Thickness and film stress effects on the martensitic transformation temperature in equi-atomic NiTi thin films

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Abstract

This paper presents the results of an experimental study of the transformation behavior and its thickness dependence of submicron Ni-50.5at %Ti thin films on substrates. Measurements were performed on thin films with a microstructure that consisted of pancake-like grains with aspect ratios in excess of 50:1 in order to minimize grain-imposed constraints. The effect of the residual stress on the martensite transformation behavior was evaluated by using different substrate materials covering a range of thermal expansion coefficients. If the thermal stress in the austenite phase exceeds ~300 MPa, the martensitic transformation occurs in a one-step process from $B_2 \rightarrow B_{19}'$, while films with a lower stress follow a two-step transformation of $B_2 \rightarrow R\text{-phase} \rightarrow B_{19}'$. The slope of the stress-temperature curve during the $B_2 \rightarrow B_{19}'$ transformation is much larger than the equilibrium value and trends up with decreasing film thickness. For films less than 400 nm in thickness, the transformation temperature decreases rapidly with decreasing film thickness. Cross-sectional TEM analysis reveals small composition shifts in the immediate vicinity of the film interfaces, but not in the bulk of the films, ruling out any composition effects

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on the transformation temperature. A simple micro-mechanics model is used to explain the observed size effects.

Keywords: Shape memory alloy thin films; Martensitic phase transformation; Substrate constraint; Thickness effect.

1. Introduction

Shape memory alloy (SMA) thin films, especially those based on NiTi, have been studied extensively over the last few decades because they are promising candidate materials for actuators in microelectromechanical systems (MEMS) (Ishida et al., 1995; König et al., 2011; McCluskey et al., 2011; Miyazaki and Ishida, 1994; Tomozawa et al., 2009; Wolf and Heuer, 1995). Several reviews of SMA process technology can be found in the literature (Fu et al., 2004; Ishida and Martynov, 2002; Winzek et al., 2004), while a detailed summary of the physical metallurgy of NiTi-based SMAs has been published by Otsuka and Ren (Otsuka and Ren, 2005). The high degree of miniaturization of current and future micro-devices has initiated efforts to develop actuators based on very thin SMA films. Use of SMA films in these applications requires a good understanding of the effect of film thickness on their transformation behavior. The martensitic transformation in an SMA material involves a series of complicated morphological changes in which martensite variants are formed to accommodate the large transformation strains (Otsuka and Wayman, 1999). The energy cost associated with the compatibility strains and with the formation of the various interfaces naturally resists the martensitic transformation, an effect one would expect to become more important with decreasing length scale.

Models for the phase transformation behavior of an SMA film constrained by a substrate have been discussed at length in the literature (Roytburd, 1998a, b; Roytburd et al., 1998; Roytburd and Slutsker, 2001, 2002). In particular, Roytburd and co-workers proposed a model for the behavior of a single crystal SMA film on a substrate based on the thermodynamics of constrained transformations (Roytburd et al., 1998). However, few systematic experimental studies on constrained transformation of SMA films have been reported. Fu et al. (Fu et al., 2006)

used the substrate curvature technique to study the effects of film thickness on the transformation of $\text{Ni}_{49.8}\text{Ti}_{50.2}$ films on silicon substrates. They claimed that a minimum film thickness of approximately 100 nm is required to show a martensitic transformation because of surface oxidation and inter-diffusion of film and substrate. König et al. (König et al., 2012) reported on the film thickness dependence of the $\text{B2} \rightarrow \text{B19}$ martensitic transformation in $\text{Ti}_{51}\text{Ni}_{38}\text{Cu}_{11}$ thin films using the four probe resistivity method. They found that the transformation temperature initially decreases with film thickness because of the decreasing grain size, but increases sharply for thicknesses below 100 nm because of the high tensile stresses in the films.

There are several factors that complicate an experimental investigation of the transformation behavior of SMA thin films on substrates. The stress level in the films varies with film thickness and changes during the measurement because of thermal mismatch between film and substrate. NiTi thin films are usually deposited by means of sputtering. Unless the deposition is performed at elevated temperature, sputtered NiTi films are amorphous in as-deposited state and need to be crystallized with an appropriate heat treatment (Wolf and Heuer, 1995). The crystallization kinetics of NiTi thin films depends on the film thickness and slows down significantly for very thin films (Wang et al., 2008). The heat treatment may result in different grain sizes for films with different thicknesses and, if the films are very thin, surface oxidation and interfacial reactions between film and underlying substrate material (typically Si or SiO_2) during the heat treatment cannot be neglected. Clearly, film stress, film thickness, grain size, surface oxidation, and interfacial reaction all play a role in the transformation behavior of SMA films making interpretation of the transformation behavior a challenge.

