Alternative smart materials

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1 PRESENTLY AVAILABLE MATERIALS

Presently, there are three types of smart materials available, ferroelectric-magnetic and -elastic materials[1]. Prototypes of the three are PZT ceramics, Terfenol-D and Nitinol. Their advantages and disadvantages are well known: Ferroelectric materials are characterized by a large elastic constant and moderate actuation strain, and their dynamical response is excellent. Some antiferroelectrics feature a larger actuation strain. Terfenol-D displays similar mechanical characteristics but its dynamical response is limited by eddy currents. This limitation can be overcome in composites. Nitinol and similar shape memory alloys feature a large elastic constant and actuation strain but suffer from inferior dynamical response which can be overcome in small sections. The ideal actuation material would display a large actuation energy and superior dynamical response. Shape memory type materials display the largest actuation strains known. It is thus natural to inquire into the possibility actuating these alloys with a magnetic field to improve their dynamical performance.

2 ALTERNATIVE CONCEPTS: FERROMAGNETIC SHAPE MEMORY MATERIALS

The concept that we wish to explore combines the desirable aspects of shape memory and magnetostrictive materials. The large strain available in shape memory materials arises from the presence of a first order martensitic transformation. However, the class of giant magnetostrictive materials all have second order transformations at the Curie temperature. The difference is illustrated in Figure 2.1, where we have schematically drawn the graph of the Helmholtz free energy function of materials that undergo first order vs. second order transformations. The magnetostrictive materials have a free energy $\varphi(\varepsilon,\ m,\ \theta)$, where ε is the strain, m is the magnetization and θ is the temperature, whereas in shape memory materials the free energy does not depend on the magnetization. For both first and second order transformations, the free energy has energy wells and there is a tendency, based on thermodynamics, for the state of the material to reside in the energy wells in the absence of applied field and stress. As described below in Section 3, the material can be made to shift between the energy wells by applying suitable combinations of stress and field.

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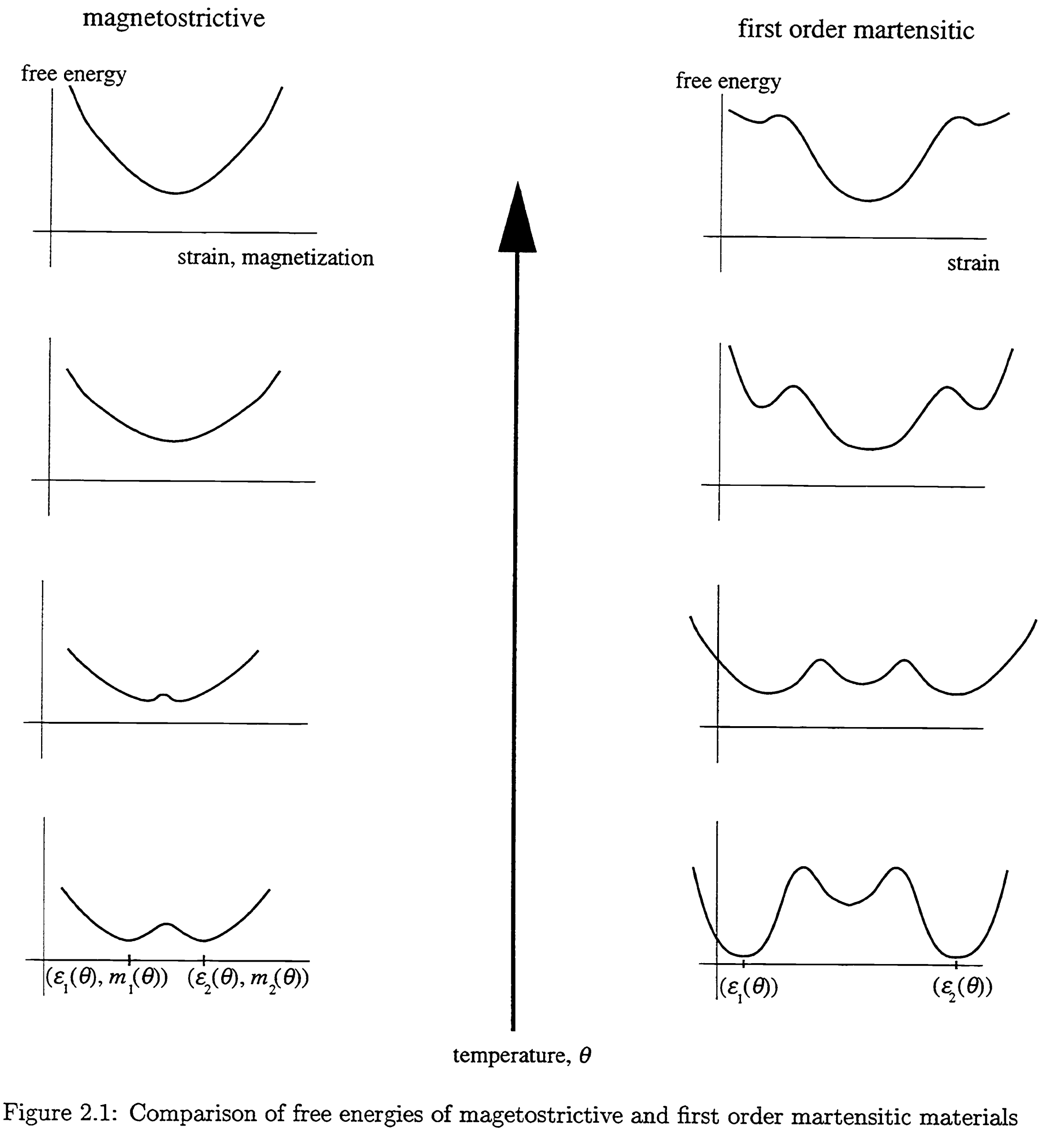

