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On the mechanism that leads to vanishing thermal hysteresis of the B2-R phase transformation in multilayered (TiNi)/(W) shape memory alloy thin films

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ABSTRACT

The film stresses in two-phase (TiNi)/(W) shape memory alloy (SMA) multilayer thin films were evaluated using synchrotron diffraction analysis. The phase transforming B2-TiNi phase is under tensile stress due to the mismatch of the coefficient-of-thermal-expansion ($\alpha_{B2\text{-}TiNi} > \alpha_W > \alpha_{Si\text{-}substrate}$) and the elastic modulus ($E_W > E_{Si} > E_{B2\text{-}TiNi}$) with respect to the bcc-W layers and the Si-substrate. The amount of stress on the B2-TiNi phase increases with increasing W amount in the film, which is proportional to the W layer thickness. This led to important changes in the behavior of the B2-R transformation. On cooling, a B2-R transformation proceeds under increasing tensile stress which increases the transformation start temperature (R_s). Upon transformation to the R phase, the TiNi layers undergo stress-relaxation by reorientation of R phase variants to accommodate the mismatch. During heating the film always starts from a relaxed stress-state, so the reverse transformation proceeds without adversely affecting the reverse transformation temperature (A_f). With increasing amount of W in the film R_s increases more on cooling, while A_f is not significantly affected on heating, and this leads to vanishing thermal hysteresis ($\Delta T_{B2\text{-}R} = A_f - R_s$).

1. Introduction

Micro-actuators driven by TiNi-based shape memory alloy (SMA) thin films can generate large recoverable strains and high-stress responses compared to other micro-actuator materials [1], making them attractive as powerful micro-actuators. Their functional behavior is due to the reversible martensitic transformation. A practical way to induce the shape memory behavior is by resistive heating and natural cooling. The driving frequency can be improved by reducing the thermal hysteresis (ΔT) of the phase transformation. Transformation temperatures higher than the operating ambient temperature can also reduce the time of cooling, due to an increased cooling gradient. Appropriate annealing and alloying are well-known methods to raise the transformation temperatures and also reduce the ΔT of TiNi-based SMA thin films [2].

Previously some of the authors introduced the concept of two-phase (TiNi)/(W) multilayer thin film SMA system where ΔT can be tailored with the amount of W [3]. The samples were made by annealing $(Ti/Ni/W)_n$ multilayer films to create a pseudo-binary (TiNi)/(W) multilayered two-phase system. By the annealing process the Ti/Ni layers are alloyed, while W undergoes negligible mixing, since it has limited solubility in the Ti-Ni phases. The W layer forms a bcc-W solid solution containing Ti and Ni within their respective solubility limit in bcc-W phase. When the atomic ratio of Ti:Ni is nearly equal, the TiNi layer forms the B2-TiNi phase by annealing. The B2-TiNi phase is responsible for the shape memory properties since it undergoes reversible martensitic transformation. The transformation path from B2-TiNi phase could either be a direct transformation to B19' phase (monoclinic martensite) or two-step path to R phase (trigonal martensite) and then to B19' phase. The presence of W phase changes the martensitic transformation path by suppressing B19' martensite transformation start temperature, M_s (R-B19' transformation with $\Delta T > 30$ K), while leaving the R phase transformation start temperature, R_s (B2-R transformation with $\Delta T < 3$ K), unaffected. This was clarified as due to grain size effects on the martensitic transformation paths of the B2-TiNi phase [4]. More interestingly it was discovered that the thermal hysteresis of the B2-R transformation ($\Delta T_{B2\text{-}R}$) can be reduced, just by adding appropriate amounts of W. This is a significant result as it presents a simple method to tailor ΔT and improve the driving frequency of TiNi-based SMA thin film actuators. However, the mechanism that leads to vanishing $\Delta T_{B2\text{-}R}$ in the Ti-Ni-W system still needs to be clarified.

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It is suggested that the physical-mechanical interaction between the W phase and B2-TiNi phase causes the observed behavior of $\Delta T_{B2\text{-}R}$. This paper explains the vanishing $\Delta T_{B2\text{-}R}$ behavior based on the development of film stresses during thermal cycling. The film stresses were evaluated from synchrotron diffraction analysis of multilayer (TiNi)/(W) SMA thin films.

2. Experimental

Using a combinatorial sputter deposition system (DCA Finland), Ti-Ni-W materials libraries were deposited from elemental sputter targets forming multilayer precursor films of $(Ti/Ni/W)_n$. After deposition, thermal annealing (500 °C for 1 h and 700 °C for 1 h) was carried out in high vacuum to alloy and induce phase formation of the as-deposited multilayer film. The internal structure of the films was observed by Scanning Transmission Electron Microscopy (STEM) with High-Angle-Annular-Dark-Field (HAADF) detector, revealing nanostructured layers of alloyed-TiNi and layers of almost immiscible W [3]. This structure is due to the limited solubility of W (<2 at.%,) in the TiNi phase, where the annealing step resulted in the formation of a pseudo-binary multilayered (TiNi)/(W) SMA thin film system. For this system the overall composition can be written as $(Ti_{100\text{-}y}Ni_y)_{100\text{-}x}W_x$. A more detailed description of the film preparation and phase characterization methods was reported previously [3,4]. The compositions of the films were measured in a scanning electron microscope (SEM, JEOL JSM 5800LV) equipped with an Oxford INCA 250 system, which consist of the INCA X-act energy dispersive X-ray (EDX) detector and INCA-EDX software for composition analysis. The phase transformation behavior was characterized by four-point probe electrical measurement during thermal cycling at a heating/cooling rate of 5 K-min^{-1}.