This paper presents the results of an experimental study of the transformation behavior of submicron near-equiatomic NiTi films supported by a substrate. In this study we have tried to

overcome the issues mentioned above by using substrates made of a range of different materials. By controlling the thermal mismatch between film and substrate, it is possible to independently evaluate the effects of both film thickness and film stress on the martensitic transformation. The heat treatment of the near-equiatomically sputtered NiTi films used in the study was tailored to maximize the NiTi grain size in the films and thus eliminate any grain size effect. Oxidation and interfacial reactions were minimized by sandwiching the NiTi films between SiN_x layers.

2. Experimental

Near-equiatomically NiTi thin films with thicknesses of 910, 470, 370, 290 and 190 nm were deposited by means of DC magnetron sputtering using NiTi and Ti targets in a confocal setup (Shih et al., 2001). The base pressure of the deposition chamber was below 5×10^{-8} Torr and the Ar working pressure was 1.5 mTorr for all depositions. The nominal target-substrate distance was 100 mm resulting in a deposition rate of approximately 12 nm/min. The substrates were rotated at a speed of 20 RPM to improve the composition and thickness uniformity of the films. The chemical composition of the as-deposited films was measured to be Ni-50.5 $\pm$ 0.2 at. % Ti by means of Rutherford backscattering spectrometry (RBS). The NiTi films were deposited onto four different types of substrates to control the stress in the films: Corning glass, Pyrex 7740 glass, (001) single-crystal silicon, and fused quartz, in order of increasing thermal mismatch with NiTi. Prior to the NiTi deposition, all substrates were coated with a SiN_x film (~50 nm in thickness) to ensure that the surfaces presented to the NiTi were identical for the different types of substrates. Immediately after deposition, a second layer of SiN_x (~30 nm in thickness) was coated onto the NiTi film surface to prevent oxidation of the films during the heat treatment. The SiN_x films were deposited with a NEXX Cirrus-150 plasma-enhanced chemical vapor deposition

(PECVD) system and the deposition conditions are listed in Table 1. The amorphous as-deposited NiTi films were crystallized by annealing them at a temperature of 450°C for 20 minutes in a vacuum furnace with a base pressure less than 5×10^{-7} Torr. During these heat treatments, the SiN_x coatings prevented reaction between the NiTi and the underlying substrate. Interfacial reactions in the NiTi/SiN_x system are significantly reduced compared to reactions in the NiTi/Si and NiTi/SiO₂ systems under similar thermal conditions (Wu et al., 2004). On cooling from the heat treatment, the thermal mismatch between the NiTi films and the various substrates resulted in different levels of residual stress in NiTi films deposited to the same thickness but on different substrates.

The annealing conditions were chosen based on a study of the crystallization kinetics of amorphous NiTi films (Wang et al., 2008; Wang and Vlassak, 2006), with a goal of precisely tailoring the microstructure of the films. Several factors went into the selection of the annealing conditions: First, the same heat treatment had to crystallize the as-deposited NiTi films over the entire range of film thicknesses. This was an important consideration because the crystallization kinetics in NiTi thin films is thickness dependent and slows down significantly for very thin films (Wang et al., 2008). Second, the main point of interest in this study was the effect of film thickness on the martensitic transformation. Consequently the ideal film microstructure was one where the grains were much larger than the film thickness. Such a microstructure was achieved by choosing annealing conditions that minimized crystallite nucleation, while allowing a reasonable crystallite growth rate. Under the selected annealing conditions crystallite nucleation occurred homogeneously inside the amorphous films, resulting in films with a random crystallographic texture (Wang and Vlassak, 2006).

The microstructure of the annealed films was examined using scanning electron microscopy (SEM, Zeiss Ultra55) and transmission electron microscopy (TEM, JEOL 2010 FEG, 200 kV). Cross-section TEM samples were prepared by mechanical tripod polishing and Ar ion beam milling. The phase composition of the films at room temperature was determined using X-ray diffraction with Cu-K α radiation on a Bruker AXS diffractometers in a θ - 2θ geometry. Scans were performed for $35^\circ < 2\theta < 55^\circ$, because the (002), (111) and (012) reflections of the B19' martensite phase and the (110) reflection of the B2 austenite phase occur in this range.