Figure 2.1: Comparison of free energies of magetostrictive and first order martensitic materials

In a second order transformation the energy wells never get very far from $\varepsilon = 0$, as the transformation strains $\varepsilon_i(\theta),\ i = 1, \dots, n$, that define the bottoms of the wells are continuous in θ and vanish at the Curie temperature. Here, n refers to the number of variants of the distorted phase. It is interesting to note the the particular crystallography given by a cubic-to-trigonal distortion in which $n = 4$, as in $\mathrm{TbDyFe_2}$, has an unusually large thermal coefficient of distortion $d\varepsilon_i/d\theta$, a feature shared by the cubic-to-trigonal R- phase transition in NiTi and NiTiCu alloys. This is evidently a particular atomic feature of the cubic-to-trigonal distortion. The relatively large magnetostriction of $\mathrm{TbDyFe_2}$ arises in this way.

In contrast, a first order martensitic transformation may have the property that the transformation strains $\varepsilon_i(\theta)$ are very different from zero at the transformation temperature, as illustrated in Figure 2.1. It is not uncommon in shape memory materials to have $|\varepsilon_i(\theta_c)|$ of the order 0.1. Typically, in shape memory materials $|\varepsilon_i(\theta) - \varepsilon_i(\theta_c)| \ll \varepsilon_i(\theta_c)$ for temperatures $\theta \leq \theta_c$. Despite the fact that the transformation strains are large in materials that undergo first order martensitic transformations, they can have mobile interfaces.

Now consider the following possibility. Suppose a material has a free energy that depends on both the strain and magnetization, as in the left of Figure 2.1, but it undergoes a first order transformation, as pictured on the right. Such a material would tend to have domains on which the strain and magnetization lie on the various energy wells, and so the domain structure could be altered by applying a field that favors one of the domains or another. In order to avoid cyclically changing the direction of the field, one would typically arrange to apply both fields and stresses, with large field favoring one domain structure and large stress favoring another. Then, by cyclically changing the magnitude of the field and loading by a constant stress, one could pass back and forth rapidly between the two domain structures. This kind of situation would be appropriate to an actuator with a compliant loading device (constant applied stress). It would be of course necessary to think carefully about crystallography, texture and suitable directions of application of load and field to maximize the work done by such an actuator, and the theory presented in Section 3 is formulated to approach such questions.

