A THERMODYNAMICAL CONSTITUTIVE MODEL FOR SHAPE MEMORY MATERIALS.
PART I. THE MONOLITHIC SHAPE MEMORY ALLOY

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Abstract

Pseudoelasticity and the shape memory effect (SME) due to martensitic transformation and reorientation of polycrystalline shape memory alloy (SMA) materials are modelled using a free energy function and a dissipation potential. Three different cases are considered, based on the number of internal state variables in the free energy: (1) Austenite plus a variable number of martensite variants; (2) Austenite plus two types of martensite; and (3) Austenite and one type of martensite. Each model accounts for three dimensional simultaneous transformation and reorientation. The single-martensite model was chosen for detailed study because of its simplicity and its ease of experimental verification. Closed form equations are derived for the damping capacity and the actuator efficiency of converting heat into work. The first law of thermodynamics is used to demonstrate that significantly more work is required to complete the adiabatic transformation than the isothermal transformation. Also, as the hardening due to the austenite/martensite misfit stresses approaches zero, the transformation approaches the isothermal, infinite specific heat conditions of a first order transformation. In a second paper, the single-martensite model is used in a mesomechanical derivation of the constitutive equations of an active composite with a SMA phase.

I. INTRODUCTION

Shape memory alloy (SMA) materials allow for the fabrication of adaptive structures with intrinsic control of shape and vibration parameters such as stiffness, natural frequency, and damping. In addition, SMA materials can function as motors and actuators that convert heat into work. The shape memory effect is due to the transformation between austenite and martensite and/or the reorientation (detwinning) of martensite variants. An active composite can be made by surrounding a prestressed martensitic SMA fiber with a non-SMA matrix material. When the

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composite is heated, usually by passing an electric current through the SMA fiber, the martensite is transformed into austenite and the fiber contracts, thereby producing the activation. Upon, cooling, the austenite transforms into martensite, and the internal stresses within the matrix partially return the composite structure to its original shape (ESCHER and HORNBOGEN [1991]; LAGOUDAS and TADJBAKHSH [1992]).

The five significant phenomena associated with monolithic SMA materials are (WARLIMONT et al [1974]; SUN and HWANG [1993]): (1) Pseudoelasticity by transformation. Isothermal stressing above the austenite start temperature results in an $A \rightarrow M$ transformation that produces a transformation strain. Upon isothermal unloading, this strain is fully recovered during the $M \rightarrow A$ transformation, albeit with hysteresis; (2) Pseudoelasticity by reorientation, sometimes known as ferroelasticity. Stress-induced reorientation of martensitic variants results in an inelastic strain. Application of a reverse stress causes the variants to return to their original orientation, resulting in a hysteretic recovery of the inelastic strain; (3) The shape memory effect (SME) by transformation. When the isothermal stress-induced $A \rightarrow M$ transformation is carried out below the austenite start temperature, the martensite and the transformation strain will remain after isothermal unloading. Subsequent heating results in the recovery of the austenite ($M \rightarrow A$) and the transformation strain; (4) The shape memory effect by reorientation. The inelastic strain produced by stress-induced reorientation of martensitic variants can be recovered by heating to complete the $M \rightarrow A$ transformation. Phenomena (3) and (4) are sometimes known as the one-way SME; (5) The two-way SME (TWSME). Cyclic thermomechanical transformation, known as "training", can be used to create a favorable residual stress field within the SMA material. After training, stress-free cooling of austenite produces a transformation strain that is hysteretically recovered during stress-free heating of the martensite.

Thermodynamics is the science of choice for constitutive modelling because it limits the possibilities for material behavior, thereby simplifying the specification of constitutive models. These restrictions are especially useful in predicting the complicated thermomechanical response inherent to SMA materials. The thermodynamical constitution of a material is given by its free energy function and dissipation potential. Furthermore, EDELEN [1974] has demonstrated that there exists a vector decomposition theorem such that the generalized fluxes appearing in the entropy production inequality can be decomposed into a dissipative component and a non-dissipative component. The dissipative fluxes must be derivable from a dissipation potential. The widely used "generalized standard material" (HALPHEN and NGUYEN [1975]) is one for which the free energy and dissipation potentials are convex and there are no non-dissipative fluxes. TANAKA and NAGAKI [1982] were evidently the first researchers to discuss martensitic transformations within the context of Edelen's formalism. Using the framework of the generalized standard material, LEXCELLENT and LICHT [1991] have compared and contrasted a number of thermodynamic models for SMA materials, considering such factors as the choice of state variables, the form of the free energy, and the transformation rate equations. BERVEILLER et al [1991] and PATOOR et al [1993] have modelled the single crystal free energy and transformation rate by assigning an internal variable to the volume fraction of the martensitic variants. The polycrystalline transformation response was then predicted by using the single crystal equations in the self-consistent micromechanics method. RANIECKI and LEXCELLENT [1994] used one internal variable, the total

martensite volume fraction, in their thermodynamical derivation of a polycrystalline phenomeno-logical model for pseudoelasticity due to transformation. SUN and HWANG [1993a,1993b]) have published perhaps the only thermodynamical model for pseudoelasticity and the shape memory effect due to both transformation and reorientation. The detailed thermodynamic analyses of ORTIN and PLANES [1988,1989,1991] are useful in developing the equations of a generalized standard material for phase transformation in SMA materials.

Thus, although a significant effort has been devoted to thermodynamic modelling of SMA materials, no phenomenological model has been developed that accounts for the five afforementioned phenomena of SMA materials. In particular, macroscopically proportional loading of inelastic composite materials generally results in microscopically nonproportional loading of the fiber and matrix. During nonproportional loading, reorientation may accompany transformation. Therefore, the present research was performed to combine and extend the research of BERVEILLER et al [1991], ORTIN and PLANES [1988,1989,1991], PATOOR et al [1987,1993], RANIECKI and LEXCELLENT [1994], and SUN and HWANG [1993a,1993b] to account for nonproportional loading, simultaneous transformation and reorientation, adiabatic deformation, and combined isotropic and kinematic hardening. The TWSME will not be included in the first paper. However, in the second paper, it is shown that the SMA composite material can undergo the TWSME even though the composite constituents can only undergo the one-way SME.

The plan of the present two-part paper in indicated in Figure 1. When viewed under a microscope, a generic point R^{macro} is seen to have a mesoscale structure consisting of fibers and matrix. In this first paper, phenomenological constitutive equations will be proposed for a generic material point at R^{meso} in V^{meso}. When viewed under a microscope, the material point R^{meso} is seen to be a representative volume element of polycrystalline SMA composed of heterogeneities separated by grain boundaries, boundaries between martensite variants, and boundaries between martensite and austenite. The microscale (z_i) distributions of these heterogeneities and boundaries are not explicitly included in the constitution of the mesoscale point R^{meso}. Instead, phase transformation and reorientation (detwinning) are modelled as chemical reactions in which internal variables specify the volume fraction of each type of heterogeneity, or "chemical species", at R^{meso}. Three scenarios will be considered, each using a different number of chemical species: (1) N species - austenite plus (N-1) variants of martensite, in section II; (2) 3 species - austenite, self accommodating martensite, and detwinned martensite, in section III; and (3) 2 species - austenite and martensite, in sections IV and V. Such a representation is possible because diffusionless allotropic phase transformations are mathematical analogs of chemical reactions with simple stoichiometric coefficients (KESTIN [1979]). Therefore, the use of internal variables to model martensitic phase changes can be indirectly credited to DeDONDER [1927], who introduced the concepts of chemical affinity and extent of reaction. Microscale observations are used to guide the development of phenomenological mesoscale constitutive equations. However, there is no actual solution of a boundary value problem in V^{micro} because, in phenomenological constitutive modelling, the constants in the equations are determined from experiments.

In the second paper, the form of the constitutive equations and the material constants for the point R^{macro} will be mesomechanically derived by first solving a boundary value problem over

V^{meso}, and then averaging the solution to obtain the constitution of point R^{macro}. The mesoscale (y_i) distributions of the phases and interfaces are not explicitly included in the constitution of the macroscale point R^{macro}.

Each of the discussions in sections II, III, and IV begin with a short statement of notation, followed by the two essential ingredients of a thermodynamic model - the free energy (thermodynamic potential) and the dissipation potential. The two species model of sections IV and V is used in the mesomechanics analysis of the second paper. Unless otherwise stated, each variable and material constant in this first paper is a function of the mesoscale coordinates y_i.

II. N Component Micromechanics Model

BERVEILLER et al [1991] and PATOOR et al [1993] modelled the single crystal free energy and transformation rate by assigning an internal variable to the volume fraction of each of the martensitic variants. Similarly, BUISSON et al ([1991]) used a transport theorem to determine the generalized force conjugate to a reorienting inter-martensitic interface. The single crystal reorientation strain rate was obtained from a consistency condition acting on a yield surface in the space of the generalized forces. In order to predict the polycrystalline response, the results of these single crystal analyses must be used in a polycrystalline averaging method, such as the self-consistent method. Because the self-consistent method yields implicit equations for the poly-crystalline properties, it is of limited use as input to the larger scale composite micromechanics analysis of the second paper. The single crystal analysis does, however, serve to guide the formu-lation of phenomenological polycrystalline constitutive equations. Therefore, the single crystal constitutive equations will be reviewed in the context of chemical reactions, and suggestions will be made for including the effects of simultaneous transformation and reorientation and the elastic stiffness difference between austenite and martensite.

II.1. Notation

Superscripts denote qualitative description of the associated variable or constant, whereas sub-scripts denote tensorial components. There is no summation on repeated superscripts unless specifically stated by a summation symbol, $\sum$. A function $\mathcal{H}$ of variables $(v^1, v^2, \cdots)$ is denoted by brackets as $\mathcal{H}\{v^1, v^2, \cdots\}$. Three assumptions are used throughout this paper: (1) All materi-als are linearly elastic; (2) The infinitesimal strain tensor is applicable; and (3) The temperature is spatially homogeneous. The fixed mass system consists of N species, each denoted by an α, where $1 \leq \alpha \leq N$. For example, for the cubic to tetragonal and monoclinic transformations, N=4 and N=25, respectively:

Species α	Type
1-(N-1)	martensite (M) variants
N	single crystal austenite (A)

The number of reactions, R, is equal to the number of combinations that can be formed from N species taken 2 at a time:

$$R = \frac{N!}{2!\,(N-2)!} = \frac{(N-1)N}{2}.\tag{1}$$

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The R "reactions", denoted by β, where $1 \leq \beta \leq R$, are labelled as

Reaction β Type
1 - (N-1)   transformation of austenite into martensite
N - R   reorientation of the martensite variants

The stoichiometric coefficients $\nu^{\alpha\beta}$ for martensitic transformations and reorientations are given by the N x R matrix

$$
\nu^{\alpha\beta} = \begin{bmatrix}
 & \underline{1} & \underline{2} & \underline{3} & \cdots & \underline{N-1} & \underline{N} & \cdots & \underline{R} \\
1\,| & 1 & 0 & 0 & \cdots & 0 & 1 & \cdots & 0 \\
2\,| & 0 & 1 & 0 & \cdots & 0 & -1 & \cdots & 0 \\
3\,| & 0 & 0 & 1 & \cdots & 0 & 0 & \cdots & 0 \\
\vdots\,| & \vdots & \vdots & \vdots & \vdots & 0 & 0 & \cdots & 1 \\
N-1\,| & 0 & 0 & 0 & \cdots & 1 & 0 & \cdots & -1 \\
N| & -1 & -1 & -1 & -1 & -1 & 0 & \cdots & 0
\end{bmatrix}
\tag{2}
$$

Note that the nonzero stoichiometric coefficients are given by either +1 or -1. The rates $\dot{c}^{\alpha}$ of each mass fraction c^{α} are obtained by summing the reaction rates $\dot{\xi}^{\beta}$, and the mass fractions are obtained by integration to yield

$$
\dot{c}^{\alpha} = \sum_{\beta=1}^{R} \nu^{\alpha\beta} \dot{\xi}^{\beta} \qquad \longrightarrow \qquad c^{\alpha} = c^{\alpha\circ} + \sum_{\beta=1}^{R} \nu^{\alpha\beta} \xi^{\beta} \, .
\tag{3}
$$

The conservation of mass is given by the constraint

$$
c^{\alpha} \geq 0 \, , \qquad \sum_{\alpha=1}^{N} c^{\alpha} = 1 \, , \qquad \sum_{\alpha=1}^{N} \dot{c}^{\alpha} = 0 \, ,
\tag{4}
$$

which requires that only N-1 of the N mass fractions be independent. The total mass density ρ is assumed to equal the mass density of each species, i.e. $\rho = \rho^{\alpha}$. The mass fractions are therefore equal to the volume fractions of the corresponding species.

