)

Where, $\delta$ is the Kronecker delta and $\beta_i$ are atomic mobilities of each element in the alloy. Equation (16) was derived for an n-component system using a similar procedure to that used in reference [68] to obtain the chemical mobilities for ternary systems. In both equations (15) and (16) n is three or four depending on the number of components considered in the simulations.

Compositions and designations of alloys used in the simulations are given in Table 4.2 along with the initial phases present in the alloys. The combination of alloys used in each diffusion couple simulation are given in Table 4.3 along with the atomic mobilities, $\beta_i$, and gradient energy coefficients, $\kappa_{jk}$. The atomic mobilities and gradient energy coefficients are given in dimensionless forms as introduced in [41]: $\hat{\beta}_i = \frac{\beta_i}{\beta}$ and $\hat{\kappa}_{jk} = \frac{\kappa_{jk}}{\Delta f l^2}$, in which $\hat{\beta}_i$ and $\hat{\kappa}_{jk}$ are the reduced form of $\beta_i$ and $\kappa_{jk}$, respectively, in which $\beta = 1\text{m/s/N}$, $\Delta f = 10\text{kJ/mol}$, and $l$ is the unit length of the system.
The isothermal section of the ternary phase diagram at $T=1083K$ with $I_1=I_2=20kJ/mol$ is shown in Fig. 4.2. The parameters were chosen so that a three-phase system with a moderately sized tie-triangle in the center of the phase diagram is obtained. The three
corners of the Gibbs triangle are the pure elements A, B and C. The three single phases at the corners of the tie-triangle in the phase diagram are denoted as $\alpha$, $\beta$, and $\gamma$, respectively. The dotted lines in the two phase regions are tie-lines while the triangle in the center of the phase diagram is the three-phase tie-triangle.

The isothermal section of the quaternary phase diagram at $T=1022K$ with $I_1=20kJ/mol$, $I_2=30kJ/mol$ and $I_3=50kJ/mol$ is shown in Fig. 4.3. Again, the parameters were chosen to obtain a suitable phase diagram with a moderately sized tie-tetrahedron. The four corners of the equilateral tetrahedron are the pure elements A, B, C, and D. Four single phase
regions appear at the corners of the tetrahedron, which are labeled as $\alpha$, $\beta$, $\gamma$, and $\delta$, respectively. The tie-tetrahedron is plotted by thick dotted lines. The ternary phase diagram is the same on each face of the tetrahedron because of the symmetry of the free energy expression. In Fig. 4.3 the phase boundaries are only shown on the front faces for clarity.

Fig. 4.3 Isothermal phase diagram of the model A-B-C-D system at 1022K.
4.3 Type 3 boundaries in ternary systems

The simulation results of type 3 boundaries are presented. The effect of atomic mobilities on the formation of type 3 boundaries through the change of eigenvector of effective diffusivity is analyzed. A comparison of our simulated diffusion paths with experimentally observed ones is also given.

4.3.1 Formation of type 3 boundaries

Simulated microstructures of the T1/T2 diffusion couple are given in Fig. 4.4. The initial microstructure here and in all the simulations consists of fine secondary phase particles randomly distributed in the matrix phase. The microstructure was produced by letting random fluctuations evolve into precipitates [55,56]. The thin grey line in the middle of the diffusion couple marks the original interface, while the white, black and grey particles are the $\alpha$, $\beta$ and $\gamma$ phases, respectively.
Fig. 4.4 Microstructural evolution of the T2/T1 diffusion couple. The white, black, and grey phases represent $\alpha$-, $\beta$- and $\gamma$, respectively. The microstructure in shorthand notation is $\alpha+\gamma|\alpha+\gamma >\beta >\alpha+\beta$ with a Type-3 boundary given by $\alpha+\gamma >\beta$. The rectangle in Fig. 4.4(c) shows the window size used to determine the local average composition in two phase region.
The diffusion path of couple T1/T2 is plotted on the ternary isotherm in Fig. 4.5. It is given by closed circles and two dashed lines. The grey closed circles are the initial average compositions of the end-alloys, while the black closed circles are compositions within the interdiffusion zone. The composition in a two-phase region relatively far from the original interface was calculated by averaging the composition in a window that was 128 grid points wide by 256 grid points high. The window is shown in Figure 4.4 by the rectangle on the left of the diffusion couple. Compositions in single-phase regions and in two-phase regions near the original interface were obtained by averaging the composition in a window that was 1 grid point wide by 256 grid points high. The dashed lines are tie-lines along which there was a jump in composition at a boundary. The arrows at T1 and T2 represent the major eigenvectors of the effective diffusivity of alloys T2 and T1. The effective diffusivity was approximated by the rule of mixtures equation:

\[
[D]^{\text{eff}} = f_\alpha [D_\alpha]^{\text{eff}} + f_\beta [D_\beta]^{\text{eff}}
\] (17)

In equation (17) \(f_\alpha\) and \(f_\beta\) are the volume fractions of phases \(\alpha\) and \(\beta\) that were obtained by applying the lever rule to the phase diagram. \([D_\alpha]^{\text{eff}}\) and \([D_\beta]^{\text{eff}}\) are effective diffusivities of phases \(\alpha\) and \(\beta\) calculated using equations [3] and [5] in reference [69]:

\[
[D_i]^{\text{eff}} = [D_i] \begin{bmatrix}
\frac{\partial X'_i}{\partial X_\beta} & \frac{\partial X'_i}{\partial X_\gamma} \\
\frac{\partial X'_i}{\partial X_\gamma} & \frac{\partial X'_i}{\partial X_\alpha}
\end{bmatrix} 
\] (i = \(\alpha\) or \(\beta\)) (18)

where \([D_i]\) is the diffusivity of single phase \(\alpha\) or \(\beta\), \(X'_j\) is the mole fraction of
component j in phase i when it is in equilibrium with the second phase, $\bar{X}_j$ is the average mole fraction of component j in a differential volume element containing more than one phase.
Fig. 4.5 The diffusion path of the T2/T1 diffusion couple. Grey dots are the initial alloy composition; black dots give the average composition in a fixed frame of the interdiffusion zone microstructure; and dashed lines give jumps in composition at boundaries between regions. The grey arrows indicate the calculated major eigenvector direction of the effective diffusivity of the initial alloys. The diffusion path crosses the $\beta$ corner of the tie-triangle to form a Type-3 boundary. The inset figure at the right top shows how the diffusion path enters the $\beta$ region and crosses the $\beta$ corner.
Using the shorthand notation introduced in reference [9], the microstructure developed after diffusion in the T1/T2 couple is $\alpha + \gamma | \alpha + \gamma > \beta > \alpha + \beta$. In both the microstructure and the diffusion path one can see the $\alpha + \gamma > \beta$ type 3 boundary.

