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Simulation of a Cubic to Tetragonal Martensitic Transformation in the Presence of Inclusions

by

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment
of the requirements for the degree of Master of Applied Science.

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Abstract

Simulated microstructure patterns formed as a result of a cubic to tetragonal martensitic transformation in the presence of inclusions are examined. Spherical and ellipsoidal inclusions constituting a variety of volume fractions within a cube of parent material are considered. Martensitic transformation strains corresponding to those of Fe-31wt %Ni are used for most of the simulations. The simulated transformation is based on a mathematical model which subdivides the cube of material into an array of smaller cubic cells then takes into account elastic strain energy, chemical energy, surface energy, and applied stress in determining the fractions of phase states within each cell of the cube as time is advanced. The transformation is studied both with and without stress applied to the cube. Complete loading and unloading cycles for a tensile stress test are simulated demonstrating the stress-strain hysteresis of the material with the inclusion.

Acknowledgement

“If I have seen so far it is by standing on the shoulders of giants”

- Issac Newton.

I humbly acknowledge the contribution of all researchers of this field before me whose insight and ideas collectively form the great assembly of knowledge without which this very meager application of science would not have been possible.

More directly, I gratefully acknowledge the intellect, wisdom and efforts of Dr. Andrei Artemev whose labor and profound understanding formed the foundation for this work.

I dedicate this document to Lancelot in loving memory, who embodied all the greatness of the German Shepherd, unequaled loyalty, integrity, and stoicism and whose friendship was a pillar of support. Lance, you are deeply missed.

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Introduction

The objective of this work is to study the crystallography of the cubic to tetragonal martensitic transformation in the presence of inclusions. The cubic to tetragonal martensitic transformation occurs in many alloys, such as iron-nickel and iron-carbon. Iron-nickel has applications as a low cost shape memory alloy. Since the martensitic microstructure is a vital determinant of the deformation properties of a shape memory material, the influence of inclusions in shaping the features of the microstructure is of interest and may hold potential for improving the shape memory properties of iron-nickel.

The study is performed using a mathematical description of the transformation energies implemented as computer code, where a cube of material is subdivided into identical smaller cubes (cells), with each cell having three possible orthogonal shape deformations of the cubic to tetragonal martensitic transformation. With each of the three tetragonal martensitic variants for each cell is associated an order parameter which describes the degree of transformation strain for each variant of the cell. A zero order parameter for each variant indicates that the state of the cell is parent phase. At each timestep of the simulation, the order parameters are updated and can be examined to determine the most energetically advantageous crystal structure at that point in time.

The energy driving the transformation is the chemical energy of the phase transformation. Opposing the transformation are elastic strain energy and surface energy as new crystal regions are created. Elastic strain energy arises as a result of the shape deformation associated with the transformation from austenite to martensite and is an infinite range field; therefore the strain energy of any given cell depends critically on the strains of all other cells of the cube. The elastic strain energy is a very significant contributor to the overall energy, which makes it instrumental in guiding the domain evolution. Key to making an efficient implementation of any simulation model is the technique used to evaluate the strain field. The technique chosen here is described in detail in Chapter 3.0. An inclusion is taken to be any non-transforming region of material. In this work two shapes of inclusion are considered, spherical and ellipsoidal. The crystallography of the transformations are obtained computationally and examined as virtual micrographs. The effect of applied stress is also considered and the code is used to simulate the repeated loading and unloading cycles of a tensile stress test.

This work was focused purely on the application of the code. The code was developed over several years through evolution by multiple contributors of the Department of Mechanical and Aerospace Engineering at Carleton University and the Department of Ceramics and Materials Engineering at Rutgers University. References 8 - 10 describe further the phase field approach which forms the basis of the program.

1.0 Martensite

Martensite is the result of a solid to solid transformation characterized by diffusionless cooperative atomic movements typically produced by rapid cooling of the austenite phase. It is observed in many alloy systems. In an Fe-C system the martensitic transformation is responsible for the hardening effect observed on quenching. In some other alloys it is fundamental to such phenomena as the shape memory effect and super elasticity. The phase of martensite is named in honor of Adolf Martens, a German metallographer credited with first observing martensite crystals in steel in about the year 1890¹⁹.

In Fe-C systems, the austenite (γ) phase has an FCC structure. At lower temperatures, the iron matrix transforms under equilibrium conditions to the ferrite phase (α), which has a BCC lattice structure. The FCC cell allows relatively high solubility of carbon in the iron matrix compared to the BCC lattice. Although the BCC lattice is less densely packed than the FCC lattice, the largest interstitial space is too small to accommodate a carbon atom, therefore the solubility limit of carbon in BCC iron is much lower than in FCC iron. If steel is cooled rapidly, carbon has insufficient time to diffuse from the iron matrix resulting in a situation of high strain energy as the FCC lattice is chemically driven to rearrange as a BCC lattice, but it is impeded by carbon atoms locked in the structure. The result is a body centered cubic unit cell distorted to a tetragonal cell, or body centered tetragonal (BCT) cell (designated the α' phase) formed rapidly by a diffusionless crystal structure transformation. The distorted BCC cell represents the lowest energy

accommodation of the carbon atoms for the least atomic displacements. This BCT structure with high strain energy contributed by the carbon atoms locked in the lattice is steel martensite and is responsible for the exceptional hardness of quenched carbon steel.

In Fe-Ni alloys, the austenite crystal structure is also FCC, but it is a substitutional solid solution rather than an interstitial solid solution⁴. Martensite forms on rapid cooling. The martensite crystal structure is BCC rather than BCT as in Fe-C alloys. The equilibrium (α) structure that is formed on slow cooling also has a BCC unit cell. The only difference between α and α' in Fe-Ni is that very regular shape deformations occur in forming the martensite structure, whereas the diffusion process leading to the α state will not exhibit any regular axial deformation pattern.

The transformation of an FCC parent lattice into a BCC or BCT lattice can be envisioned through the Bain correspondence as shown in Figure 1-1. Within an undistorted FCC lattice, a body centered structure can be observed with an axial ratio of $1/\sqrt{2}$. Therefore small atomic movements are all that are necessary to produce a BCC cell or BCT cell of different proportions as first noticed by E.C. Bain in 1924². The atomic shifts occur on three principal axes producing very regular shape changes and producing three orthogonal variants corresponding to the three orientations of tetragonal distortion.

Through techniques of X-ray diffraction, the lattice distortion has been measured for Fe-Ni as contraction on the z axis and expansion on the x-y axis (axes oriented as shown in Figure 1-2). Other cubic to tetragonal transformations can occur with expansion on one

axis and contraction on the other two. Typically the transformation volume change relative to the naturally embedded tetragon is not large. For Fe-Ni it is about 2.6%.

Body Centered Tetragon within an FCC Lattice

Distortion of the Body Centered tetragon to proportions of the observed Martensite

Figure 1-1 Bain Correspondence³

The tetragonal BCC cell inherent in the FCC lattice has an axial ratio of $1/\sqrt{2}$ as shown in Figure 1-1. Three distinct orientations of the Bain tetragons can be determined, each aligned with a different principal axis. The small atomic shifts of the martensitic

transformation result in the axial ratio of $1/\sqrt{2}$ for the basic Bain cell being altered to some other value unique to the alloy.

Given this shift of atomic positions, a crystal region that has undergone a transformation to martensite will no longer be aligned with the parent FCC lattice. Therefore a simple Bain distortion alone would produce an incoherent interface. Isolated macroscopic single martensite domains would result in enormous lattice strains as they require either stretch or compression of the parent lattice along each axis to create the tetragonal distortion. To produce a coherent interface the lattices would have to deform enormously in the region of the phase boundary implying large strain energy.

Considering there are three mutually orthogonal tetragonal distortion variants for the martensite, one way to alleviate the strain is by the formation of variant twins. The orthogonal variants could alternate in a stepped structure of expansion with respect to the parent phase for one twin, then contraction with respect to the parent phase for the other twin, resulting in a net reduction in the incoherency with respect to the parent phase over some macroscopic scale of several martensite domains. The resulting effect is a semi-coherent interface plane, termed the habit plane, between the parent lattice and the martensite lattice as illustrated in Figure 1-3.

An invariant plane strain is a deformation operation which leaves a plane, the invariant plane, undistorted by the deformation. That is no vector in the plane is changed in length, though the plane may be rotated. Simple shear (a shear on one face only) and uniaxial

extension (idealized extension, disregarding any Poisson effect) are examples of invariant plane strains as shown below. In general an invariant plane strain may be expressed mathematically as a combination of simple shear and uniaxial extension². If two crystal regions fit along an invariant plane, the elastic strain energy and the interfacial energy will be minimized, hence if the austenite to martensite transformation can be represented as an invariant plane strain, then the invariant plane is the energetically preferred candidate for the habit plane. Determining the habit plane orientation is fundamental to understanding the crystallography of martensite.

Figure 1-2 Simple Shear and Uniaxial Extension²

The habit plane is macroscopically an invariant plane, but within each region of a single tetragonal variant the interface is incoherent. Only in the habit plane will a vector within the parent phase lattice be undistorted over some macroscopic length measure under the transformation operation that produces the martensite. Since the microscopic distortion

along the habit plane is large, martensite tends to form as thin plates or laths each of a given tetragonal orientation variant. As the martensite growth process occurs, strain energy over the plate thickness builds until the energy balance favors the development of an orthogonal orientation of martensite as the adjoining plate. The result is a lamellar structure of twinned regions as shown in Figure 1-3.

In Figure 1-3, the macroscopically invariant line AI in the habit plane is composed of vectors aligned with the same principal axis of tetragonal distortion for each of the lamellar domains. The fit of least strain energy is represented by a structure where the individual martensite domains are not coherent with the austenite lattice along the habit plane, but the assembly of alternate orientation variants of martensite produces the composite effect of coherency. Thin lamellas result in a reduction in strain energy over thick lamellas as they offer a net reduction in deformation along the habit plane. Very thin lamellae can produce a coherent but distorted interface.

Only certain habit planes have been observed to occur in martensite. These habit plane variants represent the most energetically favorable fit between the martensite and the parent phase. By simple geometry as evident in Figure 1-3, the orientation of the habit plane implies a certain ratio of volume fraction of one tetragonal variant with respect to the other. Therefore, discrete ratios of plate thicknesses can be expected which correspond to the discrete values of habit plane orientation.

$$AI = AB + BC + CD + DE + EF + FG + GH + HI$$

Figure 1-3 Polytwinned martensite plate with habit plane containing invariant line AI. The regions are orthogonal orientation variants referred to as twins.²

The stepped structure of Figure 1-3 shows polytwinned martensitic plates. Crystal twins are any two regions of crystal lattice which may be brought into coincidence either by a reflection through a plane or by rotation of 180° about some axis. The plane of reflection is the twinning plane. To fit the twinned lamellae coherently along the twinning plane, requires independent rotation of each of the regions. The two dimensional analogue of this is illustrated in Figure 1-4. The drawing may be considered an atomic level picture where the circles represent atoms. Two martensite domains each distinguished by their tetragonal distortions are depicted. The mirror plane (twinning plane) lies at a 45° incline with respect to the long axis of the two rectangles in the drawing. That is to each side of this 45° mirror plane, the original (parent phase; undistorted) crystal regions were each reflections of the other, however, the rotation angle to re-establish lattice coherency is not 45° as the drawing shows.

Figure 1-4 Orthogonal tetragonal crystal variants rotated into coincidence along the twinning plane.

The complete lattice deformation consists of the Bain distortion and two rotations. One rotation, different for each of the twin regions, brings the two tetragonal domains into coherency along a twinning plane, while the other rotates the complete twinned structure into coherency with the parent phase along the invariant plane.

An alternative to the twinned structure is a slipped structure, with dislocations clustered at the habit plane, which produces the same effect as the twinned structure, as shown in Figure 1-5. The orientation variants all have like tetragonal distortions, but the slip that occurs at each layer realigns the martensite phase lattice with the parent phase lattice at the habit plane boundary. The vector sum producing the net invariant line is the sum of the principal tetragonal distortion vectors within the martensite regions and the burgers vectors at each of the slipped planes. This has been shown to be mathematically equivalent to the twinned structure².

Figure 1-5 Martensite plates formed by slip. The Burgers vector of the dislocations provides the same geometric effect as a martensite plate of orthogonal orientation variant.²

The martensitic transformation proceeds extremely rapidly with the martensite crystal growth propagating at a speed which can be as high as that of a sound wave. The phenomenon is one of apparent coordinated regimented short range atomic displacements that is metaphorically termed a “military” transformation, as opposed to a phase transformation that proceeds by long range diffusion over a much longer time scale with apparently disordered independent atomic movements referred to as a “civilian” transformation^{3,19}. In the transformation to martensite the atomic movements are not simultaneous. Instead each atomic displacement is in reaction to a neighboring displacement coupled by the elasticity of the lattice. The displacement wave propagates at near acoustic velocity like a phonon domino. Nishiyama points out this is more like Shogidaoshi, a Japanese word meaning falling one after another in succession, than a military transformation³.

The martensitic transformation is also fundamentally different from a diffusion driven transformation in the role of elastic strain energy in controlling the transformation. The high strain energy of the lattice distortion requires a strong chemical driving force and random thermal fluctuations sufficient to overcome both the chemical energy barrier and the strain energy for nucleation and growth to occur. The crystal growth is then strongly influenced by the large elastic strain energy created by the atomic displacements in forming the martensite domains. The strain energy field resulting from any transformed subsection of the crystal extends throughout the crystal volume by the infinite range elastic coupling effect of the lattice, thereby impacting the transformation of all other regions.

The geometry of the Bain distortion could be represented as shown in Figure 1-6. The circle represents a cross section of a spherical section of the austenite before the transformation. The ellipse represents a cross section of the ellipsoid produced by the tetragonal distortion. The surfaces intersect as circles passing through the points A', B', C', D'. Since the lines drawn in the figure are all radial lines for the circle, their length is unaltered by the transformation. Therefore, the lines AOC and BOD are invariant lines under the transformation. They undergo a rotation through an angle Φ , but their length is not altered. For these lines to be in an invariant plane requires that no length change occur in the plane perpendicular to the plane of the paper. Call this perpendicular axis the x_3 axis. However, for the case of the sphere intersecting the ellipsoid, the surfaces are cones with different base diameters, hence the surfaces will have undergone a distortion in the x_3 dimension.

Figure 1-6 Distortion of a circle into an ellipse showing lines which are invariant under the transformation.²

For Fe-31 wt%Ni alloy, the principal axis distortions of the Bain correspondence are as follows:

$$\eta_1 = \eta_2 = 1.132136$$

$$\eta_3 = 0.800541.$$

The measured lattice parameters of Fe-31 wt%Ni have been determined to be²:

Austenite: $a_0 = 3.591$ Angstroms.

Martensite $a = 2.875$ Angstroms.

The dimensioned martensite cell is illustrated in Figure 1-7. Note the cell is purely BCC with no tetragonal character.