Using the notation of PATOOR et al [1993], the kinematics of the reactions can be expressed in terms of the interfacial plane of normal n_i^{α} between austenite and martensite and by the dispacement g in the direction m_i^{α} of transformation. The transformation strain $\mathcal{E}_{ij}^{\alpha}$ and rotation $\mathcal{Q}_{ij}^{\alpha}$ with respect to the austenite coordinate system for each martensitic variant are given by

$$
\mathcal{E}_{ij}^{\alpha} = \frac{1}{2} (m_i^{\alpha} n_j^{\alpha} + m_j^{\alpha} n_i^{\alpha}) \, g \, , \qquad\qquad \mathcal{Q}_{ij}^{\alpha} = \frac{1}{2} (m_i^{\alpha} n_j^{\alpha} - m_j^{\alpha} n_i^{\alpha}) \, g \, .
\tag{5a-b}
$$

II.2. Free Energy

The Gibbs energy is chosen herein, instead of the Helmholtz free energy, to facilitate the comparison of model and experiments, which are often performed using stress control. The total specific

single crystal Gibbs energy $G\{\omega\}$, where $\omega = \{\sigma_{ij}, T, c^\alpha\}$, is equal to the mass weighted sum of the free energies $G^\alpha\{\sigma_{ij}, T\}$ of the species plus the free energy $G^{mix}\{\sigma_{ij}, T, c^\alpha\}$ of mixing. The free energy of each species consists of the thermal and elastic free energies of a pure substance. This is the energy that an infinitely extended species would experience under uniform stress and temperature. Accordingly,

$$
\begin{aligned}
G = G^{pure} + G^{mix} &= \sum_{\alpha=1}^{N} c^\alpha G^\alpha\{\sigma_{ij}, T\} + G^{mix}\{\sigma_{ij}, T, c^\alpha\} \\
&= G^A\{\sigma_{ij}, T\} + \sum_{\alpha=1}^{N-1} c^\alpha (G^\alpha\{\sigma_{ij}, T\} - G^A\{\sigma_{ij}, T\}) + G^{mix}\{\sigma_{ij}, T, c^\alpha\} \, ,
\end{aligned}
\tag{6}
$$

where (4) has been used to derive the second part of (6), and the superscript "A" denotes austenite. Thus, any deviation of G from the mass average is due to mixing. The free energy of each species is written as a Taylor series expansion

$$
G^\alpha = -\frac{1}{\rho}\frac{1}{2} a_{ijkl}^{\alpha 1} \sigma_{ij} \sigma_{kl} - \frac{1}{\rho} a_{ij}^{\alpha 2} \sigma_{ij} \Delta T + a^{\alpha 3} \left[\Delta T - T \, ln\left(\frac{T}{T^\circ}\right) \right] - a^{\alpha 4} \Delta T + a^{\alpha 5} \, ,
\tag{7}
$$

where $a_{ijkl}^{\alpha 1}$ is the elastic compliance, $a_{ij}^{\alpha 2}$ is the thermoelastic expansion coefficient, and $a^{\alpha 3}$ is the specific heat, $a^{\alpha 4}$ is the entropy at the reference state, $(\sigma_{ij} = 0, \ T = T^\circ, \ c^A = 1)$, $a^{\alpha 5}$ is the value of G at the reference state, and $\Delta T = T - T^\circ$. The tensorial quantities are defined with respect to the austenite coordinate system. It is assumed that all species have the same scalar properties:

$$
a^{\alpha 3} = a^{M3} \, , \quad a^{\alpha 4} = a^{M4} \, , \quad a^{\alpha 5} = a^{M5} \, , \qquad 1 \leq \alpha \leq N - 1 \, .
\tag{8}
$$

The thermoelastic moduli of each species are defined with respect to the austenite reference frame, so that

$$
a_{ijkl}^{\alpha 1} = \mathcal{Q}_{im}^\alpha \mathcal{Q}_{jn}^\alpha \mathcal{Q}_{ko}^\alpha \mathcal{Q}_{lp}^\alpha a_{mnop}^{M1} \, , \qquad a_{ij}^{\alpha 2} = \mathcal{Q}_{im}^\alpha \mathcal{Q}_{jn}^\alpha a_{mn}^{M2} \, ,
\tag{9}
$$

where a_{ijkl}^{M1} and a_{ij}^{M2} are defined with respect to the local martensite reference frame and $\mathcal{Q}_{im}^\alpha$ is approximately given by (5) when elastic rotations are excluded.

The free energy of mixing can be explained using the vocabulary of eigenstrains, inclusions and inhomogeneities (MURA [1982]). Eigenstrains are nonelastic strains such as thermal expansion and phase transformation strains that may be due to inclusions in bodies. An inclusion is a subdomain of a body that has the same elastic moduli as the surrounding material. Eigenstresses are self-equilibrated (residual, or internal) stresses that result from the incompatibility of the eigenstrains. Eigenstresses therefore store free energy in a body even if it is free of externally applied loads or constraints. An inclusion will not disturb an applied stress field. An inhomogeneity is a subdomain of a body with elastic moduli that differ from those of the surrounding material. Therefore, an inhomogeneity will disturb an applied stress field. An inhomogeneity does not, however, store free energy in the absence of applied loads because it does not produce an eigenstrain. An inhomogeneous inclusion is an inhomogeneity that contains an eigenstrain. Thus, an inhomogeneous inclusion may store free energy in the absence of applied loads, and it

will disturb an applied stress. Assuming that the free energy stored in the interfacial area between the martensite and the austenite is negligible, the specific Gibbs energy of mixing is given with respect to the austenite reference frame by

$$G^{mix}\{\sigma_{ij}, T, c^\alpha\} \;=\; G^{eig}\{\sigma_{ij}, T, c^\alpha\} \;+\; G^{interface} \;\cong\; G^{eig}\{\sigma_{ij}, T, c^\alpha\}\,. \tag{10}$$

The free energy of mixing is approximated by a series expansion

$$
\begin{aligned}
G^{eig}\{\sigma_{ij}, T, c^\alpha\} = \sum_{\alpha=1}^{N-1} c^\alpha \Bigg\{ b^{\alpha 1} - \frac{1}{\rho} b^{\alpha 2}_{ij} \sigma_{ij} + b^{\alpha 3} \Delta T + \sum_{\theta=1}^{N-1} b^{\alpha\theta 4} c^\theta - \frac{1}{\rho}\frac{1}{2} b^{\alpha 5}_{ijkl} \sigma_{ij}\sigma_{kl} \\
- \frac{1}{\rho} b^{\alpha 6}_{ij} \sigma_{ij}\Delta T + \frac{1}{2} b^{\alpha 7} (\Delta T)^2 + \sum_{\theta=1}^{N-1} b^{\alpha\theta 8} c^\theta \Delta T + \sum_{\theta=1}^{N-1} b^{\alpha\theta 9}_{ij} c^\theta \sigma_{ij} + \sum_{\theta=1}^{N-1}\sum_{\omega=1}^{N-1} b^{\alpha\theta\omega 10} c^\theta c^\omega \Bigg\}\,.
\end{aligned}
\tag{11}
$$

During the forward phase transformation, the martensite variants are inhomogeneous inclusions within the austenite matrix. G^{mix} therefore consists of several components: (1) The misfit strain energy due to the incompatibility of the transformation and reorientation eigenstrains. The $b^{\alpha 1}$ account for the self energy of each variant. $b^{\alpha\theta 4}$ and $\sum_{\theta=1}^{N-1}\sum_{\omega=1}^{N-1} b^{\alpha\theta\omega 10}$ account for hardening due to the irreversible eigenstresses; (2) Because the martensite and austenite have different thermal expansion coefficients, a homogeneous temperature change will result in misfit strain energy, modelled by the $b^{\alpha 7}$ term, due to the incompatibility of the thermal eigenstrains; (3) The interaction energy between the martensitic variants (inhomogeneities) and the applied stress. This energy contributes to the overall elastic stiffness. The terms $\sum_{\alpha=1}^{N-1} b^{\alpha 2}_{ij}$ and $\sum_{\theta=1}^{N-1} b^{\alpha\theta 9}_{ij}$ vanish because it is assumed that the reversible strain vanishes at $\sigma_{ij} = 0$ and $T = T^\circ$ (see (14a). The constants $b^{\alpha 5}_{ijkl}$ and $b^{\alpha 6}_{ij}$ contribute mixing terms to the elastic compliance and thermal expansion vector, respectively; (4) The interaction energy of the inelastic and thermal eigenstresses, which is modeled by $b^{\alpha 3}$. The $b^{\alpha\theta 8}$ account for the temperature dependence of the irreversible eigenstresses, which can be due to the temperature dependence of the elastic moduli.

The outstanding problem of thermodynamics is to provide a rigorous definition of non-equilibrium entropy, s. In the present paper, it is assumed that $s = -\frac{\partial G}{\partial T}$, which corresponds to the assumptions of local equilibrium (de GROOT and MAZUR [1962]; GLANSDORFF and PRIGOGINE, [1971]), local accompanying state (KESTIN and BATAILLE [1977]; BATAILLE and KESTIN [1979]), and quasi-homogeneity (EDELEN [1994]). These assumptions imply that the thermostatic definition of entropy as an integrating factor for the heat rate and the internal energy as an exact differential are maintained in an extended state space that includes internal variables. The free energy rate is therefore written as

$$
\begin{aligned}
\dot{G} &= \frac{\partial G}{\partial \sigma_{ij}} \dot{\sigma}_{ij} + \frac{\partial G}{\partial T}\dot{T} + \sum_{\alpha=1}^{N-1} \frac{\partial G}{\partial c^\alpha}\dot{c}^\alpha \equiv -\frac{1}{\rho}\epsilon^{te}_{ij}\dot{\sigma}_{ij} - s\dot{T} + \sum_{\alpha=1}^{N-1} \mu^\alpha \dot{c}^\alpha \\
&\equiv -\frac{1}{\rho}\epsilon^{te}_{ij}\dot{\sigma}_{ij} - s\dot{T} - \sum_{\beta=1}^{R} \mathcal{A}^\beta \dot{\xi}^\beta\,,
\end{aligned}
\tag{12}
$$

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where ϵ_{ij}^{te} is the thermoelastic, or reversible infinitesimal strain

$$\epsilon_{ij}^{te} = \epsilon_{ij} - \epsilon_{ij}^{irr} \, . \tag{13}$$

ϵ_{ij} is the total infinitesimal strain and ϵ_{ij}^{irr} is the irreversible strain due to both phase transformation and reorientation. The generalized forces are

$$\epsilon_{ij}^{te} \equiv -\rho \frac{\partial G}{\partial \sigma_{ij}} = \left(a_{ijkl}^1 + \sum_{\alpha=1}^{N-1} c^\alpha b_{ijkl}^{\alpha 5} \right) \sigma_{kl} + \left(a_{ij}^2 + \sum_{\alpha=1}^{N-1} c^\alpha b_{ij}^{\alpha 6} \right) \Delta T \, , \tag{14a}$$

$$s \equiv -\frac{\partial G}{\partial T} = \frac{1}{\rho} \left(a_{ij}^2 + \sum_{\alpha=1}^{N-1} c^\alpha b_{ij}^{\alpha 6} \right) \sigma_{ij} + a^3 ln \left(\frac{T}{T^\circ} \right) + a^4 - \sum_{\alpha=1}^{N-1} c^\alpha \left(b^{\alpha 3} + b^{\alpha 7} + \sum_{\theta=1}^{N-1} b^{\alpha \theta 8} c^\theta \Delta T \right), \tag{14b}$$

and

$$\mathcal{A}^\beta \equiv -\sum_{\alpha=1}^{N-1} \nu^{\alpha \beta} \mu^\alpha \equiv -\sum_{\alpha=1}^{N-1} \nu^{\alpha \beta} \frac{\partial G}{\partial c^\alpha} = -\sum_{\alpha=1}^{N-1} \nu^{\alpha \beta} \left(G^\alpha - G^A \right) - \sum_{\alpha=1}^{N-1} \nu^{\alpha \beta} \Bigg\{ b^{\alpha 1}$$

$$+ b^{\alpha 3} \Delta T + \sum_{\theta=1}^{N-1} b^{\alpha \theta 4} c^\theta - \frac{1}{\rho} \frac{1}{2} b_{ijkl}^{\alpha 5} \sigma_{ij} \sigma_{kl} - \frac{1}{\rho} b_{ij}^{\alpha 6} \sigma_{ij} \Delta T + \frac{1}{2} b^{\alpha 7} (\Delta T)^2$$

$$+ \sum_{\theta=1}^{N-1} b^{\alpha \theta 8} \left(c^{\theta \circ} + \sum_{\beta=1}^R \nu^{\theta \beta} \xi^\beta \right) \Delta T + \sum_{\theta=1}^{N-1} \sum_{\omega=1}^{N-1} b^{\alpha \theta \omega 10} \left(c^{\theta \circ} + \sum_{\beta=1}^R \nu^{\theta \beta} \xi^\beta \right) \left(c^{\omega \circ} + \sum_{\beta=1}^R \nu^{\omega \beta} \xi^\beta \right) \Bigg\} ,$$

$$\tag{14c}$$

where

$$a_{ijkl}^1 = a_{ijkl}^{A1} + \sum_{\alpha=1}^{N-1} c^\alpha \Delta a_{ijkl}^{\alpha 1} \, , \quad a_{ij}^2 = a_{ij}^{A2} + \sum_{\alpha=1}^{N-1} c^\alpha \Delta a_{ij}^{\alpha 2} \, , \quad a^3 = a^{A3} + \sum_{\alpha=1}^{N-1} c^\alpha \Delta a^3 \, ,$$

$$a^4 = a^{A4} + \sum_{\alpha=1}^{N-1} c^\alpha \Delta a^4 \quad a^5 = a^{A5} + \sum_{\alpha=1}^{N-1} c^\alpha \Delta a^5 \, , \tag{15a-e}$$

and

$$\Delta a_{ijkl}^{\alpha 1} = a_{ijkl}^{\alpha 1} - a_{ijkl}^{A1} \, , \quad \Delta a_{ij}^{\alpha 2} = a_{ij}^{\alpha 2} - a_{ij}^{A2} \, , \quad \Delta a^3 = a^{M3} - a^{A3} \, ,$$

$$\Delta a^4 = a^{M4} - a^{A4} \, , \quad \Delta a^5 = a^{M5} - a^{A5} \, , \tag{16a-e}$$

If the thermoelastic effect of different variant orientations with respect to the austenite reference frame is negelected, then all variants have the same free energy G^M of martensite:

$$a_{ijkl}^{\alpha 1} = a_{ijkl}^{M1} \, , \quad a_{ij}^{\alpha 2} = a_{ij}^{M2} \, , \quad b^{\alpha 1} = b^1 \, , \quad b^{\alpha 3} = b^3 \, , \quad b_{ijkl}^{\alpha 5} = b_{ijkl}^5 \, ,$$

$$b_{ij}^{\alpha 6} = b_{ij}^6 \, , \quad b^{\alpha 7} = b^7 \, , \quad b^{\alpha \theta 8} = b^8 \, , \qquad 1 \le \alpha \le N - 1 \, . \tag{17a-h}$$

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In this case, the inhomogeneity effects of each variant are equal, but the inclusion effects of each variant are not equal because the eigenstrains due to $\mathcal{E}_{ij}^{\alpha}$ differ among variants. The pure affinities then reduce to the simple forms

$$
\begin{aligned}
\mathcal{A}^{\beta pure} &\equiv -\sum_{\alpha=1}^{N-1} \nu^{\alpha\beta} \mu^{\alpha pure} \equiv -\sum_{\alpha=1}^{N-1} \nu^{\alpha\beta} \frac{\partial G^{pure}}{\partial c^{\alpha}} = \frac{1}{\rho}\frac{1}{2}\left(a_{ijkl}^{M1} - a_{ijkl}^{A\,1}\right)\sigma_{ij}\sigma_{kl} \\
&\quad + \frac{1}{\rho}\left(a_{ij}^{M2} - a_{ij}^{A2}\right)\sigma_{ij}\Delta T - \left(a^{M3} - a^{A3}\right)\left[\Delta T - T\,ln\left(\frac{T}{T^{\circ}}\right)\right] - \left(a^{M4} - a^{A4}\right) - \left(a^{M5} - a^{A5}\right), \\
\mathcal{A}^{\beta pure} &= 0, \qquad\qquad N \le \beta \le R.
\end{aligned}
$$
(18)

Therefore, if each variant has the same thermoelastic properties, then reorientation does not alter the effective material properties.

