Martensitic Transformations in Sputter-Deposited Shape Memory Ti-Ni Films

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Composition and heat-treatment dependences of the martensitic transformations in sputter-deposited shape memory Ti-Ni films were investigated by differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). Films were deposited on quartz substrates by sputtering using a target of an equiatomic TiNi alloy. The substrate temperature was kept below 423K during sputtering. The compositions of the films were determined by electron probe micro-analysis using a calibration line prepared from bulk samples of well-established compositions. The as-deposited films were found to be amorphous and to crystallize on heating above 750K. The amorphous films were heat-treated at various temperatures between 673 and 1123K and the transformation behavior of the heat-treated films was examined by DSC and TEM. Obtained results are as follows. (1) During crystallization heat treatment, no precipitation occurs in near-equiaxial Ti-Ni films, whereas T2-Ni particles precipitate in the Ti-rich films and TiNi2 particles do in the Ni-rich films. (2) The B2→R transformation temperature becomes maximum (335K) at the equiatomic composition and decreases with increasing Ni-content with a rate of 96K/at.%Ni for 50.0-50.5at.%Ni alloys which becomes a single B2 phase when crystallized by holding at 773K. It is constant (335K) in the Ti-rich side range. It also is constant in the Ni-rich range (287K with the films crystallized by holding at 773K). (3) The B2→B19 transformation temperature becomes maximum at the equiatomic composition and decreases with increasing Ni-content. It is constant in the Ti-rich range.

**keywords:** transformation temperature, sputter-deposition, shape memory, thin film, titanium-nickel

I. Introduction

Ti-Ni alloy films obtained by sputter-deposition are attracting interests as prospective material for application to actuators of micromachines. There are several published works on the structures, martensitic transformations and related properties of Ti-Ni films aiming to examine their feasibility as material for microactuators (1-6). However, due to problems that chemical composition of a sputter-deposited Ti-Ni film is different from that of the target alloy used, and that the composition is not uniform in a deposited film, the understanding of the structures and properties of the sputter-deposited films is not sufficient yet.

From investigations made on bulk Ti-Ni alloy samples, we know that a slight change in composition results in changes in structures and properties, such as (1) the increase of Ni-content in the Ni-rich side reduces the temperature of B2→B19 transformation with a rate larger than 10K/0.1at.%Ni (7); (2) for alloys with Ni-contents exceeding 50.5at.%, TiNi2 phase precipitates by aging at a temperature below 873K (8-9); (3) for alloys with Ti-contents exceeding 50.0at.%, TiNi phase forms on cooling from the melt (10). Therefore, we need to investigate the structures and properties of sputter-deposited Ti-Ni films by using specimens of well-known compositions.

The present study was undertaken to establish the ways of controlling and analyzing composition of sputter-deposited Ti-Ni films, and to make clear the composition-dependence of microstructures of the films and their effects on the martensitic transformations and the shape memory property. Fundamental understanding of the structures and properties is essential to realize the shape memory actuators.

II. Experimental

Films were deposited on quartz substrates by sputtering in argon atmosphere using a sputtering target of an equiatomic TiNi alloy. The substrate temperature was kept below 423K during sputtering. The obtained films were heat-treated at various temperatures between 573 and 1123K for 3.6ks. The composition of the films were determined by electron probe micro-analysis using a calibration line prepared from bulk samples of well-established compositions. When a prealloyed target of Ti-50.0at.%Ni was used, sputter-deposited films showed Ti depletion and Ni enrichment, probably due to oxidation of Ti during deposition operation. Therefore, the composition was controlled by partially covering the alloy target by pure Ti. In this way, films with various compositions and with a thickness of 10 μm were obtained.
Another problem was that the composition of a deposited film was not uniform; Ti content was maximum at the center of the circular substrate-table and decreased radially with a rate of 0.04%/mm as will be shown later.

The martensitic transformation behavior of the heat-treated films was examined by differential scanning calorimetry (DSC) and the structures of the films were examined by transmission electron microscopy. Thin foils for electron microscopy were prepared from discs-shaped specimens using an ion miller.