The martensitic transformation behavior of the annealed NiTi films was investigated by measuring the film stress as a function of temperature using the substrate curvature technique. Prior to the stress measurements, the specimens were dipped in liquid nitrogen for 5 minutes and allowed to come back to room temperature to insure that the NiTi films were in the low-temperature phase. The specimens were then thermally cycled between 15 and 120°C in a He atmosphere, while the curvature of the substrates was measured using a scanning laser beam (Witvrouw and Spaepen, 1993). Since the substrates were approximately three orders of magnitude thicker than the films, Stoney's equation could be used to calculate the film stress from the change in substrate curvature (Doerner and Nix, 1988). The biaxial moduli of the substrates used in Stoney's equation were 97.3, 80.0, 180.8 and 90.5 GPa for Corning glass, Pyrex glass, silicon and fused quartz respectively[†]. The stress levels in the PECVD SiN_x layers in both the as-deposited state and after heat treatment were determined from curvature measurements on a separate set of samples without NiTi films.

[†] Corning glass, Pyrex glass and fused quartz are from CORNING Inc. Elastic moduli of these glass substrates were obtained from the vendor's technical datasheets.

3. Results and discussion

3.1. Microstructure characterization

The microstructure of the crystalline NiTi films is illustrated in Fig. 1. Figure 1(a) shows a representative SEM micrograph of the surface of a 290 nm NiTi film. The surface relief caused by the martensite twins is quite evident in the micrograph. The average in-plane grain size of this film is approximately 15 μm , i.e., the aspect ratio of the pan-cake grains is approximately 50:1. Similar grain aspect ratios were also achieved for the other films. The large aspect ratio of the grains limits the interaction between adjacent grains and makes it possible to evaluate the effect of film thickness independent of the grain size. For all practical purposes, the films can be regarded as single-crystal films of random overall orientation. Figure 1(b) depicts a typical cross-section TEM micrograph of the 290 nm NiTi film. The micrograph shows that there remains an amorphous NiTi layer of approximately 15 nm at both the top and bottom interfaces after the heat treatment. TEM examination of the other films showed that these amorphous layers were present in all annealed films and that their thickness is independent of the NiTi film thickness. These amorphous layers are the result of a small shift in NiTi composition at these locations, as verified by scanning transmission electron microscope (STEM) measurements (Wang et al., 2008; Wang and Vlassak, 2006) and are instrumental in obtaining the special grain structure required for the samples. The heat treatment at 450 °C for 20 minutes is not sufficient to crystallize the amorphous layers, but they can be crystallized at a higher temperature. The inset electron diffraction pattern taken from grain 2 shows $1/3(110)$ superlattice reflections indicating that the grain is in the R-phase rather than the B19' martensite phase. Instability of B19' martensite is typical in our cross-sectional TEM specimens and may be attributed to changes in the stress state and distribution in the thin-foil geometry of TEM specimens. Figure 2 shows the

XRD spectra for the as-annealed NiTi films on Si substrates. Similar results were obtained for the films on the other substrates. The B19' martensite phase is dominant in all films except the 190 nm film, which has an austenite peak only. The scans further show that the martensitic films contain a small amount of residual austenite.

3.2. Stress-temperature curves

Figure 3 shows the residual stress in the as-deposited amorphous films at room temperature. The stress is tensile and increases slightly with increasing film thickness, indicative of a stress gradient through the thickness of the films. There is no statistically significant difference in the residual stress for films of a given thickness deposited on different types of substrates. This observation indicates that, thanks to the presence of the SiN_x coating, the structure of the as-deposited films is independent of the substrate material.

The transformation behavior of the crystallized NiTi films was characterized by measuring the stress-temperature curves during thermal cycling. Figure 4 shows typical stress-temperature curves for the films deposited on silicon substrates. These curves have the typical sigmoidal shape associated with a reversible martensitic transformation. Upon cooling from elevated temperature, the NiTi films initially consist of austenite and any variation in stress is due to the thermal mismatch between the film stack and the substrate. On continued cooling, the austenite transforms to martensite and the stress relaxes abruptly to a lower level because of the self-accommodating nature of the martensite twin structure. On subsequent heating, the reverse transformation to austenite leads to a complete recovery of the residual stress in the film. Figure 4 also shows that the stress in the austenite films varies with film thickness, but this is not necessarily a sign that there is a through-thickness stress gradient. The film stress in thermally

cycled metallic films often increases with decreasing film thickness because the yield strength of a thin film increases with decreasing film thickness (Vinci and Vlassak, 1996).