The one dimensional picture shown in Figure 2.1 is too simple to illustrate the crystallography of transformation or even the order of the transitions themselves. It can be seen easily from a study of Landau expansions of a free energy of the form $\varphi(\varepsilon,\ m,\ \theta)$ that the ferromagnetic transition and the first order martensitic transformations are unlikely to occur at precisely the same temperature, as this would require an additional identity between coefficients in the expansion that does not follow from symmetry. Let us examine this more closely. Let θ_c and θ_m be the transition/transformation temperatures, respectively, and let us assume that the parent phase is cubic. With $\theta_c < \theta_m$ we expect to see a large distortion upon cooling below θ_m. It is desirable that the martensitic phase be of low symmetry, so that there are many variants (i.e. n equals the ratio of the orders of the Laue groups of the parent and product phases[2]). Upon further cooling through $\theta = \theta_c$ we expect that the ferromagnetic transition will be second order, and the resulting state will be uniaxial, since the martensitic phase is of low symmetry. Since the free energy function is invariant under $m \to -m$, we expect to see 180° domains grow up within each each individual martensitic variant. This leads to microstructures as shown at the bottom of Figure 2.2, and the possibilities for rearranging these microstructures by applying competing fields and loads are evident. If $\theta_m < \theta_c$ we expect to see (schematically) the kinds of structures shown on the left of Figure 2.2. Upon cooling through θ_m it is expected that the easy axes will be convected by the deformation, resulting in a uniaxial state (Of course, we expect that the saturation magnetization will change discontinuously at θ_m in this case). There is an interesting third possibility. It could happen that the martensitic phase is ferromagnetic, but that its Curie temperature occurs at a higher temperature than θ_m; in other words, *if* the martensite were to remain stable above θ_m then its saturation magnetization would tend to zero at some higher temperature θ_c. In this case, the first order martensitic and the ferromagnetic transition would appear to coincide, and the ferromagnetic transition would appear first order. This situation could be confirmed by magnetomechanical experiments: one could stabilize the martensite at $\theta > \theta_m$ by applying stress, then look for the vanishing of $m_s(\theta)$.

Note that by applying all three - heat, magnetic field and stress - one can arrange to have some unusual modes of energy conversion.