A specially constructed apparatus was used to test the shape memory behavior. Using this apparatus, thermal-cycle tests under a constant load were made on the films. The specimen was cut from the central portion of the substrate as shown in Fig. 1. The gage length of the specimen was 9mm and the width was 2mm. The composition analysis of the specimen was made at the center of the gage length.

III. Results and discussions

1. Variation in composition of the sputter-deposited films

Composition of a sputter-deposited film was not uniform. Fig. 1 is an example which shows composition variation of a film formed on 50mm × 40mm quartz substrates placed on a holder of 80mm diameter. In the figure are shown the results of EPMA analysis performed on discs of 3mm diameter punched-out from the positions ①-⑥ of the substrate. The distance between ① and ⑥ is 17mm. The fact that the composition of the place ① is Ti-49.7at.%Ni and that of the place ⑥ is Ti-49.0at.%Ni shows that the Ti-content is maximum at the center of the circular holder and decreases with a rate of 0.04%/mm radially. For other several films with different compositions, we also confirmed that the Ti-content varies in the similar way and that the composition is identical at places on an identical circle on the substrate-holder. On the basis of this finding, disc specimens punched-out from an identical concentric circle of a film (see substrate in Fig. 1) were regarded to have the same composition.

2. Variation of transformation behavior due to heat-treatment

DSC investigation on martensitic transformations in Ti-Ni films with 46.8-51.5at.%Ni crystallized from amorphous state showed that transformation behavior changes depending on the heat treatment and composition. Fig. 2 shows the results of DSC measurement on Ti-46.8at.%Ni films crystallized by holding at 823K, 1023K and 1123K.

The DSC curve of the film crystallized by holding at 823K shows two peaks in both the cooling and heating processes. The first peak during cooling corresponds to B2→R transformation and the second one to R→B19' transformation. The two peaks in the heating process correspond to B19'→R and R→B2 transformations. We call this transformation type-A.

The curve of the film crystallized at 1023K shows two-step transformation of B2→R→B19' in the cooling process and direct transformation from B19' to B2 in the heating process.

![Diagram](image-url)

**Fig. 1** Composition gradience in a sputter-deposited Ti-Ni film and the position of thermal-cycle test specimen.

**Fig. 2** Three type of transformation which appear Ti-46.8at.% Ni alloy film depending on heat-treatment temperature for crystallization (T). (a) T=823K (b) T=1023K (c) T=1123K
We made similar DSC measurements on films of other compositions and found the following. Near-equatomic alloy films of single B2 phase with no precipitate-particles show the type-C transformation (one-step both during cooling and heating) for the first cycle. The films of Ni rich compositions show the type-A or type-B transformation if they are heat treated at a low temperature such that fine Ti₃Ni₄ particles precipitate. This is a confirmation of the knowledge with bulk samples.\(^{(11,12)}\).

The films of Ti-rich compositions show one of the three types of transformation behavior depending on composition and heat treatment. Fig. 3 shows composition and heat-treatment temperature dependences of transformation behavior. The type-A is shown by $\Delta$, the type-B is by $\square$, and the type-C is by $\bigcirc$. The general trend seen in Fig. 3 is the following. With a large off-stoichiometry and a low heat-treatment temperature, the type-A transformation occurs, and with decreasing off-stoichiometry and increasing heat-treatment temperature, transformation type changes from A to B and, to C. The appearance of type-A transformation with a large off-stoichiometry and a low heat-treatment temperature is a result of strengthening of the B2 matrix by the Ti₃Ni particles. Fig. 4 is a dark field electron micrograph showing fine Ti₃Ni particles dispersed in B2 matrix of Ti-46.8 at.%Ni film heat-treated at 773K. The strengthening suppresses the R→B19' transformation temperatures and has little effect on the B2→R temperatures, resulting in sufficient separation of B2→R and R→B19' transformations and also of B19'→R and R→B2. With decreasing strength of the B2 matrix due to decrease of off-stoichiometry and increase in particle size, the R→B19' transformation temperature increases and the transformation type changes from A to B and, to C. The strengthening effect is similar to that by Ti₃Ni₄ particles in alloys of Ni-rich compositions. Heat-treatment dependence of Ni-rich alloys will be discussed later.

