Heterogeneous Thin Films of Martensitic Materials with Application to Large Strain Microactuators

Y. C. Shu
Institute of Applied Mechanics
National Taiwan University
Taipei, Taiwan, ROC
yichung@spring.iam.ntu.edu.tw

ABSTRACT

We propose a multiscale modeling to study the effective behavior of a heterogeneous thin film accounting in detail for the underlying microstructure, grain sizes and the film thickness. Motivated by the recent study of shape-memory thin films, we develop our theory within the framework of 3D nonhomogeneous nonlinear elasticity enhanced with an interfacial energy. We do not require any priori selection of asymptotic expansion or ansatz in deriving our results. Under certain conditions, we show that the behavior of the films can not be predicted solely from that of identical bulk materials and can critically depend on the relative magnitudes of different material length scales. We apply our theory to martensitic materials and show that the shape-memory behavior can crucially depend on the ratios of these length scales. We comment on some novel and unusual properties that multilayer thin films made of shape-memory and elastic materials can display.

Keywords: Heterogeneous Thin Films, Martensitic Materials, Multiscale Modeling

1 Introduction

Martensitic thin films have recently attracted much interest because of their potential for application as microactuators [1]–[6]. Crystals undergoing a thermoelastic martensitic transformation often exhibit the shape-memory effect. Below the transformation temperature, they are extremely malleable - sustaining a huge deformation with strains as large as 10% under very small forces. When they are heated above the transformation temperature, the specimen springs back to its original shape as all the strain is recovered. Actuators utilizing the shape-memory effect are predicted to have the largest energy output per unit volume per cycle among a variety of common actuator systems [4]. But bulk shape-memory actuators have enjoyed limited success in temperature sensitive applications because the response is slow due to thermal inertia. On the other hand, the enhanced rate of heat transfer in thin films makes these alloys ideal for microactuator, micropump and for microelectromechanical system (MEMS) applications.

Typically, martensitic films are polycrystalline rather than monocrystalline. A polycrystal consists of a large number of single crystal grains with different orientations. The behavior of a polycrystal can be very different from that of a single crystal because of the constraining effect of neighboring grains. Depending on the deposition technique, the size of grains within the film can be larger than, comparable to or smaller than the thickness of film. Furthermore, depending on the material, the length scale of microstructure can also be larger than, comparable to or smaller than that of grains. The behavior of the film can critically depend on the relative magnitudes of these length scales, and we seek to understand this here.

The interest in microelectromechanical systems applications has recently motivated many experimental efforts to make martensitic thin films of Ti-Ni by sputtering. However, microstructure can be significantly different in thin films as compared to bulk materials. Hence, it is not clear that Ti-Ni is the ideal material in thin films. Bhattacharya and James [7] have developed a theory of martensitic single crystal thin films and Shu [8], [9] has extended this framework to bulk and thin-film polycrystals. In Section 2, we briefly describe our theoretical framework using energy minimization and study the effect of texture and grain size on recoverable strains in Section 3. We find that sputtering textures in both Ti-Ni and Cu-based shape-memory thin films are not favorable for large recoverable strain. We also use this theory to explore multilayer films and the novel properties that they may possess.

2 A Thin Film Model

Consider a heterogeneous (possibly multilayer) thin film shown in Figure 1. It occupies a reference domain

$$\Omega^h = \{\mathbf{x} \in I\!R^3 : (x_1, x_2) \in S, 0 < x_3 < h\}, \qquad (1)$$

where S is a bounded Lipschitz domain, $\{x_1, x_2, x_3\}$ are relative to an orthonormal film basis $\{\mathbf{e_1}, \mathbf{e_2}, \mathbf{e_3}\}$, and h is the film thickness. Let $\tilde{\mathbf{y}} : \Omega^h \to I\!R^3$ be the deformation of the film. The total energy of the heterogeneous thin film is

$$\tilde{e}^{(h)}[\tilde{\mathbf{y}}] = \int_{\Omega^h} \left\{ \kappa^2 |\nabla^2 \tilde{\mathbf{y}}|^2 + \varphi(\nabla \tilde{\mathbf{y}}, \frac{x_1}{d}, \frac{x_2}{d}, \frac{x_3}{h}) \right\} d\mathbf{x}, \quad (2)$$

