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New materials from theory: trends in the development of active materials

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Abstract

Active materials are materials that change shape when exposed to an applied field or a change of temperature. We review recently developed theory for active materials, with emphasis on predictions and methods that can guide the search for new materials. Special lattice parameters corresponding to certain special microstructures, texture, new concepts for large strain actuators, and the behavior of active materials at small scales are discussed. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

The usual procedure in materials science, fine-tuned from prehistoric times, is to improve materials by systematically investigating the properties of a series of samples made by varying over a limited range the controllable variables involved in synthesis or processing. While sometimes disparagingly associated with "heat and beat" metallurgy, the systematic method continues to have enormous success. The current state of the development of the most successful shape memory alloy NiTi, excepting its discovery, owes everything to this procedure (cf. Miyazaki and Otsuka, 1989).

This procedure does not, however, lend itself to the search for a totally different kind of material. Active materials such as shape memory, magnetostrictive, and ferroelectric materials often exhibit their special behavior at exceedingly special compositions: crucial differences in behavior are found in NiTi from 50.2 to 50.6 atomic % Ni. If 0.1% is regarded as an acceptable tolerance, and the alloy being investigated is at least ternary, then the systematic procedure rapidly becomes difficult. If several heat treatments are also involved, then it can be considered hopeless as a tool for discovery. Nor is the systematic method particularly effective when the method of synthesis inherently involves large changes.

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For example, when multilayer films are grown, the effects of substitution of one material for another, or the effect doubling of the thickness of a layer, often cannot be inferred from a trend based on small changes.

The usual procedure in solid mechanics is to develop mathematical models grounded in the principles of continuum mechanics and in macroscopic experiment. The models contain constitutive equations with phenomenological constants, which are evaluated from well-defined experimental procedures. The models are then used to predict the mechanical behavior, or to evaluate the reliability and strength, of solids and structures. The predictions of the most successful of these models are now carried out with the help of sophisticated numerical methods. Generally, this procedure has little impact on materials science, because of the reliance on phenomenology.

To put solid mechanics in the service of materials science, two modifications are essential. First, theories of solids have to be grounded in fundamental material constants. In active materials the most important of these are lattice parameters, symmetry and atomic structure of parent and product phases, latent heats, (electro-magneto-) elastic moduli, specific heats and saturation magnetization. Second, the procedure experiment → theory → prediction has to be reversed. Instead, it has to be replaced by the following:

1. formulate a concept of an interesting material behavior,
2. infer how such behavior could arise from certain constitutive equations that contain only fundamental material constants,
3. relate the desired material constants directly to the composition of materials,
4. formulate a procedure for synthesis.

It should be appreciated that to bring predictive science to the study of the mechanical behavior of materials, more is required than "a close cooperation between solid mechanicians and materials scientists". The standard practice of solid mechanics also has to be fundamentally changed.

This philosophy has been followed by a small group of solid mechanicians over the past five years. The purpose of this chapter to report on the progress and prospects for the future in the context of active materials. The focus is on shape memory and magnetostrictive materials, only because the methods have been applied primarily to these. The research has been most successful when it is well-focused on relatively simple behaviors. We are still quite far from assessing the implications on behavior of a complicated diffusional phase transformation in a martensitic material, let alone contemplating the first principles design of a heat treatment.

Step 2 above is difficult. That is because, when the constitutive equations contain only fundamental material constants, the complex microstructural changes in a material cannot be summarized by overall phenomenological rate laws. One must really confront microstructure. For this purpose the progress reported here has been crucially aided by concurrent research on the relation of behavior on different scales. In particular, modern mathematical methods associated with weak convergence, homogenization, γ-convergence, Young measures have proven to be useful for the problem of change-of-scale. The key question addressed by these methods is, "Precisely what (minimal) information from the microscale is needed to calculate a certain macroscale property?". It would benefit solid mechanics and materials science if these methods were more widely known: certainly anyone who deals with deformation and microstructure would be helped by knowing the so-called "minors relations" (see James, 1990; Ball and James, 1987, 1992).