Figure 1-7 Fe-31 wt%Ni martensite cell with dimensions derived from the given distortion parameters, the Bain correspondence, and the measured lattice parameter of austenite. Note the cell is cubic.

In general, as postulated by Bilby and Christian in 1955², if an undistorted plane is to result from a homogeneous distortion, such as the Bain correspondence, one of the principal distortions must be greater than unity, one must be less than unity, and the third must be unity. With the distortion illustrated in Figure 1-6, the long axis of the ellipsoid represents a greater than unity distortion of the sphere, the short axis shown is a less than unity distortion, so the prerequisite for an undistorted plane can only be fulfilled if no length change occurs in the x_3 dimension. If this were true then the invariant lines AOC and BOD of would lie in an invariant plane, but such a distortion is not consistent with the Bain distortion and it is clearly not the case for the situation of the sphere distorted to form an ellipsoid. For this reason the Bain distortion alone can not produce an invariant habit plane, nor can the Bain distortion plus a rotation produce an invariant habit plane. To produce an invariant habit plane the Bain distortion must have associated with it a rotation and a macroscopic shear.

The key ramification of this is that it is impossible for a single orientation variant of a martensite crystal to align coherently with an austenite crystal. The invariant plane is only a macroscopic semi-coherent interface where either the combination of two orthogonal orientation variants or slip supplies the necessary shear component to align the crystal lattices over a length scale that is large with respect to the individual plates.

To illustrate this point further, Figure 1-8 shows the effect of a sphere being distorted by simple shear into an ellipsoid and the cross sectional view of this. The magnitude of the shear is g and the angle is 2α . The sphere is assumed to have unit radius. Let the sphere represent any region of a crystal. By the action of the shear, some radial planes of the spherical crystal will be distorted into planes where vectors are increased in length whereas other planes will be distorted into planes in which vectors are reduced in length. One radial plane, K_2 , is undistorted. K_2 undergoes rotation to K_2' but vectors within K_2 are not altered in length. Therefore, two invariant planes are produced by the shear, the equatorial plane (shaded), and K_2 .

Figure 1-8 shows only the distortion of shear. For a crystal region undergoing a martensitic transformation, a further distortion occurs where some initial sphere of parent phase will be distorted into an ellipsoid by the transformation. The distortion of the simple shear such as is accomplished by stacked lamellae of variant twins or by slip on the planes separating lamellae, must undo the distortion of the transformation. A shear of magnitude and direction that restores some plane in the martensite crystal such that

vectors in this plane are of identical length to vectors in the original austenite crystal is a candidate for the shear of the martensite layers. The restored plane is a candidate for the habit plane.

$$\tan(\alpha) = g/2$$

All vectors on plane K2 move to K2' undistorted.
 Vectors to the left of K2 are decreased in length.
 Vectors to the right are increased in length.

Figure 1-8 Sphere being distorted into an ellipsoid by a shear of magnitude g^2 .

1.1 Algebraic Theory of Habit Plane Alignment

Wechsler, Lieberman and Read produced an algebraic solution to the habit plane orientation problem^{15,18}. Bowles and Mackenzie independently produced an alternate version¹⁶. Subsequently both theories have been shown to be identical². The following is based on the Wechsler, Lieberman and Read treatment^{2,3,15,18}.

Algebraically, the invariant plane strain can be written as:

$$P_1 = RBP, \quad (1.1)$$

where:

R = a rotation matrix,

B = the Bain correspondence tetragonal distortion matrix,

P = a shear matrix,

P₁ = the total invariant plane strain.

That this can produce an invariant plane strain can be algebraically proven as follows.

$$\text{Let } F=BP. \quad (1.2)$$

The matrix F can equivalently be expressed as the product of a symmetric matrix (Fs) and a rotation matrix (Ψ).

$$F = Fs\Psi. \quad (1.3)$$

Any symmetric matrix can be diagonalized by the principal axis transformation. The principal axis transformation has the form of:

$$\Gamma F_d \Gamma^T. \quad (1.4)$$

where F_d is a diagonal matrix and Γ is a rotation matrix.

The matrix F can then be written as:

$$F = \Gamma F_d \Gamma^T \Psi. \quad (1.5)$$

In the expression for F , all matrices except F_d are rotation matrices, hence only F_d contains strain. The diagonal matrix F_d can be written as:

$$\begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix}$$

By allowing one λ_i to be less than one, one λ_i to be greater than one and one λ_i to be equal to one, the Bilby and Christian criterion for producing an invariant plane strain is fulfilled².

To find the plane we can recognize that from the definition of invariance, any vector that lies in the habit plane must be unchanged in length by the transformation although it may be rotated. The magnitude of a vector is given as the square root of its product with its transpose. Therefore, for some habit plane vector z ,

$$z^T z = z^T P^T B^T R^T R B P z \quad (1.7)$$

Since a pure rotation can not affect the length of a vector, rotation may be ignored and the expression simplified to:

$$\begin{aligned} \mathbf{z}^T \mathbf{z} &= \mathbf{z}^T \mathbf{P}^T \mathbf{B}^T \mathbf{B} \mathbf{P} \mathbf{z} \\ &= \mathbf{z}^T \mathbf{F}^T \mathbf{F} \mathbf{z} \end{aligned} \quad (1.8)$$

Given that $\mathbf{F}$ may be decomposed into pure rotations and a diagonal matrix $\mathbf{F}_d$, we can reduce the above to:

$$\mathbf{z}^T \mathbf{z} = \mathbf{z}^T \mathbf{F}_d^T \mathbf{F}_d \mathbf{z} \quad (1.9)$$

Any expression of the form $\lambda \mathbf{x} = \mathbf{A} \mathbf{x}$, where λ is a scalar, $\mathbf{x}$ is a vector and $\mathbf{A}$ is a matrix is referred to as an eigenvalue problem. The values of λ for which the statement holds are called the eigenvalues and the vectors $\mathbf{x}$ are the eigenvectors.

Expanded, the eigenvalue equation becomes:

$$A_{11}x_1 + A_{12}x_2 + A_{13}x_3 = \lambda x_1$$

$$A_{21}x_1 + A_{22}x_2 + A_{23}x_3 = \lambda x_2$$

$$A_{31}x_1 + A_{32}x_2 + A_{33}x_3 = \lambda x_3$$

or

$$(A_{11}-\lambda)x_1 + A_{12}x_2 + A_{13}x_3 = 0$$

$$A_{21}x_1 + (A_{22}-\lambda)x_2 + A_{23}x_3 = 0$$

$$A_{31}x_1 + A_{32}x_2 + (A_{33}-\lambda)x_3 = 0$$

The eigenvalues may be found by solving the following characteristic equation:

$$\det(\mathbf{A}-\lambda \mathbf{I}) = 0 \quad (1.10)$$

It can be shown that for any real symmetric matrix $\mathbf{A}$, there exists a matrix $\mathbf{U}$ such that $\mathbf{U}^T \mathbf{A} \mathbf{U}$ is a diagonal matrix, $\mathbf{A}_d$, whose diagonal elements are the eigenvalues of $\mathbf{A}$.

Stating this the other way,

$$\mathbf{A} = \mathbf{U} \mathbf{A}_d \mathbf{U}^T. \quad (1.11)$$

The columns of $\mathbf{U}$ are the eigenvectors of $\mathbf{A}$. Therefore, the diagonal elements in the matrix $\mathbf{F}_d$ above are the eigenvalues of the matrix $\mathbf{F}_s$. The columns of the diagonalization matrix, $\mathbf{\Gamma}$, are the eigenvectors of matrix $\mathbf{F}_s$. The characteristic equation to be solved is:

$$\det(\mathbf{F}^T \mathbf{F} - \lambda^2 \mathbf{I}) = 0 \quad (1.12)$$

Now, simplify the matrix $\mathbf{P}$ by changing its basis of representation. This is done by applying some unknown rotation matrix. $\mathbf{P}$ then becomes $\mathbf{gPg}$ which is simply:

$$\begin{vmatrix} 1 & g & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

where g is the magnitude of the shear. Let $\mathbf{R}_g$ be the rotation matrix that produces this rotated $\mathbf{P}$. $\mathbf{R}_g$ is the rotation matrix that converts the basis of representation of the shear to the g basis. $\mathbf{R}_g$ is given as:

$$\mathbf{R}_g = (\mathbf{d}_2, \mathbf{p}_2, \mathbf{t}) \quad \begin{array}{l} \text{where } \mathbf{d}_2 \text{ is the direction of shear,} \\ \mathbf{p}_2 \text{ is the shear plane normal,} \\ \text{and } \mathbf{t} \text{ is } \mathbf{d}_2 \times \mathbf{p}_2 \end{array}$$

$$\text{Let } \mathbf{d}_2 = (u_1, u_2, u_3), \mathbf{p}_2 = (v_1, v_2, v_3), \mathbf{t} = \mathbf{d}_2 \times \mathbf{p}_2 = (w_1, w_2, w_3)$$

$$\mathbf{R}_g = \begin{vmatrix} u_1 & v_1 & w_1 \\ u_2 & v_2 & w_2 \\ u_3 & v_3 & w_3 \end{vmatrix}$$

Relative to this new basis $\mathbf{B}$ can be expressed as $\mathbf{R}_g^T \mathbf{B} \mathbf{R}_g$. Similarly, $\mathbf{F}$ becomes $\mathbf{R}_g^T \mathbf{F} \mathbf{R}_g$.

A new matrix, $\mathbf{gJg}$ may be defined as $(\mathbf{gFg})^T(\mathbf{gFg})$. The eigenvalues can be obtained by solving the following characteristic equation:

$$\det((\mathbf{gFg}^T)(\mathbf{gFg}) - \lambda^2 \mathbf{I}) = 0, \quad (1.13)$$

which is the same as equation 1.12 above except for the change of basis to the $\mathbf{g}$ basis. A necessary condition for an undistorted plane is that one of these eigenvalues be unity.

Applying this condition allows the equation to be solved and the value of $\mathbf{g}$ obtained.

References 2 and 3 contain the complete mathematical derivation. Two solutions for $\mathbf{g}$ are possible.

Obtaining the solution requires the initial assumption of the direction of shear $\mathbf{d}_2$ and the shear plane normal $\mathbf{p}_2$. These are as defined in Figure 1-9 relative to the austenite basis.

The shear is a macroscopic simple shear where the martensite is composed of two orthogonal variants of Bain distorted crystals. As discussed previously, the shear could also be slip shear at periodic intervals with the martensite consisting of a single orientation variant.

Figure 1-9 Shear plane and shear direction of a martensite crystal relative to the austenite basis.

From the three principal axis orientation variants and the family of four (110) type of shear planes and two possible values of g , a total of 24 possible martensite variants result. For Fe-30%Ni, the g solutions are degenerate, thus only twelve variants exist. These are termed the Nishiyama relations for habit plane alignment³. The martensitic transformation in Fe-C follows the Kurdjumov-Sachs relations for habit plane alignment where all 24 variants are possible³.

For Fe-30%Ni, the Nishiyama relations are illustrated in Figure 1-10 . These are:

$$(111)_{\gamma} \parallel (011)_{\alpha'} \quad \text{and}$$

$$[11\bar{2}]_{\gamma} \parallel [01\bar{1}]_{\alpha'} \quad \text{where } \gamma \text{ denotes the austenite lattice and } \alpha' \text{ refers to the martensite lattice.}$$

The Bain elongation is chosen as on the $[001]$ axis which is aligned for both martensite and austenite lattices. Clearly a rotation is required to first bring the plane into alignment, then a second rotation to align the vectors within the plane.

Figure 1-10 Nishiyama relations showing γ - α' alignment planes and vectors³

Breedis and Wayman (1962) have determined habit plane orientations both experimentally and algebraically for Fe-31%Ni². These are quite irrationally indexed planes given as:

Experiment	[0.1656 0.7998 0.5770]
Theory $\delta = 1.0$	[0.184765 0.594820 0.782337]
Theory $\delta = 1.00137$	[0.189454 0.788051 0.585733]

The best agreement between theory and experiment was obtained by using a dilatation parameter (δ). This dilatation parameter defines an isotropic distortion of the habit plane. Effectively it adjusts the principal distortions of the Bain correspondence. For Fe-Ni, the principal distortions determined by diffraction studies are given as $\eta_1 = \eta_2 = 1.132136$ and $\eta_3 = 0.800541$. Effectively the use of the dilatation parameter accepts that some isotropic distortion unique to the habit plane must exist. As indicated in the table a value of 0.137% was found to produce the best fit between theory and experiment.

2.0 Shape Memory Effect

Martensite twin boundaries are mobile under applied stress. Instead of undergoing plastic deformation by slip, martensitic plates can undergo large deformation by movement of the twin boundaries, i.e. the conversion of one orientation variant into another such that the natural elongation direction of the tetragonal distortion tends to the direction of applied stress. This produces shape deformation by a change in the volume fraction of orientation variants as depicted in Figure 2-1 .

Figure 2-1 Illustration of martensite superelastic behavior⁴

In response to the applied load the volume fraction with the most favorable Bain orientation grows at the expense of the other volume fractions. With a sample composed of multiple grains and multiple martensite domains within the grains any arbitrary shape

deformation to very large strains can be achieved as apparent plastic deformation, although the mechanism of shape memory is not slip but twin boundary migration.

Upon heating to the austenite temperature range, the individual martensite plates undergo a reverse transformation to the original austenite lattice producing a shape recovery of the sample. To be fully recoverable the deformation must be entirely due to martensite twin boundary movement or austenite-martensite boundary movement. Any deformation that occurs by slip impairs the material's shape memory.

2.1 *Two Way Memory Effect*

A shape memory effect is normally one-way, i.e. once transformed to the “remembered” austenite form, a subsequent transformation to martensite does not restore the deformed shape. However if a large number of martensite nucleation sites are introduced, as could be introduced as dislocations by plastic deformation through slip, then the martensite plates will repeatedly nucleate with the same configuration as guided by the dislocation nucleation sites. This can result in a two-way shape memory effect where transformation cycling from austenite to martensite and back to austenite shows a remembered shape for each phase⁴.

To produce the two way effect, some initial annealed austenite sample could be transformed to martensite. A large deformation is then produced in the sample while in its martensitic state such that many dislocations are introduced. These dislocations form

nucleation sites which stabilizes the martensite so that the same pattern of martensite habit plane variants will tend to always occur during an austenite to martensite transformation. Thermal cycling then results in shape changes between two states.

A two way shape memory effect has been observed to be induced by repeated cycling of cooling, deforming, and heating many times (hundreds of cycles). Eventually the material remembers its deformed state, so that it deforms spontaneously on cooling. The austenite state is also remembered, and a two way memory effect results. The mechanism is likely an accumulation of dislocations as a result of the repeated martensitic transformations breaking some bonds accompanied by small amounts of slip deformation with each cycle. These dislocations eventually arrange such that the lowest energy martensite crystal structure is the same as that in the deformed state.

