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Deposition and characterization of $Ti_{1-x}(Ni,Cu)_x$ shape memory alloy thin films

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Abstract

TiNiCu films with different Cu contents (up to 15 at.%) were prepared by co-sputtering of TiNi and Cu targets using a magnetron sputtering system. Film crystalline structure, phase transformation and shape memory behaviors were characterized by X-ray diffraction, differential scanning calorimeters (DSCs) and curvature method. The substitution of Ni by Cu in TiNi based films resulted in a dramatic change in martensite structure, film orientation and phase transformation behavior. With the increase of Cu content in the films, both the transformation temperatures and hysteresis decreased significantly. From DSC and curvature measurement results, the specific heat and the maximum recovery stress (corresponding to actuation force) generated during martensite transformation decreased with the increase of Cu contents, indicating the weak performance of phase transformation, especially at high Cu contents above 9 at.%. There was a maximum value for the stress increase rate (corresponding to actuation speed) at a Cu content of 9 at.%.

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1. Introduction

Thin film shape memory alloys (SMAs) have the potential to become a primary actuating mechanism for micro-actuators and biomedical applications [1,2], and great effort has been made to produce TiNi based thin films using a sputtering technique [3-10]. However, successful implementation of micro-actuators using TiNi based films requires a good understanding of the relationship among processing, microstructure and properties of TiNi films [11–13]. The shape memory characteristics of TiNi films depend significantly on metallurgical factors (such as alloy composition, annealing or aging temperatures) and sputtering conditions (such as argon gas pressure, plasma powers, substrate temperatures, etc.) [11]. Generally speaking, applications of SMAs for thermal and mechanical actuators (such as microvalves, micropumps, microgrippers, etc.) require large recovery stress, large transformation elongation and narrow transformation hysteresis (or fast response). Compared with the commonly studied TiNi binary alloys, the bulk TiNiCu alloys show less composition sensitivity to martensite transformation temperature, a narrower temperature hysteresis (thus quick actuation response), stabilization of shape memory effects, lower martensitic yield stress, suppression of Rphase transformation, increased damping capacity, superior fatigue property, etc., which make them more suitable for micro-actuator application [14–18]. So far there are a few studies on preparation and characterization of TiNiCu SMA thin films [19–22]. Successful implementation of micro-actuators using TiNiCu based films requires systematic studies on their transformation behaviors, especially for composite structures of Ti-NiCu/Si. In this paper, TiNiCu films with different Cu contents were prepared by co-sputtering of TiNi targets with separated Ti and Cu targets. Film microstructure and phase transformation behavior were characterized.

2. Experimental

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TiNiCu films were prepared by co-sputtering of TiNi, Ti and Cu targets using a magnetron sputtering equip-

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Table 1 Sputtering conditions and composition for four types of TiNiCu films

Sample	Target power			Composition			Film thickness
	TiNi (at.%) r.f. (W)	Ti DC (W)	Cu DC (W)	Ti	Ni	Cu	(µm)
TiNi	Ti50Ni50 (300)	32	0	50.2	49.6	0	4.5
TiNiCu4.5	Ti55Ni45 (300)	0	2.5	50.3	45.2	4.5	4.5
TiNiCu9	Ti60Ni40 (400)	0	8	50.1	40.8	9.1	3.5
TiNiCu15	Ti60Ni40 (400)	30	15	50.2	35	14.8	3.5

ment. The process parameters are listed in Table 1. The substrate temperature during deposition was 723 K. The base pressure of main chamber was less than 1×10^{-4} mTorr. Four-inch (1 0 0)-type silicon wafers were used as the substrates. The substrate holder was rotated during the deposition to achieve the uniform deposition. The substrate-to-target distance was 100 mm, and argon pressure was approximately 1–2 mTorr.