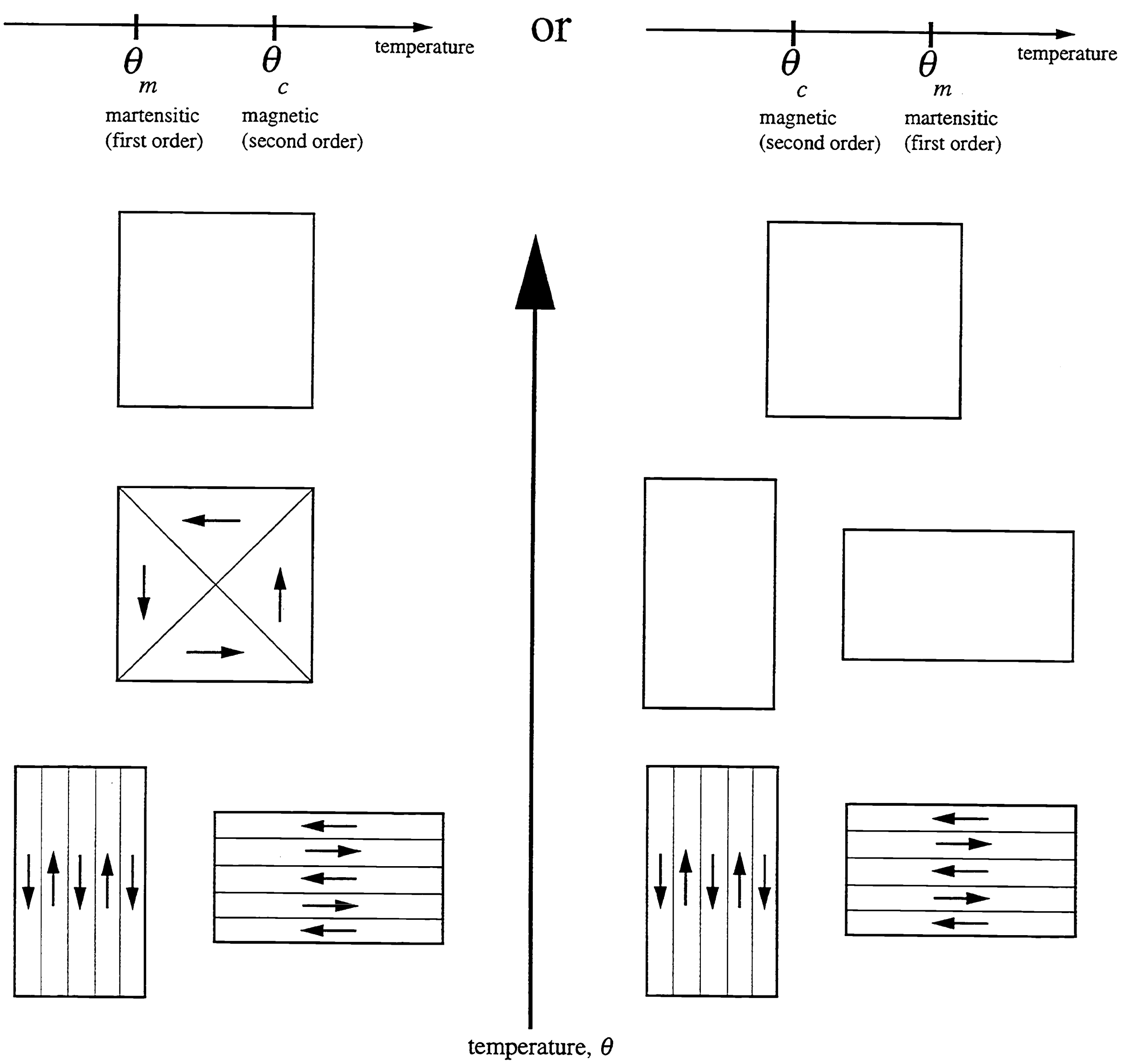

Figure 2.2: Schematic picture of domain structures for a ferromagnetic shape memory material with different ordering of transition temperatures.

3 THERMODYNAMICS OF ENERGY CONVERSION

In this section we consider in more detail the energetics of passing from one domain structure to another. A more complete elaboration of these ideas can be found in forthcoming paper[3]. There are situations that occur in shape memory materials in which geometrically nonlinear effects become important[4,2], but for simplicity we shall do our analysis using a geometrically linear model of deformations. Let us consider a material that undergoes a sequence of transformations $\theta_c \to \theta_m$ or $\theta_m \to \theta_c$ and consider a fixed temperature θ below the lowest transition. Then, the ("chemical") free energy density $\varphi(\varepsilon,\ \boldsymbol{m},\ \theta)$ has energy wells defined by certain preferred pairs $(\varepsilon_1,\ \pm\boldsymbol{m}_1)$, $(\varepsilon_2,\ \pm\boldsymbol{m}_2), \ldots, (\varepsilon_n,\ \pm\boldsymbol{m}_n)$. For example, if the material undergoes a cubic-to-tetragonal transition and the ferromagnetic state at θ is uniaxial with easy axis (100), then the expected preferred pairs are,

$$\begin{aligned}
\varepsilon_1 &= \begin{pmatrix} \varepsilon_1 & & \\ & \varepsilon_2 & \\ & & \varepsilon_2 \end{pmatrix}, \ \boldsymbol{m}_1 = m_s(100), \\
\varepsilon_2 &= \begin{pmatrix} \varepsilon_2 & & \\ & \varepsilon_1 & \\ & & \varepsilon_2 \end{pmatrix}, \ \boldsymbol{m}_2 = m_s(010), \\
\varepsilon_3 &= \begin{pmatrix} \varepsilon_2 & & \\ & \varepsilon_2 & \\ & & \varepsilon_1 \end{pmatrix}, \ \boldsymbol{m}_3 = m_s(001).
\end{aligned} \tag{3.1}$$