The training of a two way memory effect in Nitinol has been noted by Banks in reference 11 during testing of a solid state heat engine based on Nitinol wire elements. Heat engines that exploit shape memory materials as their working elements have been built by Banks and others¹¹⁻¹³. The element is typically in the form of a wire. Axial stress is applied to the wire at low temperature (in the martensite phase state), which causes large elastic deformation. The wire is heated to its austenite temperature range resulting in relaxation of the wire and enabling work to be done against a load. The work done against the load in reheating more than recovers the work done in deforming the wire as martensite. Effectively thermal energy is converted to mechanical energy through the mechanism of phase transformation. A portion of this mechanical energy is extracted in

cycling the working element between its heat source and heat sink and deforming the wire as martensite. The remainder can do work against the load.

The nucleation of martensite has been experimentally demonstrated to be a heterogeneous process. In experiments with single crystal spheres of Fe-Ni of sizes ranging from submicron to a fraction of a millimeter cooled to various temperatures below the martensite start temperature (M_s), not all particles transformed even if cooled to as low as 4 K (about 300°C below M_s). This appears to experimentally confirm that the homogeneous nucleation energy barrier is too great for random thermal fluctuations to overcome. Further tests on polycrystalline samples show that the number of nuclei increases with the degree of supercooling but it is largely independent of grain size and whether the sample is polycrystalline or single crystal. The surface did not appear to be a preferred nucleation site. Since grain boundaries and surfaces do not seem to significantly contribute nucleation sites, defects in the crystal must be the nucleation mechanism, the most likely candidate being dislocations⁵.

Through cycles of deformation dislocations could become entangled as sessile dislocation loops which form very precise sites for a particular martensite pattern growth of like oriented variants, thus enabling the two way memory effect.

2.2 Superelasticity

The martensitic transformation can be induced at a temperature above the unstressed austenite transformation start temperature (A_s) by the application of applied stress. The particular habit plane variants most favored by the applied load will dominate the martensite crystals. The martensite will show large apparent plastic deformation by the movement of twin boundaries as does a shape memory material. Since the transformation only occurred in response to the applied stress in the austenite temperature range, when the stress is removed the material reverts to austenite and to its original shape. The effect is that the material appears to have a very large elastic deformation range.

Figure 2-2 shows a typical superelastic loading/unloading curve for a titanium nickel alloy. At low stress levels, the stress-strain characteristic is that of NiTi austenite. As the applied stress is increased, stress induced martensitic (SIM) transformation starts to occur. SIM formation accounts for the slope reduction of the stress versus strain characteristic. Once the transformation has begun, further small increases in applied stress result in large strains as twin boundaries move with relative ease. Ultimately a limit is reached where opportunities for twin boundary movement are exhausted and the material shows martensite elasticity. Eventually plastic deformation would occur.

On unloading some hysteresis is observed as a driving force is required to move a given configuration of twin boundaries. The reverse transformation occurs at a stress level of less than where it occurred on loading and the material follows an austenite stress-strain

characteristic to the no load point. If no plastic deformation has occurred no residual strain should be present at zero load.

Typical Loading and Unloading Behavior of Superelastic NiTi

Figure 2-2 Hysteresis effect in Nitinol¹⁷

3.0 Martensitic Transformation Model

In modeling the martensitic transformation, energy contributions from the four sources must be accounted for. These are the elastic strain energy of the transformation, chemical energy, surface energy and the elastic strain energy of applied stress if present. The dominant contributor in shaping the crystallography of the transformation is the elastic strain energy component. It is also the most difficult to quantify as the strain energy associated with any cell is a long range field that is a function of the state of all other cells of the cube, whereas the chemical energy is simply a localized driving force and the surface energy depends only on the state of nearest neighbor cells. This chapter discusses the mathematical foundation for the modeling of each energy source beginning with the most critical of these, elastic strain energy.

3.1 *Martensitic Transformation Elastic Strain Energy Model*

The elastic strain model used in this work is a mathematical description of the energies of a martensitic phase transformation that can be used to predict the evolution of the transformation and that is amenable to implementation as a computational model. Chapter 7 of Reference 1 describes in detail the development of this theory. The salient aspects are reiterated herein. Some elements of the derivation are expounded where this detail seemed lacking in the original work. In most respects the original work will be more comprehensive and should be consulted as appropriate to form a complete description of the model.

The model is applied here in all three spatial dimensions to the martensitic transformation to predict its evolution and final morphology of domain patterns produced by the transformation. It is well known that martensitic crystal morphology is strongly influenced by elastic strain energy, so the propagation of a martensitic crystal proceeds along a path which results in overall free energy minimization. Since significant crystal lattice distortion is inherent in the martensitic transformation, strain energy is a significant component of the overall free energy of the crystal.

The driving force propelling the transformation is the chemical energy of the crystal lattice rearrangement. Opposing the transformation will be elastic strain energy and interfacial energy as new surfaces are created. These energies evolve with the transformation. Strain energy is especially difficult to model as each particle creates an energy field distributed throughout the body volume. The composite strain energy is the superposition of all such fields, so that any change in shape of any particle anywhere in the volume can influence the transformation of all other particles of the body volume.

The martensitic transformations studied in this work are all cubic to tetragonal transformations either as an ideal dilatationless transformation or as a transformation of Fe-Ni alloy. A cubic to tetragonal transformation results in three variants of the martensite phase. For Fe-Ni, each variant corresponds to contraction of the parent cubic crystal along one of its three axes with expansion on the other two. The ideal dilatationless strains were chosen with contraction on two axes and expansion on the other one. Each of these variants is described by an order parameter. Each order

parameter is accounted separately in the determination of overall free energy. The fourth possible crystal state is to remain untransformed parent phase. For a polycrystal, each grain may contain some mix of all four variants which evolves as the transformation progresses under the influence of the elastic strain fields of all phase particles within the entire system volume, the surface energy impediment presented by the surrounding regions of crystal, and the driving force of the chemical energy reduction associated with the transformation.

The elastic strain energy is the dominant effect in channeling the growth of the martensite phase and is responsible for the morphology of the transformation as the strain energy fields of the orientation variants distributed throughout the volume sum to provide certain paths of growth that are more favorable than others. If shape deformations are such that individual strain fields partially cancel then that path is energetically favored by the degree of cancellation. Shape deformations that result in additive strain fields result in a free energy increase thus they become very low probability events.

The strain field is governed by the differential equations of elasticity theory, i.e. the basic equation of the equilibrium of forces, $\partial\sigma_{ij}/\partial x_j = 0$, which in terms of the strain is simply written as $\partial(\lambda_{ijkl}\epsilon_{ij})/\partial x_j = 0$. For an isotropic solid this can be reformulated using the basic constitutive relations as:

$$\frac{E\sigma}{(1+\nu)(1-2\nu)} \frac{\partial\epsilon_{kk}}{\partial x_i} + \frac{E}{(1+\nu)} \frac{\partial\epsilon_{ij}}{\partial x_j} = 0$$

where E = Young's Modulus and ν = Poisson's ratio

From the strain field the strain energy could be easily determined. Total energy is the sum of chemical energy, surface energy, and strain energy. The crystal structure that results in the minimization of total energy will be the most probable configuration, but determining this from the governing differential equations is a very computationally difficult problem, although a solution could be obtained using finite element or finite difference techniques. The model outlined here offers a technique for the evaluation of strain energy that is much more computationally efficient than solving the elasticity differential equations directly.

3.1.1 Basic Physics of the Model

The physical foundation for the development of the equations of the computational model is based on a set of fairly simple principles of a multiphase mixture applied in a set of simple thought experiment steps. Key assumptions in this model are:

- 1) Homogeneous elastic modulus. All phases of the multiphase mixture have the same elastic modulus.
- 2) The average length dimensions of all particles are small compared to the overall system dimensions.

Note, in the simplest embodiment and in the development of the model described herein the external boundaries of the system are stress free, however extensions to the clamped or stressed crystal case may be easily made for very low computational cost. Such an extension has been included in the version of the model programmed and the effect of external stress studied. This is further described in Section 3.4 and in Chapter 4.0.

Consider some volume of crystal of parent phase and imagine the transformation to occur by the following steps.

Step 1. Arbitrarily choose a particle of the parent phase and cut this particle from the parent phase. If it is large enough such that its surface area to volume ratio is sufficiently

small, the interfacial energy associated with this can be neglected and the system energy remains unaffected.

Step 2. Let the particle transform to its new phase in the absence of any boundary constraints. This will result in a strain for the new phase relative to the untransformed parent phase, but this strain will be stress-free, hence it will have no strain energy. Let this shape transformation be described by a strain tensor, ϵ_{ij}^0 .

Step 3. Apply a boundary stress to the transformed particle such that its original shape is restored. The strain associated with this will be exactly the negative of the homogeneous transformation strain of Step 2 and by Hooke's law, the stress required will be

$\sigma_{ij} = -\lambda_{ijkl} \cdot \epsilon_{kl}^0$, where λ_{ijkl} is the general 81 component elastic modulus tensor. The strain energy stored in the particle becomes:

$$\Delta E_{\text{self}}(p) = 1/2 v_p \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0, \text{ where } v_p \text{ is the volume of the particle.}$$

Now suppose we have multiple particles all of the same size and shape. Since the particles are identical, all particles of like geometric variant of the phase transformation will have the same restoration strain energy*.

* While it is not mathematically necessary that all particles have the same size and shape, it is much more convenient to divide some macroscopic body into identical uniform particles, which is the approach taken in the application of the model within this work, hence the term particle should be interpreted as the basic uniform entity or cell assembled with all other identical cells to comprise the whole body, rather than some arbitrary shape.

So, letting $V_p = N_p v_p$, where N_p is the number of particles of any one geometric variant, V_p would be the total volume of all particles of that variant, and the energy of that variant becomes:

$$\Delta E_{\text{self}} = 1/2 V_p \lambda_{ijkl} \epsilon_{ij}^0(p) \epsilon_{kl}^0(p),$$

where $\epsilon_{ij}^0(p)$ is the transformation strain tensor for the p th phase transformation variant.

The total energy will be a summation over all variants (three variants for the cubic to tetragonal martensitic transformations studied here).

$$\Delta E_3 = 1/2 \sum_p V_p \lambda_{ijkl} \epsilon_{ij}^0(p) \epsilon_{kl}^0(p)$$

Furthermore, for the symmetrical cubic to tetragonal transformation of particles of identical size and shape, the strain energy of squeezing each variant to its original shape will be identical, so ΔE_3 can be equivalently expressed as simply: $\Delta E_3 = 1/2 N v_p E_p$, where N is the total number of transformed particles of all variants and E_p is the strain energy of any particle.

Step 4. Install the restored particles, with their surface traction still applied, back into the original matrix. This is a zero energy step as they all fit exactly in their original holes.

Step 5. Weld the particles on the matrix so that the system is again a single crystal.

Step 6. Remove the traction stress that is holding the particle shape. This will result in relaxation of the particle as some of its strain energy is transferred to the surrounding

crystal. A balance will be achieved at the point of balance of forces where the matrix exerts a force on the particle equal and opposite to that of the particle on the matrix.

Figure 3-1 Thought experiment steps in developing a model of a cubic to tetragonal martensitic transformation.

Figure 3-1 shows the steps of the thought experiment. The distortion of the lattice is depicted in great extreme.

3.1.2 Relaxation Energy

Elastic strain energy may be obtained by expanding the expression for strain energy in a power series in the strain tensor with truncation after the second term. This would be a polynomial of three terms. For any elastic material not complicated by a transformation, there is no stress if no strain exists, since $\sigma_{ij} = \partial E / \partial \epsilon_{ij}$, the linear term of this expansion will be non-existent.¹⁴ In the case of an unrestrained transformed particle, there is a stress-free transformation strain, which leads to the presence of a linear term in the relaxation energy formula.

The particle's relaxation energy power series expansion is then expressed as:

$$E = -\sigma_{ij}^0 \epsilon_{ij} + 1/2 \lambda_{ijkl} \epsilon_{ij} \epsilon_{kl}.$$

The term, σ_{ij}^0 , is the stress which would be required to produce the stress-free transformation strain if the particle were being mechanically forced to its deformed shape rather than being deformed as a consequence of a phase transformation with chemical driving energy. Therefore, $-\sigma_{ij}^0$ is the stress required to squeeze the transformed particle back to its untransformed original shape. The strain is measured from the initial untransformed shape of the particle, to which it is squeezed by the application of the imaginary stress.

If the particle relaxes only slightly in the matrix, it will experience only a small strain and the relaxation energy will be approximately $-\sigma_{ij}^0 \epsilon_{ij}$ (negative energy is energy given up by the particle to the matrix). If it relaxes fully to its stress-free transformed state, then the energy it gives up will be:

$$\begin{aligned} E &= -\sigma_{ij}^0 \epsilon_{ij}^0 + 1/2 \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 \\ &= -1/2 \sigma_{ij}^0 \epsilon_{ij}^0. \end{aligned}$$

Graphically this is depicted below. The relaxation energy of the particle is the area of the triangle under the linear stress-strain curve minus the area of the $\sigma_{ij}^0 \epsilon_{ij}$ rectangle. For very small strains, this can be approximated as work done under constant stress and is equal to $-\sigma_{ij}^0 \epsilon_{ij}$. For full relaxation of the particle, i.e. to a strain equal to the stress-free transformation strain ϵ_{ij}^0 , it becomes simply the negative of the area under the stress-strain curve ($-1/2 \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0$).

Figure 3-2 Graphical depiction of the relaxation energy of the transformed particle as it is released into the matrix. For any given relaxation ε_1 , the relaxation energy is given by the shaded region.

For the matrix, its energy is also given as:

$$E = -\sigma_{ij}^0 \varepsilon_{ij} + 1/2 \lambda_{ijkl} \varepsilon_{ij} \varepsilon_{kl},$$

but in the case of an untransformed matrix particle, its stress free transformation strain is non-existent, which removes the linear term, so this reduces to:

$$E = 1/2 \lambda_{ijkl} \varepsilon_{ij} \varepsilon_{kl},$$

which is simply the area of the triangle under its linear stress-strain curve.

The power series expansion for strain energy simply extends only to the second order term because of the assumption of linear elastic behavior. If the material were to be modeled as non-linear, higher order terms in this expansion would be required.