Film composition was determined using wavelength dispersive X-ray microanalysis using standard samples of pure Ti and Ni (purity, 99.99%), and the results are



Fig. 1. XRD analysis results for TiNi film with the change of temperature revealing the phase change during (a) heating and (b) cooling processes.

shown in Table 1. Transformation temperatures were measured using a differential scanning calorimeter (DSC, TA instrument 2920) at a heating/cooling rate of 5 K/min. The change of crystalline structures for the deposited films was analyzed using Philips PW3719 X-ray diffractor (XRD) at different temperatures. The stress changes as a function of temperature on a film-deposited wafer were measured using a Tencor FLX-2908 laser system with a heating and cooling rate of 0.5 K/min, from which the martensite transformation can be obtained [8,9,23,24].

3. Results and analysis

Fig. 1 shows the XRD results of TiNi films. At room temperature, film structure is mainly martensite (B19', monoclinic). With increase of temperature, martensite phase gradually changes to austenite as shown in Fig. 1a. During cooling process, the changes of diffraction patterns reveal clearly B2 to R-phase transformation as shown in Fig. 1b. The heights and widths of $(0\ 1\ 1)_{B2}$ peak decrease and broaden, and gradually split into two resolvable $(1\ 1\ 2)_R$ and $(3\ 0\ 0)_R$ peaks with decrease of



Fig. 2. DSC results for Ti NiCu films showing phase transformation during heating and cooling processes.



Fig. 3. Stress evolution as a function of temperature for TiNi and TiNiCu films with different Cu contents.

temperature. With further decrease in temperature, the remained austenite and R-phase gradually change to martensite. Fig. 2 shows DSC result of the TiNi films. During heating, a one-stage transformation is observed, corresponding to B19' to B2 transformation. During cooling, a two-stage transformation is observed, corresponding to transformations among B2, R-phase and B19' phase.

Fig. 3 shows stress evolution as a function of temperature for TiNi film. The stress vs. temperature plot shows a closed hysteresis loop. During heating, the stress increases significantly due to phase transformation from martensite to austenite, which forms the basis for cyclic actuation of the SMA/Si composites applicable to micro-actuator [8,23,25]. With further increase of temperature above austenite transformation finish temperature (A_f) , the transformation completes and generation of thermal stress occurs with the stress values decreasing linearly. The film intrinsic stress can be obtained by further extending the stress curves to deposition temperature of 723 K according to thermal stress changes. For TiNi film, the intrinsic stress value is 215 MPa, tensile. During cooling, tensile thermal stress develops in films. Cooling below martensite transformation start temperature (M_s) , martensitic transformation occurs and tensile stress drops significantly due to the formation and alignment of twins, shear-variant boundary motion and stress-induction of low-symmetry phases, etc. [8,25]. There is a small hump during cooling processes, indicating that there may exist a two-step transformation. The recovery stress, σ_{rec} , given by the difference between the maximum and minimum stress, is approximately 350 MPa.

XRD results of TiNiCu4.5 films are shown in Fig. 4. It reveals the existence of martensite (B19', monoclinic) at room temperature. With increase of temperature,



Fig. 4. XRD analysis results with the change of temperature for TiNiCu4.5 film revealing phase changes during heating process.

martensite gradually changes to austenite (B2, cubic), and vice versa during cooling process. No evidence of R-phase transformation can be found. Fig. 2 shows DSC results of TiNiCu4.5 films. During heating and cooling, one-stage transformation can be observed. The single peak on heating curve corresponds to martensite (monoclinic, B19') to austenite (B2, cubic) transformation, and the single peak on the cooling curve corresponds to austenite to martensitic transformation. Fig. 3 shows the measured stress as a function of temperature. The stress vs. temperature plot shows a closed hysteresis loop. During heating, the stress increases significantly due to the phase transformation from martensite to austenite. The intrinsic stress value for the film is -40 MPa, compressive. During cooling, tensile thermal stress develops in films. Cooling below M_s , martensitic transformation occurs and tensile stress drops significantly as explained above. The recovery stress is approximately 300 MPa.