The assumption is that $\varphi(\varepsilon_1,\ \pm\boldsymbol{m}_1,\ \theta) = \varphi(\varepsilon_2,\ \pm\boldsymbol{m}_2,\ \theta) = \varphi(\varepsilon_3,\ \pm\boldsymbol{m}_3,\ \theta) < \varphi(\varepsilon,\ \boldsymbol{m},\ \theta)$ for all other pairs $(\varepsilon,\ \boldsymbol{m})$. Let us denote wells $= \{(\varepsilon_1,\ \pm\boldsymbol{m}_1),\ (\varepsilon_2\ \pm\boldsymbol{m}_2),\ (\varepsilon_3,\ \pm\boldsymbol{m}_3)\}$. If we apply a field $\boldsymbol{h}$ and stress $\boldsymbol{\sigma}$ to the material, then the total free energy is (ignoring exchange),

$$\int_{\Omega} \varphi\left(\varepsilon(\boldsymbol{x}),\ \boldsymbol{m}(\boldsymbol{x}),\ \theta\right) - \boldsymbol{h}\cdot\boldsymbol{m}(\boldsymbol{x}) - \boldsymbol{\sigma}\cdot\varepsilon(\boldsymbol{x})\ dx + \frac{1}{2}\int_{\mathbb{R}^3} |\nabla\zeta|^2\ dx \tag{3.2}$$

subject to the magnetostatic equation,

$$\operatorname{div}\left(-\nabla\zeta + \boldsymbol{m}\right) = 0 \text{ on } \mathbb{R}^3. \tag{3.3}$$

Here, stable configurations are displacements $\boldsymbol{u}(\boldsymbol{x})$, with $\varepsilon_{ij}(\boldsymbol{x}) = \frac{1}{2}(u_{i,j}(\boldsymbol{x}) + u_{j,i}(\boldsymbol{x}))$ and magnetizations $\boldsymbol{m}(\boldsymbol{x})$, $|\boldsymbol{m}(\boldsymbol{x})| = m_s$, that minimize (3.2). In this minimization the final term is evaluated by solving the differential equation (3.3) for the magnetostatic potential ζ so that ζ is determined by $\boldsymbol{m}(\boldsymbol{x})$.

Typically, the magnitudes of applied fields and stresses are much smaller than the corresponding moduli that describe the "shape" of φ near its energy wells. This implies that, since φ is quadratic near its energy wells and the energy of the applied fields and loads (i.e. the second and third terms of (3.2)) are linear in $\boldsymbol{h}$ and $\boldsymbol{\sigma}$, then the values of $(\varepsilon(\boldsymbol{x}),\ \boldsymbol{m}(\boldsymbol{x}))$ on most of the volume Ω are very close to the energy wells and the first term of (3.2) is negligible (see De Simone and James [1996] for a justification of this argument). This leads to the simplified problem, which is restricted only to states on the wells:

$$\min_{(\varepsilon(\boldsymbol{x}),\ \boldsymbol{m}(\boldsymbol{x}))\ \in\ \text{wells}} \int_{\Omega} -\boldsymbol{h}\cdot\boldsymbol{m}(\boldsymbol{x}) - \boldsymbol{\sigma}\cdot\varepsilon(\boldsymbol{x})dx + \int_{\mathbb{R}^3} |\nabla\zeta|^2 dx \tag{3.4}$$

Two further simplifications render this free energy tractable. If Ω is an ellipsoid then the last term is minimized by a constant vector $\nabla\zeta = -\boldsymbol{D}\boldsymbol{m}$ on Ω, among all magnetizations with given average magnetization $\boldsymbol{m}$. Here

$\boldsymbol{D}$ is the demagnetization matrix associated with the ellipsoid Ω. In this case the magnetostatic energy (the last term of (3.4)) assumes the form $1/2(\boldsymbol{m} \cdot \boldsymbol{D}\boldsymbol{m})$. For suitable constant applied field and stress, the first two terms of (3.4) are also minimized by a constant magnetization (or, in some cases, a macroscopically constant magnetization, which is also fine) so that we have substantially simplified the minimization problem. To further simplify even further, let us assume Ω is a sphere so that $\boldsymbol{D} = \boldsymbol{I}$. Then, the magnetostatic energy does not participate at all, if the minimizer of the first two terms of (3.4) does not exhibit microstructure (since, in that case, the average magnetization satisfies $\boldsymbol{m} \cdot \boldsymbol{D}\boldsymbol{m} = m_s^2$). Thus, we get the free energy,

$$\min_{\varepsilon(\boldsymbol{x}),\ \boldsymbol{m}(\boldsymbol{x}) \in \text{ wells}} \int_{\Omega} -\boldsymbol{h} \cdot \boldsymbol{m}(\boldsymbol{x}) - \boldsymbol{\sigma} \cdot \varepsilon(\boldsymbol{x}) d\boldsymbol{x} + m_s^2(\text{vol.}\Omega) \tag{3.5}$$