The total energy of the system after relaxation of the particle is the sum of the shape restoration energy of step 3 and the relaxation energy:

$$E_{\text{elast}} = \Delta E_3 + \Delta E_{\text{relax}} = 1/2 \sum_p V_p \lambda_{ijkl} \epsilon_{ij}^0(p) \epsilon_{kl}^0(p) + \int_V [-\sigma_{ij}^0 \epsilon_{ij} + 1/2 \lambda_{ijkl} \epsilon_{ij} \epsilon_{kl}] dV$$

σ_{ij}^0 in the above equation refers to the stress applied to a particle of a given orientation variant to restore its shape. For a cluster of p particles, this could be expressed as $\sum \sigma_{ij}^0(p) \theta_p(r)$, where $\sigma_{ij}^0(p)$ is the restoration stress for the p th type of particles (i.e. one of three variants) and $\theta_p(r)$ is the shape function describing all of the p th type particle variants within the matrix. The shape function takes the value of unity within a transforming particle of the p th type and zero outside of this type of particle. The summation is taken over all variants. For the cases studied here the number of martensite variants is fixed at three. Expressing the relaxation energy where multiple transforming particles of multiple variants are involved then results in:

$$\Delta E_{\text{relax}} = \int_V [\sum \sigma_{ij}^0(p) \theta_p(r) \epsilon_{ij} + 1/2 \lambda_{ijkl} \epsilon_{ij} \epsilon_{kl}] dV \quad (3.1)$$

Solving this equation is non-trivial as it requires the evaluation of the elastic strain field throughout the volume. However, it may be simplified somewhat by decomposing the

elastic strain field into two constituent fields, a homogeneous strain field and a heterogeneous strain field, such that the total field is the sum of the two.

$$\varepsilon_{ij}(r) = \bar{\varepsilon}_{ij} + \delta\varepsilon_{ij}(r)$$

The homogeneous strain is defined as a macroscopic strain that is constant throughout the volume of the body. The heterogeneous strain field does not affect the macroscopic crystal shape and its integral over the body volume will be zero.

Substituting $\varepsilon_{ij}(r)$ in component form in equation 3.1 and expanding yields:

$$\begin{aligned} \Delta E_{\text{relax}} &= \int_V [\Sigma -\sigma^0_{ij}(p)\theta_p(r)(\bar{\varepsilon}_{ij} + \delta\varepsilon_{ij}(r)) + 1/2\lambda_{ijkl}(\bar{\varepsilon}_{ij} + \delta\varepsilon_{ij})(\bar{\varepsilon}_{kl} + \delta\varepsilon_{kl})]dV \\ \Delta E_{\text{relax}} &= \int_V [\Sigma -\sigma^0_{ij}(p)\theta_p(r)\bar{\varepsilon}_{ij} + 1/2\lambda_{ijkl}\bar{\varepsilon}_{ij}\bar{\varepsilon}_{kl}]dV + \\ &\quad \int_V [\Sigma -\sigma^0_{ij}(p)\theta_p(r)\delta\varepsilon_{ij}(r) + 1/2\lambda_{ijkl}(\delta\varepsilon_{ij}(r)\delta\varepsilon_{kl}(r) + 2\delta\varepsilon_{ij}\bar{\varepsilon}_{kl})]dV \\ &= E_{\text{homogeneous}} + E_{\text{heterogeneous}} \end{aligned}$$

where:

$$E_{\text{homogeneous}} = \int_V [\Sigma -\sigma^0_{ij}(p)\theta_p(r)\bar{\varepsilon}_{ij} + 1/2\lambda_{ijkl}\bar{\varepsilon}_{ij}\bar{\varepsilon}_{kl}]dV$$

With the average strain being constant, its integration is trivial. Recognizing the integral of the shape function over volume as simply the volume of the particle, yields:

$$E_{\text{homogeneous}} = \Sigma -\sigma^0_{ij}(p)\bar{\varepsilon}_{ij}V_p + V/2\lambda_{ijkl}\bar{\varepsilon}_{ij}\bar{\varepsilon}_{kl} \quad (3.2)$$

$E_{\text{heterogeneous}}$ can be rearranged as follows:

$$\begin{aligned} E_{\text{heterogeneous}} &= \int_V [\Sigma -\sigma^0_{ij}(p)\theta_p(r)\delta\varepsilon_{ij}(r) + 1/2\lambda_{ijkl}(\delta\varepsilon_{ij}(r)\delta\varepsilon_{kl}(r) + 2\delta\varepsilon_{ij}\bar{\varepsilon}_{kl})]dV \\ &= \int_V [\Sigma -\sigma^0_{ij}(p)\theta_p(r)\delta\varepsilon_{ij}(r) + 1/2\lambda_{ijkl}\delta\varepsilon_{ij}(r)\delta\varepsilon_{kl}(r) + \lambda_{ijkl}\bar{\varepsilon}_{kl}\delta\varepsilon_{ij}]dV \end{aligned}$$

$$= \int_V [\delta \epsilon_{ij}(r) (\sum -\sigma_{ij}^0(p) \theta_p(r) + \lambda_{ijkl} \bar{\epsilon}_{kl}) + 1/2 \lambda_{ijkl} \delta \epsilon_{ij}(r) \delta \epsilon_{kl}(r)] dV \quad (3.3)$$

The relaxation of the particle will equilibrate at a total energy minimum, which may be found by setting the derivatives with respect to strain and displacement of the functions to 0. The total energy is $\Delta E_3 + \Delta E_{\text{relax}}$, but ΔE_3 is a constant. Therefore its derivative is 0.

Setting derivatives with respect to both average strain and displacement to 0 yields:

$$\partial E_{\text{hom}} / \partial \bar{\epsilon}_{ij} = 0; \quad \partial E_{\text{heterogeneous}} / \partial u_i = 0.$$

$$\text{From 3.2, } \partial E_{\text{hom}} / \partial \bar{\epsilon}_{ij} = -\sum V_p \sigma_{ij}^0(p) + V \lambda_{ijkl} \bar{\epsilon}_{kl} \quad (3.4)$$

$$\text{Setting this to zero results in } \lambda_{ijkl} \bar{\epsilon}_{kl} = \sum w_p \sigma_{ij}^0(p) \quad (3.5)$$

where $w_p = V_p/V$ = volume fraction of all transforming particles of the pth variant.

Exploiting this result by substituting in equation 3.3 simplifies the heterogeneous relaxation energy to:

$$\begin{aligned} E_{\text{heterogeneous}} &= \int_V [\delta \epsilon_{ij}(r) (\sum -\sigma_{ij}^0(p) \theta_p(r) + \sum w_p \sigma_{ij}^0(p)) + 1/2 \lambda_{ijkl} \delta \epsilon_{ij}(r) \delta \epsilon_{kl}(r)] dV \\ &= \int_V [-\sum \sigma_{ij}^0(p) \delta \epsilon_{ij}(r) (\theta_p(r) - w_p) + 1/2 \lambda_{ijkl} \delta \epsilon_{ij}(r) \delta \epsilon_{kl}(r)] dV \\ &= \int_V [-\sum \sigma_{ij}^0(p) \delta \epsilon_{ij}(r) \Delta \theta_p(r) + 1/2 \lambda_{ijkl} \delta \epsilon_{ij}(r) \delta \epsilon_{kl}(r)] dV \end{aligned} \quad (3.6)$$

$$\text{where } \Delta \theta_p(r) = \theta_p(r) - V_p/V$$

From 3.5 and given that $\sigma_{ij}^0(p) = \lambda_{ijkl} \epsilon_{kl}^0$, we can write

$$\bar{\epsilon}_{ij} = \sum w_p \epsilon_{ij}^0$$

Substituting in equation 3.2, simplifies the homogeneous energy expression as:

$$E_{\text{homogeneous}} = -\sum \sum \lambda_{ijkl} w_p \epsilon_{ij}^0 \epsilon_{kl}^0 V_q + V/2 \sum \sum \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 w_p w_q$$

where the summations are performed twice over all particles variants in the system, p, q.

$$\begin{aligned}
 E_{\text{homogeneous}} &= -V \sum \sum \lambda_{ijkl} w_p \epsilon_{ij}^0 \epsilon_{kl}^0 w_q + V/2 \sum \sum \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 w_p w_q \\
 &= -V/2 \sum \sum \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 w_p w_q
 \end{aligned} \tag{3.7}$$

3.1.3 Heterogeneous Strain energy

By applying the infinitesimal strain approximation from elasticity theory, an approximate expression for the variation of heterogeneous strain with respect to displacement may be determined.

Applying the Lagrangian infinitesimal strain relation,

$$\delta \epsilon_{ij} = 1/2 (\partial u_i / \partial r_j + \partial u_j / \partial r_i) \tag{3.8}$$

allows the product of differential strain elements to be expressed in terms of displacement.

$$\begin{aligned}
 \delta \epsilon_{ij} \delta \epsilon_{kl} &= [1/2 (\partial u_i / \partial r_j + \partial u_j / \partial r_i)] [1/2 (\partial u_k / \partial r_l + \partial u_l / \partial r_k)] \\
 &= [1/4 (\partial u_i \partial u_k / \partial r_j \partial r_l + \partial u_j \partial u_k / \partial r_i \partial r_l + \partial u_i \partial u_l / \partial r_j \partial r_k + \partial u_j \partial u_l / \partial r_i \partial r_k)]
 \end{aligned}$$

Because of the symmetry of the tensors, this equates to:

$$\delta \epsilon_{ij} \delta \epsilon_{kl} = \partial u_k \partial u_i / (\partial r_l \partial r_j) \tag{3.9}$$

Substituting 3.9 and 3.8 in 3.6 gives:

$$E_{\text{heterogeneous}} = \int_V [-\Sigma \sigma_{ij}^0(p) [1/2(\partial u_i/\partial r_j + \partial u_j/\partial r_i)] \Delta \theta_p(r) + 1/2 \lambda_{ijkl} \partial u_k \partial u_l / (\partial r_i \partial r_j)] dV$$

Recognizing again the symmetry of the tensors, reduces this to:

$$E_{\text{heterogeneous}} = \int_V [-\Sigma \sigma_{ij}^0(p) \partial u_i / \partial r_j \Delta \theta_p(r) + 1/2 \lambda_{ijkl} \partial u_k \partial u_l / (\partial r_i \partial r_j)] dV \quad (3.10)$$

The first variation of any function $F(u)$ is defined as :

$$\delta F = \frac{\partial F}{\partial u} \delta u \quad \text{where } \delta u \text{ is the variation in } u \text{ and } \delta F \text{ is the variation in } F$$

The first variation of the heterogeneous relaxation energy may be simply written as:

$$\begin{aligned} \delta E_{\text{heterogeneous}} &= \int_V \delta [-\Sigma \sigma_{ij}^0(p) \partial u_i / \partial r_j \Delta \theta_p(r) + 1/2 \lambda_{ijkl} \partial u_k \partial u_l / (\partial r_i \partial r_j)] dV \\ &= \left(\int_V [-\Sigma \sigma_{ij}^0(p) \partial \delta u_i / \partial r_j \Delta \theta_p(r) + (1/2) \lambda_{ijkl} (\partial \delta u_k / \partial r_l) \partial u_i / \partial r_j + (1/2) \lambda_{ijkl} (\partial u_k / \partial r_l) \partial \delta u_i / \partial r_j] dV \right) \end{aligned}$$

Since the tensors are symmetric, this equates to:

$$= \left(\int_V [-\Sigma \sigma_{ij}^0(p) \partial \delta u_i / \partial r_j \Delta \theta_p(r) + \lambda_{ijkl} (\partial \delta u_k / \partial r_l) \partial u_i / \partial r_j] dV \right)$$

Integration by parts,

$$\int_0^L w dv = - \int_0^L v dw + wv \Big|_0^L$$

may be applied to each term of the $\delta E_{\text{heterogeneous}}$ expression. This gives:

$$- \int_V [\Sigma \sigma_{ij}^0(p) \partial \delta u_i / \partial r_j \Delta \theta_p(r)] dV = -\Sigma \sigma_{ij}^0(p) \Delta \theta_p(r) \delta u_i \Big|_a^b + \int_V \Sigma \sigma_{ij}^0(p) \Delta \theta_p(r) / \partial r_j \delta u_i dV$$

and

$$\int_V [\lambda_{ijkl} (\partial u_k / \partial r_l) \partial \delta u_i / \partial r_j] dV = \lambda_{ijkl} (\partial u_k / \partial r_l) \delta u_i \Big|_a^b - \int_V \lambda_{ijkl} (\partial^2 u_k / \partial^2 r_l) \delta u_i dV$$

The expression for $\delta E_{\text{heterogeneous}}$ can be simplified by assuming that the variation in strain, $\delta u_i = 0$, vanishes at the surface of the body, which is a consequence of the assumption that the heterogeneous strain field does not affect the macroscopic crystal shape. This is not strictly true and variations in the local heterogeneous strain field will exist. Variations in the strain field near the surface are minimized by using the largest number of cells practicable in the cube and with martensite feature size which is small compared to the dimensions of the cube.

By setting $\delta u_i = 0$ at the surface, the expression reduces to:

$$\delta E_{\text{heterogeneous}} = \int_V \Sigma \sigma_{ij}^0 \partial \Delta \theta_p(r) / \partial r_j \delta u_i dV - \int_V \lambda_{ijkl} (\partial^2 u_k / \partial^2 r_l) \delta u_i dV$$

Dividing both sides by δu_i gives:

$$\delta E_{\text{heterogeneous}} / \delta u_i = \int_V \Sigma \sigma_{ij}^0 \partial \Delta \theta_p(r) / \partial r_j dV - \int_V \lambda_{ijkl} (\partial^2 u_k / \partial^2 r_l) dV$$

From the total energy minimum criterion, $\delta E_{\text{heterogeneous}} / \delta u_i = 0$, therefore:

$$\begin{aligned} \int_V \Sigma \sigma_{ij}^0 \partial \Delta \theta_p(r) / \partial r_j dV &= \int_V \lambda_{ijkl} (\partial^2 u_k / \partial^2 r_l) dV \\ \Sigma \sigma_{ij}^0 \partial \Delta \theta_p(r) / \partial r_j &= \lambda_{ijkl} (\partial^2 u_k / \partial^2 r_l) \end{aligned} \quad (3.11)$$

This is the fundamental equation defining heterogeneous strain throughout the body volume.

A convenient technique for solving any differential equation is the application of the Fourier transform, defined as:

$\mathbf{f}(\mathbf{k}) = \int_V \mathbf{f}(\mathbf{r}) e^{-i\mathbf{k}\mathbf{r}} dV$, where $\mathbf{k}$ is the wave vector and $\mathbf{f}(\mathbf{k})$ becomes the transformed function in wave vector space.

