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Transformation Characteristics of Sputter Deposited SMA Thin Film

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Experimental results often show that, with the substrate-attachment, transformation intervals and transformation hysteresis are different in comparison with that of the same thin film in freestanding condition. By reasonably assuming a stress gradient through the thickness of substrate-attached film, a layer-by-layer transformation sequence is proposed and the transformation interval and hysteresis are further analyzed. The analysis results show qualitative agreement with the experimental observations.

Keywords: thin film, SMA, surface morphology, stress, hysteresis

1. INTRODUCTION

Sputter deposited thin film is generally found in a stressed condition when the substrate is still attached [1,2]. The stress existed in the substrate-attached shape memory alloy (SMA) thin film is acting as a biasing force for repeatable shape change and is of crucial importance in their applications. The present research is to investigate the effect of the stress on the transformation characteristics of deposited SMA thin films. To distinguish from other types of stresses, the stress arises from substrate attachment is termed "*substrate-induced stress*". As expressed in equation (1), the substrate-induced stress ($\overline{\sigma}_{fm}$) is composed of three components namely, *intrinsic stress* ($\overline{\sigma}_{in}$), *thermal stress* ($\overline{\sigma}_{tm}$) and *transformation stress* ($\overline{\sigma}_{tr}$).

$$\overline{\sigma}_{fm} = \overline{\sigma}_{in} + \overline{\sigma}_{tm} + \overline{\sigma}_{tr} \qquad (1)$$

Intrinsic stress, formed during the deposition process, depends on the lattice mismatch between the substrate and deposited film. *Thermal stress* originates from the difference in coefficients of thermal expansion (CTE) between the deposited film and the substrate. *Transformation stress* refers to the stress change due to phase transformation. Once the deposition process is completed, if without further treatment, the intrinsic stress as well as the thermal stress evolution are fixed. During the subsequent thermal cycles, the most significant change in the substrate-induced stress is the change of transformation stress.

In substrate-attached SMA film, stress, strain and transformation temperature are interdependent. Such film often has a smaller transformation hysteresis than that of corresponding freestanding film [3-5]. The transformation hysteresis of substrate-attached SMA thin film and its controlling factors are not well understood. In the present research, the evolution of the substrate-induced stress in a NiTiCu SMA thin film and its effect on transformation interval and hysteresis are investigated both experimentally and theoretically. The approach taken in this study is applicable to examine the transformation characteristics of other substrate-attached NiTi-base shape memory alloy thin films.

2. EXPERIMENTAL PROCEDURES

$TiNi_{48.2}Cu_{1.8}$ thin film was co-sputtered at 450°C on 4-inch (100) Si wafer of 450μm thick. The deposited thin film was about 4.5μm thick. The substrate-induced stress was calculated based on curvature change of the substrate-attached film by using Stoney equation [6]:

$$\overline{\sigma}_{fm} = \frac{1}{6}\frac{Eh^2}{(1-\nu)\Delta R t} \qquad (2)$$

E and ν are respectively the Young's modulus and the Poisson's ratio of the substrate, h, t and ΔR are the substrate thickness, the SMA film thickness and the curvature radius change before and after deposition.

3. RESULTS AND ANALYSIS

Fig. 1 is the DSC result of the freestanding film peeled off from the substrate. The film has a one-stage transformation during both cooling and heating. The transformation temperatures are indicated. The hysteresis (A_f-M_s) is about 25°C, and the transformation interval for forward (M_s–M_f) and reverse (A_f-A_s) transformation is about 7°C and 8°C, respectively.

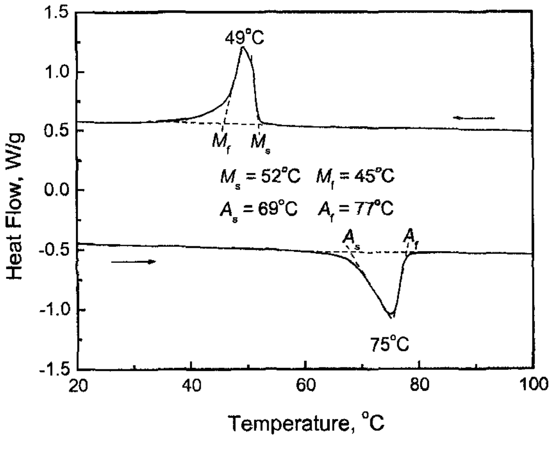


Fig 1. DSC result of a deposited $TiNi_{48.2}Cu_{1.8}$ freestanding thin film.