To investigate the effect of film stress on the martensitic transformation in the NiTi quantitatively, the stress in the crystalline NiTi layer of the film stack needs to be determined first. It is evident from Fig. 1(b) that the film stacks consist of five distinct layers: two layers of PECVD SiN_x , two layers of amorphous NiTi and one layer of crystalline NiTi. Upon transformation, the stress in the crystalline NiTi layer relaxes but the amorphous NiTi layers remain at a high stress level. To obtain the stress in just the crystalline NiTi layer, the contributions of the other layers need to be accounted for. This is especially important for the thinner films where the thickness of the other layers is comparable to that of the crystalline NiTi layer. If the SiN_x and the NiTi films (including both the amorphous and crystalline layers) have total thicknesses h_{SiN} and h_{NiTi} , respectively, the average stress in the film stack, σ_f , is given by the thickness-weighted average of the stresses in these layers

$$\sigma_f = \sigma_{\text{SiN}} \frac{h_{\text{SiN}}}{h_{\text{SiN}} + h_{\text{NiTi}}} + \sigma_{\text{NiTi}} \frac{h_{\text{NiTi}}}{h_{\text{SiN}} + h_{\text{NiTi}}}, \quad (1)$$

where σ_{SiN} and σ_{NiTi} are the stresses in the respective layers. The stress in the SiN_x films on the Si substrate was measured to be 348 ± 25 MPa and did not change appreciably over the temperature range of the curvature measurements. Given the stress in the SiN_x , the stress in the NiTi film is readily calculated using Eq. (1). After subtracting the contribution of the SiN_x coatings, the stress in the NiTi martensite (i.e., at room temperature) is still thickness dependent, increasing slightly with decreasing film thickness. This observation is somewhat surprising given the large recoverable strain associated with the martensitic transformation. Below we demonstrate that this thickness dependence does not arise because the transformation strain is

exhausted for the thinner films and thus unable to fully relax the stress in the films. Instead it is caused by the presence of the thin layers of amorphous NiTi. If we denote the amorphous and crystalline NiTi layers as layers a and c with thicknesses h_a and h_c , respectively, the stress in the NiTi film, σ_{NiTi} , is given by

$$\sigma_{\text{NiTi}} = \sigma_a \frac{h_a}{h_{\text{NiTi}}} + \sigma_c \frac{h_c}{h_{\text{NiTi}}}, \quad (2)$$

where σ_a and σ_c are the stresses in the respective layers. Rearranging Eq. (2) yields

$$\sigma_{\text{NiTi}} = \sigma_c + (\sigma_a - \sigma_c) \frac{h_a}{h_{\text{NiTi}}}, \quad (3)$$

According to Eq. (3), the stress in the crystalline section of the NiTi layer, σ_c , is given by the intercept on the stress axis of a graph of σ_{NiTi} vs. $1/h_{\text{NiTi}}$. The stress in the amorphous layers can be calculated from the slope. Figure 5 shows a graph of the stress in the NiTi layer at room temperature as a function of the reciprocal NiTi film thickness. Results for all NiTi films on silicon substrates are shown with the exception of the 190 nm film, which did not completely transform to martensite at room temperature. The stress in the martensite increases linearly with increasing reciprocal film thickness at a rate of 8.72 MPa· μm . Considering that $h_a = 30$ nm, we find that the stress in the amorphous NiTi has a value of 320 ± 42 MPa, while the stress in the martensitic NiTi is 28 ± 2 MPa. Similar analyses were conducted for the films on the Pyrex glass and fused quartz substrates and the results are summarized in Table 2. Evidently the stress in the martensite is independent of the substrate material, while the stress in the amorphous layer increases with increasing thermal mismatch between film and substrate.

3.3. Stress-related effects on transformation behavior

Figure 6(a) shows the stress in the crystallized NiTi films on the Si substrates as a function of temperature after correcting for the stress in the SiN_x and the amorphous NiTi layers. Similar results were obtained for the films on the Pyrex and fused quartz substrates and are shown in Figs. 6(b) and (c). It is evident that the hysteresis loops caused by the martensitic forward and reverse transformations shift to lower temperatures as the film thickness decreases. A direct comparison of the martensite transformation temperatures is misleading, however, because the films are at different residual stress levels when the transformation starts. The effect of stress on the transformation temperature is well documented for bulk materials (Otsuka and Wayman, 1999). For thin films, the effect of stress can be evaluated as follows. Figure 7 shows the stress-temperature curves for the 910 nm NiTi films deposited on three different substrates. The results obtained for the Corning glass substrate are not included here for reasons that will be discussed later. Because of the different thermal mismatches between film and substrate material, the stress in the austenite film is different for each type of substrate. Along with the different stress, there is also a shift in transformation temperature. Although the stress in the austenite film is different when the transformation starts, the transformation follows the same $\sigma(T)$ curve during the forward and reverse transformation. The key characteristic of the stress-temperature curve during the transformation is its slope $d\sigma/dT$, which is independent of the stress in the austenite. The values of the slopes measured in this study are plotted as a function of film thickness in Fig. 8. The slope rises from approximately 23 MPa/K for the 910 nm films to a little over 30 MPa/K for the thinnest films. Similar values were reported previously for sputter deposited NiTi films on substrates (Grummon and Zhang, 2001; Liu and Huang, 2004). Roytburd et al. (Roytburd et al., 1998) derived a modified Clapeyron-Clausius relationship to describe the equilibrium