### 4.3.2 Effect of atomic mobility on the formation of type 3 boundaries

The diffusion path and microstructures for a second ternary diffusion couple, T1/T2*, are given in Fig. 4.6. As shown in Tables 4.2 and 4.3 the alloy compositions are the same for both T1/T2 and T1/T2*, but the atomic mobilities in T1/T2 and T1/T2* are different. The result is a different eigenvector direction and a different microstructure, $\alpha + \gamma | \alpha + \gamma > \alpha + \beta$, in which there is no type-3 boundary. The notation is written indicating that there is a type 0 boundary at the initial interface of the couple. Such a boundary is predicted by local equilibrium theory, but in this case there is insufficient data with too much scatter to prove whether or not it has formed.
Fig. 4.6 Diffusion path and microstructure of T2/T1* diffusion couple. (a) Grey dots are the initial alloy composition; black dots give average compositions across the interdiffusion zone; and dashed lines give jumps in composition at boundaries between regions. The grey arrows indicate the calculated major eigenvector direction of the effective diffusivity of the initial alloys. (b) Microstructure of T2/T1 diffusion couple after t=1.0x10^7 time steps. The white, black, and grey represent α, β and γ-phase, respectively. The microstructure is α+γ|α+γ>α+β without the formation of Type-3 boundary.
4.3.3 Comparison with experiments

Figure 4.7(a) gives diffusion paths and interdiffusion microstructures for two Ni-Cr-Al diffusion couples from reference [2]. The paths were obtained from couples with initial alloys C1/S2 and C4/S2. As can be seen in the figure, initial alloys C1 and C4 are both in the $\gamma+\beta$ region of the phase diagram while S2 is in the $\gamma+\gamma'$ region. Both diffusion paths pass through the $\gamma'$ corner of the $\gamma+\beta+\gamma'$ tie-triangle to form a type 3 boundary even though their paths leading up to the $\gamma+\beta$ side of the tie-triangle are quite different. The diffusion paths are the same as in the reference except that the C1/S2 path has been altered somewhat in order to reflect the jump in average composition at the type 0 boundary. The jump is apparent in the experimental microstructure as seen in the microstructure, because of the abrupt change in volume fraction at the initial interface.
Fig. 4.7 Comparison of diffusion paths obtained by experiments and simulation. (a) Experimental diffusion paths of two diffusion couples C1/S2 and C4/S2 prepared from Ni-Al-Cr alloys [2]. The diffusion path for C1/S2 is modified from that in reference [2] as explained in the text. (b) Simulated diffusion paths of two diffusion couples T2/T1 and T3/T1 prepared from model A-B-C alloys. To simplify the comparison the corner alloys in 4.7(b) are labeled γ, β, γ′ instead of α, β, γ. Both C1/S2 and T2/T1 have a γ+β|γ+β>γ′>γ+γ′ microstructure, while both C4/S2 and T3/T1 have a γ+β<γ>γ+β>γ′>γ+γ′ microstructure although the microstructure morphologies obtained by experiment differ from those obtained by simulation.
Figure 4.7(b) gives similar diffusion paths and interdiffusion microstructures for couples T2/T1 and T3/T1 that were predicted for the model A-B-C system. In this figure the phases at the corners were labeled \( \gamma, \beta, \) and \( \gamma' \) instead of \( \alpha, \beta, \) and \( \gamma \) to simplify the comparison. With this change in notation the microstructures have the same shorthand description: \( \gamma+\beta|\gamma+\beta>\gamma+\gamma' \) for the C1/S2 and T2/T1 couples and \( \gamma+\beta<\gamma>\gamma+\beta>\gamma'>\gamma+\gamma' \) for the C4/S2 and T3/T1 couples.

In order to obtain the simulations in Fig. 4.7(b), the atomic mobilities were chosen so that the eigenvector direction of the \( \alpha+\beta \) effective diffusivity favored the formation of a type 3 boundary. The calculation of the effective diffusivity of \( \alpha+\beta \) using equation (17) and (18) is an approximation that is most accurate when the \( \alpha \) and \( \beta \) phases form as laths that are parallel to the flux direction. However in these simulations it can be seen that the second phase forms as particles, which would tend to reduce the effect of the phase with the higher diffusivity. Nevertheless the eigenvector direction that was calculated from the effective diffusivity is similar to the eigenvector direction suggested by the simulated diffusion path.

Figs. 4.5 and 4.6 show how the atomic mobilities were chosen to make the eigenvector direction favor the formation of a type 3 boundary. By changing the atomic mobilities in alloy T1/T2* to those indicated in Table 4.3 for T1/T2, the diffusion path was aligned to enter the \( \gamma' \) region. From there the path could pass through the \( \gamma' \) corner of the tie-triangle.
Once the mobilities had been adjusted in order to obtain a diffusion path like the experimental C1/S2 couple, the only change needed to form a path in the simulation that was similar to the C4/S2 couple was to move the initial composition from T2 to T4. Although a more quantitative comparison would require using thermodynamic and kinetic databases for the Ni-Cr-Al system as was done in reference [8], this example shows that the phase diagram and the eigenvector directions of the diffusivities combined with phase field simulations are robust predictors of the interdiffusion microstructure.

4.4 Type 4 boundaries in quaternary system

The diffusion path for couple Q1/Q2 in the quaternary system is plotted using two methods in Figure 4.8. In Fig. 4.8(a) it is plotted on a 3-D diagram, while in Fig. 4.8(b) the path is projected onto the 2-D X_B-X_C plane. The only phase diagram information on the projection is the location where the diffusion path crosses a phase diagram feature. These are indicated by open circles on the projections. The simulation microstructures are given in Fig. 4.9 for time steps of t=0.0, 1.0x10^6 and 4.0x10^6. From both the diffusion path and the microstructures it can be seen that the interdiffusion regions and boundaries are given by α+δ<β+γ|β+γ and that the β+γ region grows into the α+δ region to form a Type-4 boundary. As in the previous example a type 0 boundary has been included in the notation even though there was insufficient data to prove it was there.
Fig. 4.8 Diffusion path of the Q1/Q2 diffusion couple. (a) The diffusion path represented in a 3D diagram. As in the ternary diagrams, grey dots give the initial alloy composition; black dots give average compositions in the interdiffusion zone; dashed lines give jumps in composition at boundaries between regions; and open circles indicate where certain phase diagram features are crossed. (b) The diffusion path given as a 2-D projection on the $X_B$–$X_C$ plane. In both (a) and (b) it can be seen that the diffusion path jumps between edges of the tie-tetrahedron, which yields a Type-4 boundary.
Fig. 4.9 Microstructure evolution of Q1/Q2 diffusion couple illustrating the formation of a Type-4 boundary when the diffusion path jumps between edges of a tie-tetrahedron. The dark grey, black, white and light grey shades represent $\alpha$, $\beta$, $\gamma$ and $\delta$ phases, respectively. The microstructure in shorthand notation is $\alpha+\delta<\beta+\gamma|\beta+\gamma$ with a Type-4 boundary between $\alpha+\delta$ and $\beta+\gamma$. The initial compositions and diffusion path of the diffusion couple are shown in Fig. 4.8.