Step 3 above is also not very well addressed by conventional solid mechanics. But it is directly related to spectacular developments on the direct computation of material properties based on Density Functional Theory (DFT). DFT is based on the observation by Honenberg and Kohn (1964) and Kohn and Sham (1965) that the density ρ of electrons in quantum mechanics is subject to a variational principle on $\mathbb{R}^3$ (Unfortunately, one of the terms in this integrand, the exchange-correlation energy, is not precisely known from full quantum mechanics and must be "modeled" using a kind of mean field theory called the local density approximation. Despite this, DFT contains only the positions of the nuclei and their charges as data; see Parr and Yang (1989) and Friesecke (1997)). The future integration of DFT and materials science is likely in the long run to lead to truly major advances in "new materials from theory". It may one day even surpass the time honored method of preparing lots of alloys and measuring their properties.

2. Predictions that are guiding the development of active materials

We give a sample of predictions that are being used for the development of shape memory materials. As mentioned above, an underlying motivation for these results has been to understand why active materials occur at such special compositions. While part of this is related to the sensitive dependence of transition temperature on composition, another component is evidently the notion that certain microstructures that promote the shape memory effect are possible with only extremely special lattice parameters.

2.1. Special lattice parameters

Active materials have free energies with *energy wells*. That is, in the simplest case the free energy density $\varphi(\mathbf{F}, \theta)$ depends on the deformation gradient $\mathbf{F}$ and temperature θ. To take a particular example, the shape memory alloy Cu-14.0 at.%Al-3.5 at.%Ni has six energy energy wells associated with the variants of the $\gamma_1{}'$ *martensite* phase for $\theta < \theta_c$, θ_c being the transformation temperature, and a single energy well for $\theta > \theta_c$ associated with the *austenite* phase. The austenite well is defined by the identity matrix $\mathbf{F} = \mathbf{I}$ while the martensite wells are defined by specific *distortion matrices* having the form,

$$\begin{pmatrix} \frac{\alpha+\gamma}{2} & \frac{\alpha-\gamma}{2} & 0 \\ \frac{\alpha-\gamma}{2} & \frac{\alpha+\gamma}{2} & 0 \\ 0 & 0 & \beta \end{pmatrix},$$

$$\begin{pmatrix} \frac{\alpha+\gamma}{2} & 0 & \frac{\alpha-\gamma}{2} \\ 0 & \beta & 0 \\ \frac{\alpha-\gamma}{2} & 0 & \frac{\alpha+\gamma}{2} \end{pmatrix},$$

$$\begin{pmatrix} \beta & 0 & 0 \\ 0 & \frac{\alpha+\gamma}{2} & \frac{\alpha-\gamma}{2} \\ 0 & \frac{\alpha-\gamma}{2} & \frac{\alpha+\gamma}{2} \end{pmatrix},$$

$$\begin{pmatrix} \frac{\alpha+\gamma}{2} & \frac{\gamma-\alpha}{2} & 0 \\ \frac{\gamma-\alpha}{2} & \frac{\alpha+\gamma}{2} & 0 \\ 0 & 0 & \beta \end{pmatrix},$$

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$$\begin{pmatrix} \beta & 0 & 0 \\ 0 & \frac{\alpha+\gamma}{2} & \frac{\gamma-\alpha}{2} \\ 0 & \frac{\gamma-\alpha}{2} & \frac{\alpha+\gamma}{2} \end{pmatrix}. \tag{1}$$

The function $\varphi(\mathbf{F}, \theta)$ is equi-minimized for $\theta < \theta_c$ by these six matrices and, according to the principle of material frame-indifference, by all rotation matrices premultiplying these matrices (A rotation matrix is a matrix $\mathbf{R}$ satisfying $\mathbf{R}^T\mathbf{R}=\mathbf{I}$, $\det \mathbf{R}=1$, and the superscript T denotes transpose). The numbers α, β and γ are related to lattice parameters of the material, so they are known to high accuracy, e.g., for the Cu-14.0 at.%Al-3.5 at.%Ni discussed here, they are $\alpha=1.0619$, $\beta=0.9178$ and $\gamma=1.0230$.

For other martensitic materials, the structure of the energy wells can be quite different. For the monoclinic phase of the NiTi alloy mentioned above there are 12 energy wells, determined in this case by four constants, all of which are known accurately. Of course, the determination of the precise structure of the energy wells, and how they relate to X-ray measurements, has involved fundamental work in solid mechanics. In some of the more complex cases involving so-called "shuffling", there remain significant open questions.