The evolution of the substrate-induced stress during thermal cycling is shown in Fig. 2. During cooling from deposition temperature of 450°C, the thermal stress is built up due to different thermal contraction between SMA thin film and Si-substrate. Such thermal stress was completely released during martensitic transformation. Upon heating and before the onset of reverse transformation, the substrate-induced stress slightly decreases with increasing temperature due to relaxation of thermal stress in martensite. When the temperature is above A_s, the stress began to increase drastically with further increasing the temperature. When above A_f, the stress began to decrease again with further increasing temperature due also to a relaxation of the thermal stress in austenite. When in austenite state, both cooling and heating curves coincide, suggesting only thermal stress was involved. Stress increase upon reverse transformation implies a constrained shape recovery while stress decrease upon forward transformation implies a stress-induced microstructure accommodation.

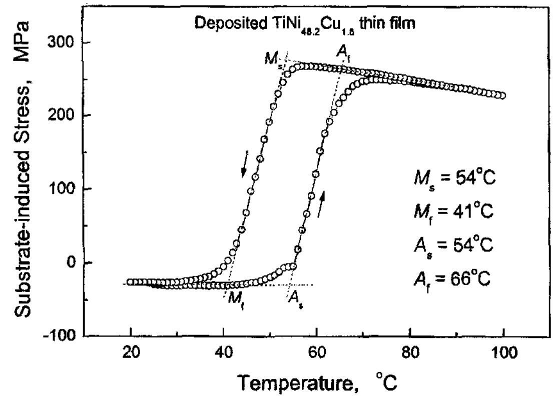


Fig 2. Substrate-induced stress of deposited TiNiCu film.

Determined from Fig. 2, the thermal stress relaxation rate, $d\bar{\sigma}_{tm}/dT$, is about –0.20MPa/°C and –1.1MPa/°C for martensite and austenite, respectively. The thermal stress relaxation rate can also be calculated [7]:

$$\frac{d\bar{\sigma}_{tm}}{dT}=\frac{E_{fm}(\alpha_{st}-\alpha_{fm})}{1-\upsilon} \tag{3}$$

E, υ, and α are respectively the Young's modulus, Poisson's ratio, and CTE. The subscripts *fm* and *st* denote the film and the substrate, respectively. The estimated CTE of the film was about 10.5×10^{-6}/°C for austenite and 6.5×10^{-6}/°C for martensite, agreeing well with the reported data. Taking 80 GPa for E_{fm} of austenite and 30 GPa for E_{fm} of martensite, 0.33 for ν and 2.6×10^{-6}/°C for α_{st}, the calculated thermal stress relaxation rate is about –0.17MPa/°C for martensite and –0.94MPa/°C for austenite. These values are in good agreement with the experimental results. The mean strain of the substrate-attached SMA film can be estimated through dividing the stress by the film's biaxial modulus [8]. If taking above values, the mean strain of this film is approximately 0.23% at M_s ($\bar{\varepsilon}_{Ms}$) and –0.07% at M_f ($\bar{\varepsilon}_{Mf}$). Obviously, the mean strain is much higher at M_s than that at M_f.

Using slope-line extension method, the estimated transformation temperatures are shown in Fig. 2. In the substrate-attached condition, the transformation intervals are wider and the hysteresis is much lower than those in freestanding mode. The substrate-induced stress was further differentiated with respect to temperature and the smoothed curve is shown in Fig. 3. The stress rate is nearly constant in both martensite and austenite regions. The constant stress rate is due to thermal expansion. Phase transformation deviates the stress rate from the constant value. As a result, a peak of the stress rate exists within the transformation region. The maximum stress rate, $d\sigma_{tr}/dT$, in both forward and reverse transformations is about 24MPa/°C.