Like couple Q1/Q2, the diffusion path for couple Q3/Q4 in the quaternary system is plotted using two methods. In Fig. 4.10(a) it is plotted on a 3-D diagram, while in Fig. 4.10(b) it is projected onto the 2-D $X_B-X_C$ plane. The simulation microstructures are given in Fig. 4.11 for $t=0$, $1.0\times10^6$ and $4.0\times10^6$ time steps. From both the diffusion path and the microstructures it can be seen that the interdiffusion regions and boundaries are
given by $\alpha+\beta+\gamma|\alpha+\beta+\gamma>\delta$ and that the $\alpha+\beta+\gamma$ region grows into the $\delta$ region to form a second kind of Type-4 boundary. In this case the type 0 boundary is clearly indicated on the diffusion path by the jump in composition at the initial interface.
Fig. 4.10 Diffusion path of the Q3/Q4 diffusion couple. (a) The diffusion path represented in a 3D diagram. Grey dots are the initial alloy composition; black dots give average compositions across the interdiffusion zone; dashed lines give jumps in composition at boundaries between regions; the open circles indicate where phase diagram features are crossed. (b) The diffusion path given as a 2-D projection on the $X_B$–$X_C$ plane. From both (a) and (b), the diffusion path jumps from a face to a corner of a tie-tetrahedron which corresponds to the formation of a second Type-4 boundary.
Fig. 4.11 Microstructure evolution of Q3/Q4 diffusion couple illustrating the formation of a Type-4 boundary when a diffusion path jumps from a face to a corner of a tie-tetrahedron. The dark grey, black, white and light grey shades represent $\alpha$, $\beta$, $\gamma$ and $\delta$ phases, respectively. The microstructure in shorthand notation is $\alpha+\beta+\gamma|\alpha+\beta+\gamma>\delta$ with a Type-4 boundary between between $\alpha+\beta+\gamma$ and $\delta$. The initial composition and diffusion path of the diffusion couple is shown in Fig. 4.10.

4.5 Summary

This work has introduced the concept of type n boundaries in $n$-component systems and demonstrated the ability of phase field models to simulate them for $n=3$ and 4. Selected simulated diffusion paths were comparable to experimental ones reported in the literature for Ni-Cr-Al diffusion couples. In addition it was shown that the number of different
kinds of type n boundaries that can form is given by the floor function \( \lfloor n/2 \rfloor \) and that all these require that the diffusion path must pass through special features on a phase diagram. Special features are those that cannot be intersected by a random line like corners of tie-triangles in a ternary system or corners or edges of a tie-tetrahedron in a quaternary system. The requirement that all type n-boundaries must pass through special features combined with the observation that few type 3 boundaries and no type 4 boundaries were found in the experimental literature suggests that type n boundaries in n-component systems will be seen infrequently. In addition any type of boundary that is greater than or equal to three will have the same problem. Therefore only type 0, 1, and/or 2 boundaries should be seen in most interdiffusion zones that form under local equilibrium conditions. However if the conditions are right for such unexpected boundaries to form, these results suggest that they may persist even if the diffusion couple compositions are varied. Finally, the simulations show that both the eigenvector direction of the initial alloy diffusivity and the composition of the initial alloys relative to the phase diagram can determine whether or not a type n boundary will form.
Chapter 5 Domain Structure at ferroelectric MPB

In this chapter, first previous works on the domain structure at MPB will be reviewed and then the models used in the phase field simulation will be given as well as the results of the simulation.

5.1 Previous works on the domain structure of ferroelectric MPB

The domain structure at ferroelectric MPB is of great interest to scientists in the ferroelectric field because researchers want to know whether the good piezoelectric property at MPB is related to the domain structure at MPB or not. Indeed, compared to domains at compositions away from MPB, the domain structure at MPB is found to be peculiar as stated below.

Through TEM observation, it was found that at MPB compositions, it is domain-within-domain hierarchical structure and the size of the domains is in nanoscale [20, 70] while no hierarchical domain structure was ever found for normal ferroelectrics with composition away from MPB and the domain size of normal ferroelectrics are always in micron size. Fig. 5.1 shows a typical hierarchical domain-within-domain structure at an
MPB composition of PZT system. It is seen that there are nanodomains embedded in the high temperature tetragonal macrodomains. The nano size of the domains at MPB can be explained by the small polarization anisotropy at MPB, as Khachaturyan has proved [71]. That is, at MPB, the energy difference of different phases (C, T, R, O and M phases) is small and as a result, the domain wall energy is small compared to normal ferroelectrics [71]. Therefore, the domain size should also be very small and goes to nanoscale level.

Fig. 5.1[18] Hierarchical domain-within-domain structure at an MPB composition of PZT system. The domains embedded in the high temperature tetragonal macrodomains are in nanoscale size.

Although the hierarchical domain-within-domain structure has been well observed by experiments, such domain structure has never been predicted by simulations. Also, the
phases of these nanodomains, is still controversial despite extensive work on it. Through CBED observations, some authors claimed that the nanodomains are of tetragonal or rhombohedral phase [35-37] while others found that monoclinic phase is also possible [18,38,72]. From thermodynamic point of view, it is proved that the conventional 6th order Landau free energy cannot generate the monoclinic phase [73]. But when the 6th order Landau free energy is extended to 8th or higher order, monoclinic phase is possible [73]. Therefore, either from experiments or from theories, it is difficult to differentiate whether the nanodomains at MPB are conventional tetragonal and rhombohedral or the newly discovered monoclinic phase.

In the current work, we aim to simulate the hierarchical domain structure at MPB and explore the phase of the domains at MPB through phase field simulations.

### 5.2 Models and Simulations

The phase field models used in the current simulation will be given as well as the parameters used in the simulations.

#### 5.2.1 Phase field models

The model system considered is a ferroelectric solid solution with C (cubic) → T and C→R transformations at the two ends of the solid solutions, respectively. The domain
structure is described by spatial distribution of spontaneous polarization \( \mathbf{P}=(P_1,P_2,P_3) \).
The total free energy of the system includes the bulk chemical free energy, domain wall energy and long range elastic and electrostatic interaction energies, i.e.,

\[
F = \int_V \left( f_{\text{bulk}} + f_{\text{grad}} + f_{\text{elas}} + f_{\text{elec}} \right) dV .
\]  

(19)

The bulk chemical free energy, \( f_{\text{bulk}} \), is approximated by a 6\(^{th}\) order Landau polynomial

\[
f_{\text{bulk}} = \alpha_i \sum_{i=1}^{3} P_i^2 + \alpha_{ij} \left( \sum_{i=1}^{3} P_i^2 \right)^2 + \alpha_{ijl} \left( \sum_{i=1}^{3} P_i \right)^2 + \frac{1}{2} \alpha_{ijl} \sum_{i,j,l=1,2,3} \epsilon_{ijl} P_i^2 P_j^2 + \alpha_{ijl} \sum_{i,j,l=1,2,3} \epsilon_{ijl} P_i^2 P_j^2 + \alpha_{ijl} \sum_{i,j,l=1,2,3} \epsilon_{ijl} P_i^2 P_j^2 P_l^2
\]  

(20)

where \( \alpha_i, \alpha_{ij}, \alpha_{ijk} \) are the expansion coefficients depending on temperature \( T \) and composition \( c \). The gradient energy density, \( f_{\text{grad}} \), in Eq. (19) is described by

\[
f_{\text{grad}} = \frac{1}{2} G_{ij} \sum_{i=1}^{3} \nabla P_i , \quad \text{where } G_{ij} \text{ is the gradient energy coefficient.}
\]