The total free energy is given by,

$$\int_{\Omega} \varphi(\nabla \mathbf{y}(\mathbf{x}),\theta)\mathrm{d}\mathbf{x} + \mathscr{L} \tag{2}$$

where $\mathscr{L}$ represents the energy of the loading device. As a consequence of energy minimization, the deformation gradient tends to lie on or near the energy wells, but since the deformation is assumed to be continuous, the deformation gradient is subject to conditions of compatibility. Precisely, the deformation gradient matrices on different wells must differ by a matrix of rank one, or, briefly, a *rank-one connection*. These conditions, together with the specific energy-well structure of the material, strongly restrict the spatial distribution of the deformation gradient, that is, the geometry of microstructure.

The ordinary *shape-memory effect* is the following. A specimen is deformed by loading at a temperature below θ_c, causing redistribution of the variants of martensite. Upon removal of the loads, the specimen retains its deformed shape (a consequence of the variants of martensite having the same free energy density). Upon heating to above θ_c, the specimen returns to its orginal shape (a consequence

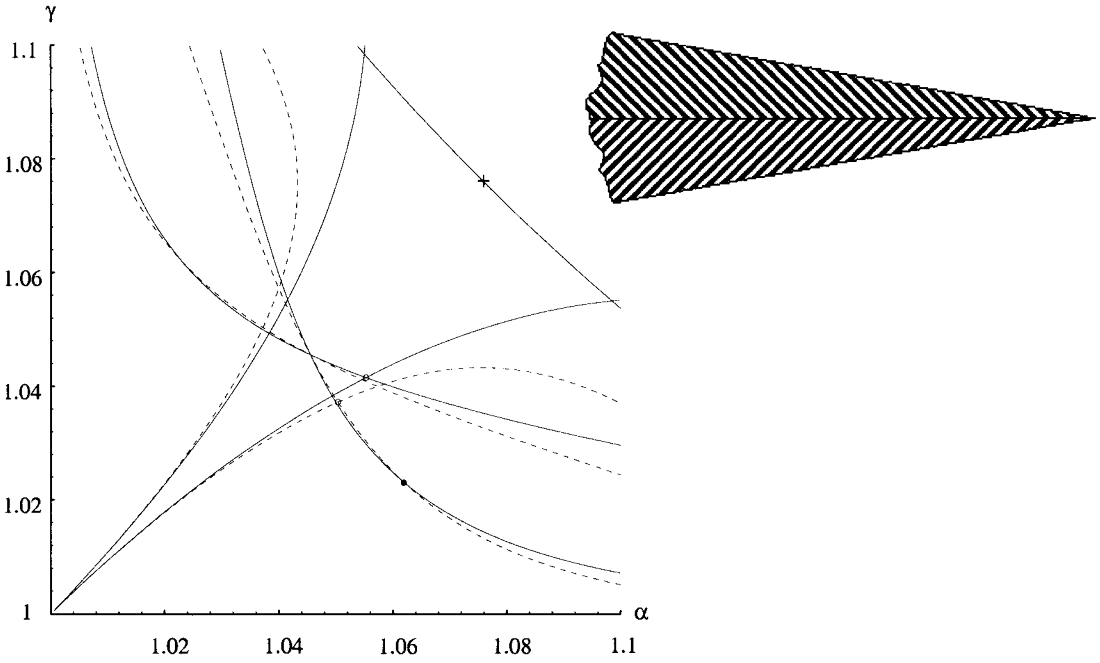

Fig. 1. Special lattice parameters for the wedge (inset) to be energy minimizing. Dashed/solid lines correspond to wedges made with Type I/Type II twins. The dot corresponds accurately to the measured lattice parameters of Cu–14.0%Al–3.5%Ni.

of there being a single energy-well for $\theta > \theta_c$). Finally, upon cooling to below θ_c, the specimen retains the original shape.

The last step is crucial. It permits the original shape to be reset. But more than that, it means that the alloy exhibits *self-accommodation*: there is a compatible arrangement of variants of martensite that exhibit no macroscopic change of shape (However, note that *microscopically* there are large distortions, since none of the matrices in Eq. (1) is close to $\mathbf{I}$). This, in turn, implies that there is an arrangement of variants of martensite that can be completely surrounded by austenite, a situation that is thought to favor easy nucleation. The precise necessary and sufficient conditions for self-accommodation are known (Bhattacharya, 1992). Except for degeneracies they are:

1. the austenite is cubic and
2. the distortion matrices have determinant 1.

This is the most fundamental tool in the search for new shape memory materials.