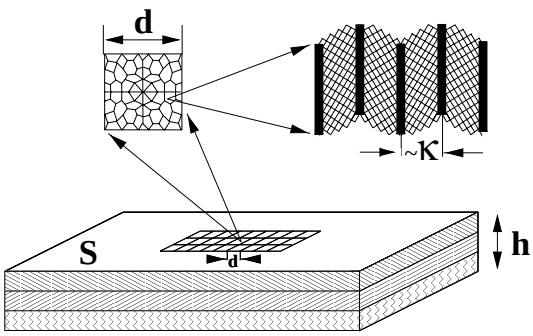

Figure 1: A heterogeneous thin film with three different length scales.

where $\varphi : I\!M^{3\times 3} \times I\!R^2 \times (0,1) \to I\!R$ is the elastic free energy density of the film and $I\!M^{m\times n}$ is the set of all $m \times n$ matrices. We assume that φ is periodic in the in-plane variables x_1 and x_2 with period $[0,1]^2$. So d scales like the typical grain size. Further, since we wish to model martensites, $\varphi(\mathbf{F}, \cdot, \cdot, \cdot)$ may have a multi-well structure and consequently nonconvex. Note that we have included the interfacial energy of the type $\kappa^2|\nabla^2\tilde{\mathbf{y}}|^2$. Minimizers of the energy (2) have oscillations on a length scale that scale with κ and hence we call κ the length-scale of the microstructure. We are interested in finding the limiting behavior of the film when all length scales κ, d and h tend to zero. Therefore, we take

$$\begin{array}{cc} \kappa = \kappa(h) > 0, & d = d(h) > 0, \\ \lim_{h\to 0}\kappa(h) = 0, & \lim_{h\to 0} d(h) = 0, \end{array} \tag{3}$$

and assume that they have fixed limiting ratios:

$$\alpha = \lim_{h\to 0}\frac{\kappa}{d}, \quad \beta = \lim_{h\to 0}\frac{h}{d}, \quad \alpha' = \lim_{h\to 0}\frac{\kappa}{h}. \tag{4}$$

Our approach is variational. We study the "variational limit" of (2) as h tends to zero. Since the energy defined in (2) scales like h as h tends to zero, we shall be interested in the limiting energy per unit thickness; i.e.,

$$\tilde{e}_1^{(h)} = \frac{1}{h}\tilde{e}^{(h)}.$$

We expect the minimum values and the minimizers of the functional $\tilde{e}_1^{(h)}$ to converge to those of a "limiting energy" $\tilde{e}_1^{(0)}$ which we seek to find. In this context, the natural tool is , -convergence as proposed by De Giorgi [10] and De Giorgi and Franzoni [11] which under a suitable technical hypothesis is nearly identical to that of convergence of minimizers. Using this notion, we show that the limiting energy is always given by

$$\tilde{e}_1^{(0)}[\mathbf{y}] = \int_S \bar{\varphi}\left(\frac{\partial \mathbf{y}}{\partial x_1}, \frac{\partial \mathbf{y}}{\partial x_2}\right) dx_1 dx_2, \tag{5}$$

Texture	Recoverable Strains (%)			
	Ti-Ni		Cu-Zn-Al	
	long	flat	long	flat
random	2.3	2.3	1.7	1.7
{111} film	5.3	8.1	1.9	5.9
{100} film	2.3	2.3	7.1	7.1
{110} film	2.3	2.3	1.7	1.7

Table 1: The predicted uniaxial recoverable extension for various textures in thin films.

where $\bar{\varphi}$ is the effective energy density and only depends on the in-plane gradient of deformation $\mathbf{y}$ and not explicitly on the position. It describes the overall behavior of the heterogeneous thin film after taking into account the martensitic microstructure, grains and multilayers.