II.3. Dissipation Potential

The total entropy production per unit volume $\dot{\zeta}$ is given as the summation of the local entropy production $\dot{\eta}$ due to microstructural rearrangements and the entropy production due to heat conduction $\dot{\gamma}$ (MALVERN [1969]), i.e., $\dot{\zeta} = \dot{\eta} + \dot{\gamma}$. According to the strong form of the second law of thermodynamics, the two entropy productions are assumed to be independently nonnegative for all processes, in which case

$$
T\dot{\eta} = \sigma_{ij}\dot{\epsilon}_{ij} - \rho\dot{\Psi} - \rho s\dot{T} \ge 0, \qquad\qquad T\dot{\gamma} = -\frac{1}{T}q_i T_{,i} \ge 0 \qquad\qquad (19a-b)
$$

where $\Psi\{\epsilon_{ij}^{te}, T, c^{\alpha}\}$ is the specific Helmholtz free energy. Using a partial Legendre transformation

$$
\Psi = G + \frac{1}{\rho}\sigma_{ij}\epsilon_{ij}^{te}, \tag{20}
$$

$T\dot{\eta}$ can be rewritten as

$$
T\dot{\eta} = \sigma_{ij}\dot{\epsilon}_{ij}^{irr} + \rho\sum_{\beta=1}^{R}\mathcal{A}^{\beta}\dot{\xi}^{\beta} \ge 0. \tag{21}
$$

Using (3), the irreversible strain is

$$
\epsilon_{ij}^{irr} = \sum_{\alpha=1}^{N-1}\mathcal{E}_{ij}^{*\alpha}\, c^{\alpha} = \sum_{\alpha=1}^{N-1}\mathcal{E}_{ij}^{*\alpha}\left(c^{\alpha\circ} + \sum_{\beta=1}^{R}\nu^{\alpha\beta}\xi^{\beta}\right). \tag{22}
$$

In general, $\mathcal{E}_{ij}^{*\alpha}$ is a function of the morphology of the c^{α}, and $\mathcal{E}_{ij}^{*\alpha} \ne \mathcal{E}_{ij}^{\alpha}$ because the irreversible strain does not volume average if the material contains elastic inhomogeneities. If $a_{ijkl}^{\alpha1} = a_{ijkl}^{M1}$, then $\mathcal{E}_{ij}^{*\alpha} = \mathcal{E}_{ij}^{\alpha}$ is exact for reorientation of 100% martensite. If $a_{ijkl}^{A1} = a_{ijkl}^{\alpha1} = a_{ijkl}^{M1}$, then $\mathcal{E}_{ij}^{*\alpha} = \mathcal{E}_{ij}^{\alpha}$ is always exact. With the net thermodynamic force Π^{β} to $\dot{\xi}^{\beta}$ given by

$$
\Pi^{\beta} = \sigma_{ij}\sum_{\alpha=1}^{N-1}\mathcal{E}_{ij}^{*\alpha}\nu^{\alpha\beta} + \rho\mathcal{A}^{\beta}, \tag{23}
$$

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the entropy production becomes

$$T\dot{\eta} = \sum_{\beta=1}^{R} \Pi^{\beta}\dot{\xi}^{\beta} \geq 0\,. \tag{24}$$

EDELEN [1974] has demonstrated that there exists a vector decomposition theorem such that the fluxes appearing in the entropy production inequality can be decomposed into a dissipative component and a non-dissipative component. Furthermore, the dissipative fluxes must be derivable from a dissipation potential. It is assumed that the individual entropy production rates, given by $T\dot{\eta}^{\beta} \equiv \Pi^{\beta}\dot{\xi}^{\beta}$, must be non-negative. In this case (24) takes the more restricted form (assuming that there are no non-dissipative fluxes)

$$T\dot{\eta}^{\beta} = \Pi^{\beta}\dot{\xi}^{\beta} \geq 0\,, \qquad\qquad 1 \leq \beta \leq R\,. \tag{25}$$

Each rate of reaction $\dot{\xi}^{\beta}$ is given by a dissipation potential $\phi^{\beta}\{\Pi^{\theta};\,\omega\}$. It is assumed that the reactions are uncoupled, so that $\phi^{\beta} = \phi^{\beta}\{\Pi^{\beta};\,\omega\}$ as

$$\dot{\xi}^{\beta} = \frac{\partial\phi^{\beta}}{\partial\Pi^{\beta}} = \frac{\partial(T\dot{\eta}^{\beta})}{\partial\Pi^{\beta}} = \frac{\partial}{\partial\Pi^{\beta}}\int_{0}^{1} T\,\dot{\eta}^{\beta}\{\tau\Pi^{\beta};\,\omega\}\frac{d\tau}{\tau} = \frac{\partial}{\partial\Pi^{\beta}}\int_{0}^{1}\Pi^{\beta}\,\dot{\xi}^{\beta}\{\tau\Pi^{\beta};\,\omega\}\,d\tau \tag{26}$$

In the case of rate independent transformation, nonzero fluxes $\dot{\xi}^{\beta}$ occur only when the force Π^{β} reaches a threshold value. The rate independent equivalent of (26) is

$$\dot{\xi}^{\beta} = \lambda^{\beta}\frac{\partial\phi^{\beta}\{\Pi^{\beta};\,\omega\}}{\partial\Pi^{\beta}}\,, \tag{27}$$

where the Lagrange multipliers λ^{β} are governed by the Kuhn-Tucker conditions

$$\lambda^{\beta} \geq 0\,, \qquad \phi^{\beta} \leq Y^{\beta}\,, \qquad \lambda^{\beta}(\phi^{\beta} - Y^{\beta}) = 0\,, \tag{28}$$

and Y^{β} is a threshold parameter similar to the yield stress of classical plasticity. For nonlinear force-flux relations, i.e. for cases in which the linear Onsager theory does not apply, there is in general no thermodynamic stability requirement, or requirement of convex ϕ^{β}:

$$\dot{\Pi}^{\beta}\dot{\xi}^{\beta} = \dot{\Pi}^{\beta}\frac{\partial\phi^{\beta}}{\partial\Pi^{\beta}} \geq 0\,. \tag{29}$$

For the cases in which the reactions are stable, i.e. (29) is applicable, the Kuhn-Tucker conditions serve to maximize the rate-independent dissipation subject to the constraints of the conservation of mass, equation (2). The widely used "generalized standard material" (HALPHEN and NGUYEN [1975]) is a special case of Edelen's general formalism in which the free energy and dissipation potentials are convex and there are no non-dissipative fluxes. Similarly, the "maximum dissipation postulate" of classical plasticity is a special case of Edelen's formalism in which the rate independent yield function is the dissipation potential and there are no non-dissipative fluxes. In the present case, the deformation is assumed to be rate independent because the temperatures

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are too low to cause significant thermal activation. Each dissipation potential is approximated by a quadratic form

$$\phi^\beta = \frac{1}{2}(\Pi^\beta)^2 \, . \tag{30}$$

From the Kuhn-Tucker conditions, an alternative statement of the consistency condition of classical plasticity, it follows that

$$0 = \dot\phi^\beta = \Pi^\beta \, \dot\Pi^\beta \qquad when \qquad \dot\xi^\beta \neq 0 \, . \tag{31}$$

Thus, rate independent deformation requires that

$$\dot\Pi^\beta \dot\xi^\beta = 0 \, , \quad or \quad \dot\Pi^\beta = 0 \quad when \quad \dot\xi^\beta \neq 0 \, . \tag{32}$$

The local entropy production can be rewritten as

$$T\dot\eta = \sum_{\beta=1}^{R} \lambda^\beta (\Pi^\beta)^2 \;=\; \sum_{\beta=1}^{R} 2\,\lambda^\beta Y^\beta \, , \tag{33}$$

from which it may be seen that the Lagrange multipliers λ^β control the history dependence of the entropy production. The Lagrange multipliers λ^β are determined by first applying (32), assuming that the $\mathcal{E}_{ij}^{*\alpha}$ are constant:

$$0 = \dot\Pi^\beta = \frac{\partial\Pi^\beta}{\partial\sigma_{ij}}\dot\sigma_{ij} + \frac{\partial\Pi^\beta}{\partial\mathcal{A}^\beta}\dot{\mathcal{A}}^\beta \, , \qquad \beta = 1, 2, 3...R \tag{34}$$

or

$$\rho \sum_{\theta=1}^{R} \frac{\partial\mathcal{A}^\beta}{\partial\xi^\theta}\dot\xi^\theta = -\left(\sum_{\alpha=1}^{N-1} \mathcal{E}_{ij}^{*\alpha}\nu^{\alpha\beta} + \rho\frac{\partial\mathcal{A}^\beta}{\partial\sigma_{ij}}\right)\dot\sigma_{ij} - \rho\frac{\partial\mathcal{A}^\beta}{\partial T}\dot T \, , \qquad \beta = 1, 2, 3...R \tag{35}$$

and then using the flow rule (27) to obtain R simultaneous equations for the R Lagrange multipliers λ^β:

$$\rho \sum_{\theta=1}^{R} \frac{\partial\mathcal{A}^\beta}{\partial\xi^\theta}\frac{\partial\phi^\theta}{\partial\Pi^\theta}\lambda^\theta = -\left(\sum_{\alpha=1}^{N-1} \mathcal{E}_{ij}^{*\alpha}\nu^{\alpha\beta} + \rho\frac{\partial\mathcal{A}^\beta}{\partial\sigma_{ij}}\right)\dot\sigma_{ij} - \rho\frac{\partial\mathcal{A}^\beta}{\partial T}\dot T \, , \qquad \beta = 1, 2, 3...R \tag{36}$$

The matrix form of these simultaneous equations yields sparcely populated matrices because most of the stoichiometric coefficients are zero. The transformation rates can be determined by using the λ^β in the flow rules (27).

II.4. Discussion

The constants in G^{eig} can be obtained by performing a micromechanics analysis in which one first solves a local boundary value problem in V^{micro} for a given arrangement of the N species, followed by an averaging method to obtain the overall single crystal coefficients. Such an analysis is extremely complicated due to the enormous number of possible variant arrangements. A very

crude solution could be obtained using the Landau-Ginzburg extension of the Landau theory of phase transformations. In the Landau theory, the strains (5) are related to the order parameters via the matrix of eigenvectors of the austenite elastic stiffness tensor. The Landau free energy is then expanded as a function of the order parameters and the stress. Minimization of the Landau energy with respect to the order parameters yields the variants that form. The Landau theory, however, is applicable only to pure substances because it does not account for the effects of variant interaction, i.e. the eigenstresses that result from the compatibility constraints among the variants. In order to account for the variant interaction, BARSCH and KRUMHANSL [1992] have augmented the Landau free energy with nonlinear and nonlocal (or strain gradient, or Landau-Ginzburg) terms which account for intermartensitic twin boundaries and a periodically modulated strain pattern. Even these analyses, however, are performed for plane problems with a small number of variants.

GANGHOFFER and coworkers ([1991]) used the finite element method to predict the transformation strain and the plastic accommodation strain. Each element of the two-dimensional, single crystal mesh represented either austenite or a martensite variant associated with one of four habit planes. Because the martensite forms in multiple variants, it is generally impossible to minimize the SMA strain energy using a continuous displacement field. BALL and JAMES [1987] have successfully overcome this difficulty by using the method of minimizing sequences with a non-convex free energy to model the twinned martensite interface, twin planes, and the austenite/finely twinned martensite interface. COLLINS and LUSKIN [1988] have used this theory to predict the arrangements of three variants in a planar problem. This finite element-like analysis is computationally intense even for this simplified geometry. Neither the advanced Landau theory nor the method of minimizing sequences accounts for dissipative effects and the associated path dependent evolution of real transformation and reorientation.