In the Cu-Al-Ni alloy used as an example above, there is a persistent microstructural feature that is seen during transformation from austenite to martensite. Termed the *wedge*, it consists of two finely-twinned martensite plates that meet back-to-back at a "midrib", pictured schematically as the inset in Fig. 1. It is also seen in quite a few other shape memory materials, e.g. specific alloys in the systems Cu-Zn-Al, Ni-Al, Ni-Mn, Ni-Zn-Cu, Fe-Ni-C, Fe-Pt, Fe-Ni-Co-Ti. Observations suggest that it provides an easy path for transformation, beginning from a point on a boundary or grain boundary. While its prevalence indicates that it is in some sense generic, nothing could be further from the truth. In fact, an analysis of the conditions under which a wedge can be energy minimizing in a free body (Bhattacharya, 1991) lead to extremely restrictive conditions on lattice parameters. A sample of Bhattacharya's results, refined and extended by Hane and Shield (1998) are shown in Fig. 1, for the case of distortion matrices as listed in Eq. (1). Here, for ease of presentation β has been set equal to 0.9178, the experimentally measured value in Cu-14.0 at.%Al-3.5 at.%Ni, and the α-γ plane is shown. For alloys with (α, γ) on the solid or dashed curves, the wedge is energy minimizing. The dot accurately shows the measured (α, γ) for Cu-14.0 at.%Al-3.5 at.%Ni.

While α, β and γ can be changed by changing composition, this Cu-14.0 at.%Al-3.5 at.%Ni alloy was not discovered by systematically adjusting composition so as to lie on one of the curves shown in Fig. 1. Rather, it was found by adjusting composition so as to have a repeatable shape memory effect and a convenient transformation temperature. The systematic use of results like that shown in Fig. 1 is extremely intriguing, and is now being followed by several groups.

The result shown in Fig. 1 really goes beyond the particular wedge microstructure. Mathematically, the special relation between α, β and γ really means that there is an "accidental" hidden rank-one connection among the energy wells, which, by symmetry, turns into lots and lots of hidden rank-one connections. This implies not only that the wedge is energy minimizing, but so are a host of other similar microstructures.

A number of other special relations among lattice parameters are now emerging corresponding to certain microstructures or behavior. Notable are the analysis of the X-interface (Ruddock, 1994), extra twins in cubic to monoclinic transformations (Pitteri and Zanzotto, 1997), general conditions for the existence of an austenite/martensite interface (Ball and Carstensen, 1997) and special relations satisfied by low hysteresis alloys (Ball et al., 1995). There is a growing belief, not confined to people deriving these relations, that they will revolutionalize the search for new active materials.

2.2. Special textures

Another class of special relations that promises to be useful is based on the analysis of special textures that promote the shape memory effect. The analysis of these involves two length scales. The microstructural length scale is assumed to be much smaller than the length scale of the grains, which in turn is assumed to be much smaller than the macroscale. To understand the behavior possible in a polycrystal, ideas from both the analysis of microstructure and homogenization are necessary. The analysis currently available covers the following kind of question: what macroscopic strains are possible in a polycrystal using essentially stress-free states from the martensite wells, allowing all possible compatible arrangements?

One of the most striking results (Bhattacharya and Kohn, 1996) is that with a cubic-to-tetragonal transformation (three energy wells for $\theta < \theta_c$) in a random polycrystal, the martensite is essentially rigid. The constraints of 1) randomness, and 2) only these three particular wells, conspire to rigidify the polycrystal. The result is robust: complete randomness is unnecessary and there is flexibility with regard to lattice parameters. What does this mean in practice? In such systems, deformation of the martensite will drive the material out of the wells. In practical terms, while a one-time shape memory effect might be observed, the severe deformations caused by the often significant departures from the wells destroys the effect after a few cycles. This is the universal observation in such systems. Yet, surprisingly, there are several large alloy development programs around the world whose goal is to find a polycrystalline shape memory alloy based on the cubic-to-tetragonal transformation, typically beginning from a martensitic steel. In the author's view such attempts, without consideration of texture, are doomed.