Let $v(\mathbf{k})$ be the the transform of $u(\mathbf{r})$, i.e.

$$v(\mathbf{k}) = \int_V u(\mathbf{r}) e^{-i\mathbf{k}\mathbf{r}} dV$$

and apply the Fourier transform to equation 3.11. This produces the following result:

$$-i\Sigma_{ij}^0 k_j \Delta\theta_p(\mathbf{k}) = \lambda_{ijkl} k_j k_k v_l(\mathbf{k}) \quad (3.12)$$

Note the Fourier transform of $du(\mathbf{r})/dr = ikv(\mathbf{k})$ and the Fourier transform of

$$d^2u(\mathbf{r})/dr^2 = -k^2v(\mathbf{k}) \text{ and } i = \sqrt{-1}.$$

The unknown function of interest is $v(\mathbf{k})$, so solving for $v(\mathbf{k})$, yields the following:

$$v_l(\mathbf{k}) = -i\Sigma_{ij}^0(p) k_j \Delta\theta_p(\mathbf{k}) (\lambda_{ijkl} k_j k_k)^{-1} \quad (3.13)$$

Writing the heterogeneous strain energy expression, 3.10 in Fourier transform space gives the following:

$$E_{\text{heterogeneous}} = \int_V [-i\Sigma_{ij}^0(p) k_j v_i(\mathbf{k}) \Delta\theta_p(\mathbf{k}) - 1/2 \lambda_{ijkl} k_j v_i(\mathbf{k}) k_l v_k^*(\mathbf{k})] dV$$

The differential volume element is dV or dr^3 . In wave vector space, the differential element is $dk/2\pi$, so expressing this fully in k space gives the following:

$$E_{\text{heterogeneous}} = \int_k [-i\Sigma_{ij}^0(p)k_j v_i(\mathbf{k})\Delta\theta_p(\mathbf{k}) - 1/2\lambda_{ijkl}k_j v_i(\mathbf{k})k_l v_k^*(\mathbf{k})]d^3k/(2\pi)^3 \quad (3.14)$$

This can be rewritten recognizing the condition of energy minimization of equation 3.11 and substituting the expression for $v(\mathbf{k})$ in equation 3.13.

$$E_{\text{heterogeneous}} = \int_k [-i\Sigma_{ij}^0(p)k_j(-i\Sigma_{jk}^0(q)k_j\Delta\theta_p(\mathbf{k})(\lambda_{ijkl}k_jk_l)^{-1})\Delta\theta_q(\mathbf{k})]d^3k/(2\pi)^3 + \\ \int_k [-1/2\lambda_{ijkl}k_jk_l(i\Sigma_{jk}^0(p)k_j\Delta\theta_p(\mathbf{k})(\lambda_{ijkl}k_jk_l)^{-1})(i\Sigma_{ij}^0(q)k_i\Delta\theta_q(\mathbf{k})(\lambda_{ijkl}k_jk_l)^{-1})]d^3k/(2\pi)^3 \quad (3.15)$$

Since $(\lambda_{ijkl}k_jk_l)(\lambda_{ijkl}k_jk_l)^{-1} = \mathbf{I}$, the second term reduces to:

$$\int_k [-1/2(i\Sigma_{jk}^0(p)k_j\Delta\theta_p(\mathbf{k})(\lambda_{ijkl}k_jk_l)^{-1})(i\Sigma_{ij}^0(q)k_j\Delta\theta_q(\mathbf{k}))]d^3k/(2\pi)^3$$

rearranging gives:

$$\int \sum_{p=1}^n \sum_{q=1}^n [1/2\sigma_{jk}^0(p)k_j\Delta\theta_p(\mathbf{k})(\lambda_{ijkl}k_jk_l)^{-1}\sigma_{ij}^0(q)k_j\Delta\theta_q(\mathbf{k})d^3k/(2\pi)^3]$$

The first term of equation 3.15 rearranges to:

$$\int \sum_{p=1}^n \sum_{q=1}^n [-\sigma_{ij}^0(p)k_j\Delta\theta_p(\mathbf{k})(\lambda_{ijkl}k_jk_l)^{-1}\sigma_{jk}^0(q)k_j\Delta\theta_q(\mathbf{k})d^3k/(2\pi)^3]$$

Adding these gives simply:

$$\int \sum_{p=1}^n \sum_{q=1}^n [-1/2\sigma_{jk}^0(p)k_j\Delta\theta_p(\mathbf{k})(\lambda_{ijkl}k_jk_l)^{-1}\sigma_{ij}^0(q)k_j\Delta\theta_q(\mathbf{k})d^3k/(2\pi)^3] \quad (3.16)$$

The total relaxation energy is the sum of the homogeneous and heterogeneous components. Adding 3.7 and 3.16 gives:

$$E_{\text{relax}} = -V/2 \sum_{p=1}^n \sum_{q=1}^n \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 w_p w_q +$$

$$\int \sum_{p=1}^n \sum_{q=1}^n [-1/2 \sigma_{jk}^0(p) k_j \Delta \theta_p(\mathbf{k}) (\lambda_{ijkl} k_j k_l)^{-1} \sigma_{ij}^0(q) k_j \Delta \theta_q(\mathbf{k}) d^3 k / (2\pi)^3]$$

The total elastic energy is the sum of the strain energy that restored the particle to its original shape (ΔE_3) and the relaxation energy above.

$$E_{\text{elast}} = \sum_{p=1}^n 1/2 V_p \lambda_{ijkl} \epsilon_{ij}^0(p) \epsilon_{kl}^0(p) - V/2 \sum_{p=1}^n \sum_{q=1}^n \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 w_p w_q +$$

$$\int \sum_{p=1}^n \sum_{q=1}^n [-1/2 \sigma_{jk}^0(p) k_j \Delta \theta_p(\mathbf{k}) (\lambda_{ijkl} k_j k_l)^{-1} \sigma_{ij}^0(q) k_j \Delta \theta_q(\mathbf{k}) d^3 k / (2\pi)^3] \quad (3.17)$$

The first two terms of 3.17 are:

$$1/2 \sum_{p=1}^n V_p \lambda_{ijkl} \epsilon_{ij}^0(p) \epsilon_{kl}^0(p) - V/2 \sum_{p=1}^n \sum_{q=1}^n \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 w_p w_q$$

Recognizing $V w_p = V_p$ gives:

$$= 1/2 \sum_{p=1}^n V_p \lambda_{ijkl} \epsilon_{ij}^0(p) \epsilon_{kl}^0(p) - 1/2 \sum_{p=1}^n \sum_{q=1}^n \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 V_p w_q$$

$$= 1/2 \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 \left(\sum_{p=1}^n V_p - \sum_{p=1}^n \sum_{q=1}^n \frac{V_p V_q}{V} \right)$$

These terms can be equivalently combined under a single pair of summations using the Kronecker delta, as only repeated indices of the Kronecker delta are non-zero.

$$\begin{aligned}
&= \frac{1}{2} \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 \sum_{p=1}^n \sum_{q=1}^n \delta_{pq} V_p - \sum_{p=1}^n \sum_{q=1}^n \frac{V_p V_q}{V} \\
&= \frac{1}{2} \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 \sum_{p=1}^n \sum_{q=1}^n \left(\delta_{pq} V_p - \frac{V_p V_q}{V} \right) \quad (3.18)
\end{aligned}$$

From the definition of $\Delta\theta(p)$, $\Delta\theta_p(r) = \theta_p(r) - V_p/V$, and given that the integral of the shape function over the system volume is the volume of the particle variant, we can write the following:

$$\begin{aligned}
\int_V \Delta\theta_p(r) \Delta\theta_q(r) dV &= \int_V (\theta_p(r) - V_p/V) (\theta_q(r) - V_q/V) dV \\
&= \int_V (\theta_p(r) - w_p) (\theta_q(r) - w_q) dV \\
&= \int_V (\theta_p(r)\theta_q(r) - w_p\theta_q(r) - w_q\theta_p(r) + w_p w_q) dV \\
&= \int_V [(\theta_p(r)\theta_q(r) dV] - w_p V_q - w_q V_p + w_p w_q V \\
&= \int_V [(\theta_p(r)\theta_q(r) dV] - w_p V_q - w_q V_p + w_p V_q \\
&= \int_V [(\theta_p(r)\theta_q(r) dV] - w_q V_p
\end{aligned}$$

Now, the product of shape functions can only be non-zero if the indices are the same, because a particle can not be simultaneously part of two variants at once. Respecting this, allows the above to be reduced to:

$$= \int_V [(\theta_p(r))^2 dV] - w_q V_p$$

Since $\theta_p(r)$ is either equal to one inside the particle or zero outside of it, this further reduces to simply:

$$\begin{aligned}
&= \int_V [(\theta_p(r)dV) - w_q V_p] \\
&= V_p - w_q V_p
\end{aligned}$$

This can be expressed in matrix form as:

$$\begin{aligned}
&= \delta_{pq} V_p - w_q V_p \\
&= \delta_{pq} V_p - V_q V_p / V
\end{aligned}$$

Annotating 3.18 with this equivalency, allows 3.18 to be rewritten as:

$$1/2 \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 \sum_{p=1}^n \sum_{q=1}^n \int_V \Delta \theta_p(r) \Delta \theta_q(r) dV$$

In k-space this becomes:

$$1/2 \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 \sum_{p=1}^n \sum_{q=1}^n \int d^3k / (2\pi)^3 \Delta \theta_p(\mathbf{k}) \Delta \theta_q^*(\mathbf{k})$$

Exploiting this result to rewrite the complete expression for elastic strain energy (3.17), by substituting it for the first two terms of that equation, results in the following:

$$\begin{aligned}
E_{\text{elast}} &= 1/2 \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 \sum_{p=1}^n \sum_{q=1}^n \int d^3k / (2\pi)^3 \Delta \theta_p(\mathbf{k}) \Delta \theta_q^*(\mathbf{k}) + \\
&\sum_{p=1}^n \sum_{q=1}^n \int [-1/2 \sigma_{jk}^0(p) \mathbf{k}_j \Delta \theta_p(\mathbf{k}) (\lambda_{ijkl} k_j k_l)^{-1} \sigma_{ij}^0(q) \mathbf{k}_j \Delta \theta_q^*(\mathbf{k}) d^3k / (2\pi)^3] \\
&= 1/2 \sum_{p=1}^n \sum_{q=1}^n \int d^3k / (2\pi)^3 \Delta \theta_p(\mathbf{k}) \Delta \theta_q^*(\mathbf{k}) [\lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 - \sigma_{jk}^0(p) \mathbf{k}_j (\lambda_{ijkl} k_j k_l)^{-1} \sigma_{ij}^0(q) \mathbf{k}_j] \quad (3.19)
\end{aligned}$$

The Fourier transform of $\Delta\theta_p(r)$ is:

$$\int dV(\theta_p(r) - V_p/V)e^{ikr}$$

If $k=0$, this reduces to:

$$\begin{aligned} & \int dV(\theta_p(r) - V_p/V) \\ &= V_p - V_p \\ &= 0 \end{aligned}$$

For $k \neq 0$,

$$\begin{aligned} & \int dV(\theta_p(r) - V_p/V)e^{ikr} \\ & \int dV(\theta_p(r))e^{ikr} \end{aligned}$$

which is simply represented symbolically as $\theta_p(\mathbf{k})$.

Therefore, equation 3.19 can be written in terms of $\theta(\mathbf{k})$ with the 0^{th} term excluded from the integration.

$$E_{\text{elast}} = \frac{1}{2} \sum_{p=1}^n \sum_{q=1}^n \oint [\lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 - \sigma_{jk}^0(p) \mathbf{k}_j (\lambda_{ijkl} k_j k_l)^{-1} \sigma_{ij}^0(q) \mathbf{k}_j] d^3k / (2\pi)^3 \theta_p(\mathbf{k}) \theta_q^*(\mathbf{k}) \quad (3.20)$$

where $\oint$ signifies the exclusion of the 0th term.

The fact that the 0^{th} term in k-space evaluates to 0 in the above equation implies that the homogeneous strain energy must be zero, as the homogeneous strain energy is by definition uniform throughout the body. This is in apparent contradiction to the approach in the derivation where homogeneous and heterogeneous strain energies were separately derived then combined to produce the composite strain energy. However, it becomes an

acceptable intuitive result when one considers that a body that is unconstrained can not contain any uniform strain energy throughout its volume as it has no boundary traction to supply a reaction force. Therefore simple physics dictates that the $\mathbf{k}=(0,0,0)$ strain energy term must vanish.

Equation 3.20 gives the value of strain energy for all particles integrated over the volume of the cube, but to determine the evolution of the individual phase states of all of the cells, requires the determination of the strain energy driving force. For any cell the driving force propelling a change in its state is the energy differential between its current state and the alternate states. Mathematically this is described as the variational derivative of strain energy with respect to order parameter. Taking the variational derivative of equation 3.20, yields the strain energy component of the transformation driving force as:

$$\frac{\delta E_{\text{elast}}}{\delta \theta_p(\mathbf{k})} = 1/2 \sum_{p=1}^n [\lambda_{ijkl} \varepsilon_{ij}^0 \varepsilon_{kl}^0 - \sigma_{jk}^0(\mathbf{p}) \mathbf{k}_j (\lambda_{ijkl} \mathbf{k}_j \mathbf{k}_l)^{-1} \sigma_{ij}^0(\mathbf{q}) \mathbf{k}_j] \theta_p(\mathbf{k}) \quad (3.21)$$

Equation 3.21 is the equation implemented in the computer code. In this format it allows quite efficient implementation as the only evolving quantity is the shape function in $\mathbf{k}$ -space. This evolves as particles transform in the most energetically favorable orientation. Assuming the system to be composed of particles of uniform size, the stress-free transformation strain and the restoration stress will be the same for any particle of a given orientation variant anywhere in the system. Young's modulus is also assumed to have a constant value throughout the volume and be the same for both parent phase and martensite phase particles.

3.2 Chemical Energy

The chemical energy of a cell is expressed as some function of the cell's order parameters such that equivalent minima exist for the value of the order parameter which corresponds to each orientation variant. The total chemical energy for the cube is the sum of all the individual cell energies.

The chemical energy of a cell is given as a function of the order parameters by the following Landau polynomial⁹:

$$E(r) = E_0 + C_1 \cdot [\theta_1^2(r) + \theta_2^2(r) + \theta_3^2(r)] - C_2 \cdot [\theta_1^3(r) + \theta_2^3(r) + \theta_3^3(r)] + C_3 \cdot [\theta_1^2(r) + \theta_2^2(r) + \theta_3^2(r)]^2 \quad (3.22)$$

$\theta_n(r)$ refers to the order parameter for the nth tetragonal orientation variant. The forth state is parent phase, but it is characterized as a value of 0 for all three tetragonal variant order parameters.

For any cell its choices are to remain in its current state or to assume one of the other phases, therefore the energy differentials from its current state to the alternate states define the driving forces motivating each possible change of state.

