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Martensitic transformation in $Ni_{50}Ti_{50}$ films

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Abstract

The elasticity and anelasticity of $Ni_{50}Ti_{50}$ films deposited on Si substrates were studied, yielding information on the damping and modulus softening. It was found that the transformation behavior strongly depends on the film thickness and approaches bulk $Ni_{50}Ti_{50}$ behavior as the film becomes a few microns thick. For the same film thickness the transformation depends on the film–substrate adhesion. In films with good adhesion, cross-sectional transmission electron microscopy reveals a thin parent phase layer which does not transform, while the bulk part of the $Ni_{50}Ti_{50}$ film transforms. It is thus proposed that interface constraints stabilize the B2 structure. A microscopic interpretation in terms of transformation strains at the interface is given.

1. Introduction

As an actuator material, shape memory alloys (SMAs) suffer from low response speeds, since the memory kinetics is controlled by the thermal diffusivity. Laminates of thin SMA and Si films promise faster responses [1]. This promise has drawn attention to the shape memory effect in thin films [2–7]. Compared with this intense focus on applications, little is known concerning the nature of the structural transformation in film/substrate composites. A thin film SMA is not simply a thinner bulk material. Additional complications arise, the most important being the interface effect. Because the substrate does not transform at all, it imposes strong boundary constraints on the transformation. The nature and effect of this constraint are still unknown. Therefore an understanding of the interface accommodation for the thin film martensitic transformation is desirable.

The purpose of the current investigation is to study the influence of the film–substrate interface on SMA transformations. Systematic cross-sectional transmission electron microscopy (TEM) studies accompany the macroscopic mechanical measurements to gain direct insight to the microstructural mechanisms. Since mechanical damping is sensitive to microstructures in general and the martensitic transformation in particular, it is used as the main parameter guiding the thermal treatment of the SMA/substrate composites.

2. Experimental techniques

$Ni_{50}Ti_{50}$ films of various thickness were deposited on oxidized Si(100) substrates by d.c. magnetron sputtering. The target material was $Ni_{50}Ti_{50}$. The base vacuum in the deposition apparatus was in the range 6×10^{-8}–2×10^{-7} Torr and the films were sputtered in Ar at a pressure of 10 mTorr. The deposition rate was about 1 Å s^{-1} and the substrate was kept at room temperature during deposition. Each deposition run included four specimens deposited simultaneously, one of which was shadowed to provide a sharp edge for thickness detection by a Sloan Dektak thickness scanner with a resolution of a few nanometers. The as-deposited films have an internal stress as high as 700 MPa [7]. At these levels of stress any contamination of the substrate may result in the failure of the deposited films. Various substrates have been used for deposition, including Si, oxidized Si, quartz and glass. Films on all these substrates appeared to be adhering well in the as-deposited state, but showed adhesion problems after heat treatments. The only exception is SiO_2/Si with 2000 Å SiO_2 serving as a diffusion barrier, which shows very good adhesion through all heat treatments.

The damping was measured employing a clamped–free reed arrangement where the reed is comprised of the film/substrate composite [8–10]. The experimental arrangement permitted the determination of the stress [11] in the deposited film which was traced in the course of heat treatments and transformations.

The composition–depth profile of the films and its development with heat treatment were monitored by Rutherford backscattering (RBS). The crystal structure

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of the films was analyzed using X-ray diffraction and their microstructure was studied by both plane view and cross-sectional TEM.

3. Experimental results

A typical result of an RBS analysis is shown in Fig. 1, in which a RUMP [12] code simulated composition profile is plotted as curve 2. A comparison of the actual and simulated profiles shows that the NiTi film was $Ni_{50}Ti_{50}$ and had a constant composition profile. Heat-treated films display the same RBS pattern, indicating that the composition is not altered and no interface reactions occur. The as-deposited film exhibits a broad amorphous X-ray diffraction peak as reported before [2, 7]. Annealing at 560 °C leads to recrystallization of the film as indicated by the (110) peak of B2 $Ni_{50}Ti_{50}$ shown in Fig. 2(a). Further annealing at temperatures above 640 °C results in grain growth.

The X-ray diffraction spectra of co-processed films demonstrate clearly that well-adhering and detachable films exhibit different structures. The adhering films on SiO_2/Si always consist of strongly (110)-textured B2, while the non-adhering films on bare Si have already transformed to the B19 martensite structure, as shown in Figs. 2(a) and 2(b). A 1 μm poorly adhering film shows the same characteristics as Fig. 2(b).