transformation of austenite to martensite in a single crystal on a substrate and calculated a slope of approximately 7 MPa/K for a single-crystal NiTi film with a (110) orientation. The basic assumptions underlying this thermodynamic model are that the martensite plates are very thin compared to the film thickness and that the plates are finely distributed throughout the film. It was shown by Shu and Bhattacharya (Shu and Bhattacharya, 1998) that the recoverable strain for a film with a (110) texture should be the same as for a film with a random texture, so that the value of the equilibrium slope should be the same as well. By contrast much larger values of the slope are observed in this study. It has also been suggested that the slope is the result of a stress gradient through the thickness of the austenite film and that the temperature range over which the transformation occurs is a measure for the stress gradient in the film (Liu and Huang, 2004). The stress gradient model cannot explain, however, why the slopes in this study are significantly larger than the slope predicted by the thermodynamic model. If anything, a stress gradient would result in an even shallower slope. We will show later that the austenite to martensite transformation in a thin single-crystal SMA film on a substrate occurs at a fixed temperature that depends on the stress in the film, at least as long as the martensite plates form through the thickness of the film and the austenite is perfectly constrained by the substrate. The finite slope observed in the experiments can then be attributed to the relaxation of the stress in austenite adjacent to martensite plates, as well as to the grain-to-grain variation of the stress in the austenite that arises because of the elastic anisotropy of the austenite grains – larger thermal stresses develop in grains with larger in-plane moduli.

The results in Fig. 7 show that the stress in the martensite film is very small and independent of the stress in the austenite film. Furthermore, there is a temperature range over which the stress in the martensite is nearly constant, i.e., no thermal stress develops. Since most of the austenite

has transformed to martensite in this temperature range (e.g., see XRD spectra in Fig. 2), this region of stress invariance can be attributed to a simple rearrangement of the martensite variants on further cooling. Both of these observations are clear indications that the transformation strain is not exhausted by the stress drop as noted in the previous section (Roytburd and Slutsker, 2002).

When the thermal stress in the austenite is less than ~ 300 MPa, the transformation path from austenite to martensite is changed. Figure 9 shows the stress-temperature curve in a 910 nm NiTi film on a SiN_x -coated Corning glass substrate. The thermal mismatch between Corning glass and NiTi is small and as a result the residual stress in the austenite is quite low after annealing. As shown in Fig. 9, the stress-temperature behavior of this film is qualitatively different from the behavior for the other substrates. Rather than one stress relaxation step, there are two distinct stress drops on cooling. XRD results (not shown) indicate that the first stress drop is due to formation of the R-phase, while the second drop is caused by formation of B19' martensite. The presence of the R-phase is further confirmed by the small temperature hysteresis between the forward and reverse transformations that occurs if the film is reheated before the B19' phase forms (open symbols in the figure). This observation indicates that the film stress affects the transformation sequence and product, in agreement with reports in the literature that bulk NiTi material undergoes a two-step transformation, $B_2 \rightarrow \text{R-phase} \rightarrow B19'$, if the applied stress is low (Craciunescu et al., 2003; Stachowiak and McCormick, 1988). The reverse transformation, however, is a one-step transformation to austenite.

3.4. Thickness-dependent transformation behavior

As illustrated in Fig. 6 and Fig. 7, the martensitic transformation temperature shifts to lower temperature as the film thickness or the film stress decreases. The austenite-to-martensite transformation start temperature, M_s , and the film stress at which the transformation starts, σ_A ,

can be determined for each film as the point of first deviation in the cooling path of stress-temperature curve. Figure 10 shows the transformation temperature as a function of film stress and thickness. The figure demonstrates that the M_s temperature shifts to lower values as the film thickness decreases, while an increasing film stress has the opposite effect.