The elastic energy density, \( f_{\text{elas}} \), is calculated by

\[
f_{\text{elas}} = \frac{1}{2} C_{ijkl} \epsilon_{ij} \epsilon_{kl} = \frac{1}{2} C_{ijkl} (\epsilon_{ij} - \epsilon_0^0)(\epsilon_{kl} - \epsilon_0^0) , \quad \text{where } \epsilon_0^0, \epsilon_{ij}, \epsilon_0^0
\]

denote the elastic strain, total strain and spontaneous strain, respectively. The spontaneous strain is related to the polarization \( \mathbf{P} \) by

\[
\epsilon_0^0 = \xi Q_{ijkl} P_i P_j
\]

where \( Q_{ijkl} \) is the electrostrictive coefficient of the single crystal and \( \xi \) is a parameter introduced to describe the magnitude of electrostrictive coefficients. The electrostatic energy density, \( f_{\text{elec}} \), is described by

\[
f_{\text{elec}} = -\frac{1}{2} E_i P_i , \quad \text{where } E_i \text{ denotes the inhomogeneous electrical field due to dipole-dipole interaction [74]. It can be obtained by solving the electrostatic equilibrium equation } D_{ij} = 0 \text{ where } D_i \text{ is the electric displacement given by } D_i = \epsilon_0 (\eta \epsilon_b) E_i + P_i
\]

where \( \epsilon_0 \) is the dielectric permittivity of vacuum, \( \epsilon_b \) is the background dielectric.
permittivity [75,76] and \( \eta \) is a parameter introduced to describe the magnitude of background dielectric permittivity.

The temporal evolution of the spontaneous polarization field can be obtained by solving the time-dependent Ginzburg-Landau equation

\[
\frac{dP(r,t)}{dt} = -M \frac{\delta F}{\delta P_i(r,t)}
\]

where \( M \) is the kinetic coefficients and \( t \) is time.

### 5.2.2 Parameters used in the simulations

Both \( \xi \) and \( \eta \) are set to be 1.0 unless otherwise specified. The elastic constants and electrostrictive coefficients adopt the experimentally measured values of BaTiO\(_3\) [77]. The Landau coefficients in Equation (20) used in our simulations are modified from the measured values of pure BaTiO\(_3\) [77] by assuming certain temperature- and composition-dependence of \( \alpha_{i1} \) and \( \alpha_{i2} \) that determine the order of ferroelectric phase transition and \( \alpha_{i12}, \alpha_{i13} \) that determine the polarization anisotropy along with \( \alpha_{i2} \). The temperature and composition dependence of them are as follows: \( \alpha_i = \alpha_i^0(T-T_C) \),

\[
\alpha_{i1} = \alpha_{i1}^0|T-T_P| + \alpha_{i11}^0 |c-c_p|, \quad \alpha_{i11} = \alpha_{i11}^0, \quad \alpha_{i12} = \alpha_{i12}^0(T-T_P) + \alpha_{i12}^{00}(c-c_p), \quad \alpha_{i12} = \alpha_{i12}^0(c-c_p),
\]

and \( \alpha_{i13} = \alpha_{i13}^0(c-c_p) \), where \( \alpha_{i1}^0, \alpha_{i11}^0, \alpha_{i12}^0, \alpha_{i13}^0, \alpha_{i111}, \alpha_{i112}, \alpha_{i113} \) are constants, \( T_P, c_p \) are the temperature and composition at the triple point, \( T_C = T_C^{00}+bc \) in which \( T_C^{00} \) is the Curie temperature at \( c=0 \) and \( b \) is a constant. The constants in these equations are (in SI units...
unless otherwise specified): \( \alpha_1^0 = 4.124 \times 10^5 \), \( \alpha_{11}^0 = -5 \times 10^5 \), \( \alpha_{111}^0 = -5 \times 10^8 \), \( \alpha_2^0 = 8 \times 10^5 \), \( \alpha_{12}^0 = 8 \times 10^8 \), \( \alpha_{111}^0 = 1.294 \times 10^9 \), \( \alpha_{1111}^0 = 1.5 \times 10^9 \), \( \alpha_{11111}^0 = 7.5 \times 10^5 \), \( c_v = 0.4 \), \( T_v = 105^\circ C \), \( T_c = 65^\circ C \), \( b = 100^\circ C \). Based on the experimental observations [16], the triple point is also a tricritical point for their system. It is seen from our Landau polynomial that the value of \( \alpha_1 \) determines the order of cubic (C) to tetragonal (T) transition (second order if \( \alpha_1 > 0 \) and first order if \( \alpha_1 < 0 \)) and the value of \( \alpha_1 + \alpha_{12} / 3 \) determines the order of C to rhombohedral (R) transition (second order if \( \alpha_1 + \alpha_{12} / 3 > 0 \) and first order if \( \alpha_1 + \alpha_{12} / 3 < 0 \)). We set \( \alpha_1 = \alpha_{11}^0 |T-T_v| + \alpha_{11}^0 |c-c_v| \) and \( \alpha_{12} = \alpha_{12}^0 (T-T_v) + \alpha_{12}^0 (c-c_v) \) where \( \alpha_{11}^0 = -5 \times 10^5 \), \( \alpha_{11}^0 = -5 \times 10^8 \), \( \alpha_{12}^0 = 8 \times 10^5 \), \( \alpha_{12}^0 = 8 \times 10^8 \) so that at the triple point \( (c_v=0.4, T_v=105^\circ C) \) both \( \alpha_1 \) and \( \alpha_1 + \alpha_{12} / 3 \) vanish but \( \alpha_1 < 0 \) for all other C to T transition point and \( \alpha_1 + \alpha_{12} / 3 < 0 \) for all other C to R transition point, that is, the triple point is also set to be a tricritical point. \( \alpha_1, \alpha_{12} \) and \( \alpha_{13} \) are set to be: \( \alpha_{12} = \alpha_{12}^0 (T-T_v) + \alpha_{12}^0 (c-c_v) \) and \( \alpha_{13} = \alpha_{13}^0 (c-c_v) \) where \( \alpha_{12}^0 = 8 \times 10^5 \), \( \alpha_{12}^0 = 8 \times 10^8 \), \( \alpha_{13}^0 = 1.5 \times 10^9 \), \( \alpha_{13}^0 = 7.5 \times 10^5 \) so that there is a T to R transition near the triple point and the polarization anisotropy is small near the MPB. Taking \( c=0.5 \) and \( T=20^\circ C \), for example, the six Landau coefficients (all in SI units) are: \( \alpha_1 = -3.9 \times 10^4 \), \( \alpha_{11} = -9.3 \times 10^7 \), \( \alpha_{12} = 1.2 \times 10^7 \), \( \alpha_{111} = 1.3 \times 10^9 \), \( \alpha_{112} = 1.5 \times 10^8 \), \( \alpha_{113} = 7.5 \times 10^7 \). It is seen that \( \alpha_{12} = -\alpha_{11} / 8 \), \( \alpha_{112} = \alpha_{111} / 9 \), \( \alpha_{113} = \alpha_{111} / 17 \) and thus the three anisotropy terms are small and the energy cost for changing the orientation of polarization is low, which is an indication that the polarization anisotropy is small near the MPB. In reference [77], it is
seen that for pure BaTiO3, $\alpha_{12} \approx -6\alpha_{11}$, $\alpha_{112} \approx -4.5\alpha_{111}$, and $\alpha_{113} \approx -8\alpha_{111}$ (note that the form of Landau polynomial in ref. [74] is different from ours and thus the Landau coefficients need to be rearranged before making a comparison). The magnitude of anisotropy coefficients in pure BaTiO3 are comparable to that of isotropy coefficients, which indicate that the polarization anisotropy is much larger in pure BaTiO3 as compared to that at MPB in our simulated system. Therefore, with our choices of Landau parameters, the phase equilibria of the system include C→T and C→R transformations at the two ends of the solid solution (c=0 and c=1), respectively, and an MPB between T and R phase starting from the triple point $(c_d, T_{tr})$ that is also set to be a tricritical point where the free energy of all phases (C, T and R) are equal. The polarization anisotropy is small at MPB because according to our choices of the Landau parameters, near the MPB the anisotropy coefficients $\alpha_{12}$ and $(\alpha_{112}, \alpha_{113})$ are small as compared to the corresponding isotropy coefficients $\alpha_{11}$ and $\alpha_{111}$, respectively. Our system can be regarded as an approximation of BaTiO3 based BZT-BCT system as reported in reference [16] where it is found that the triple point is also a tricritical point and the polarization anisotropy at the MPB is small.