There are a number of other results on texture. The results are quantitative, e.g. precise values or precise bounds on recoverable strains, but I shall just describe them qualitatively. It turns out that the [110] texture produced naturally by drawing NiTi wires is an ideal texture for producing large recoverable strains (no surprise!). The natural texture of sputtered films NiTi is also [110], but this is an extremely bad texture for producing large recoverable strains, a result that is borne out by experiment, but which was puzzling prior to these theoretical results. However, the texture produced by melt spinning is ideal. In Cu-based shape memory materials there are similar quantitative results, and a similar significant effect of texture on recoverable strain, which has motivated new attempts to grow films of these materials.

3. New concepts: ferromagnetic shape memory

Magnetostriction is the strain in a solid produced by the application of a magnetic field. In the early 1970's Clark and Belson (1972) measured unusually large magnetostriction at room temperature in certain R-Fe_2 alloys, where R is a rare earth element, approaching the magnetostriction observed in pure crystals of Tb and Dy at very low temperatures. While these alloys have naturally large magnetostriction, they are otherwise conventional ferromagnetic materials. They have a Curie temperature, at which a second order transformation takes place. The free energy density φ may be thought of as depending additionally on magnetization, $\varphi(\mathbf{F}, \mathbf{m}, \theta)$. Above θ_c, it has a single energy well, while below θ_c it has wells defined by certain pairs $((\mathbf{U}_1, \mathbf{m}_1),..., (\mathbf{U}_k, \mathbf{m}_k))$, $(\mathbf{U}_i, \mathbf{m}_i)$ dependent on temperature. Because of the second order nature of the Curie transformation, each of these pairs tends continuously to $(\mathbf{I}, \mathbf{o})$ as $\theta \rightarrow \theta_c$ from below.

For actuator applications these giant magnetostrictive materials had a deficiency: they had large hysteresis loops. This means that the magnetic domains are subject to pinning by defects. Clark and coworkers formulated a brilliant strategy to solve this problem. By mixing appropriate amounts of $TbFe_2$ and $DyFe_2$, they arranged for the alloy to have a nearly ambiguous easy axis (either [100] or [111]), near the boundary between two magnetic phases. This has the effect of reducing the anisotropy constants of the material, broadening domain walls, and thereby weakening the effect of pinning.

This intentional ambiguity is a recurring theme in the development of active materials, and it lacks a clear theoretical foundation. A very similar example is found in ferroelectrics, which are often arranged to be near the morphotropic boundary, a nearly vertical line in the phase diagram of $PbZr_xTi_{1-x}O_3$ that separates tetragonal from trigonal phases (Jaffe et al., 1971; Newnham, 1997). The intuitive idea, explained in terms of the energy-well picture, is that the presence of an extra set of wells, where ordinarily there would be barriers, has the effect of removing lots of barriers and thereby facilitating the polarization (or magnetization) process. A related idea, close to the arguments in the preceeding section, is that more wells means more microstructures available to ease the passage between two given states. But all this is all very vague, and one of the outstanding theoretical problems in "new materials from theory" is to lend some predictive understanding to this strategy.

Before continuing, let us make the "ambigous phase" strategy slightly more quantitative. In the simplest model of magnetostriction $\varphi(\mathbf{F}, \mathbf{m}, \theta)$ is approximated by its geometrically linear counterpart $\tilde{\varphi}(\mathbf{E},\mathbf{m},\theta)$, where the small strain matrix $\mathbf{E}$ approximates $(\mathbf{F}^T\mathbf{F})^{1/2}$-$\mathbf{I}$, and the form of $\tilde{\varphi}$ is such that the energy wells are pairs $((\mathbf{E}_1, \mathbf{m}_1),..., (\mathbf{E}_k, \mathbf{m}_k))$, where $\mathbf{E}_i = \tilde{E}(\mathbf{m}_i)$, and the magnetizations $(\mathbf{m}_1,..., \mathbf{m}_k)$ minimize the *anisotropy energy*,

$$\frac{\kappa_1}{m_s^4}\left(m_1^2 m_2^2 + m_2^2 m_3^2 + m_1^2 m^{2_3}\right) + \frac{\kappa_2}{m_s^6}\left(m_1^2 m_2^2 m_3^2\right) \tag{3}$$

Here κ_1 and κ_2 are called anisotropy constants and m_s is the saturation magnetization, $|\mathbf{m}| = m_s$. Clark's strategy is related to the fact that *both* κ_1 and κ_2 have opposite signs in $TbFe_2$ and $DyFe_2$. Tetragonal/trigonal ambiguity is achieved at $\kappa_2 = -9\kappa_1$. Perfect ambiguity is achieved at $\kappa_1 = \kappa_2 = 0$.