Cross-sectional TEM characterization was difficult owing to the fact that the ion-beam-milling rate of $Ni_{50}Ti_{50}$ is much lower than that of SiO_2/Si. A special process was thus designed to prepare good TEM cross-section specimens. A Model 590 tripod polish-mounting stage was used to grind the cross-sectioned specimen to a thickness of about 1 μm. The specimen was then ion milled at a very small angle until the film portion was a few thousand angstroms thick.

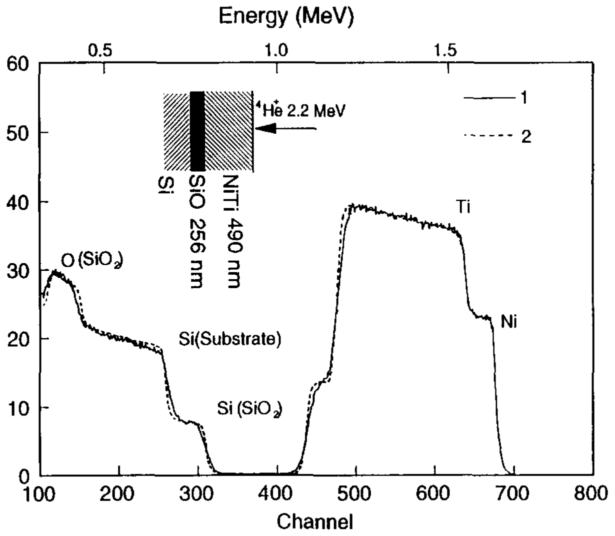

Fig. 1. RBS spectrum of as-deposited $Ni_{50}Ti_{50}/SiO_2/Si$. The dotted curve (curve 2) is the simulated spectrum.

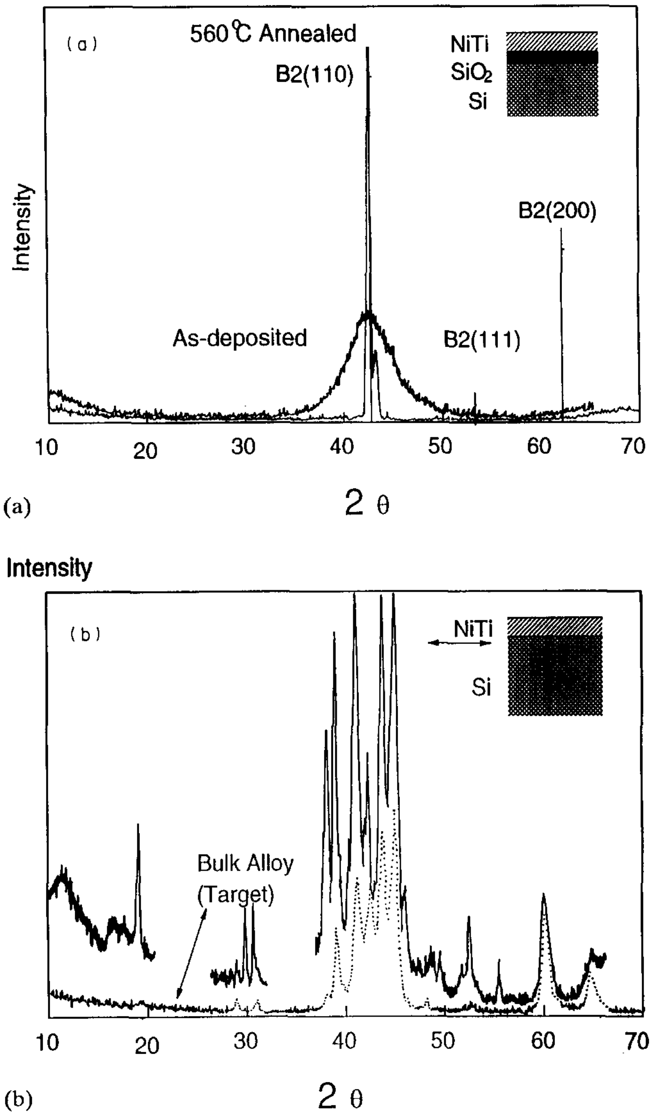

Fig. 2. (a) Room temperature X-ray diffraction spectra of a 2 μm $Ni_{50}Ti_{50}$ film on an SiO_2/Si substrate as deposited and annealed at 560 °C. Peaks associated with the B2 structure are indexed. (b) Room temperature X-ray diffraction spectrum of a 2 μm $Ni_{50}Ti_{50}$ film on an Si substrate annealed at 660 °C. The dotted curve is the spectrum of the target alloy, which is martensitic at this temperature.