The effect of film thickness on the martensite transformation temperature is illustrated further in Fig. 11, which shows the M_s temperature at a reference stress of 500 MPa as determined from curve fits to the data in Fig. 10. The precise equation for the curve fit does not have a large effect on the result and will be discussed later. It is evident that the martensitic transformation shifts to lower temperatures as the film thickness decreases. The effect is small for thick films, but becomes quite pronounced for films thinner than 400 nm. The films in this study have a small composition shift in the amorphous layers at the NiTi/SiN_x interfaces (Wang and Vlassak, 2006). The crystalline layer, however, has the same near-equiatomic composition as the as-deposited amorphous film. The depression of the transformation temperature cannot be attributed to a shift in composition caused by a reaction with the SiN_x layers. The transformation temperature of the 290 nm film is approximately 25°C lower than that of the 910 nm film. If this change were due to a shift in composition, the entire film would have to be approximately 0.25 at.% richer in Ni, based on the composition dependence of the transformation temperature of bulk NiTi (Tang, 1997). If the 190 nm film is considered, the composition shift would have to be nearly 1 at.%. This is impossible for the annealing conditions in this study given the slow diffusion in amorphous NiTi (Janicki and Grundy, 1986). We conclude that the observed decrease in transformation temperature with film thickness is an intrinsic size effect.

It was reported in a TEM study by Waitz and coworkers (Waitz and Karnthaler, 2004; Waitz et al., 2004) that a two-step transformation, B2 → R-phase → B19', occurs in both isolated NiTi

nano-crystals embedded in an amorphous matrix and in nano-crystals in nanocrystalline alloys when the crystallite size decreases below a critical value. This transformation path leads to the formation of (001) B19' compound twins in the martensite. We have not seen any evidence for such a two-step transformation with decreasing film thickness, although a two-step transformation does occur for films with low values of residual stress. We also have not observed any (001) B19' compound twins in our films. It is possible that much smaller film thicknesses are required for the two-step transformation to occur or compound twins to form.

3.5. Micromechanics of constrained transformation behavior

We have investigated the transformation behavior of NiTi films constrained by a substrate. The effect of film thickness on the transformation temperature suggests that the substrate constraint has a significant effect on the transformation. Here we develop a simple micromechanics model to explain the observed effect.

As illustrated schematically in Fig. 12, a poly-domain martensite plate forms through the thickness of an austenite grain. Following our experimental results, we assume that the martensite variants in this plate are those that relax the stress in the plate to zero. The martensite plate also reduces the stress state in the adjacent austenite. If the spacing between the martensite plates is large compared to the film thickness, the stress in the adjacent austenite is only partially relaxed because of the constraint imposed by the substrate. The extent of relaxation depends on the precise geometry and the elastic mismatch between film and substrate. Here we only consider the limiting case where the stress relaxation in the austenite is negligible, i.e., the stress profile approaches a step function across the austenite/martensite interface. The free energy for such an austenite-martensite mixture constrained by a substrate is given by:

$$f(\alpha) = (1-\alpha)f_A^0 + \alpha f_M^0 + e(\alpha) + W_s(\alpha), \quad (4)$$

where α is the martensite volume fraction. The quantities f_A^0 and f_M^0 are the free energies per unit volume of the unstressed austenite and martensite. The term $e(\alpha)$ is the internal energy of the self-accommodated martensite, which consists of the energy associated with the various interfaces in the film and the elastic energy of the short-range internal stresses. This term can be written as $e_0\alpha$ where e_0 is the corresponding energy density (Roytburd et al., 1998). The term $W_s(\alpha)$ is elastic strain energy due to the residual stress in the austenite. Assuming isotropic elasticity and no stress relaxation in the austenite, Eq. (4) can be rewritten as

$$f(\alpha) = f_A^0 + \alpha(f_M^0 - f_A^0 + e_0) + (1-\alpha)\frac{\sigma^2(1-\nu)}{E}, \quad (5)$$

where E and ν are Young's modulus and Poisson's ratio of the film. It is evident from Eq. (5) that the transformation from austenite to martensite will occur if

$$f_M^0 - f_A^0 + e_0 = \frac{\sigma^2(1-\nu)}{E}, \quad (6)$$

i.e., the transformation starts and finishes at a single temperature, which depends on the austenite film stress. The resulting stress-temperature curve has an infinite slope at the transformation temperature. The infinite slope is the result of the rather simplistic assumption that no stress relaxation occurs in the austenite adjacent to the martensite plates. In actual practice, some relaxation does occur and the slope will be finite. In addition to stress relaxation, any stress heterogeneity in the film, either grain to grain or across the film thickness, will further act to reduce the slope. It should be emphasized that this simple model is valid only if the martensite plates grow through the thickness of the film with a width that is comparable to or greater than

the film thickness. The image in Fig. 1(a) suggests that this is a reasonable assumption for the films in this study. If the martensite plates are very thin and finely distributed throughout the film, the thermodynamic analysis by Roytburd and coworkers (Roytburd et al., 1998) should provide a better description. The model is also consistent with the observation that the stress-temperature slope increases when the grain size and hence the martensite plate width increases (Roytburd et al., 1998).