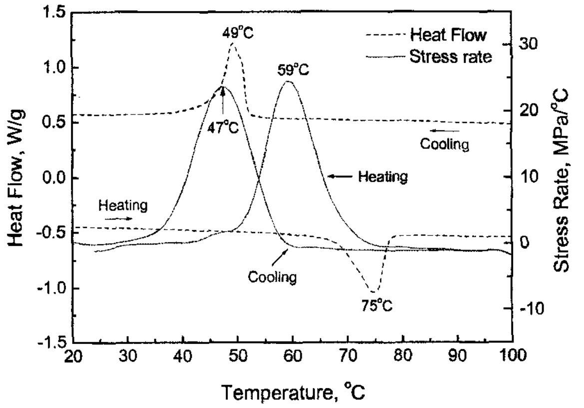


Fig 3. Substrate-induced stress rate as a function of temperature in $TiNi_{48.2}Cu_{1.8}$ film. DSC curve of the corresponding freestanding film is also plotted.

Based on the stress rate vs. temperature curve, the transformation temperatures can also be estimated by using the slope-line extension method. The estimated values are respectively, M_s = 57°C, M_f = 37°C, A_s = 50°C and A_f = 69°C. All these values are different from those determined based on stress-temperature curve in Fig. 2. Since the stress-rate is more sensitive to the change of the volume fraction of the transformation product than does the stress magnitude, the transformation temperature determined based on the stress-rate curve should be a closer estimation. If taking (A_f–M_s) as the transformation hysteresis, it is about 12°C for the substrate-attached film, a significantly lower value than that of the freestanding film (25°C).

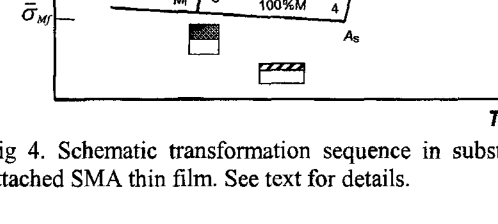
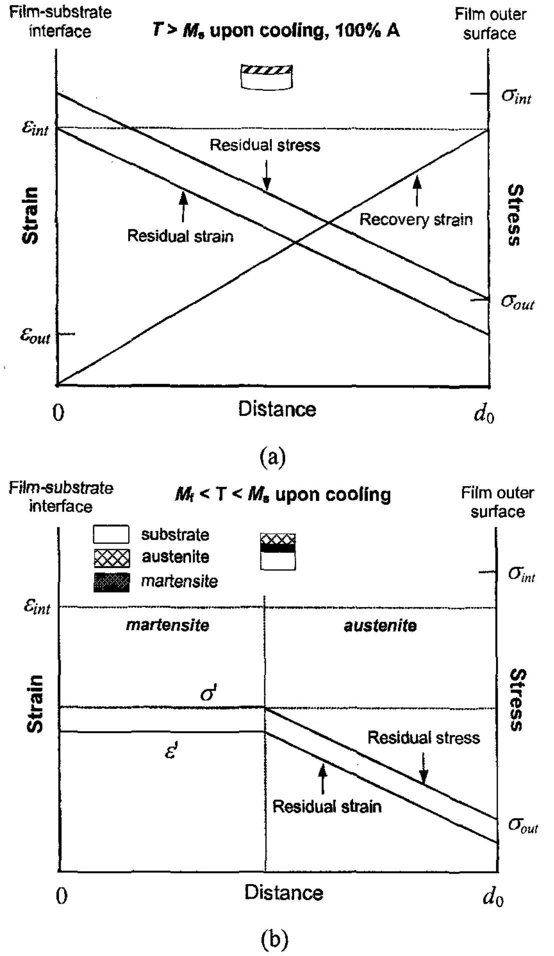


Fig 4. Schematic transformation sequence in substrate-attached SMA thin film. See text for details.

The temperature dependence of the average stress is schematically illustrated in Fig. 4. In the substrate-attached austenitic film, the residual strain is not evenly distributed through the thickness. At the film-substrate interface, the residual strain is the highest before forward transformation due to strong constraint exerted by substrate. On the outer film surface, the residual strain is the lowest due to relatively less-constrained shape recovery. Thus, above M_s, the film's residual stress at the substrate-film interface is the highest, while that at the outer surface layer is the lowest.