The domain wall energy for 90° domain walls is assumed to be ~0.1 J/m², which yields a length scale $l_0$ (the numerical grid size) of ~2.0 nm. The simulations were carried out in both 2D and 3D and the simulation cell sizes are $512 \times 512$ and $128 \times 128 \times 128$, respectively, with periodic boundary conditions applied in all dimensions.
5.3 Formation of monoclinic nanodomains at MPB

The simulated hierarchical domain structure in 2D is shown and the phases of the domains are analyzed. Also, the effect of elastic and electrostatic energies on the formation of monoclinic phase at MPB is explored. Finally, a 3D simulation result is given.

5.3.1 Hierarchical nanodomain structure at MPB

Fig. 5.2 shows the microstructure evolution upon step cooling of a system with \( c = 0.5 \) in 2D. At \( T = 45^\circ C \), the domain structure is a typical polytwin consisting of different variants of the T phase (Fig. 5.2(a)). At \( T = 15^\circ C \), new domains start to appear at the twin boundaries of the existing T domains (Fig. 5.2(b)). When \( T \) reaches \(-45^\circ C\) (Fig. 5.2(c)), the high-temperature polytwin domains are filled with new nanodomains, forming a domain-in-domain hierarchical structure. Such a hierarchical structure is stable with further cooling down to \(-115^\circ C\) and \(-265^\circ C\), as shown in Figs. 5.2(d) and (e), respectively. The simulated hierarchical domain structures (Fig 5.2(c)-(e)) agree well with those found in PZT and BZT-BCT having compositions at MPB by direct TEM observations [18-21].
Fig. 5.2 (a-e) Domain structure evolution (in 2D) in a ferroelectric system with composition c=0.5 upon cooling. (f) The change of angle between polarization vector on the dashed line shown in Fig. 5.2(a) and [1,0] direction at different temperatures.
5.3.2 Monoclinic phase

By examining closely the polarization vector in Figs. 5.2(a)-5.2(e), it is found that the nanodomains in Fig. 5.2(c) are neither T (P₁=0 or P₂=0) nor R (|P₁| = |P₂|), instead, they are M (|P₁| ≠ |P₂|, P₁≠0, P₂≠0). To better illustrate this, Fig. 5.2(f) shows the angle $\theta$ between vector [P₁, P₂] and direction [1,0] across the dashed line shown in Fig. 2(a) at different temperatures. It thus can be seen in Fig. 5.2(f) that as temperature decreases the change of $\theta$ in the microstructures shown in Fig. 5.2(a)-(e) indicates a T (Fig.5.2(a))→T+M (Fig.5.2(b))→M (Fig.5.2(c))→M+R (Fig.5.2(d))→R (Fig.5.2(f)) transition and the M phase in Figs. 5.2(c) is homogeneous in each nanodomain. Although it is still controversial whether the nanodomains in the hierarchical structure observed by TEM are T(R) or M phase, more and more experimental evidences show that they are either pure M phase or T(R)+M mixture [18,19,72,78], which supports our predictions.

Fig. 5.3(a) shows the phase diagram of the system constructed from the simulation results. Fig. 5.3(b) shows how the transition temperatures in Fig. 5.3(a) are defined through the variation of the volume fraction of the M phase ($V_I$) with temperature using a solution of $c=0.5$ as an example. The transition temperatures of T→M ($T_{T-M}$) and M→R ($T_{M-R}$) transitions in Fig. 5.3(a) are defined on the curve in Fig. 5.3(b) by the points where the volume fraction of the M phase exhibits the most rapid increase and decrease, respectively. The temperature at which the M phase starts to coexist with the T phase ($T_{allT}$) and the temperature at which the M phase no longer coexists with the R phase
(T\textsubscript{allR}) are defined by the temperatures at which the slope of the curve at respectively the high and low temperature ends starts to deviate significantly from zero.

It is seen from Fig. 5.3(a) that there is a single M phase field in between the T- and R-phase fields, separated by two two-phase fields. The phase diagram constructed based on the simulation results resembles those measured by experiments for PZT and PMN-PT systems [24,79], although the phase boundary between M and R was not reported in the experiments.

Fig. 5.3 (a) Phase diagram calculated by 2D phase field simulations. (b) Definition of the transition temperatures in (a).
5.3.3 Effect of electrostatic and elastic energies on the formation of monoclinic nanodomains

According to a 6th order Landau free energy polynomial, an M phase should not be expected because the free energy landscape does not have any extrema point at the M phase except on the MPB line where the Landau free energy of all three phases are equal [73]. However, the M phase does form in our simulations within a relatively wide temperature or composition range around the MPB. This suggests that it is the elastic and/or electrostatic interactions considered in our simulations that stabilize the M phase.

In order to explore the effect of elastic energy on the formation of the M nanodomain structure, $\xi$ is decreased to 0.75 while the other parameters are kept the same for the same cooling process. By decreasing $\xi$ the electrostriction is decreased and hence the elastic energy will take less effect during the formation of domain structures. Similar simulations are carried out by increasing $\eta$ to 2 while the other parameters are kept the same. By increasing $\eta$ the electric field caused by inhomogeneous polarization is decreased and thus the electrostatic energy will take less effect during the formation of domain structures. The temperature ranges for the existence of the M phase (the range between the red and blue line in Fig. 5.3(a)) as defined above in Fig. 5.3(b) are plotted for both cases in Figs. 5.4(a) and 5.4(b), respectively. It can be seen that the temperature range is narrowed in both cases, which confirms that both the elastic and electrostatic energies stabilize the M phase. Also, when both $\xi$ and $\eta$ are set to 0 which corresponds to a bulk homogeneous ferroelectric state, it is seen that the M phase does not appear and
only a T→R transition is observed. The T→R transition temperature is denoted by the solid line in Figs. 5.4(a) and 5.4(b) as a comparison.