XRD results for TiNiCu9 films during heating are shown in Fig. 5. It reveals the existence of martensitic (B19, orthorhombic) phase at room temperature. With



Fig. 5. XRD analysis results with the change of temperature for TiNiCu9 film revealing phase changes during heating process.



Fig. 6. XRD analysis results with the change of temperature for TiNiCu15 film revealing phase changes during heating process.

increase of temperature, the orthorhombic phase gradually changes to austenite (B2) phase, and vice versa during cooling process. No intermediate phase can be found. Fig. 2 shows DSC results of the TiNiCu9 films. During heating and cooling, a one-stage transformation can be observed, corresponding to transformation between B19 and austenite phase. Fig. 3 shows stress evolution as a function of temperature for this film. The stress vs. temperature plot shows a closed hysteresis loop. The intrinsic stress value for the film is 42 MPa, tensile. The recovery stress is approximately 190 MPa.

Fig. 6 shows XRD results of TiNiCu15 films at different temperatures. At room temperature, there is B19 (orthorhombic) phase and large amount of precipitates of $Ti_2(Ni,Cu)$ and $Ti(Ni,Cu)_3$ phases co-existed in the films. During heating process, B19 phase gradually changes to austenite, and vice versa during cooling process. The precipitates do not change apparently during heating and cooling process. DSC curve of TiNiCu15 film (see Fig. 2) shows only one broad peak during both heating and cooling, verifying the transformation between B2 and B19 phases. Fig. 3 shows the measured stress as a function of temperature for this film. The stress vs. temperature plot still shows a closed hysteresis loop. The intrinsic stress value is 158 MPa, tensile. The recovery stress is approximately 148 MPa.

4. Discussions

Films of TiNi, TiNiCu4.5 are very ductile, and when Si substrate is broken, the attached films still remain unbroken. TiNiCu9 film is still ductile, and micro-tensile testing is being performed to quantitatively evaluate film ductility. However, TiNiCu15 film is quite brittle, which is the same as reported that TiNiCu bulk materials with Cu content larger than 10% are so brittle that plastic deformation is almost impossible [16]. There is large



Fig. 7. Transformation temperatures for TiNi and TiNiCu films obtained from DSC and curvature methods.

amount of precipitates of $Ti_2(Ni,Cu)$ and $Ti(Ni,Cu)_3$ phases existed in TiNiCu15 films. These precipitates probably cause the brittleness of the film [26], since these oriented precipitates often exert long-range stress fields arising from coherency strains. Of course, the ductility of films also depends much on coating structure (e.g. columnar structure, porosity) or Ti/Ni composition, and detailed investigations are needed.

From both DSC and stress measurement results, transformation temperatures decrease with increase of Cu content up to 9%, while increase slightly with further increase in Cu content to 15% as shown in Fig. 7. The transformation hysteresis also shows a strong dependence on Cu content as shown in Fig. 8, in which both stress measurement and DSC results are shown. With the increase of Cu contents, the hysteresis decreases significantly with Cu content up to 9%, while with



Fig. 8. Transformation hysteresis for TiNiCu films obtained from both stress measurement and DSC results (above).



Fig. 9. Stress increase rates (the differentiated stress) vs. temperature for TiNi and TiNiCu films (right side).

further increase in Cu content, the hysteresis increases slightly. These results are identical to those of bulk TiNiCu materials [14–18]. TiNiCu films on Si substrate show narrower hysteresis (obtained from curvature method) compared with those for freestanding films obtained from DSC tests (see Fig. 8). It is well known that temperatures of phase transformation depend on the magnitude of residual or externally applied stresses. In the constrained TiNi and TiNiCu films on Si substrate, the residual stress caused by thermal and deposition processes, and stress evolution during heating and cooling processes could cause the changes in transformation behaviors. The stress in TiNi and TiNiCu films is biaxial plane stress. Tensile residual stress favors austenite to martensite phase transformation and promotes the martensite transformation, while it will hinder martensite to austenite transformation [27], thus making the hysteresis much smaller (see Fig. 8).