According to Clausius-Clapeyron equation, applied stress increases the transformation temperatures. Thus, the forward transformation will start from the substrate-film interface where the highest stress exists and thus the highest M_s temperature. During cooling and above M_s (point 1), the sample is completely austenitic. The overall average stress is $\bar{\sigma}_{Ms}$ which is the highest stress value experimentally determined. As soon as the martensite is formed (point 2), the stress is released, meanwhile, the stress is redistributed through the film thickness. The transformation front propagates outwards layer-by-layer through the film thickness. Due to strong constraint by the substrate, it is unlikely that the reverse transformation will start from the film-martensite interface. Upon reverse transformation (point 4), the austenite transforms from the film outer surface and the transformation front propagates inwards layer-by-layer.



(a)

(b)

Fig 5. Distribution of the residual stress and strain through film thickness upon cooling for (a) temperatures higher than M_s, and (b) between M_s and M_f.

The distribution of the residual strain and stress through the film thickness is illustrated in Fig. 5. σ_{int} refers to the residual stress of austenite at the substrate-film interface, while σ_{out} refers to the residual stress of austenite at the outer surface layer. Above M_s, the residual stress and strain are a linear distribution through the film thickness. In Fig. 5a, the lowest shape recovery corresponds to the highest residual strain, thus the highest residual stress at the substrate-austenite interface. As shown in Fig. 5b, during forward transformation, the overall stress relaxes due to self-accommodation of martensite variants. The residual strain as well as residual stress at the substrate-film interface decrease. During martensitic transformation, the stress redistributes through the film thickness. Similar to forward transformation, in the reverse transformation, the interfacial stress between martensite and austenite increases with increasing the volume fraction of austenite and plays a critical role in controlling the reverse transformation process.

Assuming a linear distribution of the stress from the substrate-film interface to the outer surface as shown in Fig. 5a, before transformation at $T = M_s$, we have,

$$\bar{\sigma}_{Ms} = \frac{\sigma_{int} + \sigma_{out}}{2} \quad \text{or} \quad \sigma_{int} = 2\bar{\sigma}_{Ms} - \sigma_{out} \tag{4}$$

$\bar{\sigma}_{Ms}$ is the average stress of austenitic film ($T = M_s$). When a martensite layer is formed, the force applied to the film is the sum of the forces shared by both martensite and austenite:

$$F_{fm} = F_M + F_A \quad \text{or} \quad \bar{\sigma}_{fm} A_{fm} = \bar{\sigma}_M A_M + \bar{\sigma}_A A_A \tag{5}$$

Alternatively, we have

$$\bar{\sigma}_{fm} = \bar{\sigma}_M V_M + \bar{\sigma}_A (1 - V_M) \tag{6}$$

Subscripts A and M denote austenite and martensite. F is the force, $\bar{\sigma}$ is the average stress, A is the cross-sectional area, V is the volume fraction. Based on the stress analysis shown in Figure 5b, during phase transformation, we further have

$$\bar{\sigma}_M = \sigma' \quad \text{and} \quad \bar{\sigma}_A = \frac{\sigma' + \sigma_{out}}{2} \tag{7}$$

Substituting Eq. (7) into (6) leads to

$$\begin{aligned} \bar{\sigma}_{fm} &= \sigma' V_M + \frac{\sigma' + \sigma_{out}}{2}(1 - V_M) \\ &= \frac{\sigma'}{2}(1 + V_M) + \frac{\sigma_{out}}{2}(1 - V_M) \end{aligned} \tag{8}$$

$$\text{and} \qquad \sigma' = \frac{2\bar{\sigma}_{fm} - \sigma_{out}(1 - V_M)}{1 + V_M} \tag{9}$$

From Fig. 2, the average stress in thin film is a function of volume fraction of martensite and it can be estimated experimentally. For simplicity, its dependence on temperature is assumed to be a linear function and can be expressed by the following simple equation:

$$\bar{\sigma}_{fm} = \bar{\sigma}_{Mf} V_M + \bar{\sigma}_{Ms}(1 - V_M) \tag{10}$$