The ambiguous phase strategy is not the only way to achieve large field-induced strains. In fact, the author, together with Manfred Wuttig and Robert Tickle, has been pursuing a strategy that in a sense is

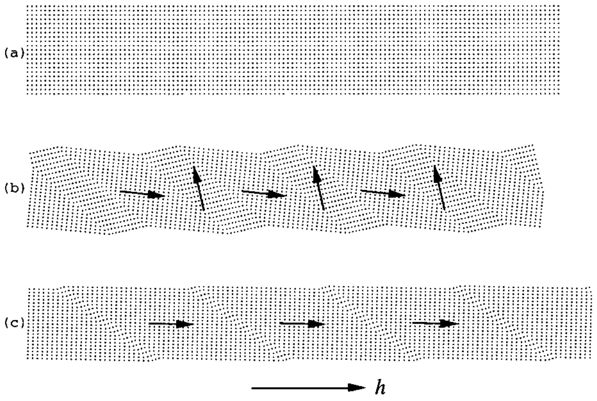

Fig. 2. Ferromagnetic shape memory illustrated using two tetragonal variants of martensite.

exactly opposite to the ambiguous phase strategy. That is, in certain ferromagnetic martensitic materials, we have been trying to make $|\kappa_1|$ and $|\kappa_2|$ as large as possible.

To explain how opposite strategies can give similar results, it is helpful to return to ordinary martensitic materials. The usual way of thinking about martensitic materials is in terms of soft moduli, or, from the theorist's perspective, linearized theory. Upon cooling, the presence of the first order phase transformation is signaled by the rapid decrease of certain elastic moduli whose associated eigenmodes resemble the impending transformation strain. But, in the 1970s and 1980s, it was noticed that while some softening was evident in most cases, it was not always pronounced. That is, there are martensites with very large transformation strains, modest softening, and very mobile twin boundaries (Krumhansl, 1987). Briefly: linearized theory does not tell the whole story. As an example, two compound twinned variants of martensite in single crystals of Cu-14.0 at.%Al-3.5 at.%Ni can be made to move back and forth large distances with a critical resolved shear stress of 1.5 MPa, and this for hundreds of thousands of cycles (Abeyaratne et al., 1996).

Therefore, one can conceive the following idea. Arrange to have a material with a martensitic transformation and a Curie temperature, so that the martensitic phase is ferromagnetic, has mobile twin boundaries and high anisotropy. The latter is quite consistent with large transformation strain since high structural anisotropy correlates with high magnetic anisotropy. With high magnetic anisotropy, the magnetization stays rigidly attached to easy axes, and the application of a field $\mathbf{h}$ favors variants of martensite with magnetization parallel to $\mathbf{h}$, owing to the presence of the term $-\mathbf{h}\cdot\mathbf{m}$ in the energy density. This is illustrated in Fig. 2 for two tetragonal variants of martensite. Why is the material relatively easy to magnetize? Because the magnetization process is due to redistribution of martensite variants with mobile interfaces. Of course, depending on the direction of the field, it might be very difficult to *fully* magnetize the material, because that would entail magnetization rotation, but that does not matter. The deep question is: what really governs the mobility of interfaces?

Using this strategy on alloys in the system NiMnGa, field-induced strains some 50 times those of giant magnetostrictive materials have been observed at moderate fields (Tickle et al., 1999; Tickle and James, 1999; James and Wuttig, 1996James and Wuttig, 1998; Ullakko et al., 1996). While issues remain, it appears that these will develop into an important class of actuator materials.