Fig. 5.4 Narrowing of the temperature range for M phase field in the phase diagram with decreasing ξ (a) and increasing η (b), respectively.

The appearance of the M phase thus could be understood as the following. When a polytwinned T domain structure is further cooled, as the Landau free energy of the R phase becomes lower and lower as compared to that of the T phase, the R phase has a tendency to nucleate in these T domains by developing polarization in the direction where the T domains have zero polarization value. Since near the MPB the polarization anisotropy is small and the free energy of M phase is close to that of R phase, the
difference in the long-range elastic and electrostatic interaction energies of the two
different M and R nanodomain structures (for example, Figs. 5.2(c) and 5.2(e)) could
outweigh that in the chemical free energy and the total free energy of the M nanodomain
structure could be lower than that of R nanodomain structure. As a consequence, the
polarization in the new direction does not develop fully into that of an R phase, but rather
into an M phase (Fig. 5.2(c)). With further cooling, the chemical free energy difference
between the M and R phases becomes much larger and dominant over the effect of the
elastic and electrostatic energy contributions and thus the R phase forms as shown in Fig.
5.2(e).

To confirm the above arguments we convert the M nanodomains obtained at T=-45°C in
the solid solution with c=0.5 (Fig. 5.2(c)) to R nanodomains and let the system relax at
the same temperature. It is seen that the R nanodomain structure returns spontaneously to
the M nanodomain structure. Fig. 5.5 shows the various energy changes associated with
this relaxation process and it is readily seen that although the chemical free energy
increases, both the electrostatic and elastic energies decrease and the total free energy
decreases as well.
Fig. 5.5 Variation of different energy terms with time during the relaxation of an artificial R nanodomain structure made from that in Fig. 5.2(c) back to an M nanodomain structure.

In fact, it has been reported that the M phase can be induced by epitaxial strain in ferroelectric thin films [80-83]. This indicates that the long-range elastic interaction can actually stabilize the M phase, although our results are different in that it is the coherency strain in bulk samples rather than epitaxial strain in thin films. Also, the M phase is found stable in PbZr$_{0.5}$Ti$_{0.5}$O$_3$ (a composition near the MPB of PZT system) by first principle calculations where both elastic and electrostatic interactions are accounted for [84].

Note that the appearance of M phase has been explained by Vanderbilt and Cohen [73] who extended the traditional 6th order Landau polynomial to at least 8th order. However,
the need of 8th and higher order terms may not be a necessary condition to have a stable M phase at the MPB, as it has been shown recently that the M phase could be stable with a 6th order or even 4th order Landau polynomial when two order parameters are involved [85-87]. Our work, on the other hand, suggests that even though the chemical free energy characterized by the Landau theory does not support a stable M phase, with the presence of long-range elastic and electrostatic interactions in a multi-domain state when the polarization anisotropy is small, an M phase can be stable.

5.3.5 3D simulations

Although the above simulations are carried out in 2D, 3D simulations show similar transformation sequence and hierarchical domain structures. An example is presented in Fig. 5.6, where it is shown that an initial T microdomain structure (Fig. 5.6(a)) transforms into an M nanodomain hierarchical structure (Fig. 5.6(b)) in a system with c=0.5 upon cooling from T=100°C down to T=20°C. T1 and T2 are the two types of T domains with polarization vector along the [100] and [010] directions, respectively. Within the T1 microdomains, M1 and M2 nanodomains form with polarization vectors [0.32, 0, 0.11] and [0.32, 0, -0.11], respectively, and within the T2 microdomains, M3 and M4 nanodomains form with polarization vectors [0, 0.32, -0.11] and [0, 0.32, 0.11], respectively.
It is to be noted that the initial T structure is formed by quenching from the cubic phase field into the T phase field in the phase diagram (simulated by random fluctuations in the phase field simulations). Due to the limited 3D system size, however, only two types of the T domains (T1 and T2) form at T=100 °C and, as a consequence, the polarization does not change along the [001] direction as seen in Figs. 5.6(a) and 5.6(b).

![Fig. 5.6 Formation of hierarchical M domain structure in 3D. (a) Initial T domain structure. (b) M domain structure upon cooling.](image)

5.4 Summary

In conclusion, the domain-within-domain hierarchical nanodomain structure has been successfully predicted by phase field simulations and the phase of the nanodomains are
found to be monoclinic. Our work suggests that the appearance of M phase at MPB could be a natural consequence of the interplay between small polarization anisotropy at MPB characterized by a 6th order Landau free energy polynomial and the effect of long-range elastic and electrostatic interactions. Although the conventional 6th order Landau free energy does not support the monoclinic phase, the elastic and electrostatic energy stabilize it. As long as the polarization anisotropy is small, i.e., the chemical free energy of monoclinic phase is not so large compared to that of tetragonal or rhombohedral phase, monoclinic phase can form due to the elastic and electrostatic interactions. Also, our results tell that the extended 8th order Landau free energy is a sufficient condition for the formation of monoclinic phase but it may not be necessary. A 6th order Landau free energy with small anisotropy combined with long range elastic and electrostatic energies can generate monoclinic phase itself.

This finding is scientifically interesting and technologically important because (i) it resolves a long-standing critical issue about the very existence of the M phase at MPB and reveals a new physical origin of it, and (ii) it could shed light on new ways of enhancing piezoelectric response of ferroelectrics through strain engineering, e.g., by tuning coherency strain in bulk samples to enlarge the composition and temperature range of the M phase field as suggested by Fig. 5.4(a), which is in parallel to strain engineering by tuning epitaxial strain between ferroelectric thin films and substrates widely used in the field to stabilize the M phase [80-83].
Chapter 6 Piezoelectric property at ferroelectric MPB

In this chapter, the two prevailing theories on the origin of superior piezoelectric property at MPB are reviewed. Then the phase field models used in our simulation are given. The simulation results and discussion are followed.

6.1 Two theories on the origin of good piezoelectric property at ferroelectric MPB

The origin of superior piezoelectric property at MPB is under extensive research but is still under serious debate. There are mainly two theories on it, the “polarization rotation model” and the “adaptive phase model”. In the following, we discuss both two models.