Regardless of the method used to predict the arrangement of species, the single crystal response must be used in a micromechanics solution over V^{micro} to obtain the average response of a polycrystalline SMA material. For the case of pseudoelasticity due to transformation, PATOOR et al [1993] have obtained excellent agreement between theory and experiment using the self-consistent method for a Cu-Zn-Al SMA material with the following assumptions: (1) The martensite variants and the austenite have the same elastic moduli; and (2) G^{eig} is given by the simplified equation

$$G^{eig} = \sum_{\alpha=1}^{24} \sum_{\theta=1}^{24} b^{\alpha\theta 8} c^{\alpha} c^{\theta} . \tag{37}$$

Furthermore, the interaction matrix $d^{\alpha\theta}$ was approximated using only two terms (FASSI-FEHRI et al [1987]), one for self accommodating variants and one for non-self accommodating variants. Despite its demonstrated accuracy, this polycrystalline model is not useful as input to the larger scale micromechanics analysis of the second part of this paper because the self-consistent method does not yield closed form solutions for the effective polycrystalline properties. It is therefore necessary to derive phenomenological equations for the polycrystalline SMA material. BHATTACHARYA and KOHN [1993] have derived the effective free energy function of polycrystals in which each crystal contains a small number of martensitic variants. Dissipative effects were not included.

III. Three Component Phenomenological Model

TANAKA [1986] has presented a one-dimensional phenomenological SMA model that is similar to nonlinear elasticity, or deformation plasticity, in that the martensitic volume fraction is given by a piecewise equation of state rather than an incremental flow rule that uses a dissipation potential. BRINSON [1993] has extended the model of TANAKA [1986] by decomposing the martensitic volume fraction into two parts, self accommodating martensite, which does not produce transformation strain, and non-self accommodating (or detwinned) martensite, which produces transformation strain. BOYD and LAGOUDAS [1993] have proposed a three dimensional, thermodynamically based extension of this concept that includes three components: austenite, self accommodating martensite, and non-self accommodating (or detwinned) martensite. Section III of the present paper is a review of the model of BOYD and LAGOUDAS [1993].

III.1. Notation

The fixed mass system consists of three species undergoing three "reactions":

Species α	Type	Reaction β	Type
1	self accommodating polycrystalline martensite	I	$3 \to 1$
2	detwinned polycrystalline martensite	II	$3 \to 2$
3	polycrystalline austenite	III	$1 \to 2$

The stoichiometric coefficients $\nu^{\alpha\beta}$ are given by

$$\nu^{\alpha\beta} = \begin{bmatrix} 1 & 0 & -1 \\ 0 & 1 & 1 \\ -1 & -1 & 0 \end{bmatrix} \tag{38}$$

The rates $\dot{c}^\alpha$ of each mass fraction c^α are obtained by summing over each reaction, and the mass fractions are obtained by integration to yield

$$\dot{c}^\alpha = \sum_{\beta=I}^{III} \nu^{\alpha\beta}\dot{\xi}^\beta \qquad \longrightarrow \qquad c^\alpha = c^{\alpha\circ} + \sum_{\beta=I}^{III} \nu^{\alpha\beta}\xi^\beta \,. \tag{39}$$

Equation (38) can be used in (39) to obtain

$$c^1 = c^{1\circ} + \xi^I - \xi^{III} \,, \qquad c^2 = c^{2\circ} + \xi^{II} + \xi^{III} \,, \qquad c^3 = c^{3\circ} - \xi^I - \xi^{II} \,. \tag{40}$$

The conservation of mass is given by the constraint

$$c^\alpha \geq 0 \,, \qquad \sum_{\alpha=1}^{3} c^\alpha = 1 \,, \qquad \sum_{\alpha=1}^{3} \dot{c}^\alpha = 0 \,, \tag{41}$$

which requires that only 2 of the 3 mass fractions are independent. The total mass density ρ is assumed to equal the mass density of each species. The mass fractions c^α are therefore equal to the volume fractions of the corresponding species.

III.2. Free Energy

The total specific Gibbs energy $G\{\omega\}$ of a polycrystalline SMA, where $\omega = \{\sigma_{ij}, T, c^1, c^2, \kappa_{ij}\}$, is equal to the mass weighted sum of the free energy $G^\alpha\{\sigma_{ij}, T\}$ of each species plus the free energy $G^{mix}\{\sigma_{ij}, T, c^1, c^2, \kappa_{ij}\}$ of mixing. The internal variable κ_{ij} will be discussed in section III.3., after the introduction of the transformation tensor. The total Gibbs energy is

$$G = G^{pure} + G^{mix} = G^{pure} + G^{eig} + G^{surface} \cong G^{pure} + G^{eig}$$

$$= \sum_{\alpha=1}^{3} c^\alpha G^\alpha\{\sigma_{ij}, T\} + G^{eig}\{\sigma_{ij}, T, c^1, c^2, \kappa_{ij}\} \,, \tag{42}$$

where G^{eig} now includes the stored energy of the eigenstresses due to polycrystalline effects. Equation (41) can be used to rewrite (42) as

$$G = G^3\{\sigma_{ij}, T\} + c^1(G^1\{\sigma_{ij}, T\} - G^3\{\sigma_{ij}, T\}) + c^2(G^2\{\sigma_{ij}, T\} - G^3\{\sigma_{ij}, T\})$$
$$+ G^{mix}\{\sigma_{ij}, T, c^1, c^2, \kappa_{ij}\} \,. \tag{43}$$

The free energy rate is given by

$$\dot{G} = \frac{\partial G}{\partial \sigma_{ij}}\dot{\sigma}_{ij} + \frac{\partial G}{\partial T}\dot{T} + \sum_{\alpha=1}^{2} \frac{\partial G}{\partial c^\alpha}\dot{c}^\alpha + \frac{\partial G}{\partial \kappa_{ij}}\dot{\kappa}_{ij}$$

$$\equiv -\frac{1}{\rho}\epsilon_{ij}^{te}\dot{\sigma}_{ij} - s\dot{T} + \sum_{\alpha=1}^{2} \mu^\alpha \dot{c}^\alpha + g_{ij}\dot{\kappa}_{ij} \tag{44}$$

$$\equiv -\frac{1}{\rho}\epsilon_{ij}^{te}\dot{\sigma}_{ij} - s\dot{T} - \sum_{\beta=I}^{III} \mathcal{A}^\beta \dot{\xi}^\beta + g_{ij}\dot{\kappa}_{ij} \,.$$

III.3. Dissipation Potential

Using the method of section II.3., the local dissipation rate can be written as

$$T\dot{\eta} = \sigma_{ij}\dot{\epsilon}_{ij}^{irr} + \rho \sum_{\beta=I}^{III} \mathcal{A}^\beta \dot{\xi}^\beta - \rho g_{ij}\dot{\kappa}_{ij} \geq 0 \,. \tag{45}$$

The irreversible strain rate is decomposed as

$$\dot{\epsilon}_{ij}^{irr} = \sum_{\alpha=1}^{2} \mathcal{F}_{ij}^{*\alpha}\dot{c}^\alpha = \sum_{\alpha=1}^{2}\sum_{\beta=I}^{III} \mathcal{F}_{ij}^{*\alpha}\nu^{\alpha\beta}\dot{\xi}^\beta = \sum_{\beta=I}^{III} \Lambda_{ij}^\beta\{\sigma_{ij}, T, c^1, c^2, \kappa_{ij}\}\dot{\xi}^\beta \,, \tag{46}$$

where Λ_{ij}^β is the transformation tensor. In the case of the N-1 component model, each transformation tensor was rigorously defined by $\mathcal{E}_{ij}^\alpha$ when $a_{ijkl}^{A1} = a_{ijkl}^{\alpha 1} = a_{ijkl}^{M1}$. In the phenomenological polycrystalline model, however, the transformation tensors $\mathcal{F}_{ij}^{*\alpha}$ and Λ_{ij}^β are only approximate.

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By definition, the self accommodating martensite does not produce transformation strain, so

$$\Lambda_{ij}^{I} = 0 \,. \tag{47}$$

A logical choice for Λ_{ij}^{II} and Λ_{ij}^{III} can be made by considering the symmetry changes that occur during phase transformation and reorientation. During the forward phase transformation, the material is changing from a high symmetry, cubic, to a lower symmetry, usually either tetragonal or monoclinic. Thus, there are many possible variants, and the variants that actually form will be biased by the applied stress. During the reverse transformation, however, all of the variants must return to the same parent symmetry. Thus, the reverse form of Λ_{ij}^{II} should be governed strictly by kinematical, or symmetry considerations. In effect, the manner in which the variants return to the parent phase should depend on the manner in which they previously transformed into the product phase. If κ_{ij} is chosen to represent some average measure of the symmetry changes incurred during the forward transformation, then the reverse form of Λ_{ij}^{II} should depend predominately on κ_{ij}. The sequence of variant annihilation during the reverse transformation is frequently opposite to the sequence of variant formation during the forward transformation. SUN and HWANG [1993a] have used a reverse form of Λ_{ij}^{II} that is given by a memory functional of the state that existed during the forward transformation. An approximate form of Λ_{ij}^{II} is

$$\Lambda_{ij}^{II} = \begin{cases} \Lambda_{ij}^{II}\{\sigma_{ij}\} \,, & \dot{\xi}^{II} > 0 \\ \Lambda_{ij}^{II}\{\kappa_{ij}\} \,, & \dot{\xi}^{II} < 0 \end{cases} \tag{48}$$

The growth and disappearance of the variants during reorientation is determined by the applied stress, so that an approximate form of Λ_{ij}^{III} is given by $\Lambda_{ij}^{III}\{\sigma_{ij}\}$.

The symmetry changes that are represented by κ_{ij} would occur even if there were no eigenstresses to store free energy. Thus, it is assumed that the principle importance of κ_{ij} is not to represent G^{eig}, but rather to specify the reverse form of Λ_{ij}^{II}. Accordingly, it is assumed that

$$0 = \frac{\partial G}{\partial \kappa_{ij}} = g_{ij} \,. \tag{49}$$

With the net thermodynamic force Π^{β} to $\dot{\xi}^{\beta}$ given by

$$\Pi^{\beta} = \sigma_{ij}\Lambda_{ij}^{\beta} + \rho\mathcal{A}^{\beta} \,, \tag{50}$$

the local entropy production becomes

$$T\dot{\eta} = \sum_{\beta=1}^{III} \Pi^{\beta}\dot{\xi}^{\beta} \,. \tag{51}$$

Assuming that the reactions are uncoupled, each rate of reaction is given by a rate independent dissipation potential ϕ^{β} as in section II.3., but with only three reactions.

III.4. Discussion

This three component phenomenological model has several shortcomings: (1) By definition, the self accommodating martensite produces no transformation strain, i.e. $\Lambda_{ij}^I = 0$, and a stress-induced transformation will result in non-self accommodating martensite, as shown by $\Lambda_{ij}^{II} \neq 0$. In reality, if the transformation results in a volume change, then there will be no purely self accommodating martensite, even in a stress-free transformation. Thus, the very definition of self accommodating martensite is invalid if the transformation is not purely deviatoric; (2) The formalism can be confusing because there are cases in which the forward transformation leads to a decrease in c^1; (3) BOYD and LAGOUDAS [1993] chose the three component model partly because of BRINSON's [1993] interesting extension of TANAKA's [1986] model. The models of Tanaka and Brinson, however, used a constant transformation tensor. In those cases, it is necessary to use two different volume fractions of martensite; and (4) It may be impossible to experimentally distinguish between c^1 and c^2 using resistivity measurements. It would then be necessary to measure c^1 and c^2 using microscopy or x-ray diffraction. In this case, it is really the N components of section II that are being measured.

Because of these shortcomings, the present authors have chosen the following two component phenomenological model.

IV. Two Component Phenomenological Model

RANIECKI and LEXCELLENT [1994] used one internal variable, the total martensite volume fraction, in their two-component thermodynamical derivation of a polycrystalline phenomenological model for pseudoelasticity due to transformation. The two-component model of SUN and HWANG [1993a,1993b]) is perhaps the only published thermodynamical method for pseudoelasticity and the shape memory effect due to both transformation and reorientation. The present section is an extension of these analyses to account for the simultaneous transformation and reorientation that can occur within the composite material of the second paper.

IV.1. Free Energy

The total specific Gibbs energy $G\{\omega\}$ of a polycrystalline SMA, where $\omega = \{\sigma_{ij}, T, c^M, \epsilon_{ij}^{irr}\}$, is equal to the mass weighted sum of the free energy $G^\alpha\{\sigma_{ij}, T\}$ of each species plus the free energy $G^{mix}\{\sigma_{ij}, T, c^M, \epsilon_{ij}^{irr}\}$ of mixing:

$$G = G^A\{\sigma_{ij}, T\} + c^M \left(G^M\{\sigma_{ij}, T\} - G^A\{\sigma_{ij}, T\} \right) + G^{mix}\{\sigma_{ij}, T, c^M, \epsilon_{ij}^{irr}\} . \qquad (52)$$

The free energy of each species is written as

$$G^\alpha = -\frac{1}{\rho}\frac{1}{2}a_{ijkl}^{\alpha 1}\sigma_{ij}\sigma_{kl} - \frac{1}{\rho}a_{ij}^{\alpha 2}\sigma_{ij}\Delta T + a^{\alpha 3}\left[\Delta T - T\,ln\left(\frac{T}{T^\circ}\right)\right] - a^{\alpha 4}T + a^{\alpha 5} . \qquad (53)$$

SUN and HWANG [1993] and RANIECKI and L'EXCELLENT [1994] included the temperature dependence of $a_{ijkl}^{\alpha 1}$ to account for the softening of the austenite near the martensite start temperature.