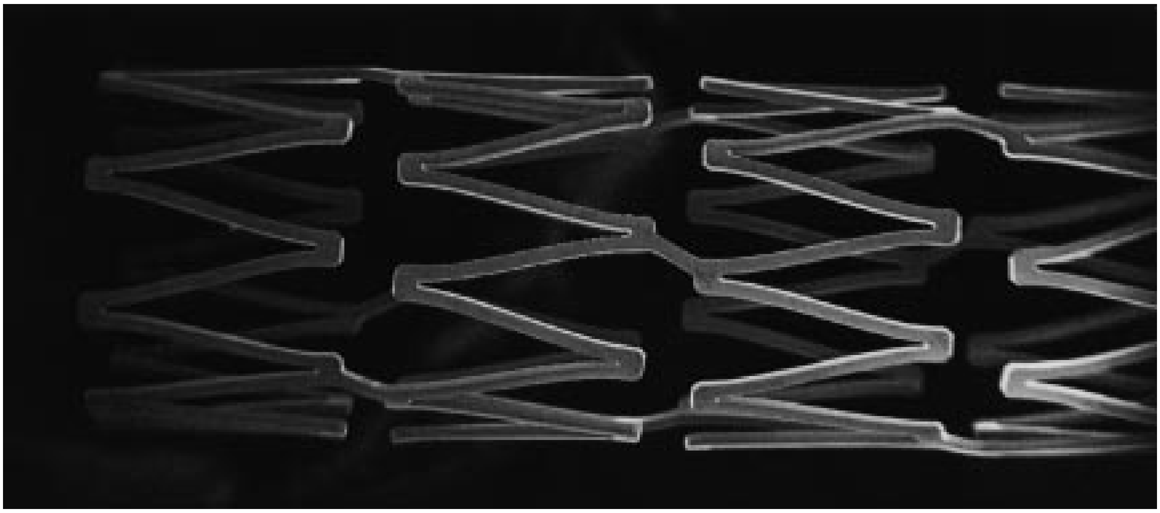

Fig. 3. Stent laser machined from a tube of NiTi. Using the property of superelasticity, the stent expands to hold an artery open. Courtesy of Brian Berg, Boston Scientific–SciMed. Width of strips is approximately 200 μm.

4. The outlook for active materials at large and small scales

Applications of active materials have been growing rapidly. Areas of particular promise are in vibration and motion control systems, pumps and valves, and data processing and storage. Biomedicine has been a particularly fertile area for shape memory materials. In Fig. 3, we picture a beautiful stent made of delicate fine strips of NiTi.

In applications of active materials, the moving parts of a machine are replaced by the movements of microstructure. The value of active materials for applications arises from two features,

1. by cooperative microstructural changes, a small piece of material can efficiently undergo a large motion, and
2. they serve as energy conversion devices.

So it is interesting to ask, What happens if we scale a piece of shape memory material smaller and smaller, say, even smaller than its own microstructural features? Will a small specimen of shape memory material still display the shape memory effect?

Let us consider first the macroscopic viewpoint, represented by Table 1. This shows work output per unit volume of various actuators. It was obtained from macroscopic data, e.g., the entry for NiTi was calculated by multiplying stress × recoverable strain in a shape memory cycle. Note the high value for this alloy, sugggesting that, because of “per unit volume”, this will be a good candidate for microactuators. This is partly due to the first order phase transformation that is being exploited, a fact that has motivated the search for both ferromagnetic shape memory materials and relaxor ferroelectrics based on first order phase transformations (Park et al., 1998).

The values in Table 1 are also *per cycle*. The feature that hampers the use of shape memory materials in many bulk applications is that they are slow to heat and especially slow to cool. But in thin film form, the heat transfer rates are significantly increased. One estimate gives a frequency for the shape memory cycle at several hundred Hz for a micron thick film. This has motivated much recent interest in the growth of films.

Table 1
Work per unit volume for various microactuators, after Krulevitch et al. (1996)