Combining Eqs. (9) and (10) leads to

$$\sigma' = \frac{2\bar{\sigma}_{Mf} V_M + (2\bar{\sigma}_{Ms} - \sigma_{out})(1 - V_M)}{1 + V_M} \tag{11}$$

Equation (11) gives the estimation of the stress at the martensite-austenite interface as a function of volume fraction of martensite. It can be verified that when $V_M = 0\%$, $\sigma' = 2\bar{\sigma}_{Ms} - \sigma_{out}$ (the stress at the substrate-austenite interface). When $V_M = 100\%$, $\sigma' = \bar{\sigma}_{Mf}$, which is the average stress existed in the martensite and can be obtained from the experimental result shown in Fig. 2.

If $\bar{\sigma}_{Mf}$ is negligibly small as in the present case,

$$\sigma' = \frac{(2\bar{\sigma}_{Ms} - \sigma_{out})(1 - V_M)}{1 + V_M} \tag{12}$$

Employing Clausius-Clapeyron equation and neglecting the deduction details, we have:

$$\begin{aligned} M_s(\sigma'_{Ms}) - M_f(0) &= M_s(0) - M_f(0) + \left(\frac{d\sigma}{dT}\right)^{-1} \sigma'_{Ms} \\ A_f(\sigma'_{Af}) - A_s(0) &= A_f(0) - A_s(0) + \left(\frac{d\sigma}{dT}\right)^{-1} \sigma'_{Af} \end{aligned} \tag{13}$$

$[M_s(\sigma'_{Ms}) - M_f(0)]$ and $[A_f(\sigma'_{Af}) - A_s(0)]$ are respectively forward and reverse transformation intervals of substrate-attached film. $[M_s(0) - M_f(0)]$ and $[A_f(0) - A_s(0)]$ are respectively forward and reverse transformation intervals of the stress-free samples.

The above equations suggest that the transformation intervals of substrate-attached SMA thin film are always wider than those of stress-free sample of the same material. Such prediction agrees qualitatively with the experimental results shown in Fig 3. In addition to the present result, the transformation hysteresis has also been observed to decrease in various other substrate-attached SMA thin films [3-5] including NiTi, NiTiCu with Cu-content up to 25%, and NiTiPd thin films. Zero-hysteresis [3] and even "negative hysteresis" [9] have been reported.

It is known that the thermoelastic transformation is due to a local balance between chemical and non-chemical forces [10-13]. The equilibrium condition in thermoelastic transformation is that the chemical force equals to the non-chemical force,

$$\Delta H^{A\to M} - T\Delta S^{A\to M} = \Delta E_{el}^{A\to M} + \Delta E_{fr}^{A\to M} \tag{14}$$

$$\Delta H^{M\to A} - T\Delta S^{M\to A} = -\Delta E_{el}^{M\to A} + \Delta E_{fr}^{M\to A} \tag{15}$$

where ΔE_{el} is the change of elastic strain energy, and ΔE_{fr} the frictional energy. The stored elastic energy during forward transformation acts as driving force for the reverse transformation. It can be assumed that $\Delta E_{el}^{A\to M} = \Delta E_{el}^{M\to A} = \Delta E_{el}$, $\Delta E_{fr}^{A\to M} = \Delta E_{fr}^{M\to A} = \Delta E_{fr}$ and $\Delta S^{A\to M} = -\Delta S^{M\to A}$.

Near to the completion of the reverse transformation, the residual strain in the untransformed martensite layer reaches its maximum value. In such a transformation process, an extra chemical driving force is required to compensate the extra strain energy (ΔE_{ex}) needed for proceeding the transformation. The extra strain energy built up during the reverse transformation is a part of the driving force for the forward transformation. Thus, we have the following equilibrium condition for the substrate-attached SMA film.

$$T_0 - T^{A\to M} = \left(\Delta E_{el} + \Delta E_{fr} - \Delta E_{ex}^{A\to M}\right) / \Delta S^{A\to M} \tag{16}$$

$$T_0 - T^{M\to A} = \left(-\Delta E_{el} + \Delta E_{fr} + \Delta E_{ex}^{M\to A}\right) / \Delta S^{M\to A} \tag{17}$$