Differentiating the Landau polynomial with respect to order parameter, for any single order parameter (let this be θ_1), then gives the chemical energy driving force as follows:

$$\partial E(r) / \partial \theta_1(r) = 2 \cdot C_1 \cdot \theta_1(r) - 3 \cdot C_2 \cdot \theta_1^2(r) + 4 \cdot C_3 \cdot [\theta_1^3(r) + \theta_1 \cdot \theta_2^2(r) + \theta_1 \cdot \theta_3^2(r)] \quad (3.23)$$

The value of the equilibrium order parameter may be determined by allowing $\theta_2 = \theta_3 = 0$ in equation 3.23, setting the value of $\partial E(r)/\partial \theta_1(r) = 0$, and solving for θ_1 . This gives the following equation:

$$0 = 2 \cdot C_1 \cdot \theta_1(r) - 3 \cdot C_2 \cdot \theta_1^2(r) + 4 \cdot C_3 \cdot \theta_1^3(r),$$

so,

$$0 = 2 \cdot C_1 - 3 \cdot C_2 \cdot \theta_1(r) + 4 \cdot C_3 \cdot \theta_1^2(r) \quad (3.24)$$

This is a simple quadratic equation in $\theta_1(r)$ and has roots given by the quadratic formula.

$$\theta_1(r) = \frac{3 \cdot C_2 \pm \sqrt{9 \cdot C_2^2 - 32 \cdot C_1 \cdot C_3}}{8 \cdot C_3} \quad (3.25)$$

The equilibrium order parameter is the order parameter value for which there is no driving force between states. The equilibrium order parameter value is used to normalize the value of the transformation strain.

3.3 Surface Energy

The surface energy associated with any cell is related to the derivative of the transformation strain tensor with respect to space, i.e. the gradient. Since the transformation strain tensor is a function of the order parameter, the surface energy can be expressed directly in terms of the order parameter. The surface energy is given as the product of the gradient strain tensors and proportionality tensor, β^{10} .

$$E_s(\mathbf{r}) = \beta_{imnjsp} \cdot \nabla_i \epsilon_{c\ mn}^0(\mathbf{r}) \cdot \nabla_j \epsilon_{c\ sp}^0(\mathbf{r}) \quad (3.26)$$

For this work β_{imnjsp} is a diagonal matrix with a constant scale factor on elements of the diagonal. $E_s(\mathbf{r})$ is the surface energy function throughout the cube which must be integrated over the cube volume to obtain the total contribution to surface energy.

The strain field, $\epsilon_{c\ mn}^0(\mathbf{r})$ of equation 3.26 refers to the composite transformation strain field which is composed of contributions from all p variants, and may be expressed as a function of the order parameters and their associated individual stress-free transformation strains as¹⁰:

$$\epsilon_{c\ mn}^0(\mathbf{r}) = \sum_{p=1}^n \theta_p(\mathbf{r}) \cdot \epsilon_{mn}^0(p, \mathbf{r}) \quad (3.27)$$

where the summation is over all variants, n , and $\epsilon_{mn}^0(p, \mathbf{r})$ is the stress-free transformation strain of variant p .

so,

$$E_s(\mathbf{r}) = \beta_{imnjsp} \cdot \nabla_i \sum_{p=1}^n \theta_p(\mathbf{r}) \cdot \epsilon_{mn}^0(p, \mathbf{r}) \cdot \nabla_j \sum_{p=1}^n \theta_p(\mathbf{r}) \cdot \epsilon_{sp}^0(p, \mathbf{r}) \quad (3.28)$$

The stress-free transformation strain, $\epsilon_{sp}^0(p, \mathbf{r})$, is simply a known constant for each variant. Therefore it could be defined as part of the term β_{imnjsp} and the expression simplified to:

$$E_s(\mathbf{r}) = \beta_{imnjsp} \cdot \nabla_i \sum_{p=1}^n \theta_p(\mathbf{r}) \cdot \nabla_j \sum_{p=1}^n \theta_p(\mathbf{r}) \quad (3.29)$$

This is much more conveniently calculated in k -space where the gradient simply becomes $k \cdot \theta(\mathbf{k})$.

$$E_s(\mathbf{k}) = \beta_{\text{imnjsp}} \cdot \sum_{p=1}^n \mathbf{k} \theta_p(\mathbf{k}) \cdot \sum_{p=1}^n \mathbf{k} \theta_p(\mathbf{k}) \quad (3.30)$$

Equation 3.30 defines the surface energy of the transformation in k-space for all order parameters, but to determine the driving force for a change of state, the change in the value of the surface energy with respect to each order parameter is the quantity of interest. Taking the derivative of the surface energy with respect to order parameter for each of the order parameters yields the following expression:

$$\begin{aligned} \frac{\partial E_s(\mathbf{k})}{\partial \theta_p(\mathbf{k})} &= \frac{\partial [\beta_{\text{imnjsp}} \cdot \mathbf{k}^2 \theta_p(\mathbf{k}) \cdot \theta_p(\mathbf{k})]}{\partial \theta_p(\mathbf{k})} \\ &= \beta_{\text{imnjsp}} \cdot \mathbf{k}^2 \theta_p(\mathbf{k}) \end{aligned}$$

The inverse Fourier transform must be applied to the above to arrive at a result in real space.

3.4 Applied Stress

Applied stress affects the transformation by interacting with the transformation strains.

The transformation strains multiplied by the applied stress gives the work done by the transformation against the applied load.

$$E_{\text{load}} = -\sigma_{ij}^{\text{applied}} \cdot \sum_{p=1}^n \int_V \epsilon_{ij}^0(p,r) \cdot \theta_p(r) dV$$

The negative sign indicates that any applied load component that coincides with the direction of a transformation strain will act to reduce the free energy of the transformation.

The driving force is obtained by taking the variational derivative with respect to order parameter of the above expression, which gives:

$$\frac{\delta E_{\text{load}}}{\delta \theta_p(r)} = -\sigma_{ij}^{\text{applied}} \cdot \epsilon_{ij}^0(p,r)$$

The further affect of the applied load is linear elastic strain of the material which is taken into account and is significant in determining the overall strain in the stress versus strain test, but it has no impact on the transformation driving force.

4.0 The Program

The computer code that performs the martensite crystal growth simulation used for this study was developed over a period of several years with contributions from multiple contributors from the department of mechanical and aerospace engineering at Carleton University and the department of ceramic and materials engineering at Rutgers University. The code follows the phase field model theory outlined in References 8-10.

The program describes the evolution of a cubic array of cells. Each cell may become one of three tetragonal variants or it may remain in its parent phase state. Associated with each cell is an order parameter. The order parameter is a one dimensional array of real numbers representing the phase state of the cell by expressing its degree of strain for each of the possible phase states. The extent to which every cell is inclined to each of its strain states is determined by a calculation of overall energy minimization for the entire cube of cells. The order parameter contains three elements per cell, one element corresponding to each of the three tetragonal variants. A normalized value of one for the order parameter corresponding to any of the variants with a value of zero for the other two indicates the cell is entirely in that state. Zeroes for all elements of the order parameters indicates the cell has no tetragonal transformation character and is therefore 100% parent phase.

During the simulation the state of a given cell is not absolutely determined as exclusively one variant, rather the order parameters may take on a continuous range of values with cells being a mixture of some degree of all three variants. With the resolution of the specified time step of the simulation, a driving force calculation for the entire cube is

performed and the order parameter values are updated. At the conclusion of some specified elapsed time marking the end of the simulation, the resulting order parameter array is post-processed and a hard decision is made for the state of each cell by comparing each of its order parameter values against a threshold. Any cell with an order parameter value for any variant above threshold is taken as consisting of 100% of that phase state. The microstructure is viewed by plotting these cell states throughout the cube.

Three primary contributors to the total energy equation exist. These are the chemical energy, the surface energy and the elastic strain energy. The chemical energy driving force is the change in Gibbs free energy of the martensitic transformation. The elastic strain energy is computed in reciprocal space using the closed form derived in Chapter 3. This is a field ranging throughout the volume of the space and therefore all particles of the volume influence the energy balance for all other particles. The gradient energy is controlled by the value of the gradient coefficient. Since the order parameter indicates the orientation variant, it is an expression of strain. Surface energy is given as the tensor product of the spatial derivative of strains multiplied by the gradient coefficient, which effectively makes all energy units relative to elastic strain energy as the elastic to chemical energy ratio is provided as an input parameter and the gradient energy is a function of differential strain.

The program allows the variants to dynamically “self-assemble” in the most energetically favorable configuration without restriction to any a priori imposed static theoretical

optimal habit plane orientation such as those discussed in Chapter 1. The most energetically favorable orientation should be the orientation that minimizes strain energy.

The computations are performed in wave vector space where the fast Fourier transform implemented in three dimensions is used to convert from real space to k-space. In k-space the differential equations of a strain field can be algebraically manipulated. This technique offers significant computational benefit over competing numerical techniques such as the finite element method or a finite difference technique for solving the differential equations of the strain field.

To further obtain computational efficiency advantage is taken of the fact that the product of the stress-free transformation strains is a fixed value for all three correspondence variants and that the elastic modulus is uniform for all cells and for both austenite and martensite, thus allowing a precomputed matrix of strain energies which minimizes the amount of dynamic updating for the program.

4.1 Program Details

Prior to the main computational loop, a number of initialization routines are called. These initialize the grain structure for a multigrain simulation, initialize elasticity arrays, precompute a matrix “Bpq” to reduce the computational load in the main loop, and initialize the state of the cells of the cube (these may be set to the output of a previous simulation so that it may be continued).

The pre-computed matrix B_{pq} is essential to accelerating the program execution.

Equation 3.20 gives strain energy as:

$$E_{\text{elast}} = \frac{1}{2} \sum_{p=1}^n \sum_{q=1}^n \oint [\lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 - \sigma_{jk}^0(p) \mathbf{k}_j (\lambda_{ijkl} k_j k_l)^{-1} \sigma_{ij}^0(q) \mathbf{k}_j] d^3k / (2\pi)^3 \theta_p(\mathbf{k}) \theta_q^*(\mathbf{k})$$

where $\oint$ signifies the exclusion of the 0th term.

The portion to the left of the integral expression is composed of static values, i.e. Young's modulus, stress-free transformation strain, strain-free transformation stress, and the wave vector. This is the B_{pq} array in the program and is computed as:

$$B_{pq} = \frac{1}{2} \sum_{p=1}^n \sum_{q=1}^n [\lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 - \sigma_{jk}^0(p) \mathbf{k}_j (\lambda_{ijkl} k_j k_l)^{-1} \sigma_{ij}^0(q) \mathbf{k}_j]$$

B_{pq} is computed once at the outset of the program execution, which substantially reduces the total execution time.

In the main loop of the program there are just two primary computational routines. Also in the main loop at each simulation time step, energy values are updated and a print routine called to update output files. The two primary computational routines are “Transformation_Forces” and “Evolvestructure”.

4.1.1 Transformation_Forces

The driving force for a transformation is the energy difference between states. Four sources contribute to the driving force. These are elastic strain energy, surface energy, chemical energy, and applied stress.

The variable `General_Force` is an array of the cube size with a fourth dimension equal to the product of the number of variants and the number of grains (recognizing that any cell may take on the character of any variant of any grain) which holds a composite energy derivative term indicating the driving force for transformation of that cell to each grain/domain type. This is effectively one cubic array for each possible grain and orientation variant. For the simulations of this study the cube was restricted to a single crystal and the number of orientation variants was that of Fe-Ni, which is three. A positive driving force for a given variant in any cell indicates a positive bias for transformation to that variant.

Strain Energy

The strain driving force contribution is obtained by multiplying the pre-computed B_{pq} matrix with the existing order parameter array in k-space and integrating over the number of grain-domains[♦]. Effectively this implements the integration operation of equation 3.20 differentiated with respect to the order parameter to obtain the strain energy driving force.

For a given cell the change in energy with respect to the order parameter yields a delta value for each of the order parameters indicating the tendency of the cell to transform from its current state to any other state. Notwithstanding interactions with other cells, all states of a cell are energetically equivalent, so the change in energy with respect to order parameter would be zero for an isolated cell. For a cell within the matrix, the change in

[♦] Let grain-domain be the product of the number of grains and the number of domains in the model. For a single crystal, the number of grains is one. For Fe-Ni, the number of domains is the number of orthogonal variants = 3.

energy with respect to order parameter indicates the degree to which transformation to that alternate state is favored or disfavored.

Since B_{pq} is an integral expression, the variational derivative is used, which is then inverse Fourier transformed to obtain a result in real space.

$$E(k) = B_{pq} * |\theta(k)|^2$$

$$\frac{\delta E(k)}{\delta \theta(k)} = 2 * B_{pq} * \theta(k)$$

$$\frac{\delta E(r)}{\delta \theta(r)} = \text{ifft}\left(\frac{\delta E(k)}{\delta \theta(k)}\right)$$

$$\text{General_Force} = \text{General_Force} - 0.5 \cdot \frac{\delta E(r)}{\delta \theta(r)} \quad (4.1)$$

Surface Energy

The surface energy is calculated in k-space by applying equation 3.30, i.e.,

$$E_s(k) = \beta_{\text{imnjsp}} \cdot \sum_{p=1}^n k \theta_p(k) \cdot \sum_{p=1}^n k \theta_p(k)$$

To avoid the discontinuity of having k change slope in the center of the cube, the sine function can be used as a substitute. It also acts as a window function to reduce the leakage effects in the FFT or inverse FFT, which arise as the result of the finite length sequence. Since the cube size is small in any given dimension, typically 64 for most simulations, the spectral leakage effect can be significant.

The calculation of the surface energy then becomes:

$$E_s(k) = \beta_{\text{imnjsp}} \cdot \sum_{p=1}^n \sin(k)\theta_p(k) \cdot \sum_{q=1}^n \sin(k)\theta_q(k)$$

This defines the surface energy in wave vector space, but what is of interest is the change in this surface energy with respect to the order parameter, as this will describe the driving forces propelling a change to the alternate states throughout the matrix. The change in surface energy with order parameter can be expressed as the variational derivative as follows:

$$\frac{\delta E_s(k)}{\delta \theta_p(k)} = 2 \cdot \beta_{\text{imnjsp}} \cdot \sin^2(k)\theta_p(k)$$

In the code, the implementation of the driving force update becomes:

$$\frac{\delta E(k)}{\delta \theta_p(k)} = -2.0 \cdot \text{Gradient_coefficient} \cdot \sin^2(k_i \pi / N) \cdot \theta(k_i)$$

$$\frac{\delta E(r)}{\delta \theta_p(r)} = \text{ifft}\left(\frac{\delta E(k)}{\delta \theta_p(k)}\right)$$

$$\text{General_Force} = \text{General_Force} + \frac{\delta E(r)}{\delta \theta_p(r)} \quad (4.2)$$

Applied Stress

For each cell of the cube, the General_Force array is updated by a term representing the product of the applied stress tensor and the transformation strains of the cell (one strain tensor per grain-domain) divided by the equilibrium order parameter. This results in one energy value for each grain-domain and biases the transformation driving force such that

orientation variants with elongations in the direction of applied tension or contractions in the direction of applied compression are favored.

$$\frac{\partial E(r)}{\partial \theta_p(r)} = \text{Transformation_Strain}_{ij} * \text{Applied_Stress}_{ij} / \text{Equilibrium_order_parameter}$$

$$\text{General_Force} = \text{General_Force} + \frac{\partial E(r)}{\partial \theta_p(r)} \quad (4.3)$$

Chemical Energy

The chemical energy driving force is calculated as a function of the order parameters in real space using the polynomial of equation 3.23:

$$\partial E(r) / \partial \theta_1(r) = 2 \cdot C_1 \cdot \theta_1(r) - 3 \cdot C_2 \cdot \theta_1^2(r) + 4 \cdot C_3 \cdot [\theta_1^3(r) + \theta_1 \cdot \theta_2^2(r) + \theta_1 \cdot \theta_3^2(r)] \quad (3.23)$$

Integration over volume is accomplished by accumulating the result for each cell in the general force array to produce the total driving force for the entire cube:

$$\text{General_Force} = \text{General_Force} + \partial E(r) / \partial \theta_1(r).$$

The coefficients are chosen so as to produce a reasonable transformation energy barrier with a potential energy minimum for the martensite state. The coefficients used for this work were empirically determined by Dr. Artemev and are as follows:

$$A=0.5, B=5.0, C=1.8.$$

4.1.2 Evolve_Structure

This routine updates the order parameters based on the transformation driving forces, generates a random noise signal which can initiate a transformation, optionally imposes substrates and inclusions, and updates the overall average strain and volume fractions. An inclusion is any non-transforming region. A substrate is a non-transforming region that covers the entire face of a cube with some specified thickness.