Actuator type	W/v (J/m^3)	Equation	Comments
1. Ni–Ti SMA	2.5×10^7	$\sigma{\cdot}\epsilon$	max. one-time output: $\sigma = 500$ MPa, $\epsilon = 5\%$
	6.0×10^6	$\sigma{\cdot}\epsilon$	thousands of cycles: $\sigma = 300$ MPa, $\epsilon = 2\%$
2. Solid–liquid phase change	4.7×10^6	$1/3(\Delta v/v)^2 k$	k = bulk modulus = 2.2 GPa (H_2O) 8% volume change (acetamide)
3. Thermo–pneumatic	1.2×10^6	$F{\cdot}\delta/v$	measured values: $F = 20$ N, $\delta = 50$ µm, $v = 4$ mm × 4 mm × 50 µm^3
4. Thermal expansion	4.6×10^5	$\frac{1}{2}\frac{(E_s}{} + E_f)2(\Delta\alpha \cdot \Delta T)^2$	ideal, nickel on silicon, s = substrate, f = film, $\delta T = 200$°C
5. Electro–magnetic	4.0×10^5	$\frac{F\cdot\delta}{v} F = \frac{-M_s^2 \cdot A}{2\mu}$	ideal, variable reluctance: v = total gap volume, $M_s = 1$ V sec/m^2
	2.8×10^4	$F{\cdot}\delta/v$	measured values, variable reluctance: $F = 0.28$ mN, $\delta = 250$ µm, $v = 100 \times 100 \times 250$ µm^3
	1.6×10^3	T/v	measured values, external field: Torque = 0.185 mN m, $v = 400 \times 40 \times 7$ µm^3
6. Electrostatic	1.8×10^5	$\frac{F\cdot\delta}{A\cdot \mathrm{gap}} F = \frac{\epsilon V^2 A}{2\delta^2}$	ideal: $V = 100$ volts, δ = gap = 0.5 µm
	3.4×10^3	$F{\cdot}\delta/v$	measured values, comb drive: $F = 0.2$ mN (60 volts), $v = 2 \times 20 \times 3000$ µm^3 (total gap), $\delta = 2$ µm
	7.0×10^2	$F{\cdot}\delta/v$	measured values, integrated force array: v = device volume, 120 volts
7. Piezoelectric	1.2×10^5	$1/2(d_{33}E)^2 E_f$	calculated, PZT: $E_f = 60$ GPa (bulk), $d_{33} = 500$ (bulk), $E = 40$ kv/cm
	1.8×10^2	$1/2(d_{33}E)^2 E_f$	calculated, ZnO: $E_f = 160$ GPa (bulk), $d_{33} = 12$ (bulk), $E = 40$ kv/cm
8. Muscle	1.8×10^4	$1/2(\sigma{\cdot}\epsilon)$	measured values: $\sigma = 350$ kPa, $\epsilon = 10\%$
9. Microbubble	3.4×10^2	$F{\cdot}\delta/v_b$	measured values: bubble diam. = 71 µm, $F = 0.9$ µN, $\delta = 71$ µm

But we expect a breakdown of this kind of macroscopic reasoning at small scales. A classical estimate for the width of the twin bands present in the most common martensitic microstructure gives const. $L^{1/2}$, where L is the length of the twin bands measured parallel to the bands. This yields the impossible conclusion that for a cube of size L, with L sufficiently small, the twin bands will be wider than the specimen. Obviously, the calculation breaks down, but we lack a reasonable one to replace it.

Anyway, the suggestion is that small particles will be single domain, like small magnetic particles. This, combined with the likely absence of nucleation sites in small particles, suggests that small particles would not transform at all. Experimental evidence from the 1950s suggested exactly that. But more recently, conflicting evidence has surfaced; a beautiful example of a martensitic transformation has been identified by Olson and Hartman (1982) in the nanoscale virus Bacteriophage T4. It exhibits a remarkable 50% transformation strain. It also seems to have a built-in scheme for nucleation.

In films there are some unexpected recent predictions. One of these says that for a suitably oriented, sufficiently thin, single crystal film, exact austenite/martensite interfaces are stable, i.e., without the fine twinning that is almost always seen in bulk (Dong et al., 1999). Small scale structures based on these would exhibit spontaneous strains significantly larger than seen in bulk because of the elimination of cancellation of strain due to the fine twinning. Could we really access directly the full transformation strain of an active material at small scales, without the compromises of microstructure?

In a famous after dinner talk in the 1960s, Feynman imagined a scenario of milliscale machines making microscale machines (Feynman, 1993a, 1993b [reprinted]), these making still smaller nanoscale machines, which would compute, store information, even provide entertainment (The ultimate non-virtual game: operator driven microscale vehicles under the microscope at war with a sea of protozoa). This has launched a huge, dynamic, international effort to understand the behavior of materials at small scales and do engineering at these scales. Mechanics is likely to play an important role in this activity, especially as technology makes the transition from macroscopic methods like surface micromachining, self-assembly and conventional patterning, to the essentially microbotic vision of Feynman, a development that already can be predicted from the spectacular success of the atomic probe microscope. With suitable development of small scale engineering one can imagine, for example, a small scale vehicle that is injected into the bloodstream and is powered by active materials drawing energy from a remotely applied field, which simultaneously could serve for imaging. The vehicle could carry surgical tools and thereputic drugs. A whole new strategy for therapy is suggested: rather than apply medicines at essentially constant concentration over the body, with associated side effects, deliver much stronger medicines, but with short lifetimes, directly to the affected area.

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