Finally, note that this is a two-dimensional problem rather than a three-dimensional problem and $\bar{\varphi}$ depends only on the in-plane derivatives of the deformation. So, if we knew $\bar{\varphi}$, (5) is a much easier problem than (2). A detailed characterization of $\bar{\varphi}$ is provided in Shu [9]. Here, we discuss the main features and use it to study specific examples. The most important finding is that $\bar{\varphi}$ depends qualitatively on the relative magnitudes of length scales or on the ratios of $\frac{\kappa}{d}$, $\frac{h}{d}$ and $\frac{\kappa}{h}$.

3 Results

3.1 Films with Columnar Grains

Shape-memory thin films are often made by sputtering [1]–[3], [12]. The grains in these films are typically columnar (eg., see Figure 2 of [2]). Further, the microstructure is usually smaller than the grains (eg., see Figure 5 in [12]). So we assume that $\varphi = \varphi(\nabla\mathbf{y}, x_1, x_2)$ in (2) and $d >> \kappa$. We can show that the behavior of the film depends on the ratio of the film thickness h to the typical size of grains d. Table 1 contrasts the behavior of films with long or rod-like ($h >> d$) grains and films with flat or pan-cake shaped ($h << d$) grains. It lists the predicted recoverable strains for films with different textures in Ti-Ni and Cu-Zn-Al. Note that they are larger for flat grains compared to long grains. We also note here that neither the random nor {110} texture which is common for BCC materials [1], [3] are ideal textures for large recoverable strain. The ideal textures appear to be {100} for Cu-Zn-Al (this texture can be produced by melt-spinning) and {111} for Ti-Ni.

We now briefly explain the ideas behind these results. Consider first the case $h << d$. The grains are flat and thin and have a "pan-cake" shape. The intergranular constraints are now only in-plane; any out-of-plane incompatibility is easily overcome with very small elastic energy. Further, within each grain the interface condition is an "invariant line" rather than an "invariant plane" condition. Therefore, the effective behavior of

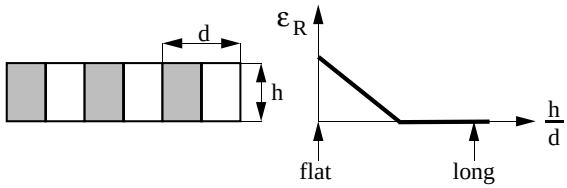

Figure 2: The recoverable extension versus aspect ratio of the grain $\frac{h}{d}$ for a polycrystalline thin film with a periodic texture containing two orientations: "grey" and "white" columnar grains.

the film is obtained by taking the thin-film limit and then homogenizing in the plane of the film. Indeed, the effective energy density can be shown to be [9]

$$\bar{\varphi}(\bar{\mathbf{F}}) = \inf_{\substack{k\in N\\ \boldsymbol{\omega}}} \fint_{kX} \varphi_0(\bar{\mathbf{F}} + \nabla_p \boldsymbol{\omega}, \mathbf{x}_p) d\mathbf{x}_p,$$
$$\varphi_0(\bar{\mathbf{F}}, \mathbf{x}_p) = \inf_{\mathbf{b}\in I\!R^3} \varphi(\bar{\mathbf{F}}|\mathbf{b}, \mathbf{x}_p),$$

where $X = (0,1)^2$, $\mathbf{x}_p = (x_1, x_2)$, $\bar{\mathbf{F}} \in I\!M^{3\times 2}$ and ∇_p is the in-plane gradient operator such that $\nabla_p \boldsymbol{\omega} = \boldsymbol{\omega}_{,1} \otimes \mathbf{e}_1 + \boldsymbol{\omega}_{,2} \otimes \mathbf{e}_2$.