Now we can consider a typical situation. Consider a compressive stress $\boldsymbol{\sigma} = \sigma(100)$ and field $\boldsymbol{h} = h(100)$ applied along (100), $\sigma \leq 0$ and $h > 0$. It is easy to check from (3.5) that the free energy minimizer is the state $(\varepsilon(\boldsymbol{x}),\ \boldsymbol{m}(\boldsymbol{x})) = (\varepsilon_1,\ \boldsymbol{m}_1)$ for $\boldsymbol{\sigma} \cdot \varepsilon_1 + \boldsymbol{h} \cdot \boldsymbol{m}_1 > \boldsymbol{\sigma} \cdot \varepsilon_2 + \boldsymbol{h} \cdot \boldsymbol{m}_2$, while a suitable minimizer is $(\varepsilon(\boldsymbol{x}),\ \boldsymbol{m}(\boldsymbol{x})) = (\varepsilon_2,\ \pm \boldsymbol{m}_2)$ for $\boldsymbol{\sigma} \cdot \varepsilon_2 + \boldsymbol{h} \cdot \boldsymbol{m}_2 > \boldsymbol{\sigma} \cdot \varepsilon_1 + \boldsymbol{h} \cdot \boldsymbol{m}_1$, and our assumptions are justified in this case. According to energy minimization, transformation takes place when $\boldsymbol{\sigma} \quad \varepsilon_2 + \boldsymbol{h} \cdot \boldsymbol{m}_2 = \boldsymbol{\sigma} \cdot \varepsilon_1 + \boldsymbol{h} \cdot \boldsymbol{m}_1$, i.e. when

$$\sigma\left(\varepsilon_2 - \varepsilon_1\right) = hm_s \tag{3.6}$$

To understand what we might expect quantitatively in a favorable situation, let us take the desirable condition (for self accommodation) of no volume change $\varepsilon_2 = -\varepsilon$, $\varepsilon_1 = 2\varepsilon$ with $\varepsilon = 0.01$ and $m_s = 1400$ emu/cm^3 for Co. This gives $h = -(3\varepsilon/m_s)\sigma \equiv 200\frac{\text{Oe}}{\text{MPa}}\sigma$. Thus a stress of 10 MPa over a strain of 1% can be produced by a moderate field of 2000 Oe.

Of course, this is the ideal situation of switching (without hysteresis) between energy minimizers. These values of the field would tend to be increased somewhat by the presence of hysteresis. The calculations given above can be studied in more detail to understand domain structures and low energy pathways.

4 STRATEGIES FOR FINDING FERROMAGNETIC SHAPE MEMEORY MATERIALS

It must be expected that the candidate alloys contain a traditional ferromagnetic element, Fe, Ni and/or Co. Furthermore, the candidate potential ferromagnetic shape memory material should belong to a known class of shape memory alloys. The intersection of both classes contains ferromagnetic Heusler alloys, steels in a wider sense and Co based alloys. More specifically promising candidates will be found in NiMnX, Fe(Ni, Mn, Pt, Pd)X and CoNiX alloys. among those, the compositions Ni_2MnGa and Fe based invars have, in principle, the desired characteristics[5]). However, at this time, the martensitic and ferromagnetic, transition temperatures of the known compositions in the Ni_2MnGa and Fe-based systems are located at technologically uninteresting temperatures. Off stochiometric compositions promise better operating temperatures. For instance, the martensitic and ferromagnetic transition temperatures of Ni_2MnGa can be changed from 150K to 300K by changing composition[6].

Optimum action can be expected for highly metastable reversible systems, i.e. if the desired actuation can be achieved reversibly with the least amount of work. It follows that the microstructure of the alloys, once identified, should be controlled. This principle has been successfully applied for the development of Terfenol-D solidification microstructures and must be utilized in the candidate alloys as well. In general, the self-accommodating martensitic microstructure must be mesoscopically ordered. A polydomain single crystal[7,8] represents an extreme but energetically most efficient material. Highly textured materials will form a technologically acceptable engineering equivalent.

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