Noise generation is applied as a random signal of adjustable amplitude active for a specified length of time. The time and amplitude of the signal are set in the “martensite.data” file.

Substrates and inclusions are imposed by forcing the order parameters for all cells of the inclusion to zero (parent phase). The substrate can be defined by setting a switch in the martensite data file and setting a parameter to define the substrate thickness. Code is installed for both spherical and ellipsoidal inclusions. Removing the comment characters and setting size and location parameters as required installs the inclusion.

Updates for inclusions and noise are applied in real space. Conversion to k-space completes the order parameter updates.

Volume fractions are updated by calculating the ratio of the magnitude of the order parameters for each cell to the equilibrium order parameter value then comparing this result with a threshold level. If the result for any variant exceeds the threshold, the cell is

declared to be of that variant and its volume fraction incremented. The three tetragonal volume fractions are expressed as percentages. The remainder is parent phase.

The average strain is efficiently computed in k-space using the 0th term of the order parameters. The 0th term of the k-space order parameter array represents the homogeneous order parameter.

$$\text{Average_Strain} = \frac{\text{Grain_Trans_Strains} * \text{Order_Parameters_k}(0,0,0)}{\text{System_Volume} * \text{Equilibrium_Order_Parameter}}$$

4.2 *The Fourier Transform in Three Dimensions*

The three dimensional Fourier transform is defined as:

$$f(\mathbf{k}) = \int_V f(\mathbf{r}) e^{-i\mathbf{k}\mathbf{r}} dV$$

For the elements of the cube this can be computed by calculating the one-dimensional Fourier transforms of the rows of data on one face of the cube, then on the rows of data on each slice through the cube parallel to the chosen face. The result is stored as a cubic array and all of the one-dimensional Fourier transforms for all columns of this result, starting from the same face as the row computation and working through each slice of the cube, is computed. This result is stored as a cubic array and the Fourier transform of rows of this data starting on an orthogonal face and working through each slice perpendicular to the slices of the first transform calculation is computed. The composite calculation is the Fourier transform of the Fourier transform of the Fourier transform, where each

transform is calculated on an orthogonal dimension of the cube. Figure 4-1 illustrates the computation of an FFT in three dimensions.

For speed of calculation a radix-2 fast Fourier transform is used. This is implemented as a subroutine and called as required to convert from real space to wave vector space and vice versa.

Figure 4-1 Three Dimensional FFT

4.3 Controlling the Simulation

The file ‘martensite.data’ is used to provide simulation control. The parameters of this file are read within the initialization section of the main program routine (‘PCPMartensite’). The sixteen lines of a sample ‘martensite.data’ file are shown below with annotations below each line indicating the meaning of the numbers and a description column to provide some brief additional elaboration. The values in the data column of the table are representative of the parameters used for the simulations discussed in Chapter 5.0.

#	Data	Description
1	0.1,500.0,0.0,500.0,10,500	
	time_step = 0.1, sim_length = 500.0, print_start_time=0.0, print_stop_time=500.0, print_period=10, backup_period=500	Time resolution of the simulation. Total simulation length. The starting time for recording output The stop time for recording output Period of updating the output files Generates a backup file at this interval. Allows partial recovery of data if the simulation crashes.
2	F,20.0,0.2	
	make_noise=False,	Enables the generation of a Gaussian noise signal. Always set to false if the initial simulation state is to be read from a file. Always set to true otherwise as this is the source of martensite nucleation events. Without noise to start the process, no martensitic transformation will occur.

	noise_length=20.0, noise_amplitude=0.2	Length of time for the noise. This was set to 20 for all simulations. Power level of the noise. Fixed at 0.2 for all simulations.
3	F,T,F	
	constrained_system=False, read_initial_state=True, has_defects=False	Defines the system cube boundaries as fixed or mobile. This was set to False for all simulations. Reads the starting structure from a file – “Martensite.Start”. The format is identical to the output file “Martensite.Final”, hence any simulation can always be continued. Defect cells (non-transforming cells) can be inserted using this option. If set to true, a file (Defects.dat) with an entry for each element of the cube is read. A ‘1’ in the file will define that cell to be a normal cell. A ‘0’ will define it to be an inclusion or defect cell. This option was not used in these experiments.
4	F,13	
	substrate=False, substrate_thickness=13	Defines a substrate to be present or not. Substrate thickness in units of the cube
5	0.5,5.0,1.8	
	potential_coefficients=0.5,5.0,1.8	The coefficients for the Landau polynomial defining the chemical potential energy curve. The values given were the values used for all simulations.
6	0.01	
	gradient_coefficients=0.01	The proportionality constant relating order parameter gradient to surface energy. This was usually set to 0.01 for all results presented in Chapter 5.0.
7	40	
	elastic_chem_energy_ratio=40	The dimensionless ratio relating the magnitude of elastic strain

		energy to chemical driving force.
8	0.3	
	poisson_ratio=0.3	Poisson's ratio.
9	3	
	number_of_variants=3	Number of tetragonal variants. Always set to three for this work. The implicit forth variant is parent phase.
10	0.1322,0.1322,-0.1994,0.0,0.0,0.0	
	$\epsilon_{11}, \epsilon_{22}, \epsilon_{33}, \epsilon_{32}, \epsilon_{31}, \epsilon_{21}$	3x3 strain matrix for the first variant relative to parent phase. The matrix is symmetrical. The numbers are the transformation strains for Fe-Ni.
11	0.1322,-0.1994,0.1322,0.0,0.0,0.0	
	$\epsilon_{11}, \epsilon_{22}, \epsilon_{33}, \epsilon_{32}, \epsilon_{31}, \epsilon_{21}$	3x3 strain matrix for the second variant relative to parent phase. The matrix is symmetrical. The numbers are the transformation strains for Fe-Ni.
12	-0.1994,0.1322,0.1322,0.0,0.0,0.0	
	$\epsilon_{11}, \epsilon_{22}, \epsilon_{33}, \epsilon_{32}, \epsilon_{31}, \epsilon_{21}$	3x3 strain matrix for the third variant relative to parent phase. The matrix is symmetrical. The numbers are the transformation strains for Fe-Ni.
13	64,64,64	
	system_size=64,64,64	Cube size. The dimensions must be equal and a power of 2 to satisfy the radix-2 FFT algorithm.
14	1	
	number_of_grains=1	Number of grains. If greater than one, the grain structures must be defined with a 'GrainStructure.data' file.
15	0.00,-4.0,0.0,0.0,0.0,0.0	
	applied_stress=0.0,-4.0,0.0,0.0,0.0,0.0	Applied stress as $\sigma_x, \sigma_y, \sigma_z, \tau_x, \tau_y, \tau_z$
16	0.75	

	critical_order_parameter=0.75	For each variant of each grain of each cell the final decided order parameter is either 0 or 1. This parameter sets the threshold value for the decision. This value was fixed at 0.75 for all simulations.
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In addition to the Fe-Ni simulations with strains as defined in the above table, a few simulations were also run using a set of ideal dilatationless transformation strains. The ideal dilatationless transformation strains are as follows:

0.1,-0.05,-0.05,0.0,0.0,0.0

-0.05,0.1,-0.05,0.0,0.0,0.0

-0.05,-0.05,0.1,0.0,0.0,0.0

The above defines a transformation strain with 10% elongation on one axis and 5% contraction on two others. This is in contrast to the Fe-Ni strains which have 13% elongation on two axes with 20% contraction on the third.

5.0 Results

The objective of this work was to examine the effect of inclusions on martensitic domain structures formed as a result of the transformation of a single crystal of austenite. Two types of inclusion morphology were considered, spherical and ellipsoidal. Minor code modifications were implemented to model either shape of inclusion of selectable radii and center position. An inclusion for the purposes of this work is merely any region which does not undergo transformation. The creation of an inclusion in the program code was accomplished by forcing all cells within the boundary of the equation describing the inclusion shape to have an order parameter of zero.

Simulations were run for two sets of transformation strains, ideal dilatationless strains and Fe-31wt%Ni transformation strains for both spherical and ellipsoidal inclusions composing several different volume fractions of the cube. A variety of elastic to chemical energy ratios and gradient energy coefficients were applied initially, but high values of the elastic to chemical energy ratio with small coefficients for the gradient energy term were found to be the most conducive to the result of a multivariant pattern, so elastic to chemical energy ratios in the range of 20-40 were used with a gradient energy coefficient typically set to 0.01.

For the most multivariant of resulting crystal structures, a tensile stress-strain test for two complete loading and unloading cycles of a single sample was executed. One test was executed for each inclusion shape, spherical and ellipsoidal.

5.1 Inclusion Simulation Micrographs

Figure 5-1 shows three cross-sections of a simulation of a 64x64x64 cube with a radius 15 (5.4% volume fraction) spherical inclusion. The transformation strains are ideal dilatationless (+10% on one axis and -5% on the other two). The elastic to chemical energy ratio was set to 40 and the gradient coefficient to 0.01. After achieving equilibrium in the simulation the crystal consisted of two martensite domains with volume fractions of 56% and 36%. About 8% of austenite remained untransformed, of which 5.4% was the inclusion volume.

Figure 5-1 Central cross-section contour plots of the cube with spherical inclusion and ideal dilatationless martensite strains. Spherical volume fraction = 5.4%. Elastic to Chemical energy ratio = 40. Gradient energy coefficient = 0.01.

Figure 5-2 shows the micrographs of an identical simulation with the elastic to chemical energy ratio reduced to 20. A high elastic to chemical energy ratio results in a finer structure as thinner plates lead to reduced strain energy at the austenite to martensite interfaces, therefore the martensite plates can be expected to get coarser as the elastic to chemical energy ratio is reduced. This is borne out in Figure 5-2. For this case, the

volume fractions were 54% and 40%. About 6% of austenite remained untransformed, of which 5.4% was the inclusion volume. Negligible third orientation variant was present.

Figure 5-2 Central cross-section contour plots of the cube with spherical inclusion and ideal dilatationless martensite strains. Spherical volume fraction = 5.4%. Elastic to Chemical energy ratio = 20. Gradient energy coefficient = 0.01.

Figure 5-3 shows the result of a simulation without the inclusion. A much coarser structure is developed as the inclusion is not present to affect the elastic strain field. Note the plots are contour plots, where the bands denote a transition in levels rather than absolute levels, hence they represent boundaries between domains. The transformation reached equilibrium with the entire cube volume composed of two martensite domains with volume fractions of 66% and 34%. These domains are labeled as “1” and “2” in Figure 5-3.

Figure 5-3 Central cross-section contour plots of the cube with no inclusion and ideal dilatationless martensite strains. Elastic to Chemical energy ratio = 40. Gradient energy coefficient = 0.01.

With an inclusion of very small volume fraction, the impact on the microstructure of the transformation becomes insignificant. Figure 5-4 shows the effect of a 0.8% volume fraction spherical inclusion with ideal dilatationless martensitic transformation strains. Comparing this to Figure 5-3, illustrates the minimal effect of the small inclusion.

Figure 5-4 Central cross-section contour plots of the cube with spherical inclusion and ideal dilatationless martensite strains. Spherical volume fraction = 0.8%. Elastic to Chemical energy ratio = 40. Gradient energy coefficient = 0.01.

Figure 5-5 shows the effect of growing the inclusion size to 1.6%. A few additional lamellae appear, but the microstructure is not substantially altered. Increasing the inclusion size further results in the formation of a finer structure with each increment of inclusion size.

Figure 5-5 Central cross-section contour plots of the cube with spherical inclusion and ideal dilatationless martensite strains. Spherical volume fraction = 1.6%. Elastic to Chemical energy ratio = 40. Gradient energy coefficient = 0.01.

Figure 5-6 shows the central slices of an Fe-31%Ni cube with a 17% volume fraction spherical inclusion. The martensite plates are thinner than those of Figure 5-1 and Figure 5-2 and the larger inclusion has significantly affected the strain field over most of the

volume of the cube. All three orientation variants of martensite are present in the volume fractions of 14%, 48%, 11%, with 27% of untransformed austenite remaining.

x-y

x-z

y-z

Figure 5-6 Central cross-section contour plots of the cube with a 17% volume fraction inclusion and Fe-31 wt% Ni transformation strains. Elastic to Chemical energy ratio = 40. Gradient energy coefficient = 0.01.

Figure 5-7 shows an ellipsoidal inclusion with major to minor axis ratio of 3 constituting a 4.9% volume fraction in Fe-Ni. Note the y-z slice indicates the martensite domains have formed as mostly needles and laths. The volume fractions obtained were 53% and 39%. The remainder was parent phase. Negligible third variant was present.

x-y

x-z

y-z

Figure 5-7 Ellipsoidal Inclusion in Fe-Ni. Volume Fraction = 4.9%. Elastic to chemical energy ratio = 40. Gradient energy = 0.01.

Figure 5-8 shows the view of the y-z face of the same cube of Figure 5-7. The fine structure of the needles and laths extend to the boundary of the cube as far removed as possible from the inclusion.

Figure 5-8 Micrograph of the y-z face of the cube of Figure 5-7

Figure 5-9 shows an ellipsoidal inclusion of approximately 13% volume fraction in Fe-31%Ni. The increase in inclusion size resulted in further refinement of the domain structure. The volume fractions of the martensite domains were 35% and 48% with 17% untransformed parent phase. Again, negligible third orientation variant was present. With a major to minor axis ratio of three, the ellipse slightly exceeds the boundary of the cube.

Figure 5-9 Ellipsoidal Inclusion in Fe-Ni. Volume Fraction = 13%. Elastic to chemical energy ratio = 40. Gradient energy = 0.01.

Figure 5-10 shows the circular cross-section of an ellipsoidal inclusion of 15.4% volume fraction in Fe-Ni at three different time intervals. The first is the output of the simulation

at $t=800$ time units, and has associated volume fractions of 33%, 33%, 11%, with 22% of untransformed parent phase. Clearly two distinct types of twinned regions are evident.