We now turn to another extreme case $h >> d$. The grains are now long and rod-like; and it is no longer possible to overcome out-of-plane constraints. Therefore, the intergranular constraints are fully three-dimensional. Consequently, the effective behavior is obtained by homogenizing in three dimensions and then taking the thin-film limit. Thus, the recoverable strains for such films is essentially the same as bulk materials. The explicit form of the effective energy density in this case can be shown to be [9]

$$\begin{aligned}
\bar{\varphi}(\bar{\mathbf{F}}) &= Q\varphi_0^H(\bar{\mathbf{F}}),\\
\varphi_0^H(\bar{\mathbf{F}}) &= \inf_{\mathbf{b}\in I\!R^3} \varphi^H(\bar{\mathbf{F}}|\mathbf{b}),\\
\varphi^H(\mathbf{F}) &= \inf_{\substack{k\in N\\ \hat{\boldsymbol{\omega}}}} \fint_{k\hat{X}} \varphi(\mathbf{F} + \nabla\hat{\boldsymbol{\omega}}, \mathbf{x}_p) d\mathbf{x}
\end{aligned}$$

where $Q\varphi_0^H(\bar{\mathbf{F}})$ is the lower quasi-convex envelope of φ_0^H, $\hat{X} = (0,1)^3$, $\mathbf{F} = (\bar{\mathbf{F}}|\mathbf{b}) \in I\!M^{3\times 3}$ and ∇ is a 3D gradient operator such that $\nabla\hat{\boldsymbol{\omega}} = \hat{\boldsymbol{\omega}}_{,1} \otimes \mathbf{e}_1 + \hat{\boldsymbol{\omega}}_{,2} \otimes \mathbf{e}_2 + \hat{\boldsymbol{\omega}}_{,3} \otimes \mathbf{e}_3$.

While these extreme cases are instructive, the film thickness and the grain size are on the same order of magnitude in sputtered films. The analysis is then difficult but reflects the trends suggested by the extreme cases. Let us use the following example to demonstrate it. Consider a two-dimensional polycrystalline film with a texture containing two orientations ("grey" and "white" grains) as shown in Figure 2. Assuming that the martensite has two variants, we can calculate the recoverable strain exactly for any value of the ratio $\frac{h}{d}$. The result is shown schematically in Figure 2. The dependence is striking, and the recoverable strain is maximum at $\frac{h}{d} = 0$ (flat grains) and minimum at $\frac{h}{d} = \infty$ (long grains) as expected.

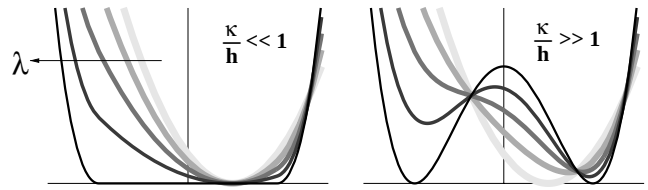

Figure 3: The effective behavior of a multilayer thin film is determined by the energies above for small and large values of $\frac{\kappa}{h}$.

Before closing this subsection, we should mention the effect of the ratio $\frac{\kappa}{d}$ of the size of the microstructure to that of the grain. Above, we took this ratio to be zero; however, this may not be true when the grain size becomes very small (on the order of tens of nanometer). We can show that if $\kappa >> d$, it costs materials more energy to form microstructure inside each grain and consequently strains can not be recovered unless the texture is exceptional. Once again, the analysis on the case of comparable κ and d is difficult but it interpolates the two extreme cases.

3.2 Multilayers

Consider a multilayer film made up of a finite number of alternating layers of a martensitic material and a purely elastic material. Let λ be the volume fraction of the martensitic material and let ϵ_m be the mismatch strain of the elastic material relative to the austenite phase of the martensitic material. The effective behavior is some combination of the behavior of these two materials; however, the nature of the behavior depends on the ratio $\frac{\kappa}{h}$ of the microstructure size to the thickness. Figure 3 shows the behavior for small and large $\frac{\kappa}{h}$ assuming a two-variant martensite for simplicity. The dark line is the energy of the martensitic material and the thick light line is the energy of the elastic material. The behavior of the multilayer is shown by lines of increasing greylevel for decreasing volume fraction λ (also see [7]). For small $\frac{\kappa}{h}$, the martensitic material freely forms microstructure and the multilayer is like an elastic material with soft-modulus. For large $\frac{\kappa}{h}$ on the other hand, the multilayer behaves like a phase transforming material: it has two variants with transformation strains which may be different from those of the original martensitic material, and one variant is preferred over the other. Hence, this multilayer film will display a two-way SME. Further notice that the multilayer is internally stressed so that the minimum energy is not zero. Finally, the multilayer can form "macroscopic twins": these are not twins confined to the martensitic material but encompass both the elastic and the martensitic material. Thus, multilayers promise to be a means of making apparently new