Selected samples were used for synchrotron diffraction experiments. These samples have a constant Ti:Ni atomic ratio of 55:45 in order to remove compositional influence on the phase transformation behavior of B2-TiNi. The selected samples exhibit only the B2-R phase transformation within the same temperature interval. They have different W contents of 4.4 at.%, 17.1 at.% and 28.1 at.%, and they represent the overall behavior of $\Delta T_{B2\text{-}R}$ with respect to W content. The nominal layer thicknesses of the W layer are 1.2 nm (4.4 at.%), 4.1 nm (17.1 at.%) and 6.7 nm (28.1 at.%). The synchrotron diffraction experiments were carried out in the synchrotron beam line at Stanford Synchrotron Radiation Lightsource (SSRL) SLAC MSD Hard X-rays, Menlo Park California USA. The wavelength of the beam was 0.09758 nm, and the sample to detector (2D area detector) distance was 150 mm. A LaB_6 standard sample was used for calibration of the experimental geometry, such as the beam center, rotation angle and angle of detector tilt. The films are substrate attached so they were measured using a glancing incidence set-up. The sample stage is equipped with a heater making it possible to perform diffraction experiments at various constant temperatures. The diffraction raw data were treated using fit2d software [5] and they were transformed into ASCII text format for residual stress analysis. Peak profile fitting using Gaussian function was employed to determine the diffraction peak positions as a function of ψ-angle. The stresses were calculated using the $\sin^2\psi$ method [6]. For a biaxial stress-state the analysis can be carried out using the linear equation:

$$\frac{d_{\varphi\psi}-d_0}{d_0}=\frac{1+\upsilon}{E}\sigma_\varphi\sin^2\psi-\frac{\upsilon}{E}(\sigma_{11}+\sigma_{22})\rightarrow y=m*x+b,\ \text{linear equation} \tag{1}$$

Where d_0 = unstressed d-spacing (normally estimated at $\psi = 0°$), $d_{\phi\psi}$ = d-spacing at ϕ and ψ, E = Young's Modulus, υ = Poisson number, σ_ϕ = residual stress in-plane, $\sigma_{11}+\sigma_{22}$ = stress components parallel to the surface of the film. The ψ angle is the tilt angle whereas the ϕ angle is the in-plane angle. The stress of the B2-TiNi phase is evaluated from the slope, m, as follows,

$$\sigma_\varphi=m*\frac{E}{1+\upsilon}*\frac{1}{d_0} \tag{2}$$

The elastic moduli used for the evaluation of stress in the TiNi layer were 84 GPa and 60 GPa, for austenite and martensite, respectively [7]. The Poisson ratio used was 0.3 for both austenite and martensite.

3. Results and discussion

3.1. Composition dependence of $\Delta T_{B2\text{-}R}$

Typical resistance-temperature curves, R(T), are shown in Fig. 1(a) for $(Ti_{55}Ni_{45})_{100\text{-}x}W_x$ films. The heating-cooling curves show reversible non-linear changes of resistance with temperature, that is typical of a B2-R transformation in TiNi based SMA. The transformation temperatures indicated as R_s and A_f, are the B2-R transformation start temperature and B2-R reverse transformation finish temperature, respectively. The hysteresis width ($\Delta T_{B2\text{-}R} = A_f - R_s$) for all samples is characteristically narrow, and varies with W content. For example when W is 4.4 at.% the value of ΔT is 1.9 K, it vanished to 0 when W is 17 at.%, and it shows a negative value when W is 28 at.%. Fig. 1(b) shows a plot of $\Delta T_{B2\text{-}R}$ as a function of W content for two sets of films annealed at 500 °C and 700 °C. The plot reveals that $\Delta T_{B2\text{-}R}$ decreases almost linearly with increasing W content, where it approaches zero and decreased further towards negative values. This behavior is not due to the Ti:Ni

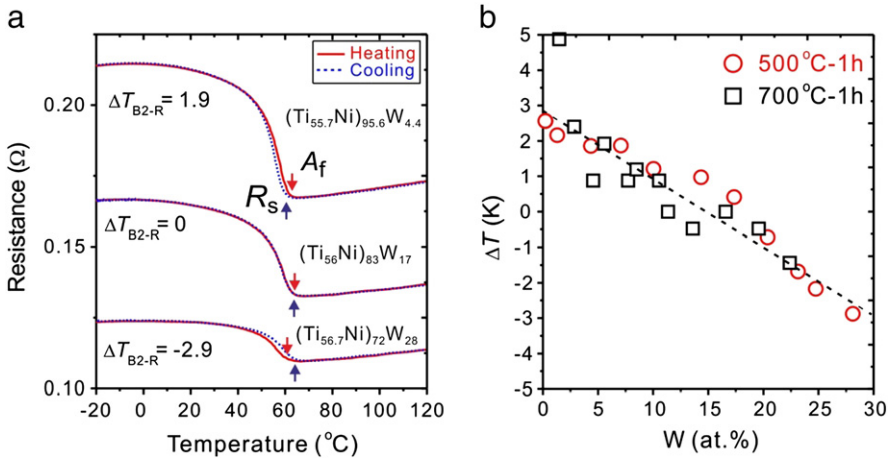

Fig. 1. (a) Resistance-temperature curves of $(Ti_{55}Ni)_{100\text{-}x}$-$W_x$ multilayer films annealed at 500 °C for 1 h. (b) Plot of $\Delta T_{B2\text{-}R}$ as a function W content for films annealed at 500 °C and 700 °C.