The second micrograph is the same cross-section after 1600 time units. The diagonal central band has narrowed and the proportion of third orientation variant has declined to 8%. The third micrograph shows the simulation result after 2800 time units. The structure has coarsened such that the diagonal band has disappeared and the third martensite orientation variant has been entirely consumed. The volume fractions at 2800 units are 35% and 46%, with 19% untransformed parent phase.

Figure 5-10 X-Y cross-section at three points of elapsed time of an ellipsoidal Inclusion in Fe-Ni. Volume Fraction = 13%. Elastic to chemical energy ratio = 40. Gradient energy = 0.01.

The simulations shown by the micrographs of Figure 5-10 were run with an elastic to chemical energy ratio of 40. The modulus of elasticity of the material can be very reasonably approximated as independent of temperature for the temperature range of interest, but the chemical driving force scales with temperature. Temperatures far below the martensite start temperature result in much higher chemical driving forces, therefore

they correspond to lower values of elastic to chemical energy ratios. The crystal structures produced at lower temperatures are not very strongly martensitic, i.e. the plates of martensite tend to be thicker and the structures not as varied because the strain energy contribution is much smaller. This is evident in Figure 5-1 and Figure 5-2 where the effect of changing the elastic to chemical energy ratio from 40 to 20 is illustrated.

By dynamically lowering the value of the elastic to chemical energy ratio as a simulation progresses (as would be the case in cooling a sample), it can be expected that the more multi-variant high temperature structures can be frozen. This was done in a very simple two step adjustment for the 800 time step output of Figure 5-10. Lowering the elastic to chemical energy ratio to 4 from 40 at 800 time units, then resuming the simulation, resulted in the diagonal band persisting and approximately no change in the volume fractions to 2800 time units. The overall energy values reported by the simulator were showing no evolution at 2800 units, so this was most likely an equilibrium structure.

Figure 5-11 shows an ellipsoidal inclusion of 15.4% volume fraction in Fe-Ni. The ellipse is rotated so that its major axis aligns with the cube diagonal. This allows the inclusion to fully fit within the cube. The volume fractions of the martensite domains were 33%, 44%, and 3% with 20% untransformed parent phase.

x-y

x-z

y-z

Figure 5-11 Rotated ellipsoidal Inclusion in Fe-Ni. Volume Fraction = 15.4%. Elastic to chemical energy ratio = 40. Gradient energy = 0.01.

Figure 5-12 shows two Fe-Ni spherical inclusions occupying a total volume fraction of 15.7% of the cube. With the elastic to chemical energy ratio set to 40, the volume

fractions after 1000 time units were, 3%, 55%, 21%, with a remainder of 21% of untransformed parent phase.

x-y

x-z

y-z

Figure 5-12 Two spherical inclusions in Fe-Ni. Total volume fraction = 15.7%. Elastic to chemical energy ratio = 40. Gradient energy = 0.01.

Figure 5-13 indicates the quite significant crystallographic impact of reducing the elastic to chemical energy ratio to 20. The same two Fe-Ni spherical inclusions of Figure 5-12 are shown. The volume fractions after 1000 time units were, 28%, 49%, 4%, with a remainder of 19% of untransformed parent phase.

x-y

x-z

y-z

Figure 5-13 Two spherical inclusions in Fe-Ni. Total volume fraction = 15.7%. Elastic to chemical energy ratio = 20. Gradient energy = 0.01.

Figure 5-14 shows a simulation where the inclusion is an inert substrate layer. The substrate volume fraction is 15.7%. The volume fractions after 1000 time units stabilized at 39%, 40%, 0%, with a remainder of 20% of untransformed parent phase. The patterns are predictably an assembly of thin plates, needles, and laths forming domain twins with their long axis perpendicular to the substrate. The x-z slice indicates the edge view of these structures.

x-y

x-z

y-z

Figure 5-14 Substrate inclusion in Fe-Ni. Substrate volume fraction = 15.7%. Elastic to chemical energy ratio = 40. Gradient energy = 0.01.

5.2 *The Effect of Applied Stress*

The effect of uniaxial applied stress was examined with a 64x64x64 cube containing a single spherical inclusion of 19.4% volume fraction. The crystal patterns through the central slices of this cube are shown in Figure 5-15 for the case of no applied stress. The volume fractions after 800 simulator time units were 11%, 44%, 14%, with 30% remaining as parent phase. For the application of a very small tensile load set to a normalized value of 0.005 on the y axis, the crystal pattern changes remarkably as illustrated in Figure 5-16.

Figure 5-15 Spherical inclusion in Fe-Ni. Total volume fraction = 19.4%. Elastic to chemical energy ratio = 40. Gradient energy = 0.01. No applied stress.

The volume fractions shown in Figure 5-16 after 1600 simulator time units were 21%, 18%, 30%, with a parent phase remainder of 31%. Only very low values of applied stress were found to cause the generation of substantial volume fractions of all three martensite variants. Increasing this stress further to a normalized value of 0.1 caused almost total

disappearance of the third orientation variant. The volume fractions became 34%, 0%, 36%, with 28% untransformed parent phase.

x-y

x-z

y-z

Figure 5-16 Spherical inclusion in Fe-Ni. Total volume fraction = 19.4%. Elastic to chemical energy ratio = 40. Gradient energy = 0.01. Y-axis applied tensile stress of 0.005.

Figure 5-17 shows the effect of a further increase in the normalized applied tensile load to 1.0. The domain patterns become much less multivariant as the tetragonal variants reorient to a more favorable alignment with respect to the applied stress. The volume fractions shown are 37%, 0%, 32%, with 29% untransformed parent phase. The patterns remain similar for increases in applied stress up to 10.0. At a uniaxial stress level of 10.0, the volume fractions were changed slightly to 38%, 0%, 38%, with 23% remaining untransformed.

x-y

x-z

y-z

Figure 5-17 Spherical inclusion in Fe-Ni. Total volume fraction = 19.4%. Elastic to chemical energy ratio = 40. Gradient energy = 0.01. Y-axis applied tensile stress of 1.0.

Under small uniform tri-axial compressive loads of less than 1.6 with the elastic to chemical energy ratio set to 40 and the gradient coefficient set to 0.01, the Fe-Ni cube transforms producing crystal structures that are not substantially different from the no-load case. As the tri-axial load was increased beyond 1.6, the transformation was completely inhibited and the cube remained parent phase. This is an expected result as Fe-Ni transformation strains result in a slight volume expansion. A uniform compressive load will oppose the transformation thereby supplying a negative driving force.

Uniform tri-axial tensile loads have little impact on the crystal structure patterns. This is also an expected result as a uniform tension would be favorable to the net volumetric expansion of the crystal which is a natural consequence of transformation to martensite for Fe-Ni.

5.3 Tensile Stress-Strain Plots

Figure 5-18 shows a strain versus stress plot for a 64x64x64 cube with a 19.4% spherical inclusion for two cycles of loading and unloading. The elastic to chemical energy ratio was set to 40 and the gradient energy term to 0.01. The applied stress was initially tension on one axis of the cube. The stress was increased in steps until a clear change in the apparent elastic modulus was noted. At this point the sample was unloaded in steps through the region of low elastic modulus until the slope of the strain versus stress curve was again reduced, which necessitated applying compressive stress to the sample. This was repeated to produce a second complete loading and unloading cycle.

Significant hysteresis can be observed in the plots. The strain versus stress characteristic can be observed to be quite repeatable after the initial loading, as the second loop of the curve overlays almost exactly on the first.

Figure 5-18 Stress-Strain Plot for two loading/unloading cycles with 19.4% spherical inclusion.

Figure 5-19 shows a strain versus stress plot for a 64x64x64 cube with a 15.4% ellipsoidal inclusion for two cycles of loading and unloading. The ellipsoid is rotated so that its major axis lies approximately on the cube diagonal. The micrographs for the transformation under no applied stress are shown in Figure 5-11. The elastic to chemical energy ratio was set to 40 and the gradient energy term to 0.01. As in the spherical inclusion test, the applied stress was initially tension on one axis of the cube. This was increased in steps until a flattening of the strain vs. stress curve was noticed. At this point the sample was unloaded in steps through the region of low elastic modulus until the slope of the strain versus stress curve was again reduced, which necessitated applying compressive stress to the sample. This was repeated to produce a second complete loading and unloading cycle.

The hysteresis loop is clear and near perfect agreement exists between the second loading/unloading cycle and the first. Despite the smaller volume fraction of the ellipsoidal inclusion, it produces a broader hysteresis loop than the spherical inclusion.

Figure 5-19 Stress-Strain Plot for three loading/unloading cycles with a 15.4% ellipsoidal inclusion.

5.4 Relating Simulation Units to Absolute Units

The simulation program accepts input parameters as relative rather than absolute units.

Temperature is not expressly given; rather it is implicit within the elastic to chemical energy ratio. Knowing the change in enthalpy of the transformation (ΔH) for a material at the equilibrium transformation temperature (T_0) and Young's modulus allows elastic strain energy to be determined as a ratio of chemical energy (ΔG) for any other temperature. Assuming the specific heat to be unaffected by the transformation, the driving force at a reduced temperature (T_1) is easily calculated from basic thermodynamic relations as:

$$\Delta G = \frac{\Delta H \cdot (T_1 - T_0)}{T_0}$$

An isotropic material is assumed, so elastic strain energy is obtained as:

$$E = 1/2 \lambda \epsilon_{ii}^2 + \mu \epsilon_{ik}^2$$

Given the principal axes strains of the transformation, this reduces to:

$$E = 1/2 \lambda \epsilon_{ii}^2$$

Expressing both E and ΔG in terms of the same unit volume, allows an elastic to chemical energy ratio to be expressed as $E/\Delta G$, which varies with the reduced temperature T_1 .

The gradient energy coefficient is not well quantified, but it produces a small effect compared to strain energy and chemical energy. Adjusting the gradient coefficient provides scaling of dimensions as a small value of the gradient coefficient reduces the impediment to the creation of new surfaces allowing finer structures in the martensite.

Relating simulator time units to real time is also not straightforward. From the observation of crystal structures produced within certain simulator time units and analogous structures produced in real samples over a period of real time, an approximate scale for simulator time can be inferred.

The units of the elastic strain energy component associated with applied stress are normalized to the value of the equilibrium order parameter of the cube, whereas the value of transformation strain energy is normalized to the value of the square of the equilibrium order parameter of the cube. Effectively this introduces a scale factor difference in the units of applied load in that the actual load is the equilibrium order parameter times the stated applied load. As a ratio of Young's Modulus, the applied stress is then:

$$\sigma_{\text{relative}} = \frac{\sigma_{\text{applied}} \cdot \text{EOP}}{\lambda}$$

The values used in these simulations with Fe-Ni were $\lambda = 1335$, $\text{EOP} = 2.01$, and $\sigma_{\text{applied}} < 10$, so the stress levels did not exceed approximately 1.5% of Young's Modulus.

The simulator output can be used for qualitative comparisons and analysis, but precision of feature size or reaction time is not readily available. Temperature can be reasonably accurately deduced knowing the enthalpy of the transformation and Young' modulus. Units of length and time are best approximately quantified by relating simulated results on virtual samples to observed results on real samples.

6.0 Conclusions

The crystallographic impact of the presence of spherical and ellipsoidal inclusion shapes within a block of mono-crystalline material has been examined through simulation. The presence of an inclusion clearly affects the microstructure in that it leads to a finer structure of martensite, with the inclusion defining a fixed “habit” surface against which the martensite plates, needles and laths must be accommodated while minimizing strain and interface energy.

Very small volume fractions of inclusions have a negligible impact on the final microstructure. An inclusion volume fraction of less than about 1% appears to have approximately no microstructure impact. At a volume fraction of about 1.6% a few additional lamellae can be observed in the cube, but the microstructure is still substantially unchanged from the 0% inclusion simulation. Progressively finer structures are produced as the inclusion size is increased.

That the presence of the inclusion does not tend to produce more multi-domain structures with an approximately balanced composition of all three martensitic variants throughout the cube was an unexpected result as the habit plane of a spherical or an ellipsoidal inclusion is the continuously varying surface tangent plane, which could be expected to promote the growth of martensitic structures of a multiplicity of orientation variants. The simulations show that typically only two orthogonal orientation variants of martensite

predominate, evidence that the elastic strain energy and gradient energy to accommodate the inclusion in a simple two variant single domain structure is less than that required to accommodate the inclusion with a multi-domain structure where all three orientation variants are present. A multi-domain structure would be expected to more optimally accommodate the inclusion but strain energy and interface energy between domains evidently make it a less energetically preferred morphology. An interesting exception is illustrated in Figure 5-16, where a crystal structure in the presence of very small values of applied stress is shown to be quite multi-variant, consisting of a number of distinct twinned lamellar regions. For this structure to be favored by a very small value of applied stress, but not under the case of no load or under more substantial levels of applied stress suggests that a polycrystalline material would be more multi-variant in the presence of inclusions as the transformations in neighboring grains should influence any single grain with an effect analogous to the influence of an applied stress.

Under large values of tensile stress the simulated material with the inclusion contains approximately balanced volume fractions of the two variants. This is an expected result for Fe-Ni as the transformation strains exhibit elongation on two axes with contraction on the other axis thus leading to the equally favored growth of two variants under the applied load.

Hydrostatic compressive loads tend to inhibit the transformation as expected. The martensitic transformation strains of Fe-Ni result in a slight volumetric expansion, so a load of hydrostatic compression will simply provide a force of resistance to the

transformation. Hydrostatic tensile loads would tend to provide a driving force in favor of the transformation, but as the load is uniform and aligned with the axes of tetragonal distortion of the martensite it has little effect on the crystal structure or volume fractions of the result.

The tensile strain versus stress plots show a region of apparent plastic deformation as expected of twinned or polytwinned martensite^{*}. The loading/unloading cycles show significant hysteresis indicating an energy barrier to the movement of the twin boundaries. Very likely this barrier is contributed by the presence of the inclusion but to quantify the impact through simulation would require a cube with twinned martensite morphology and no inclusion, however even the very coarse twins of a monocrystalline cube without the inclusion merge into a single variant structure under large applied load, so such a direct test can not be conveniently carried out. An interesting further investigation beyond the scope of this work would be a stress test conducted on a polycrystalline cube and compared with the result for the mono-crystalline cube with inclusion.

The strain versus stress plot for the ellipsoidal inclusion shows slightly greater hysteresis than the similar result for the spherical inclusion despite the fact that the ellipsoidal inclusion occupies a smaller volume fraction of the cube than the spherical inclusion. This is probably a consequence of the larger surface area of the ellipsoid which exposes a larger “habit” surface. The greater hysteresis of the ellipsoid compared to the sphere also

^{*} The plastic deformation is by the movement of twin boundaries rather than slip.

clearly demonstrates that the inclusion has the effect of introducing some energy barrier to the movement of the twin boundaries.

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