The polarization rotation model is based on the newly discovered monoclinic phase and it attributes the high piezoelectric coefficients at MPB to the monoclinic phase. It believes that the polarization vector rotation within the monoclinic plane is responsible for the high piezoelectric coefficients at MPB. Fig. 6.1 shows schematically how polarization rotation under external electric field would cause the deformation of the MPB samples. Under this model, the good piezoelectric property at MPB is intrinsic and without the monoclinic phase, the high piezoelectric property cannot be realized.
The adaptive phase model is based on the nano T or nano R domain structure assumed in the adaptive phase theory and claims that the domain wall movement under electric field on a nanoscale is responsible for the high piezoelectric coefficients at MPB. Due to the small polarization anisotropy and the low domain wall energy at MPB, the domain wall movement is easy so that a small external electric field can generate a large response and thus the piezoelectric coefficient at MPB is high. Fig. 6.2 shows schematically how domain wall movement under external electric field would cause the deformation of the MPB samples. Under the adaptive phase model, the good piezoelectric property at MPB is extrinsic and monoclinic phase is not necessary at MPB.
For both models, there are many supports both from experimental observations and calculations. For example, for polarization rotation model, experimentally the existence of monoclinic phase has been reported [22-25]; also, it was calculated by first principles that polarization rotation within monoclinic plane was a key path for polarization vector under electric field [29]; finally, thermodynamically it is found that when the conventional 6\textsuperscript{th} order Landau theory was extended to 8\textsuperscript{th} order or higher order, monoclinic phase can be stabilized [73]. For adaptive phase model, experimentally nanodomain structure at MPB was observed [18-21]; also, some CBED observation seem to support that the nanodomains at MPB are T or R phase [35-37]; finally, thermodynamic calculations have found that nanodomains at MPB themselves can generate high piezoelectric property and monoclinic phase is not necessary [71].
Although both models have some merits in them, neither of them is perfect. The polarization rotation model emphasizes the role of monoclinic phase but it neglects the possible role of nanodomains at MPB. As mentioned in the last chapter, the nanodomain structure is well observed by experiments. The adaptive phase model, on the other hand, although provides a possibility that monoclinic phase can be an average effect of nano T or R, it cannot exclude the possibility that monoclinic phase does exist and might play a big role in the good piezoelectric property at MPB. More and more experiments show that the nanodomains at MPB are monoclinic themselves. Also, both models cannot explain why the strain-electric field loops of poled MPB samples are hysteresis for some compositions but anhysteresis for others [90-92]. Fig. 6.3 shows one typical strain-electric field loops with large hysteretic found at an MPB composition [90] and Fig. 6.4 shows one typical strain-electric field loop with nearly no hysteresis found at a different MPB composition.
Fig. 6.3[90] A typical hysteresis strain-electric field loop found at an MPB composition for PZN-PT system.
Fig. 6.4 A typical anhysteresis strain-electric field loop found at another MPB composition for PZN-PT system.

Therefore, disregard of extensive research, it is still not clear which of the two models explains the good piezoelectricity at MPB. In the current work, phase field simulation is employed to investigate the domain structure and piezoelectric property of poled samples at MPB.
6.2 Models and Simulations

In the current work, we adopt similar models for the simulation of domain structure at MPB except that poling is needed to study the piezoelectric properties of samples, i.e., external electric field will be added to samples.

Still, the model system considered is a ferroelectric solid solution with $C \rightarrow T$ and $C \rightarrow R$ transformations at the two ends of the solid solutions, respectively. The total free energy is also calculated by equation (19) in chapter 5. All the other free energy terms are calculated using the same method as in Chapter 5 except the electrostatic energy because now the external electric field will be added to the samples. The electrostatic energy density, $f_{elec}$, is described by $f_{elec} = \frac{1}{2} E_i P_i - E_{ex}^i P_i$, where $E_i$ denotes the inhomogeneous electrical field due to dipole-dipole interaction and $E_{ex}^i$ is the external electric field.

The temporal evolution of the spontaneous polarization field can be obtained by solving equation (21) in chapter 5 and the parameters used in the simulations are the same as those used in chapter 5. The phase diagram of unpoled samples is shown in Fig. 5.3(a).

The domain wall energy for $90^\circ$ domain walls is assumed to be $\sim 0.1 \text{ J/m}^2$, which yields a length scale $l_0$ (the numerical grid size) of $\sim 2.0$ nm. The simulations were carried out
in 2D and the simulation cell sizes are 512×512, with periodic boundary conditions applied in all dimensions.

Composition c=0.2, 0.3, 0.4, 0.5, 0.55, 0.6, 0.65, 0.7, 0.8, 0.9 are simulated and the temperature T is fixed at 25°C.

6.3 Pizeoelectric property at MPB

The initial domain structure of poled samples and the piezoelectric property of these poled samples including the strain-electric field loops and the d33 coefficients will be given. Also, the mechanism of the good piezoelectric property at MPB will be analyzed.

6.3.1 Initial domain structure of poled samples

The initial domain structure of poled samples are obtained by adding an external field of about ~100kV/cm along [100] direction to a fresh sample and then retreating the electric field and letting the sample relax for a certain amount of time.

It is seen in Fig. 6.5 that there are three types of domain structure after poling the sample along [100] direction. The R macordomain structure (a), the intermediate M nanodomain structure (b) and the T macrodomain structure (c). The M nanodomain structure has been observed in reference [72] and exhibit striking similarity with our simulated one.
Fig. 6.5 Three types of domain structure after poling the samples along [100] direction. (a) Rhomohdral macrodomain structure. (b) Monoclinic nanodomain structure. (c) Tetragonal macrodomains structure. The arrows in (a) and (c) represents the direction of the polarization vector. Different colors represent domains with different polarization vectors.

It is found that at composition c=0.2-0.5, the poled samples exhibit R macordomain structure; at c=0.55-0.6, the poled samples exhibit M nanodomain structure and at c=0.65-0.9, the poled samples exhibit T macrodomain structure. It should be noted that the phase of domains for poled samples can be different from those of the fresh samples for the same composition, especially for compositions near MPB. This is because the poling history will result in a residual electric field in the samples and this residual
electric field could alter the phases of domains at MPB because samples at MPB compositions are fragile and sensitive to the poling history [93].

6.3.2 **Strain-Electric field loops of poled samples**

The strain-electric field loops of poled samples are then measured by calculating the strain of the sample during the process of adding the electric field gradually along [100] direction again and then gradually retreating the field to zero. Fig. 6.6 shows the strain-electric field loops of samples at different compositions.

![Fig. 6.6 The strain-electric field loops of poled samples at different compositions.](image-url)
It is seen that for composition with T macrodomain structures, the strain-electric field loops are linear and hysteresis free. For compositions with M nanodomain structures, the strain-electric field loops are with large hysteresis. For compositions with R nanodomain structures, the loops are anhysterelis at low electric field but hystereiss at higher electric field. Similar strain-electric field loops, both the hysteresis ones and anhystereiss ones, as well as the ones anhysteresis at low field but hysteresis at high fields, are all found near MPB in experiments [89-92].

Why the strain-electric field loops are hysteresis at some cases but anhysteresis at other cases can be understood as the following. For composition with T macrodomain structures, under a [001] electric field, only extension of polarization vector occurs and such process is reversible. As a result, the strain is small and anhysteresis. For composition with R macrodomain structure, at low [001] fields, only polarization rotation occurs and such process is reversible and so the strain-electric field loops are anhysteresis. At high [001] fields, the domain wall between two alternating R domains disappear and R to T transition occurs. The disappearance and reappearance of domain wall between two R domains are irreversible because there should be barrier for such process. Therefore, hysteresis appears at high fields. For compositions with M nanodomain structure, under external [001] field, both polarization rotation and domain wall movement occurs. Although polarization rotation is a reversible process, the domain wall movement can be irreversible and thus the strain-electric field loops become hysteresis.
6.3.3 \( d_{33} \) coefficients

The \( d_{33} \) coefficients of poled samples can be calculated from the slope of the strain-electric field loops at zero field. Fig. 6.7 gives the change of \( d_{33} \) coefficients with compositions. It is seen that the highest \( d_{33} \) appears at a composition with R macrodomain structure, which is consistent with experiments [88, 92].