We call this transformation type-B. With a specimen which shows the type-B transformation, if cooling is stopped before the start of R→B19' transformation, the reverse R→B2 transformation appears on subsequent heating.

The curve of the film crystallized at 1123K shows only one peak in both the cooling and heating processes corresponding to B2↔B19' transformation. We call this transformation type-C.

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**Fig. 3** Variation of transformation behavior due to changes in composition and heat-treatment temperature.

**Fig. 4** Dark field image of densely dispersed Ti$_3$Ni precipitate particles in a Ti-46.8 at.%Ni alloy film.

**Fig. 5** B2→R transformation temperatures of Ti-Ni alloy films crystallized by holding at 773K for 3.6ks, plotted against Ni contents.
transformation in the first cycle and B2→R transformation does not appear. However, repeated complete thermal cycling causes gradual decrease of the B2→B19' transformation temperature while it does not affect the B2→R transformation temperature, resulting in appearance of the B2→R transformation before the R→B19' transformation (33). For the films of near-equiatomic compositions, the peak temperatures of the B2→R transformation revealed in the above way were plotted in Fig. 5. The figure reveals that the B2→R transformation temperature is constant (335K) in the composition range of 46.8~50.0at.%Ni and also in the range of 50.5~52.6at.%Ni (287K) and that it decreases with increasing Ni-content with a rate of 96K/at.%Ni in the range of 50.0~50.5at.%Ni. The B2→R transformation temperatures in Fig. 5 are for the Ti-Ni films heat-treated at 773K. In order to know their dependence on heat-treatment temperature, DSC measurements were made on the Ti-46.8at.%Ni and Ti-51.5at.%Ni films crystallized by holding at several different temperatures. Obtained B2→R transformation temperatures of the Ti-46.8at.%Ni films are plotted in Fig. 6 and those of the Ti-51.5at.%Ni films are plotted in Fig. 7 against heat treatment temperatures for crystallization. It is seen in Fig. 6 that the B2→R transformation temperature of Ti-46.8at.%Ni alloy shows no heat-treatment temperature dependence. This is true for other Ti-rich alloys. This is considered to have resulted from the fact that in the Ti-Ni phase diagram the boundary between region of (Ti2Ni+B2) and single B2 is extremely steep and Ti-content of the B2 phase coexisting with Ti2Ni has no change with alloy composition and holding temperature. On the other hand, it is seen in Fig. 7 that B2→R transformation temperature of Ti-51.5at.%Ni alloy decreases with increasing heat-treatment temperature. This can be understood from the fact that the single B2 phase range in the phase diagram widens towards Ni-rich side with increasing temperature and thus Ni-content of the B2 phase in the Ti-51.5at.%Ni alloy increases with increasing holding temperature, resulting in decrease in the B2→R transformation temperature.

4. Composition dependence of the B19' transformation temperature

Temperatures of the R→B19' transformation (□) or of the B2→B19'(○), and those of the B19'→R(■) or of the B19'→B2(●) were plotted against Ni-content in Fig. 8. Alloys of the near-equiatomic compositions in the range from 49.6at.%Ni to 50.5at.%Ni show the direct B2→B19' transformation, i.e. the type C in the first cycle and B2→R transformation does not appear. For these alloys of type C transformation, the B2→B19' transformation temperatures for the first cycle were plotted in Fig. 8. In the alloys with Ni-content less than 49.6at.%, type A transformation (two-step both in cooling and heating process) occurs as was already shown in Fig. 3. The R→B19' transformation temperatures were plotted for these Ti-rich alloys in Fig. 8. These R→B19' transformation temperatures