Figure 3 shows a schematic micrograph of a crystallized film annealed at 560 °C. This film has a grain size of about 50 nm. The interlayer at the film–substrate interface has an even finer columnar grain structure. Microdiffraction data indicate that this interlayer consists of the same phase as the bulk of the film. The sharp film–SiO_2 interface suggests that there is neither reaction nor interdiffusion between film and substrate, confirming the RBS results. The interlayer retains its columnar grain structure upon further heat treatment. *An important observation is that the interlayer never*

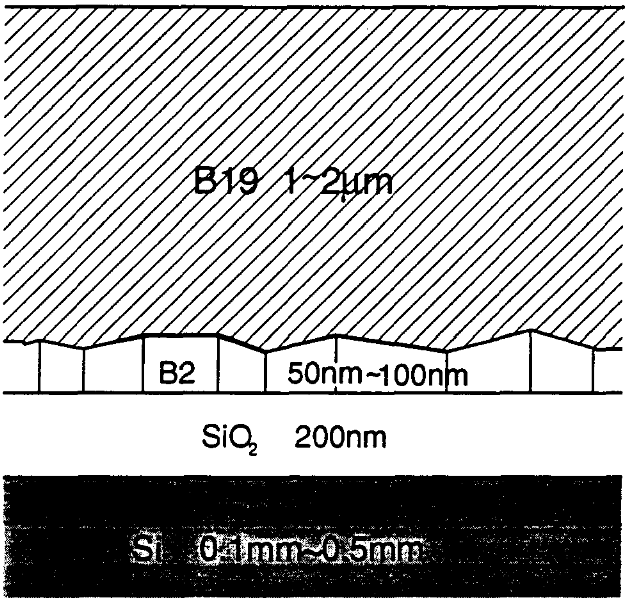

Fig. 3. Schematic cross-sectional transmission electron micrograph of an annealed $Ni_{50}Ti_{50}/SiO_2/Si$ specimen.

transforms even though the above layer shows a clear transformation microstructure. Such an untransformed interlayer consisting entirely of parent phase and about 50–100 nm thick has been found in films of various thicknesses.

The internal friction of the film/substrate composite reeds has been analyzed using the known equation [8, 12]

$$Q_c^{-1}=Q_s^{-1}+3\frac{E_f}{E_s}\frac{d_f}{d_s}Q_f^{-1} \qquad (1)$$

where Q^{-1}, E and d represent the internal friction, Young's modulus and the thickness respectively. The subscripts "c", "s" and "f" specify composite, substrate and film respectively.

The changes in internal friction due to the martensite transformation were determined from the difference given by eqn. (1) [12]. The results obtained for various film thicknesses are shown in Fig. 4. The internal friction of the target material is included as a reference. For $Ni_{50}Ti_{50}$ bulk material the change in internal friction at about 100 °C corresponds to the transformation from martensite to austenite (target material in Fig. 4). The transformation temperature is the same as that measured by differential scanning calorimetry. Curves referring to film thicknesses from 2 to 0.43 μm correspond to specimens annealed at 670 °C. Figure 4 shows clearly that the martensitic transformation behavior depends on the film thickness and tends to approach bulk characteristics as the film thickness approaches a few microns. The temperature interval in which the transformation occurs tends to increase as the film becomes thinner. It should also be noticed that below a certain grain size the transformation, if it occurs at all, does not take place in the temperature region accessible for this study (bottom curve in Fig. 4).