Fig. 9 shows the stress increase rates (the differentiated stress) vs. temperature for TiNi and TiNiCu films derived from Fig. 3. These curves show similar information for phase transformation to those from DSC curves in Fig. 2, but the obtained transformation temperatures are slightly different. Figs. 10 and 11 show the recovery stress and maximum stress increase rates vs. temperature for the films with different Cu contents. With the increase of Cu contents, the recovery stress, corresponding to the driving force to actuate microactuators, decreases to about half of the values with the increase of Cu contents up to 15%. From DSC results, the specific heat values of martensite to austenite trans-



Fig. 10. Recovery stress vs. temperature for TiNiCu films with different Cu contents.

formation also decrease with the increase of Cu contents in films (25.4, 25.08, 20.7 and 10.35 J/g, respectively, for four specimens), which shows that the transformation becomes weaker with the introduction of Cu contents in TiNi films. However, for the stress increase rate, there is a maximum value for film with Cu content of 9%, indicating that the actuation speed is maximum for TiNiCu9 film. From this point of view, TiNiCu9 film is probably more suitable for micro-actuator applications regarding to response time (hysteresis) and actuation speed (stress increase rate). Results also show that with the increase of Cu contents, phase transformation behaviors become less sensitive to Ti/Ni composition, which was well reported in Refs. [14–18].

The substitution of Ni by Cu in TiNi based films results in apparent change in martensite structure. TiNi film shows the typical B19' martensite phase at room temperature, with R-phase as an intermediate phase when cooling down from austenite phase. For TiNiCu film with Cu content of 4%, there is still transformation between monoclinic structure and austenite, but no R-



Fig. 11. Maximum stress increase rates vs. temperature for the films with different Cu contents.

phase is observed during heating and cooling. For TiNiCu9 and TiNiCu15 films, transformations between orthorhombic structures (B19) and austenite can be observed in these films. For TiNiCu films with different Cu contents, the preferred orientation of austenite phases is also guite different. Here we use the ratio of austenite peak intensities $(I(1 \ 1 \ 0)/I(2 \ 0 \ 0)/I(2 \ 1 \ 1))$ obtained from XRD results to roughly compare the texture of films. The ratio for random oriented TiNi austenite phase is 100:40:60. The ratios for TiNi, TiNiCu4.5, TiNiCu9 and T1NiCu15 films are 100:11:12, 100:23:59, 100:365:11 and 100:160:55, respectively. The above results indicate that without Cu addition into TiNi films, the preferred orientation is B2 $(1 \ 1 \ 0)$. With the gradual introduction of Cu into TiNi films, the preferred orientation of B2 (110) becomes weak, and at Cu content of 9%, there is a preferred orientation of B2 (200). With the further increase of Cu content, the preferred orientation is still B2 (200), but slightly weaker. The addition of Cu into TiNi films also significantly changes the lattice constants of austenite phases. The lattice constant of austenite phase for TiNi film is 0.3013 nm, which is close to that of TiNi binary alloys (0.3015 nm). With the increase of Cu contents from 0-15%, lattice parameters are 0.3013, 0.3028, 0.3036 and 0.3052 nm for four types of films, respectively, which means Cu elements are solid-solutioned into ternary TiNiCu alloys.

5. Conclusions

The substitution of Ni by Cu in TiNi films resulted in a dramatic change in martensite structure, film orientation and phase transformation behavior. With the increase of Cu content in the films, both the transformation temperatures and hysteresis decreased significantly. From DSC and curvature measurement results, the specific heat and the maximum recovery stress (corresponding to actuation force) generated during martensite transformation decreased with the increase of Cu contents, indicating the weak performance of phase transformation, especially at high Cu contents above 9 at.%. There is a maximum value for the stress increase rate (corresponding to actuation speed) at a Cu content of 9 at.%.

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