![Fig. 6.7 The \( d_{33} \) coefficients of poled samples with different compositions.](image)

It should be noted that for polycrystals, the highest piezoelectric coefficients always appear at MPB compositions, which is different from our result that R phase has the
highest $d_{33}$. This is because in our simulation, we only measure the $d_{33}$ of a single crystal along [001] direction. Under this direction, R phase near MPB has the largest $d_{33}$ and T phase has very small $d_{33}$. In other directions, for example, [111] direction, R phase should have minimal $d_{33}$ coefficients and T phase near MPB might have the largest $d_{33}$. In all directions, MPB compositions always have high $d_{33}$, albeit not the highest. Therefore, for the $d_{33}$ of polycrystals, which is a measure of average $d_{33}$ of all grains, the highest $d_{33}$ always appears at MPB compositions.

### 6.3.4 Polarization rotation VS adaptive phase model

By looking closely at the polarization vector change under electric field in our sample, it can be seen that the polarization vector gradually rotates with increasing electric field in the samples which exhibit high piezoelectric coefficients such as those with macro R domain structures and nano M domain structures initially. Fig. 6.8 gives the change of $\Phi$ (the angle between the polarization vector of one grid point within one domain and the poling direction [001] within one domain) with electric field at two samples. The red symbols are for one sample with R macrodomain structure and the blue symbols are for one sample with M nanodomain structure. $\Phi$ does not change for samples with T macrodomain structure (always zero) and thus is not shown here. It is seen from Fig. 6.8 that the polarization vector gradually rotates from its original direction to [001] the electric field direction. After the polarization vector is aligned with the poling direction, only polarization extension occurs while the direction of the polarization vector does not
change and thus at high fields a plateau occurs. It is to be noted that for M nanodomain structure, $\phi$ changes sharply from a certain angle to zero as seen in Fig. 6.8, telling that domain wall movement also occurs in these M nanodomain structure.

Therefore from our simulation results, it is seen that polarization rotation takes an important role in the high piezoelectric coefficients at MPB for poled samples with R macrodomain structure because for R macrodomain structure, only polarization rotation occurs. For M nanodomain structure, it is seen that polarization rotation and domain wall movement take place simultaneously but it is difficult to differentiate which mechanism takes a more important role. Therefore it is possible that both the mechanisms take a role in the high piezoelectric property of poled samples with M nanodomain structures.
It is to be noted that no matter which mechanism take an important role, the polarzaition rotation or the domain wall movement, small polarization anisotropy is a key element for both mechanisms to generate high piezoelectric coefficients. In other word, small polarization anisotropy is a necessary condition for good piezoelectric property. For compositions away form MPB, both domain wall movement and polarization rotation (with a very small angle) may also occur under external electric field. However, the response should be weak due to the high barrier between different phases and as a result, the piezoelectric property is not good. Only at small anisotropy like at MPB, the barrier
between different phases is low thus both polarization rotation and domain wall movement can be easily activated by external electric field and therefore the piezoelectric property is good.

6.4 Summary

The above work on the piezoelectric property of ferroelectric MPB indicates that both polarization rotation and domain wall movement can play important roles for the high piezoelectric coefficients at MPB. For compositions near MPB which have a R macrodomain structure after poling, polarization rotation is the only origin of good piezoelectric property. For MPB compositions with monoclinic nanodomains after poling, polarization rotation and domain wall movement takes place simultaneously during the application of electric field but it is difficult to tell which mechanism takes a more important role. For compositions with R macrodomain structures after poling, the strain-electric field loops can be anhysteresis at low electric field, but hysteresis will appear at high enough fields because R to T transition will happen at high electric field. For compositions with M nanodomain structures after poling, the strain-electric field loops will be with large hysteresis due to the domain wall movement. No matter which mechanism, one necessary condition for high piezoelectricity is that the polarization anisotropy should be small because only at small polarization anisotropy both the mechanisms can exhibit strong response to external electric field.
Chapter 7 Summary and Future Work

7.1 Summary

Phase field method has been applied successfully to two areas of materials science, interdiffusion microstructure of high temperature coatings and the domain structure and piezoelectric property at the morphotropic phase boundary of ferroelectric solid solutions. The following conclusions can be summarized from the simulation work in the current thesis.

1. For interdiffusion microstructure of high temperature coatings, interdiffusion microstructure maps can be a useful guide for designing alloys of appropriate compositions. The fundamentals of interdiffusion microstructure maps (IMMs) derived in the current work, such as the topology of the IMMs, the three mechanisms of microstructure change on an IMM and the principles of drawing IMMs, can be instructive for plotting interdiffusion microstructure maps for real systems.

2. Type n boundaries ($n \geq 3$) are infrequent in interdiffusion microstructures of high temperature coatings because their diffusion paths have to pass through a special feature
that cannot be intersected by a random line. However, both our simulations and experimental observations show that under the right condition, they can occur and once they occur, it will persist even if we vary the initial alloy compositions.

3. The ferroelectric domain structure at the morphotropic phase boundary of ferroelectric solid solutions is with hierarchical nanodomain structure as simulated by our phase field methods as well as observed by experiments. The phases of the nanodomains, however, can be monoclinic even under a sixth order Landau free energy which does not support a monoclinic phase and it was found that the monoclinic nanodomains are stabilized by the long range elastic and electrostatic energies as revealed by our simulations.

4. The good piezoelectric property at morphotropic phase boundaries of ferroelectric solid solutions is revealed to be related to both the polarization rotation within the monoclinic plane as well as domain wall movement under external electric field. For poled samples with R macrodomain structure, polarization rotation is the only origin of the good piezoelectric property but for poled samples with M nanodomain structure, both the polarization rotation and domain wall movement take place but it is hard to tell which mechanism plays a more important role. No matter which mechanism takes role, the small polarization anisotropy is the key element determining the good piezoelectric property at MPB. The $d_{33}$ coefficients are found to be highest at composition with R macrodomain structure for poling direction [001], which agrees with experiments.
7.2 Future Work

Along with the work that has been done in this thesis, a lot more work can be done both in the area of interdiffusion microstructure of high temperature coatings and in the area of ferroelectric morphotropic phase boundary and are suggested below:

1. For interdiffusion microstructure of high temperature coatings, although type n boundaries \((n \geq 3)\) has been successfully simulated and has been proved to persist even if the composition varies when the right condition occurs, the origin of why such boundaries will occur is still unclear, i.e., why the nature will choose such peculiar diffusion path rather than other alternatives, is still a mystery and remains to be answered. It is hoped that a comparison between such diffusion path and other alternatives will provide an answer.

2. For ferroelectric morphotropic phase boundaries, it is interesting to investigate why overpoling effect occurs for some MPB compositions [94, 95]. Also, it should be interesting to know whether the peculiar hierarchical domain-within-domain structure formed at MPB is related to the treatment history of the sample.
Bibliography