Re-arranging above equations we obtain an expression of transformation hysteresis (ΔT):

$$\Delta T = \Delta T_0 + \left(\Delta E_{ex}^{M\to A} - \Delta E_{ex}^{A\to M}\right) / \Delta S^{A\to M} \tag{18}$$

Where ΔT_0 is the transformation hysteresis under stress-free condition, $\Delta E_{ex}^{A\to M}$ and $\Delta E_{ex}^{M\to A}$ are respectively the extra strain energy for forward and reverse transformation. When $\Delta E_{ex}^{A\to M} = \Delta E_{ex}^{M\to A} = 0$, it is the stress-free condition. When $\Delta E_{ex}^{A\to M} = \Delta E_{ex}^{M\to A} \neq 0$, it is the conventional constraint shape recovery under uniaxial stress. In this case, the transformation hysteresis is unchanged and, in principle, it is the same as that of stress-free condition. However, if $\Delta E_{ex}^{A\to M} > \Delta E_{ex}^{M\to A}$, the transformation hysteresis decreases. According to Fig. 2, such assumption is experimentally valid. The stress level at A_f is lower than that at M_s. Such thermal stress difference is solely due to temperature difference between M_s and A_f. Further, the difference in CTEs between martensite and austenite should further add to the difference in thermal stresses between that at substrate-austenite interface ($T = M_s$) and that at substrate-martensite interface ($T = A_f$). By further taking into account Fig. 5 and equation (4), it is envisaged that the first austenite layer transforming to martensite should have been under a much higher stress level than that of the last martensite layer transforming to austenite. Thus, we can reasonably expect that $\Delta E_{ex}^{A\to M} > \Delta E_{ex}^{M\to A}$, and this is responsible for the observed decrease of the transformation hysteresis in substrate-attached SMA thin films.

4. CONCLUSIONS

This article presents an attempt to understand the effect of substrate-induced stress on the transformation interval and transformation hysteresis of sputter deposited NiTi-base SMA thin films. By assuming a stress gradient through the thickness of substrate-attached SMA thin film due to different amount of shape recovery, a layer-by-layer transformation sequence is proposed. The transformation front propagates from the substrate-film interface outwards during forward transformation and inwards during reverse transformation. The transformation interval and hysteresis are further analyzed based on above transformation sequences. The analysis confirms that, in the substrate-attached SMA thin films, due to the presence of the interfacial thermal stress, the transformation intervals increase while the transformation hysteresis decreases.

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REFERENCES

[1] P. S. Alexopoulos, T. C. O'Sullivan, *Annu. Rev. Mater. Sci.*, **20**, 391 (1990).

[2] T. A. Thornton, Coating Deposition by Sputtering, in *Deposition Technologies for Films and Coatings: Developments and Applications,* Edited by R. F. Bunshah, *et al.*, Noyes Publications, New Jersey, USA., 1982, Chapter 5, pp.170-243.

[3] B. Winzek, E. Quandt, *Mat. Res. Soc. Symp. Proc.* **604**, 117 (2000).

[4] B. Winzek, E. *Quandt, Metallk.*, **90**, 769 (1999).

[5] X. Huang, Y. Liu, S. F. Ling, H. H. Zhang, W. M. Huang, *Surf. Coat. Technol.* **167**, 148 (2003).

[6] W. D. Nix, *Metall. Trans.* **A20**, 2217 (1989).

[7] J. P. Zhang, D. S. Grummon, *Mat. Res. Soc. Symp. Proc.* **459**, 451 (1997).

[8] P. Krulevtich, A. P. Lee, P. B. Ransey, J. C. Trevino, J. Hamilton, M. A. Northrup, *J. Microelctromech. Syst.* **5**, 270 (1996).

[9] X. Huang, Y. Liu, *Proceedings of SPIE, Smart Materials II*, **4934**, 210 (2002).

[10] G. B. Olson, M. Cohen, *Scripta Metall.* **9**, 1247 (1975).

[11] H. C. Tong , C. M. Wayman, *Acta Metall.* **23**, 209 (1975).

[12] J. Ortin, A. Planes, *Acta Metall.* **37**, 1433 (1989).

[13] J. Ortin, A. Planes, *Acta Metall.* **36**, 1873 (1988).

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