Using Turnbull's approximation, $f_A^0 - f_M^0 \approx L(T_0 - T)/T_0$, for the free energy in Eq. (6) shows that the transformation temperature increases with the square of the residual stress in the film:

$$M_s \approx T_0 + \frac{T_0}{L} \left(\frac{\sigma^2(1-\nu)}{E} - e_0 \right), \quad (7)$$

where T_0 is the stress-free equilibrium temperature between austenite and martensite and L is the latent heat of transformation. The data in Fig. 10 were fitted using this equation. The equation further indicates that the transformation temperature decreases with increasing internal energy density e_0 , i.e., with decreasing film thickness as we will demonstrate below.

When the austenite transforms to martensite, the large transformation strains are accommodated through the formation of a poly-domain microstructure that contains many martensite variants or twins and that minimizes the overall incompatibility between the martensite and austenite. The condition for the onset of the transformation can be written as

$$f_A^0 - f_M^0 = U_B, \quad (8)$$

where U_B represents the energy barrier to transformation, which comprises the energy per unit volume associated with the various interfaces, the elastic energy of the internal stresses, and an energy dissipation term we refer to as a friction term:

$$U_B = \Gamma_{PB} + \Gamma_{PA} + \Gamma_S + W_{PS} - W_{Au} + F_C. \quad (9)$$

The components of U_B are illustrated schematically in Fig. 13, which shows twinned martensite plates in an austenite film. Γ_{PB} is the interfacial energy between martensite plates; Γ_{PA} is the energy of the martensite/austenite interfaces; Γ_S is the change in interfacial energy between film and substrate or capping layer as a result of the transformation. W_{PS} is the strain energy caused by the interaction between the martensite plates and the substrate or the capping layer. F_C is the friction term that represents the work dissipated per unit volume of martensite as a result of inelastic processes. This term scales with the degree of incompatibility between the austenite and the martensite and is in part responsible for the transformation hysteresis between heating and cooling (James and Zhang, 2005; Zarnetta et al., 2010). The term W_{Au} represents the strain energy associated with the residual stresses in the austenite. Because of its self-accommodating nature, formation of the martensite phase results in a local reduction of the residual stresses in the coating and hence in a reduction of the strain energy. Consequently, the presence of residual stresses in the austenite lowers the transformation barrier. The various energy terms in Eq. (9) scale differently with film thickness and martensite plate width. Writing these dependencies explicitly, we obtain

$$U_B = \frac{\gamma_{PB} + \gamma_{PA}}{d} + \frac{\gamma_S}{h} + w_{PS} \frac{d}{h} - W_{Au} + F_C, \quad (10)$$

where d represents the martensite plate width, h the film thickness, and where γ_{PB} , γ_{PA} , γ_S , and w_{PS} are defined through a term-by-term comparison of Eqs. (9) and (10). The friction term

depends on the incompatibility between the martensite and austenite crystal structures, and its scaling with microstructure is not clear. However, given that the transformation hysteresis does not change much with film thickness, we take this term to first order independent of any microstructural length scales. Minimizing the energy barrier with respect to d shows that the plate width scales with the square root of the film thickness. Equation (10) can then be rewritten as

$$U_B = 2\sqrt{\frac{(\gamma_{PB} + \gamma_{PA})W_{PS}}{h}} + \frac{\gamma_S}{h} - W_{Au} + F_C. \quad (11)$$

According to this expression, the barrier to transformation increases with decreasing film thickness. Using the Turnbull approximation, $f_A^0 - f_M^0 \approx L(T_0 - T)/T_0$, it is possible to estimate the transformation start temperature from Eqs. (8) and (11). Figure 14 shows the transformation start temperature as a function of film thickness based on material parameters for NiTi taken from literature (Waitz et al., 2007) as shown in Table 3. The experimental transformation temperatures obtained in this study are also shown. The theory clearly predicts the correct trend, but the experimental data drop off faster. The lack of quantitative agreement is of course not entirely unexpected given the complexity of martensitic transformation process and the uncertainty in the energy terms in theory.

4. Conclusions

The following conclusions can be drawn based on our experimental observations:

1. The grain size of sputtered NiTi thin films can be tailored by choosing an appropriate heat treatment to crystallize the amorphous as-deposited coatings. Very large grain

aspect ratios can be obtained for a wide range of coating thicknesses. These large aspect ratios ensure that the martensitic transformation is not affected by the grain size of the coatings.