3. Composition dependence of the R-phase transformation temperature

Utilizing the gradual composition change of 0.04at%/mm in the deposited films, composition dependence of the R-phase transformation temperature was examined. Films with Ni-contents between 46.8 and 52.6at.% crystallized by holding at 773K for 3.6ks were examined by DSC for the B2→R transformation temperatures. Obtained temperatures of the B2→R transformation (△) and those of the R→B2 (△) were plotted against Ni-content in Fig. 5. Alloys of the near-equiatomic compositions show the direct B2→B19'
Fig. 8 R→B19' transformation temperature of Ti-Ni alloy films crystallized by holding at 773K for 3.6ks, plotted against Ni-content.

Fig. 9 R→B19' transformation temperatures of a Ti-46.8at.% Ni alloy film, plotted against heat treatment temperatures for crystallization.

Fig. 10 R→B19' transformation temperatures of a Ti-5.15at.% Ni alloy film, plotted against heat treatment temperatures for crystallization.

B19' transformation temperatures for the Ti-rich alloys increase. An example of Ti-46.8at.%Ni is shown in Fig. 9. By heat-treatment at 1073K for 3.6ks this alloy shows the type B transformation. The level of the R→B19' transformation temperatures and that of the B19'→B2 are shown by the broken lines in Fig. 8. It is seen in Fig. 9 that with increasing heat-treatment temperature the temperatures of the R→B19' and B19'→B2 transformations approach those of B2→B19' and B19'→B2 of near-equiatomic alloys.

In the alloys of Ni-content of nearly 50.5at.%, the type B transformation occurs and in alloys of Ni-contents exceeding 50.5at.% the type A transformation (two-step both in cooling and heating process) occurs. The R→B19' transformation temperatures decrease with increasing Ni-content when the heat-treatment temperature is 773K. In order to know their dependence on heat-treatment temperature, DSC measurements were made on the Ti-51.5at.%Ni films crystallized by holding at several different temperatures. Obtained R→B19' transformation temperatures of the Ti-51.5 at.%Ni films are plotted in Fig. 10 against heat treatment temperatures for crystallization. It is seen in Fig. 10 that R→B19' transformation temperature shows no heat-treatment temperature dependence while the B19'→R transformation temperature decreases with increasing heat-treatment temperature. Reason for these changes is not clear yet at present.

5. Shape memory behavior

In order to examine the shape memory behavior of sputter-deposited films, thermal-cycle testings under a constant load
were made on several samples of different compositions and heat-treatments. Fig. 11 shows an elongation-temperature curve of a Ti-51.6at.%Ni alloy film crystallized by holding at 973K and aged at 773K for 3.6ks. The testing was made under a constant load of 117MPa. The film shows a very good shape memory. The first step at 307K during cooling is due to the B2 → R transformation and the second at 287K is due to the R → B19' transformation. Only one step appears at 307K in the heating process. This is due to the direct transformation from B19' to B2. Similar elongation-temperature curves were obtained for films of Ti-rich and near-equiatomic composition.

IV. Conclusion

As-deposited films are amorphous when the substrate temperature is kept below 423K during sputtering, and crystallize on heating above 750K. During crystallization heat-treatment, no precipitation occurs in near-equiatomic alloy films, whereas Ti,Ni precipitates in the Ti-rich films and Ti,Ni does in the Ni-rich films.

B2 → R transformation temperature becomes maximum (335K) at the equiatomic composition and decreases with increasing Ni-content with a rate of 96K/at.%Ni (in the range of 50.0-50.5at.%Ni when heat-treated at 773K). It is constant (335K) in the Ti-rich side range of the phase diagram of above 50.0at.%Ti. It also is constant in the Ni-rich range of above 50.5at.%Ni (287K when heat-treated at 773K).

B2 → B19' (or R → B19') transformation temperatures become maximum at the equiatomic composition and decrease with increasing Ni-content. They are nearly constant in the Ti-rich range when fully annealed.

The films show a very good shape memory.

References