In choosing an equation for G^{mix}, it is assumed that the elastic compliance and the thermal expansion coefficient are not altered by mixing. This assumption is supported by the analysis of BOYD and LAGOUDAS [1994], in which the Mori-Tanaka micromechanics method was used to predict the effective elastic stiffness of polycrystalline (Nitinol, $E^A = 30$ GPa, $E^M = 13$ GPa) austenite containing martensitic inhomogeneities. It was found that the effective elastic stiffness differed by no more than 15% from the volume average. It is also assumed that the thermal eigenstresses are small relative to the irreversible eigenstresses. Furthermore, it is assumed that the self energy of thin plate martensite is negligible relative to the interaction energies (FASSI-FEHRI et al [1987]; PATOOR et al [1987]), so that the first order terms containing c^M and ϵ_{ij}^{irr} are omitted. From the operational point of view, the constants associated with the first order term in c^M are experimentally inseparable from Δa^5. Accordingly, the series expansion of G^{mix} is truncated at second order as

$$G^{mix} = \frac{1}{2}b^1(c^M)^2 + \frac{1}{2}b_{ijkl}^2\epsilon_{ij}^{irr}\epsilon_{kl}^{irr} + b_{ij}^3\epsilon_{ij}^{irr}c^M \ . \tag{54}$$

This equation for G^{mix} is analogous to the form used in plasticity for linear kinematic and isotropic hardening, in which ϵ_{ij}^{irr} serves as a kinematic hardening variable. SUN and HWANG [1993] and RANIECKI and L'EXCELLENT [1994] included the temperature dependence of b^1. This effect could arise because, for a given eigenstrain, the eigenstresses and stored energy depend on the elastic moduli, which may be functions of temperature. Also, it may be necessary to include c^M dependence in the hardening moduli of (54) to account for the fact that the austenite and martensite have different elastic moduli. SUN and HWANG [1993] included the volume fraction of transformed martensite and reoriented martensite as separate internal variables, whereas the present model makes no attempt to decompose the the martensite volume fraction. The volume fraction of martensite, c^M, can be experimentally correlated with the resisitivity, whereas multiple martensitic volume fractions suffer from the experimental difficulties discussed in section II.B.4.

The free energy rate is

$$\dot{G} = \frac{\partial G}{\partial \sigma_{ij}}\dot{\sigma}_{ij} + \frac{\partial G}{\partial T}\dot{T} + \frac{\partial G}{\partial c^M}\dot{c}^M + \frac{\partial G}{\partial \epsilon_{ij}^{irr}}\dot{\epsilon}_{ij}^{irr} \equiv -\frac{1}{\rho}\epsilon_{ij}^{te}\dot{\sigma}_{ij} - s\dot{T} + \mu^M\dot{c}^M + \mu_{ij}^{irr}\dot{\epsilon}_{ij}^{irr} \ , \tag{55}$$

where the strain decomposition $\epsilon_{ij}^{te} = \epsilon_{ij} - \epsilon_{ij}^{irr}$, equation (13), remains valid. The generalized forces are

$$\epsilon_{ij}^{te} = a_{ijkl}^1\sigma_{kl} + a_{ij}^2\Delta T \ , \qquad s = \frac{1}{\rho}a_{ij}^2\sigma_{ij} + a^3 ln\left(\frac{T}{T^\circ}\right) + a^4 \ , \qquad \mu_{ij}^{irr} = b_{ijkl}^2\epsilon_{kl}^{irr} + b_{ij}^3 c^M$$

$$\mu^M = -\frac{1}{\rho}\frac{1}{2}\Delta a_{ijkl}^1\sigma_{ij}\sigma_{kl} - \frac{1}{\rho}\Delta a_{ij}^2\sigma_{ij}\Delta T + \Delta a^3\left[\Delta T - T ln\left(\frac{T}{T^\circ}\right)\right] - \Delta a^4 T + \Delta a^5$$

$$+ b^1 c^M + b_{ij}^3\epsilon_{ij}^{irr} \ ,$$

$$\tag{56a-e}$$

where

$$a_{ijkl}^1 = a_{ijkl}^{A1} + c^M\Delta a_{ijkl}^1 \ , \quad a_{ij}^2 = a_{ij}^{A2} + c^M\Delta a_{ij}^2 \ , \quad a^3 = a^{A3} + c^M\Delta a^3 \ ,$$

$$a^4 = a^{A4} + c^M\Delta a^4 \ , \quad a^5 = a^{A5} + c^M\Delta a^5 \ ,$$

$$\tag{57a-e}$$

and

$$\Delta a_{ijkl}^1 = a_{ijkl}^{M1} - a_{ijkl}^{A1}, \quad \Delta a_{ij}^2 = a_{ij}^{M2} - a_{ij}^{A2}, \quad \Delta a^3 = a^{M3} - a^{A3},$$
$$\Delta a^4 = a^{M4} - a^{A4}, \quad \Delta a^5 = a^{M5} - a^{A5}. \tag{58a-e}$$

IV.2. Dissipation Potential

Following the method of section II.3., the local dissipation rate is given by

$$T\dot{\eta} = \sigma_{ij}\dot{\epsilon}_{ij}^{irr} - \rho\mu^M \dot{c}^M - \rho\mu_{ij}^{irr}\dot{\epsilon}_{ij}^{irr}$$
$$= (\sigma_{ij} - \rho\mu_{ij}^{irr})\dot{\epsilon}_{ij}^{irr} - \rho\mu^M \dot{c}^M = \sigma_{ij}^{eff}\dot{\epsilon}_{ij}^{irr} - \rho\mu^M \dot{c}^M \geq 0, \tag{59}$$

where

$$\sigma_{ij}^{eff} = \sigma_{ij} - \rho\mu_{ij}^{irr}. \tag{60}$$

The irreversible strain rate is decomposed into a part $\dot{\epsilon}_{ij}^t$ due to transformation and a part $\dot{\epsilon}_{ij}^r$ due to reorientation:

$$\dot{\epsilon}_{ij}^{irr} = \dot{\epsilon}_{ij}^t + \dot{\epsilon}_{ij}^r, \qquad\qquad \epsilon_{ij}^{irr} = \epsilon_{ij}^t + \epsilon_{ij}^r, \tag{61a-b}$$

where

$$\dot{\epsilon}_{ij}^t = \Lambda_{ij}\{\sigma_{ij}, T, c^M, \epsilon_{ij}^{irr}\}\dot{c}^M. \tag{62}$$

In general, there is no unique relationship between ϵ_{ij}^t and c^M. However, for proportional loading, $\sigma_{ij} = K_{ij}\bar{\sigma}$, where K_{ij} are constants, and the incremental equations (62) can be integrated in closed form to obtain an equation of state $\epsilon_{ij}^t = \epsilon_{ij}^t\{\sigma_{kl}, T, c^M\}$. The local dissipation rate, (59), can be rewritten using (61) and (62) as

$$T\dot{\eta} = \sigma_{ij}^{eff}\dot{\epsilon}_{ij}^t + \sigma_{ij}^{eff}\dot{\epsilon}_{ij}^r - \rho\mu^M \dot{c}^M = (\sigma_{ij}^{eff}\Lambda_{ij} - \rho\mu^M)\dot{c}^M + \sigma_{ij}^{eff}\dot{\epsilon}_{ij}^r$$
$$= \Pi\dot{c}^M + \sigma_{ij}^{eff}\dot{\epsilon}_{ij}^r \geq 0, \tag{63}$$

where

$$\Pi = \sigma_{ij}^{eff}\Lambda_{ij} - \rho\mu^M. \tag{64}$$

Note that neither ϵ_{ij}^t nor ϵ_{ij}^r are independent state variables, although $\dot{\epsilon}_{ij}^r$ is an independent flux. In fact, although ϵ_{ij}^{irr} is infinitesimal, the strains ϵ_{ij}^t and ϵ_{ij}^r can accumulate and grow large under cyclic loading. It is assumed that the transformation rate and the reorientation rate separately obey the Clausius-Duhem inequality:

$$T\dot{\eta}^M = \Pi\dot{c}^M \geq 0, \qquad\qquad T\dot{\eta}^r = \sigma_{ij}^{eff}\dot{\epsilon}_{ij}^r \geq 0. \tag{65a-b}$$

In this case, there are two separate dissipation potentials, $\phi^t\{\Pi, \sigma_{ij}^{eff}; \omega\}$ and $\phi^r\{\Pi, \sigma_{ij}^{eff}; \omega\}$. The generally anisotropic form of the dissipation potentials can contain coupling terms in Π and σ_{ij}^{eff}. However, in order to emphasize a different coupling effect due to the form (54) for G^{mix}, it is assumed that there are no coupling terms in ϕ^t and ϕ^r, i.e. $\phi^t = \phi^t\{\Pi; \omega\}$ and $\phi^r = \phi^r\{\sigma_{ij}^{eff}; \omega\}$:

$$\dot{c}^M = \lambda^t \frac{\partial\phi^t\{\Pi; \omega\}}{\partial\Pi}, \qquad\qquad \dot{\epsilon}_{ij}^r = \lambda^r \frac{\partial\phi^r\{\sigma_{kl}^{eff}; \omega\}}{\partial\sigma_{ij}^{eff}}. \tag{66a-b}$$

The Kuhn-Tucker conditions for transformation and the conservation of mass are

$$\lambda^t \geq 0 \,, \qquad \phi^t \leq Y^t \,, \qquad \lambda^t(\phi^t - Y^t) = 0 \,, \qquad when \qquad 0 \leq c^M \leq 1 \,. \tag{67}$$

For inelasticity due to transformation and reorientation, the maximum irreversible strain is limited by the extent of transformation and/or reorientation. Therefore, the dilatational and the effective irreversible strains are assumed to be less than the maximum values $\left(\bar{\epsilon}^{irr}\right)^{max}$ and $\epsilon_{mm}^{irr\,max}$ associated with fully oriented martensite:

$$\bar{\epsilon}^{irr} \leq c^M \left(\bar{\epsilon}^{irr}\right)^{max} \,, \qquad\qquad \epsilon_{mm}^{irr} \leq c^M \epsilon_{mm}^{irr\,max} \,, \tag{68}$$

where $\bar{\epsilon}^{irr} = \left(\frac{2}{3}\epsilon_{ij}'^{irr}\epsilon_{ij}'^{irr}\right)^{\frac{1}{2}}$. Reorientation can occur only when

$$\lambda^r \geq 0 \,, \qquad \phi^r \geq Y^r \,, \tag{69}$$

and the irreversible strain rate is such that the kinematic limitation (68) is not violated. These criteria differ from the the Kuhn-Tucker conditions in that ϕ^r can exceed the threshold value, Y^r. As demonstrated in section V, this phenomena can occur during transformation under proportional loading. It is assumed that reorientation occurs at constant ϕ^r:

$$\dot{\phi}^r = 0 \qquad when \qquad \dot{\epsilon}_{ij}^r \neq 0 \,. \tag{70}$$

The potentials ϕ^t and ϕ^r are assumed to be the convex quadratic functions

$$\phi^t = \frac{1}{2}(\Pi)^2 \,, \qquad\qquad \phi^r = \frac{1}{2}N_{ijkl}\sigma_{ij}^{eff}\sigma_{kl}^{eff} \,, \tag{71a-b}$$

where the constant N_{ijkl} is symmetric: $N_{ijkl} = N_{klij}$. Note that Π is constant during nonzero $\dot{c}^M$. Therefore, the local entropy produced during a complete cycle of isothermal transformation is given by

$$\begin{aligned}
\eta &= \frac{1}{T}\left(\int_{c^M=0}^{c^M=1} \Pi d\,c^M + \int_{c^M=1}^{c^M=0} \Pi d\,c^M\right) = \frac{1}{T}2\Pi \\
&= \frac{1}{T}\left(\int_{c^M=0}^{c^M=1} (2Y^t)^{\frac{1}{2}}d\,c^M - \int_{c^M=1}^{c^M=0} (2Y^t)^{\frac{1}{2}}d\,c^M\right) = \frac{1}{T}2(2Y^t)^{\frac{1}{2}} \,.
\end{aligned} \tag{72}$$

The Lagrange multipliers can be derived by first using (67) and (70),

$$0 = \dot{\phi}^t = \Pi\dot{\Pi} \,, \qquad 0 = \dot{\phi}^r = \frac{\partial\phi^r}{\partial\sigma_{ij}^{eff}}\dot{\sigma}_{ij}^{eff} = N_{ijkl}\sigma_{ij}^{eff}\dot{\sigma}_{kl}^{eff} \,, \tag{73a-b}$$

which results in the two coupled equations

$$-\left(\frac{\partial\Pi}{\partial c^M} + \frac{\partial\Pi}{\partial\epsilon_{ij}^{irr}}\Lambda_{ij}\right)\dot{c}^M - \frac{\partial\Pi}{\partial\epsilon_{ij}^r}\dot{\epsilon}_{ij}^r = \frac{\partial\Pi}{\partial\sigma_{ij}}\dot{\sigma}_{ij} + \frac{\partial\Pi}{\partial T}\dot{T} \,, \tag{74a}$$

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$$
-\frac{\partial \phi^r}{\partial \sigma_{kl}^{eff}}\left[\left(\frac{\partial \sigma_{kl}^{eff}}{\partial c^M} + \frac{\partial \sigma_{kl}^{eff}}{\partial \epsilon_{ij}^{irr}}\Lambda_{ij}\right)\dot{c}^M + \frac{\partial \sigma_{kl}^{eff}}{\partial \epsilon_{ij}^{irr}}\dot{\epsilon}_{ij}^r\right] = \frac{\partial \phi^r}{\partial \sigma_{kl}^{eff}}\left(\dot{\sigma}_{kl} + \frac{\partial \sigma_{kl}^{eff}}{\partial T}\dot{T}\right). \qquad (74b)
$$

The flow rules (66) can now be used to solve for the Lagrange multipliers:

$$
-\left(\frac{\partial \Pi}{\partial c} + \frac{\partial \Pi}{\partial \epsilon_{ij}^{irr}}\Lambda_{ij}\right)\frac{\partial \phi^t}{\partial \Pi}\lambda^t - \frac{\partial \Pi}{\partial \epsilon_{ij}^{irr}}\frac{\partial \phi^r}{\partial \sigma_{ij}^{eff}}\lambda^r = \frac{\partial \Pi}{\partial \sigma_{ij}}\dot{\sigma}_{ij} + \frac{\partial \Pi}{\partial T}\dot{T}, \qquad (75a)
$$

and

$$
-\frac{\partial \phi^r}{\partial \sigma_{kl}^{eff}}\left[\left(\frac{\partial \sigma_{kl}^{eff}}{\partial c^M} + \frac{\partial \sigma_{kl}^{eff}}{\partial \epsilon_{ij}^{irr}}\Lambda_{ij}\right)\frac{\partial \phi^t}{\partial \Pi}\lambda^t + \frac{\partial \sigma_{kl}^{eff}}{\partial \epsilon_{ij}^{irr}}\frac{\partial \phi^r}{\partial \sigma_{ij}^{eff}}\lambda^r\right] = \frac{\partial \phi^r}{\partial \sigma_{kl}^{eff}}\left(\dot{\sigma}_{kl} + \frac{\partial \sigma_{kl}^{eff}}{\partial T}\dot{T}\right). \quad (75b)
$$

The nonzero fluxes are obtained by using equations (75) for the nonzero Lagrange multipliers in the flow rules (66). When the criterion for transformation and reorientation are simultaneously satisfied, one obtains simultaneous equations for the fluxes $\dot{c}^M$ and $\dot{\epsilon}_{ij}^r$. The simultaneous equations are due to the coupling terms in G^{mix}, which means that the internal state developed during transformation affects subsequent reorientation, and visa-versa. Note that equations (71) for the dissipation potentials excludes explicit coupling due to cross terms in Π and σ_{ij}^{eff}. For G given by (52), (53) and (54), $\frac{\partial \sigma_{ij}^{eff}}{\partial T} = 0$.