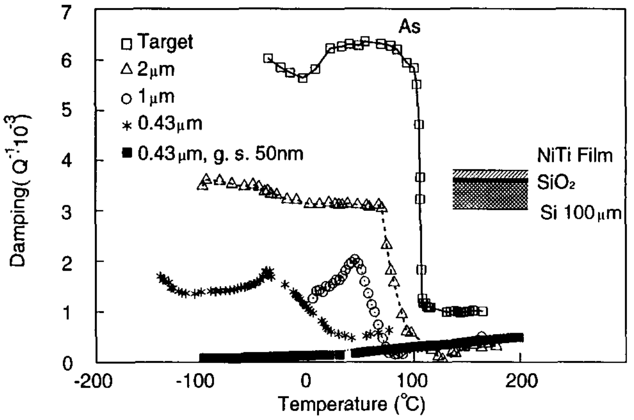

Fig. 4. Intrinsic internal friction of $Ni_{50}Ti_{50}$ films of various thicknesses. The substrate effect has been subtracted. Measurement frequencies are around 300 Hz.

4. Discussion

The martensitic transformation in NiTi alloys involves strains up to 8%. In the bulk this large strain is largely accommodated through twinning. In the present case of thin film martensitic transformations the semiconducting substrate cannot respond to the transforming film to accommodate the potential discontinuity at the interface. Therefore the transforming film has to accomplish the strain accommodation at the interface by itself. The untransformed interlayer observed by cross-sectional TEM is playing this role since it accommodates the strain through a gradient, eliminating the potential discontinuity at the interface.

The fact that the interlayer does not transform explains the thickness dependence of the internal friction measurements. As the film thickness is reduced to a few thousand angstroms and the thickness becomes comparable with the thickness of the interlayer, the transformation will not occur in the film. With increasing film thickness the influence of the interlayer decreases and the film behaves more like the bulk material.

The mechanism of interface stabilization of the parent B2 structure may be understood by considering the strong (110) B2 texture. The transformation requires (110) planes to shrink from the parent phase parameters $a_p=2.998$ Å, $b_p=4.240$ Å and $c_p=4.239$ Å to the parameters of the martensitic phase, $a_m=2.889$ Å, $b_m=4.120$ Å and $c_m=4.622$ Å. For ease of comparison these parameters are quoted in the parent phase coordinate system and indexed "p" for parent and "m" for martensite (see Fig. 5). It can be seen that an expansion as large as 10% occurs in the c direction

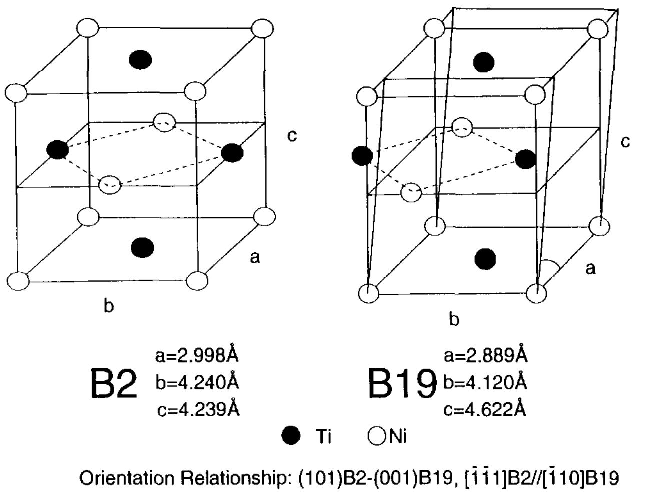

Fig. 5. Schematic unit cells of B2 and B19. The *c* axis was chosen along (110) in B2 and along (001) in B19.

perpendicular to the (110) plane. For a perfectly (110)-textured film the *c* direction is free of constraints so the martensitic expansion need not be accommodated in the film/substrate composite reed. However, the shrinkage of (110) planes is blocked at the film–substrate interface. Strong interfacial adhesion will thus stabilize the B2 structure. As the film thickness increases, a larger volume fraction of the film is sufficiently distant from the interface that its constraining effect is reduced. Hence the martensitic transformation will approach its bulk behavior for thicker films.

5. Summary

A parent phase interlayer was found to accommodate the martensitic transformation strain in $Ni_{50}Ti_{50}$ films deposited on SiO_2/Si substrates. If the overall thickness of the film approaches the thickness of the interlayer, at about 100 nm, the transformation is suppressed to temperatures below liquid nitrogen temperature. Films thicker than about 10 μm assume bulk transformation characteristics. If the constraint accommodated by the interlayer is released by poor film–substrate adhesion, even very thin films behave like bulk material. The texture of the film determines the sign of the average stress induced in the film by the martensitic transformation.

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