2. By measuring the residual stress in SiN_x-capped NiTi coatings as a function of temperature using the substrate curvature technique, it is possible to evaluate the effects of film stress and film thickness on the martensitic transformation temperature even for very thin films. The martensite transformation temperature decreases rapidly with increasing film stress and decreasing film thickness.
3. The stress drop associated with the transformation occurs over a narrow temperature range, much narrower in fact than predicted by existing models. This observation is attributed to the constraint imposed on the NiTi coatings by the underlying substrate when the martensite plate size is on the order of the film thickness.
4. The decrease in transformation temperature with decreasing film thickness is not caused by a change in composition and must therefore be attributed to microstructural and geometric factors. A simple model shows that the energy barrier for the martensitic transformation indeed increases with decreasing film thickness, causing a commensurate decrease in transformation temperature.
5. The level of film stress can change the transformation sequence and product. If the residual stress in the NiTi films is low, a two-step transformation of B₂ → R-phase → B19' occurs instead of the direct B₂ → B19' transformation for films with larger residual stress.

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TABLES

TABLE 1. Deposition conditions of PECVD SiN_x film

Base pressure (Torr)	1×10^{-7}
Working pressure (mTorr)	10
Ar (sccm)	20
N ₂ (sccm)	5.8
SiH ₄ (sccm)	40
Microwave (W)	265
Deposition rate (Å/s)	1.1

TABLE 2. Results of stress determination in NiTi films

Substrate	Stress in SiN _x , σ_{SiN} (MPa)	Stress in martensite NiTi, σ_c (MPa)	Stress in amorphous NiTi, σ_a (MPa)
Pyrex	285 ± 31	32 ± 3	263 ± 43
Silicon	348 ± 25	28 ± 2	320 ± 42
Fused quartz	530 ± 47	22 ± 8	501 ± 140

TABLE 3. Material parameters for NiTi (Waitz et al., 2007)

Elastic constants of NiTi	$E = 58 \text{ GPa}, \nu = 0.42$
Interfacial energy	$\gamma_{PB} = 0.01 \text{ J/m}^2, \gamma_{PA} = 0.1 \text{ J/m}^2, \gamma_S = 0.1 \text{ J/m}^2$
Strain energy	$w_{PS} = E\varepsilon_T^2/2(1+\nu) = 2 \times 10^8 \text{ J/m}^3 (\varepsilon_T=0.1),$ $W_{Au} = \sigma_f^2(1-\nu)/E = 2.5 \times 10^6 \text{ J/m}^3 (\sigma_f=500 \text{ MPa})$
Work of friction	$F_c = 5.8 \times 10^6 \text{ J/m}^3$
Latent heat	$L = 1.85 \times 10^8 \text{ J/m}^3$
Temperature of chemical equilibrium	$T_0 = 370 \text{ K}$

LIST OF FIGURE CAPTIONS

Figure 1. Microstructure of a 290 nm NiTi film after the heat treatment. (a) SEM micrograph of the film surface showing the surface relief caused by martensitic transformation. (b) Cross-section TEM micrograph showing multiple layer structure of NiTi film. The inset electron diffraction pattern taken from grain 2 shows $1/3(110)$ superlattice reflections indicating the grain is in the R-phase.

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Figure 5. Film stacks on silicon substrates: Residual stress at room temperature as a function of reciprocal film thickness after subtracting the contributions of the SiN_x coatings.

Figure 6. Stress in the crystalline layers of the NiTi films as a function of temperature: (a) Films on silicon substrates; (b) Films on Pyrex substrate; (c) Films on fused quartz substrate.

Figure 7. Film stress in 910 nm film on different substrates as a function of temperature.

Figure 8. The slope $d\sigma/dT$ of the stress-temperature curve along the transformation path upon cooling.

Figure 9. Stress-temperature curve for a NiTi film on a Corning glass substrate. The inset shows the thermal history in the measurement; open symbols in the inset correspond to open symbols in the stress-temperature curve.

Figure 10. Transformation temperature as a function of film stress and film thickness. Curve fits are based on Eq. (7) in the text using the same coefficient B for the stress term for all data sets.

Figure 11. M_s transformation temperature at a film stress of 500MPa as a function of film thickness. Transformation temperatures were calculated at the reference stress using the curve fits in Fig. 10.

Figure 12. Stress profile inside the two-phase film.

Figure 13. Energy terms associated with transformation.

Figure 14. Comparison of the model with experiment for transformation temperature.

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(a)

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