For the case in which $\dot{\epsilon}_{ij}^r = 0$ and $\dot{c}^M \neq 0$, (53), (54) and (64) can be used to solve (75) and (74) for $\dot{c}^M$ as

$$
\dot{c}^M = (\mathcal{D}^1)^{-1}\left(\frac{\partial \Pi}{\partial \sigma_{ij}}\dot{\sigma}_{ij} + \frac{\partial \Pi}{\partial T}\dot{T}\right), \qquad (76)
$$

where

$$
\mathcal{D}^1 = -\frac{\partial \Pi}{\partial c^M} - \frac{\partial \Pi}{\partial \epsilon_{ij}^{irr}}\Lambda_{ij} \qquad (77)
$$

For proportional loading, $\sigma_{ij} = K_{ij}\bar{\sigma}$, where K_{ij} are constants, and the incremental equations (76) can be integrated in closed form to obtain an equation of state $c^M = c^M\{\sigma_{ij}, T\}$. When higher order terms are included in the free energy, the integrated form of the incremental thermodynamic formulation can be made to converge to the the exponential equation of state postulated by MAGEE [1970] for ferrous martensitic transformations, and sometimes used to model SMA materials (SATO and TANAKA [1988], ZHANG et al [1991], BRINSON [1993]). Some SMA materials, however, exhibit essentially linear behavior through most of their stress-strain response.

For pure reorientaiton, $\dot{c}^M = 0$ and $\dot{\epsilon}_{ij}^r \neq 0$, and the irreversible strain rate is given by (74b) and (75b):

$$
\dot{\epsilon}_{ij}^r = -\left(\frac{\partial \phi^r}{\partial \sigma_{kl}^{eff}}\frac{\partial \sigma_{kl}^{eff}}{\partial \epsilon_{mn}^{irr}}\frac{\partial \phi^r}{\partial \sigma_{mn}^{eff}}\right)^{-1}\frac{\partial \phi^r}{\partial \sigma_{op}^{eff}}\frac{\partial \phi^r}{\partial \sigma_{ij}^{eff}}\dot{\sigma}_{op}. \qquad (78)
$$

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The tangent compliance tensor, $\mathcal{M}^2_{ijkl}$, and the tangent thermal expansion vector, $\mathcal{M}^3$, are defined by the general equation

$$\dot{\epsilon}_{ij} = \mathcal{M}^2_{ijkl}\dot{\sigma}_{kl} + \mathcal{M}^3_{ij}\dot{T}, \tag{79}$$

and have the specific forms

$$\mathcal{M}^2_{ijop} = a^1_{ijop} - \left(\frac{\partial \phi^r}{\partial \sigma^{eff}_{kl}} \frac{\partial \sigma^{eff}_{kl}}{\partial \epsilon^{irr}_{mn}} \frac{\partial \phi^r}{\partial \sigma^{eff}_{mn}} \right)^{-1} \frac{\partial \phi^r}{\partial \sigma^{eff}_{ij}} \frac{\partial \phi^r}{\partial \sigma^{eff}_{op}}, \quad \mathcal{M}^3_{ij} = a^2_{ij}. \tag{80a-b}$$

For pure reorientation, the tangent compliance tensor is symmetric. This is exactly the result obtained for linear kinematic hardening of dislocation-based plasticity, augmented by the constraint (68).

IV.3. Adiabatic, Isothermal, and Constant Stress Transformation of SMA

During adiabatic transformation, the temperature is not a known input to the problem. The temperature rate must therefore be found using the adiabatic form of the first law. Also, it is useful to have an equation for the transformation rate as a function of the heat input. Toward this end, the first law is written, with $\dot{\epsilon}^r_{ij} = 0$, as

$$\rho\dot{u} = \sigma_{ij}\dot{\epsilon}_{ij} + \rho\dot{Q} = \sigma_{ij}(\dot{\epsilon}^{te}_{ij} + \Lambda_{ij}\dot{c}^M) + \rho\dot{Q}, \tag{81}$$

where the specific heat input rate $\dot{Q}$ is due to a heat source term, r, possibly due to resistance heating, and a heat flux term, $-q_{i,i}$:

$$\dot{Q} = r - q_{i,i}. \tag{82}$$

The Legendre transformation

$$\rho u = \rho G + \sigma_{ij}\epsilon^{te}_{ij} + \rho T s. \tag{83}$$

can be used in (81) to derive the equation

$$T\dot{s} = \frac{1}{\rho}\Pi\dot{c}^M + \dot{Q}. \tag{84}$$

Alternatively, (84) could be written directly from the balance of entropy:

$$\dot{s} = \frac{1}{T}\left(\frac{1}{\rho}\dot{\eta} + \dot{Q}\right) = \frac{1}{T}\left(\frac{1}{\rho}\Pi\dot{c}^M + \dot{Q}\right). \tag{85}$$

The definition of entropy, $s = -\frac{\partial G}{\partial T}$, can be used in (84) to write

$$\dot{Q} = -T\left(\frac{\partial^2 G}{\partial\sigma_{ij}\partial T}\dot{\sigma}_{ij} + \frac{\partial^2 G}{\partial T^2}\dot{T}\right) - \left[T\left(\frac{\partial^2 G}{\partial c^M\partial T} + \frac{\partial^2 G}{\partial\epsilon^{irr}_{ij}\partial T}\Lambda_{ij}\right) + \frac{1}{\rho}\Pi\right]\dot{c}^M. \tag{86}$$

The $\dot{c}^M$ term in (86) can be eliminated using the flow rule, (76):

$$\dot{Q} = \left(\frac{1}{\rho}a^2_{ij}T - \mathcal{D}^2\frac{\partial\Pi}{\partial\sigma_{ij}}\right)\dot{\sigma}_{ij} + \left(a^3 - \mathcal{D}^2\frac{\partial\Pi}{\partial T}\right)\dot{T}, \tag{87}$$

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where $a^3 = -T \frac{\partial^2 G}{\partial T^2}$ and $-\frac{1}{\rho} a_{ij}^2 = \frac{\partial^2 G}{\partial \sigma_{ij} \partial T}$, and

$$\mathcal{D}^2 = (\mathcal{D}^1)^{-1} \left(\frac{1}{\rho} \Pi + T \mathcal{D}^3 \right), \tag{88}$$

where, using (52)-(54),

$$\mathcal{D}^3 = \frac{\partial^2 G}{\partial c^M \partial T} + \frac{\partial^2 G}{\partial \epsilon_{ij}^{irr} \partial T} \Lambda_{ij} = -\frac{1}{\rho} \Delta a_{ij}^2 \sigma_{ij} - \Delta a^3 \, ln \left(\frac{T}{T^\circ} \right) - \Delta a^4 \ . \tag{89}$$

Equation (87) motivates the study of three types of transformation: adiabatic, isothermal, and constant stress. During **adiabatic** transformation, $\dot{Q} = 0$, and (87) can be used to write the temperature rate as a function of the stress rate:

$$\dot{T} = -\left(a^3 - \mathcal{D}^2 \frac{\partial \Pi}{\partial T} \right)^{-1} \left(\frac{1}{\rho} a_{ij}^2 T - \mathcal{D}^2 \frac{\partial \Pi}{\partial \sigma_{ij}} \right) \dot{\sigma}_{ij} \ . \tag{90}$$

Equation (90) can now be substituted into (76) to eliminate $\dot{T}$ in the rate equation for $\dot{c}^M$:

$$\dot{c}^M = (\mathcal{D}^1)^{-1} \left[\frac{\partial \Pi}{\partial \sigma_{ij}} - \frac{\partial \Pi}{\partial T} \left(a^3 - \mathcal{D}^2 \frac{\partial \Pi}{\partial T} \right)^{-1} \left(\frac{1}{\rho} a_{ij}^2 T - \mathcal{D}^2 \frac{\partial \Pi}{\partial \sigma_{ij}} \right) \right] \dot{\sigma}_{ij} \ . \tag{91}$$

The **isothermal** transformation rate is obtained from (76) as

$$\dot{c}^M = \left(\mathcal{D}^1 \right)^{-1} \frac{\partial \Pi}{\partial \sigma_{ij}} \dot{\sigma}_{ij} \tag{92}$$

Neither the adiabatic nor the isothermal transformations can occur at constant stress.

The present model contains no rate dependence in the pointwise constitutive equations. Therefore, if the deformation rate of a test specimen is fast enough to be truely adiabatic, i.e. there is insufficient time for significant heat transfer from the specimen, then the present model will exhibit no apparent rate dependence. However, MCCORMICK et al [1993] have experimentally demonstrated that if the deformation of Nitinol is slow enough to allow for significant heat transfer from the specimen, then there is an apparent rate dependence in the behavior of the test specimen. This apparent rate dependence is not a material effect, but rather a structural phenomenon that arises from the solution of the heat conduction equation. This structural heat transfer may account for the reported (GRAESSER and COZZARELLI [1991]) rate dependence of Nitinol.

During **constant stress** transformation, the flow rule (76) gives

$$\dot{c}^M = \left(\mathcal{D}^1 \right)^{-1} \frac{\partial \Pi}{\partial T} \dot{T} \ . \tag{93}$$

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The heat rate can be introduced into (93) by setting $\dot{\sigma}_{ij} = 0$ in (87) to get

$$\dot{T} = \left(a^3 - \mathcal{D}^2 \frac{\partial \Pi}{\partial T}\right)^{-1} \dot{Q}, \tag{94}$$

and using this result in (93)

$$\dot{c}^M = \left[\mathcal{D}^1 \left(a^3 - \mathcal{D}^2 \frac{\partial \Pi}{\partial T}\right)\right]^{-1} \frac{\partial \Pi}{\partial T} \dot{Q} = \left[a^3 \mathcal{D}^1 - \left(\frac{1}{\rho}\Pi + T \mathcal{D}^3\right)\frac{\partial \Pi}{\partial T}\right]^{-1} \frac{\partial \Pi}{\partial T} \dot{Q}, \tag{95}$$

from which it may be seen that the constant stress transformation cannot occur adiabatically. Also, the constant stress transformation cannot occur isothermally (first order) because G^{mix} renders the transformation second order rather than first order. As the hardening term $\mathcal{D}^1 \to 0$, the transformation approaches isothermal, or first order conditions $\dot{T} \to 0$. Consider the response to constant stress and constant heat rate, $\dot{Q}$. For the case of a non-hardening transformation, the following limits are valid for finite $\frac{\partial \Lambda_{ij}}{\partial T}$ in $\frac{\partial \Pi}{\partial T}$:

$$\lim_{\mathcal{D}^1 \to 0} \dot{T} = \lim_{\mathcal{D}^1 \to 0} \left(a^3 - \mathcal{D}^2 \frac{\partial \Pi}{\partial T}\right)^{-1} \dot{Q} = 0, \tag{96}$$

and

$$\lim_{\mathcal{D}^1 \to 0} \dot{c}^M = -\left(\frac{1}{\rho}\Pi + T \mathcal{D}^3\right)^{-1} \dot{Q} = -\left[\pm\frac{1}{\rho}(2Y^t)^{\frac{1}{2}} + T \mathcal{D}^3\right]^{-1} \dot{Q}, \tag{97}$$

and the heat of the transformation, which is isothermal, consists of a dissipative part, $\pm\frac{1}{\rho}(2Y^t)^{\frac{1}{2}}$, and a reversible part $\mathcal{D}^3 T$. For the forward transformation,

$$Q^t = \int_0^1 \frac{1}{\rho}\left[(2Y^t)^{\frac{1}{2}} + \mathcal{D}^3 T\right] d\,c^M = \frac{1}{\rho}\left[(2Y^t)^{\frac{1}{2}} + \mathcal{D}^3 T\right]. \tag{98}$$

For **reversible** transformation, $Y^t = \Pi = 0$, and

$$\lim_{\Pi \to 0} \dot{c}^M = \left(a^3 \mathcal{D}^1 - \mathcal{D}^3 \frac{\partial \Pi}{\partial T} T\right)^{-1} \frac{\partial \Pi}{\partial T} \dot{Q}. \tag{99}$$

For reversible transformation with no hardening:

$$\lim_{\Pi \to 0,\,\mathcal{D}^1 \to 0} \dot{c}^M = -\left(\mathcal{D}^3 T\right)^{-1} \dot{Q}, \tag{100}$$

from which the reversible latent heat of transformation can be calculated, noting that the non-hardening transformation must be isothermal, as

$$Q^t = -\int_0^1 \left(\mathcal{D}^3 T\right) d\,c^M = -\mathcal{D}^3 T = \left[\frac{1}{\rho}\Delta a_{ij}^2 \sigma_{ij} + \Delta a^3 \, ln\left(\frac{T}{T^\circ}\right) + \Delta a^4\right] T. \tag{101}$$