materials.

4 Conclusion

1. The behavior of heterogeneous thin films can not be predicted solely from that of identical bulk materials and can critically depend on the relative magnitudes of different material length scales.

2. Common sputtering texture is not ideal for shape-memory effect in both Ti-Ni and Cu-Zn-Al thin films (Table 1).

3. Flat grains are preferable to long grains in columnar films (Figure 2).

4. Multilayer thin-films provide a promising avenue for making materials with novel properties (Figure 3).

Acknowledgements. Part of this research was conducted during the visit to the Max-Planck-Institute for MIS, Leipzig and the author is very grateful for their hospitality.

REFERENCES

[1] K. R. C. Gisser, J. D. Busch, A. D. Johnson, and A. B. Ellis. Oriented Nickel-Titanium Shape Memory Alloy Films Prepared by Annealing During Deposition. *Appl. Phys. Lett.*, **61**:1632–1634, 1992.

[2] A. Ishida, A. Takei, and S. Miyazaki. Shape Memory Thin Film of Ti-Ni Formed by Sputtering. *Thin Solid Films*, **228**:210–214, 1993.

[3] Q. Su, S. Z. Hua, and M. Wuttig. Martensitic Transformation in $Ni_{50}Ti_{50}$ Films. *J. Alloys and Compounds*, **211/212**:460–463, 1994.

[4] P. Krulevitch, A. P. Lee, P. B. Ramsey, J. C. Trevino, J. Hamilton, and M. A. Northrup. Thin Film Shape Memory Alloy Microactuators. *Journal of Microelectromechanical Systems*, **5**:270–282, 1996.

[5] L. W. Chang and D. S. Grummon. Structure Evolution in Sputtered Thin-Films of Ti-X(Ni,Cu)(1-X) .1. Diffusive Transformations. *Phil. Mag. A*, **76**:163–189, 1997.

[6] L. W. Chang and D. S. Grummon. Phase-Transformations in Sputtered Thin-Films of Ti-X(Ni,Cu)(1-X) .2. Displacive Transformations. *Phil. Mag. A*, **76**:191–219, 1997.

[7] K. Bhattacharya and R. D. James. A Theory of Thin Films of Martensitic Materials with Applications to Microactuators. *J. Mech. Phys. Solids*, 47:531–576, 1999.

[8] Y. C. Shu and K. Bhattacharya. The Influence of Texture on the Shape-Memory Effect in Polycrystals. *Acta Materialia*, **46**:5457–5473, 1998.

[9] Y. C. Shu. Heterogeneous Thin Films of Martensitic Materials. *To appear in Archive for Rational Mechanics and Analysis*, 2000.

[10] E. De Giorgi. Sulla convergenza di alcune successioni di integrali del tipo dell'area. *Rendi Conti di Mat.*, **8**:277–294, 1975.

[11] E. De Giorgi and T. Franzoni. Su un tipo di convergenza variazionale. *Atti. Accad. Naz. Lincei Rend. Cl. Sci. Mat.* (8), **58**:842–850, 1975.

[12] P. Krulevitch, P. B. Ramsey, D. M. Makowiecki, A. P. Lee, M. A. Northrup, and G. C. Johnson. Mixed-Sputter Deposition of Ni-Ti-Cu Shape Memory Films. *Thin Solid Films*, **274**:101–105, 1996.