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In this special case of reversible non-hardening transformation, $\mathcal{D}^3$ is the entropy of transformation. Another form of the heat of transformation for a reversible non-hardening transformation can be obtained by noting that the transformation corresponds, with $0 = b^1 = b^2_{ijkl} = b^3_{ij}$, to

$$0 = \Pi = \sigma_{ij}\Lambda_{ij} + \frac{1}{2}\Delta a^1_{ijkl}\sigma_{ij}\sigma_{kl} + \Delta a^2_{ij}\sigma_{ij}\Delta T - \rho\left\{\Delta a^3\left[\Delta T - T\,ln\left(\frac{T}{T^\circ}\right)\right] - \Delta a^4 T + \Delta a^5\right\}. \quad (102)$$

Now define the energy of transformation, $\mathcal{E}^t$, the entropy of transformation, $\mathcal{S}^t$, the work of transformation, $\mathcal{W}^t$, and the partial heat of transformation, $\mathcal{H}^t$, as

$$\mathcal{E}^t = Q^t = \mathcal{S}^t T = \mathcal{W}^t + \mathcal{H}^t. \quad (103)$$

For the case of reversible non-hardening transformation, comparison of (101),(102) and (103) yields

$$\mathcal{W}^t = -\frac{1}{\rho}\sigma_{ij}\Lambda_{ij}, \qquad \mathcal{S}^t = \frac{1}{\rho}\Delta a^2_{ij}\sigma_{ij} + \Delta a^3\,ln\left(\frac{T}{T^\circ}\right) + \Delta a^4,$$

$$\mathcal{H}^t = \frac{1}{\rho}\left[-\frac{1}{2}\Delta a^1_{ijkl}\sigma_{ij}\sigma_{kl} + \Delta a^2_{ij}\sigma_{ij}T^\circ + \rho\left(\Delta a^3\Delta T + \Delta a^5\right)\right]. \quad (104a-c)$$

IV.4. Damping Capacity and Engine (Actuator) Efficiency of SMA

The energy dissipation due to transformation and reorientation can be used to control structural damping. Also, a SMA material can be used as an engine that converts heat into work, thereby allowing for the thermally controlled actuation of structures. For these applications, material performance measures are needed for the dissipation-to-heat-rate ratio, $\frac{T\dot{\eta}}{\rho Q}$, the dissipation-to-work-rate ratio, $\frac{T\dot{\eta}}{W}$, and the actuation efficiency ratio, $\frac{\dot{W}}{\rho Q}$. Throughout section IV.4., it is assumed that there is no reorientation, i.e., $\dot{\epsilon}^r_{ij} = 0$. The dissipation-to-mixing power ratio, $\frac{T\dot{\eta}}{\rho\dot{G}^{mix}}$, can be obtained from (65) and (54):

$$\frac{T\dot{\eta}}{\rho\dot{G}^{mix}} = \pm(2Y^t)^{\frac{1}{2}}\left[\rho\left(\frac{\partial G^{mix}}{\partial c^M} + \frac{\partial G^{mix}}{\partial \epsilon^{irr}_{ij}}\Lambda_{ij}\right)\right]^{-1}. \quad (1025$$

The work rate is

$$\dot{W} = \sigma_{ij}\dot{\epsilon}_{ij}. \quad (106)$$

The total strain rate $\dot{\epsilon}_{ij}$ is obtained by taking the time derivative of Hooke's Law,

$$\epsilon_{ij} = \epsilon^{te}_{ij} + \epsilon^{irr}_{ij} = \epsilon_{ij} = a^1_{ijkl}\sigma_{kl} + a^2_{ij}\Delta T + \epsilon^{irr}_{ij} \quad (107)$$

and then solving for $\dot{\epsilon}_{ij}$, with $\dot{\epsilon}^r_{ij} = 0$:

$$\dot{\epsilon}_{ij} = a^1_{ijkl}\dot{\sigma}_{kl} + \dot{a}^1_{ijkl}\sigma_{kl} + a^2_{ij}\dot{T} + \dot{a}^2_{ij}\Delta T + \Lambda_{ij}\dot{c}^M = a^1_{ijkl}\dot{\sigma}_{kl} + a^2_{ij}\dot{T} + \mathcal{M}^1_{ij}\dot{c}^M, \quad (108)$$

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where

$$\mathcal{M}^1_{ij} = \Lambda_{ij} + \Delta a^1_{ijkl}\sigma_{kl} + \Delta a^2_{ij}\Delta T \, . \tag{109}$$

Now use the flow rule (76) in (108) to get

$$\dot{\epsilon}_{ij} = \mathcal{M}^2_{ijkl}\dot{\sigma}_{kl} + \mathcal{M}^3_{ij}\dot{T} \, , \tag{110}$$

where the tangent compliance tensor $\mathcal{M}^2_{ijkl}$ and the tangent thermal expansion vector $\mathcal{M}^3_{ij}$ are

$$\mathcal{M}^2_{ijkl} = a^1_{ijkl} + (\mathcal{D}^1)^{-1}\mathcal{M}^1_{ij}\frac{\partial \Pi}{\partial \sigma_{kl}} \, , \qquad \mathcal{M}^3_{ij} = a^2_{ij} + (\mathcal{D}^1)^{-1}\mathcal{M}^1_{ij}\frac{\partial \Pi}{\partial T} \, . \tag{111a-b}$$

Note that the tangent compliance tensor is not, in general, symmetric. Finally, the strain rate in (106) can be eliminated using (110), resulting in

$$\dot{W} = \sigma_{ij}(\mathcal{M}^2_{ijkl}\dot{\sigma}_{kl} + \mathcal{M}^3_{ij}\dot{T}) \, . \tag{112}$$

During **constant stress** transformation, the instantaneous motor or actuator efficiency of converting heat into work is obtained by using (112) and (94) with $\dot{\sigma}_{ij} = 0$ to get

$$\frac{\dot{W}}{\rho\dot{Q}} = \sigma_{ij}\mathcal{M}^3_{ij}\left[\rho\left(a^3 - \mathcal{D}^2\frac{\partial \Pi}{\partial T}\right)\right]^{-1} \, . \tag{113}$$

The instantaneous dissipation-to-heat-rate-ratio can be derived using (65a) and (95):

$$\frac{T\dot{\eta}}{\rho\dot{Q}} = \pm(2Y^t)^{\frac{1}{2}}\frac{\partial \Pi}{\partial T}\left[\rho\mathcal{D}^1\left(a^3 - \mathcal{D}^2\frac{\partial \Pi}{\partial T}\right)\right]^{-1} \, . \tag{114}$$

The instantaneous dissipation-to-work-rate-ratio, which is the mechanical damping rate, can be derived using (65a), (93) and (111), with $\dot{\sigma}_{ij} = 0$:

$$\frac{T\dot{\eta}}{\dot{W}} = \pm(2Y^t)^{\frac{1}{2}}\left(\mathcal{D}^1\right)^{-1}\frac{\partial \Pi}{\partial T}(\sigma_{ij}\mathcal{M}^3_{ij})^{-1} \, . \tag{115}$$

For **isothermal** proportional loading, such that $\dot{\sigma}_{ij} = K_{ij}\dot{\bar{\sigma}}$, the three performance measures can be derived as

$$\frac{\dot{W}}{\rho\dot{Q}} = \bar{\sigma}K_{ij}\mathcal{M}^2_{ijkl}K_{kl}\left[\rho\left(\frac{1}{\rho}a^2_{mn}T - \mathcal{D}^2\frac{\partial \Pi}{\partial \sigma_{mn}}\right)K_{mn}\right]^{-1} \, , \tag{116}$$

$$\frac{T\dot{\eta}}{\rho\dot{Q}} = \pm(2Y^t)^{\frac{1}{2}}(\mathcal{D}^1)^{-1}\frac{\partial \Pi}{\partial \sigma_{ij}}K_{ij}\left[\rho\left(\frac{1}{\rho}a^2_{mn}T - \mathcal{D}^2\frac{\partial \Pi}{\partial \sigma_{mn}}\right)K_{mn}\right]^{-1} \, , \tag{117}$$

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and

$$\frac{T\dot{\eta}}{\dot{W}} = \pm(2Y^t)^{\frac{1}{2}}\mathcal{D}^1\frac{\partial\Pi}{\partial\sigma_{ij}}K_{ij}\left(\bar{\sigma}K_{mn}\mathcal{M}^2_{mnop}K_{op}\right)^{-1}. \tag{118}$$

Similar results can be derived for hydrostatic loading, $\dot{\sigma}_{ij} = \dot{\sigma}_{mm}\delta_{ij}$.

For **adiabatic** transformation under proportional or hydrostatic loading, it is possible to derive a closed form (but long) equation for $\frac{T\dot{\eta}}{\dot{W}}$.

V. RESULTS AND DISCUSSION

In order to use the two component model of section IV, it is necessary to specify the transformation tensor, $\Lambda_{ij}\{\sigma_{ij}, T, c^M, \epsilon^{irr}\}$, and the constants

$$a^{\alpha 1}_{ijkl}, \ a^{\alpha 2}_{ij}, \ a^{\alpha 3}, \ \Delta a^4, \ \Delta a^5, \ \rho, \ T^\circ, \ b^1, \ b^2_{ijkl}, \ b^3_{ij}, \ Y^t, \ Y^r. \tag{119}$$

The SMA is assumed to be isotropic. In choosing a function for Λ_{ij}, it is assumed that the symmetry changes incurred during the transformation and reorientation can be expressed as a function of the deviatoric irreversible strain. Specifically, and consistent with the discussion preceeding (48),

$$\Lambda_{ij} = \Lambda'_{ij} + \frac{1}{3}\Lambda_{kk}\delta_{ij}, \tag{120}$$

where

$$\Lambda_{ij} = \begin{cases} \frac{3}{2}H\left(\bar{\sigma}^{eff}\right)^{-1}\sigma'^{eff}_{ij} + \frac{1}{3}I\delta_{ij}, & \dot{c}^M > 0 \\ H\left(\bar{\epsilon}^{irr}\right)^{-1}\epsilon'^{irr}_{ij} + \frac{1}{3}I\delta_{ij}, & \dot{c}^M < 0 \end{cases} \tag{121}$$

and

$$\sigma'^{eff}_{ij} = \sigma'_{ij} - \rho\mu'^{irr}_{ij}, \tag{122}$$

$$\bar{\sigma}^{eff} = \left(\frac{3}{2}\sigma'^{eff}_{ij}\sigma'^{eff}_{ij}\right)^{\frac{1}{2}} = \left[\frac{3}{2}(\sigma'_{ij} - \rho\mu'^{irr}_{ij})(\sigma'_{ij} - \rho\mu'^{irr}_{ij})\right]^{\frac{1}{2}}, \tag{123}$$

and $\bar{\epsilon}^{irr} = \left(\frac{2}{3}\epsilon'^{irr}_{ij}\epsilon'^{irr}_{ij}\right)^{\frac{1}{2}}$ and H and I are constants. With respect to (68), it is assumed that the the effective irreversible strain is limited to the amount accumulated during uniaxial proportional loading:

$$\bar{\epsilon}^{irr} \leq c^M H, \qquad\qquad \epsilon^{irr}_{mm} \leq c^M I. \tag{124}$$

The isotropic form of G^{mix}, equation (54), with (120), (121) and (62) simplifies to

$$G^{mix} = \frac{1}{2}b^1(c^M)^2 + \frac{1}{2}b^4\epsilon'^{irr}_{ij}\epsilon'^{irr}_{ij} + \frac{1}{2}b^5(Ic^M + \epsilon^r_{mm})^2 + b^6(Ic^M + \epsilon^r_{mm})c^M. \tag{125}$$

It is assumed that each variant has the same dilatational strains $\mathcal{E}^\alpha_{mm}$ and $\mathcal{E}^{*\alpha}_{mm}$ given by (5) and (22), respectively. Under these conditions, the dilatational reorientation strain vanishes, i.e. $\epsilon^r_{mm} = 0$, and (125) simplifies to

$$G^{mix} = \left[\frac{1}{2}b^1 + \frac{1}{2}b^5(I)^2 + b^6I\right](c^M)^2 + \frac{1}{2}b^4\epsilon'^{irr}_{ij}\epsilon'^{irr}_{ij} = \frac{1}{2}b^7(c^M)^2 + \frac{1}{2}b^4\epsilon'^{irr}_{ij}\epsilon'^{irr}_{ij}. \tag{126}$$

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The thermodynamic force Π is given by

$$\Pi = \sigma_{ij}^{\prime eff} \Lambda_{ij}' + \frac{1}{3}\sigma_{mm}I + \frac{1}{2}\Delta a_{ijkl}^1 \sigma_{ij}\sigma_{kl} + \Delta a_{ij}^2 \sigma_{ij}\Delta T - \rho\Delta a^3 \left[\Delta T - T\ln\left(\frac{T}{T^\circ}\right)\right] + \rho\Delta a^4 T$$
$$- \rho\Delta a^5 - \rho b^7 c^M \ .$$

(127)

For the case in which $\dot{\epsilon}_{ij}^r = 0$ and $\dot{c}^M \neq 0$, the terms in the flow rule (76) can be explicitly written using (64) and (120)-(123):

$$\mathcal{D}^1 = \rho\left[b^7 + \frac{3}{2}(H)^2 b^4\right] , \qquad \frac{\partial\Pi}{\partial T} = \Delta a_{ij}^2 \sigma_{ij} + \rho\left[\Delta a^3 \ln\left(\frac{T}{T^\circ}\right) + \Delta a^4\right] ,$$

$$\frac{\partial\Pi}{\partial\sigma_{ij}} = \Lambda_{ij} + \mathcal{D}_{ij}^4 , \qquad \mathcal{D}_{ij}^4 = -\rho\frac{\partial\mu^M}{\partial\sigma_{ij}} = \Delta a_{ijkl}^1 \sigma_{kl} + \Delta a_{ij}^2 \Delta T .$$

(128a − d)

When (76) is used, $b^4 = 0$, if $\dot{\epsilon}_{ij}^{\prime t} = 0$, i.e if $\Lambda_{ij}' = 0$. For the choice (121) for Λ_{ij}, the tangent compliance tensor, equation (111a), is symmetric because

$$\mathcal{M}_{ij}^1 = \frac{\partial\Pi}{\partial\sigma_{ij}} \ .$$

(129)

The equality (129) follows from the fact that

$$\sigma_{kl}^{\prime eff} \frac{\partial\Lambda_{kl}}{\partial\sigma_{ij}} = 0$$

(130)

for both the forward and the reverse transformations.

A Clausius-Clapeyron type equation can be derived for the case of proportional loading, $\dot{\sigma}_{ij} = K_{ij}\dot{\sigma}$, by setting $\dot{c}^M = 0$ in the flow rule, (76):

$$\frac{\dot{\sigma}}{\dot{T}} = -\left\{\Delta a_{ij}^2 \sigma_{ij} + \rho\left[\Delta a^3 \ln\left(\frac{T}{T^\circ}\right) + \Delta a^4\right]\right\}\left[(\Lambda_{ij} + \Delta a_{ijkl}^1 \sigma_{kl} + \Delta a_{ij}^2 \Delta T)K_{ij}\right]^{-1} .$$

(131)

The isotropic form of ϕ^r is

$$\phi^r = \frac{1}{2}\sigma_{ij}^{\prime eff}\sigma_{ij}^{\prime eff} \ .$$

(132)

For the isotropic case, the following 18 constants must be determined:

$$E^\alpha , \ v^\alpha , \ \alpha^\alpha , \ a^{\alpha 3} , \ \Delta a^4 , \ \Delta a^5 , \ \rho , \ T^\circ , \ b^4 , \ b^7 , \ Y^t , \ Y^r , \ H , \ I , \qquad \alpha = A, M$$

(133)

where E^α, v^α and α^α are the phase elastic moduli, elastic Poisson ratios, and thermal expansion coefficients, respectively. In discussing the operations necessary to determine the material constants, it is assumed that σ_{ij}, ϵ_{ij} and T can be measured using a load cell, extensometer and

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thermocouple, and that c^M can be correlated with resistivity measurements. It is not necessary to measure the heat rate, $\dot{Q}$ to get the constants. If the difference in specific heats, Δa^3, is assumed to be negligible, as in Table 1, then all of the constants in the present model can be obtained from three phase transformation tests and one reorientation test. The thermoelastic constants E^α, v^α, α^α and $a^{\alpha 3}$ were chosen from the data reported by JACKSON et al [1972]. However, small differences in heat treatment and alloying can significantly alter the thermomechanical repsonse of Nitinol.

V.1. Transformation

A cycle of stress-free thermal loading can be used to determine the thermoelastic expansion coefficients α^α, the specific heats $a^{\alpha 3}$, the transformation dilatation factor I, and the stress-free austenite and martensite start and finish temperatures, A^s, A^f, M^s and M^f. An isothermal stress-strain plot can be used to determine the elastic moduli E^α and the Poisson ratios v^α. The maximum transformation strain under uniaxial stress is $H + \frac{1}{3}I$, which can be used to determine H. When another isothermal stress-strain plot is obtained for a different temperature, the Clausius-Clapeyron equation (130) can be used to determine Δa^4 by measuring the ratio $\frac{d\sigma^{yield}}{dT}$. The term $\Delta a_{ij}^2 \sigma_{ij}(T - T^\circ)$ is small. Therefore, for this case in which the difference in specific heats, Δa^3, is negligible, the choice of T° is relatively unimportant. The isotropic hardening modulus, b^7, can then be calculated by integrating (76) using the results from the stress-free thermal loading test:

$$b^7 = \left(M^s - M^f\right)\Delta a^4 \,. \tag{134}$$

The kinematic hardening modulus, b^4, can then be calculated by integrating the isothermal form of (76). It is now necessary to determine the latent heat of transformation, which includes the reversible part Δa^5 and the irreversible part due to entropy production, which is determined by Y^t. The energy within the stress-strain hysteresis loop of a complete, isothermal thermodynamic cycle is given by (72) as $2(2Y^t)^{\frac{1}{2}}$. The remaining constant, Δa^5, can be determined from the condition that, during transformation, $\Pi = (2Y^t)^{\frac{1}{2}}$, where Δa^5 is the only remaining unknown quantity in Π.

For cases in which Δa^3 is not negligible, T° may play a significant part in the transformation. In the Clausius-Clapeyron equation, the term $\rho \Delta a^3 \, ln\left(\frac{T}{T^\circ}\right)$ counteracts the term $\Delta a_{ijkl}^1 \sigma_{ij}\sigma_{kl}$, making the ratio $\frac{d\sigma^{yield}}{dT}$ more linear.

The pseudoelastic response, Figure 2, occurs when the chemical force for transformation is large (negative) relative to the (positive) mechanical force.

The adiabatic and isothermal transformations are compared in Figure 3. Both cases begin at the same initial temperature, $293^\circ K$. The reversible latent heat hinders the forward transformation (exothermic) and assists the reverse transformation (endothermic). The dissipated energy inhibits both the forward and the reverse transformations. The adiabatic stress-strain response exhibits greater hardening than the isothermal response. This "thermal hardening" that occurs during adiabatic transformation of SMA materials is in contrast to the thermal softening associated with plasticity due to dislocation glide and diffusion. The thermal hardening of SMA materials is due

to the temperature dependence of the chemical potential, μ^M; increasing the temperature lowers the thermodynamic force, Π, at constant stress. These adiabatic and isothermal results agree qualitatively with the partial transformation curves of MCCORMICK et al [1993]. The high stresses required to complete the adiabatic transformation, especially under cyclic conditions, may lead to dislocation slip that results in a premature loss of memory relative to isothermal loading.

The energetics of isothermal (T=323° K) pseudoelasticity is depicted in Figure 4. The work expended in a complete thermodynamic cycle is equal to the dissipation, $2(2Y^t)^{\frac{1}{2}}$. The units of time are arbitrary because the deformation is rate independent.

Figures 5a, 5b and 6 demonstrate the ability of SMA materials to convert heat into work using the shape memory effect (SME) by transformation. The first step of the SME, Figure 5a, consists of an isothermal transformation at a temperature that is low enough to prevent pseudoelastic recovery of the transformation strain. The second step of the SME, Figure 5b, consists of a constant stress heating that results in the recovery of the transformation strain, thereby converting heat into work. From Figure 6, it can be seen that the net work of the SME does not equal the dissipation, as it did for the pseudoelasticity of Figure 4.

Because the martensite is fully oriented in the test cases of Figures 2 thru 6, the equalities (68) and (124) are active, i.e. $\bar{\epsilon}^{irr} = c^M \left(\bar{\epsilon}^{irr}\right)^{max} = c^M H$. Thus, although the coupled equations (75) indicate that $\lambda^r > 0$, and ϕ^r may be greater than Y^r, the kinematic constraints (68) and (124) require that $\dot{\epsilon}^r_{ij} = 0$. The uncoupled form of (75) is therefore used to determine λ^t.

V.2. Reorientation

Finally, the reorientation yield parameter, Y^r, can be correlated with the yield stress of 100% self accommodating martensite ($c^M = 1$, $\bar{\epsilon}^{irr} = 0$) by performing a stress-strain test at a temperature, below M^f, that was reached by stress-free thermal loading. Figures 7a and 7b, analogous to Figures 5a and 5b, demonstrate the ability of SMA materials to convert heat into work using the shape memory effect (SME) by reorientation. The first step of the SME, Figure 7a, consists of an isothermal reorientation followed by a partial unloading. The reorientation is stopped when the limit $\bar{\epsilon}^{irr} = c^M H = 0.05$ is reached, after which time the martensite deforms elastically. The second step of the SME, Figure 7b, consists of a constant stress heating that results in the recovery of the irreversible strain, thereby converting heat into work.

A reorientation test could also be used to determine the kinematic hardening modulus, b^4.

V.3. Simultaneous Transformation and Reorientation

As illustrated in Figures 8a and 8b, non-proportional loading paths can lead to simultaneous transformation and reorientation. The isothermal loading input is indicated in Figure 8a. The initial loading, $\dot{\sigma}_{33} > 0$, results in fully oriented martensite with $c^M = 0.5$. Subsequent loading by $\dot{\sigma}_{22} > 0$ initiates the transformation of the remaining austenite at approximately 400 time steps. Reorientation of the martensite formed during the initial loading, $\dot{\sigma}_{33} > 0$, begins when

the reorientation threshold, $\phi^r > Y^r$ is satisfied at approximately 420 time steps. At this point, the coupled equations (74) must be used for λ^t and λ^r.

VI. SUMMARY

The analyses of PATOOR et al [1993], RANIECKI and LEXCELLENT [1994], and SUN and HWANG [1993] were combined and extended to account for pseudoelasticity and the shape memory effect (SME) due to martensitic transformation and reorientation of polycrystalline shape memory alloy (SMA) materials. The constants and variables in the model can be experimentally obtained from macroscopic measurments of stress, strain, temperature and resistivity. Simultaneous transformation and reorientation were modelled by treating $\dot{\epsilon}^t_{ij}$ and $\dot{\epsilon}^r_{ij}$ as separate fluxes in the dissipation inequality, although the internal state variable for kinematic hardening was assumed to be the total irreversible strain, ϵ^{irr}_{ij}. Closed form equations were derived for the damping capacity and the actuator efficiency of converting heat into work. The first law of thermodynamics was used to demonstrate that significantly more work is required to complete the adiabatic transformation than the isothermal transformation. As the "hardening" due to the austenite/martensite misfit stresses approaches zero, the transformation approaches the isothermal, infinite specific heat conditions of a first order transformation. In a second paper, the phenomenological equations derived in sections IV and V of this first paper are used in a mesomechanical derivation of the thermomchanical constitutive equations of an active composite wiht a SMA phase.

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Table 1. SMA fiber and elastomer matrix properties

NiTi material properties

$$D^A = 30.0 \times 10^3 \; MPa$$
$$D^M = 13.0 \times 10^3 \; MPa$$
$$\nu = 0.33$$
$$\alpha^A = 11.0 \times 10^{-6}/^\circ C$$
$$\alpha^M = 6.6 \times 10^{-6}/^\circ C$$
$$M^s = 23^\circ C$$
$$M^f = 5^\circ C$$
$$A^s = 29^\circ C$$
$$A^f = 51^\circ C$$
$$C^M = 11.3 \; MPa/^\circ C$$
$$C^A = 4.5 \; MPa/^\circ C$$
$$\Omega = -0.91 \times 10^3 \; MPa$$

Polymer material properties

$$D = 2.0 \times 10^3 \; MPa$$
$$\nu = 0.45$$
$$\alpha = 75 \times 10^{-6}/^\circ C$$

Material	$(\frac{3}{2} B_{ij33}'^{fea} B_{ij33}'^{fea})^{\frac{1}{2}}$	$(\frac{3}{2} B_{ij33}'^{fem} B_{ij33}'^{fem})^{\frac{1}{2}}$	$(\frac{3}{2} b_{ij}'^{fea} b_{ij}'^{fea})^{\frac{1}{2}}$	$(\frac{3}{2} b_{ij}'^{fem} b_{ij}'^{fem})^{\frac{1}{2}}$
elastomer	3.950	3.101	0.390	0.320
aluminum	0.455	0.208	0.187	0.077
tool steel	0.178	0.079	0.000	0.010
isotropic graphite	0.039	0.015	0.018	0.001

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Table 1. NiTi Material properties

$$E^A = 30.0 \times 10^3 \ MPa$$

$$E^M = 13.0 \times 10^3 \ MPa$$

$$v^A = v^M = 0.33$$

$$\alpha^A = 11.0 \times 10^{-6}/°C$$

$$\alpha^M = 6.6 \times 10^{-6}/°C$$

$$a^{A3} = a^{M3} = 4.000 \times 10^{-4} \ MJ/(kg \, °K)$$

$$b^4 = 324.7 \times 10^{-4} \ MJ/kg$$

$$b^7 = 7.519 \times 10^{-4} \ MJ/kg$$

$$\Delta a^4 = -57.84 \times 10^{-6} \ MJ/(kg \, °K)$$

$$\Delta a^5 = -17.00 \times 10^{-3} \ MJ/kg$$

$$H = 0.050$$

$$I = 0.000$$

$$Y^t = 30.00 \ (MPa)^2$$

$$Y^r = 7500 \ (MPa)^2$$

$$As = 301°K$$

$$Af = 316°K$$

$$Ms = 273°K$$

$$Mf = 260°K$$

Table 1. NiTi Material properties

$$E^A = 30.0 \times 10^3 \ MPa$$
$$E^M = 13.0 \times 10^3 \ MPa$$
$$v^A = v^M = 0.33$$
$$\alpha^A = 11.0 \times 10^{-6}/^\circ C$$
$$\alpha^M = 6.6 \times 10^{-6}/^\circ C$$
$$a^{A3} = a^{M3} = 4.000 \times 10^{-4} \ MJ/(kg\,^\circ K)$$
$$b^2 = 324.7 \times 10^{-4} \ MJ/kg$$
$$b^1 = 7.519 \times 10^{-4} \ MJ/kg$$
$$\Delta a^4 = -57.84 \times 10^{-6} \ MJ/(kg\,^\circ K)$$
$$\Delta a^5 = -17.00 \times 10^{-3} \ MJ/kg$$
$$H = 0.050$$
$$I = 0.000$$
$$Y^t = 30.00 \ (MPa)^2$$