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Crystallization of Sputter-deposited Ti-Ni Amorphous Thin Films

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The crystallization process of amorphous Ti-Ni thin films of various composition was investigated. The Ti-$Ni_{(x)}$ ($0.3<x<0.75$) thin films were fabricated by a r.f. magnetron sputter-deposition method. Crystallization temperatures of the thin films were measured by DSC with various heating rates of 5, 10, 20 and 30K/min. The thin films with Ni-content from 35 to 65at% were amorphous in an as-sputtered condition, whereas those with Ni-content more than 67.6at% were crystallized during the sputtering process. The crystallization temperature and activation energy exhibited the minimum value at the equiatomic composition, and increased with increasing Ni-content or Ti-content. The amorphous thin films with Ni-content between 35 and those with Ni-content of 64.7at% are crystallized to Ti-Ni and $TiNi_3$, respectively, by heating at the crystallization temperature.
Key words: Ti-Ni, sputtering, thin film, amorphous, activation energy, crystallization

1. INTRODUCTION

Ti-Ni alloys are considered to be one of the most promising materials for actuators of MEMS (micro-electro-mechanical systems) because of its large recovery strain and recovery force [1]. In order to apply the Ti-Ni alloy to MEMS, it is required to make them thin down to micron size. Rolling and melt spinning are available for making thin plates with a thickness larger than 20 μm. Only sputter-deposition is availed for making thin films with a thickness less than 10 μm. As-sputter-deposited Ti-Ni thin films are amorphous when deposited without heating substrates. Therefore, proper crystallization heat treatment is needed to induce the shape memory effect with large recovery force and strain. The shape memory behavior of Ti-Ni thin films crystallized at various temperatures has been investigated[2-8]. It is well known that the shape memory properties are sensitively dependent on microstructure. So the understanding of crystallization behavior of Ti-Ni thin films is necessary to obtain good shape memory properties. Although the crystallization behavior of Ti-Ni melt-spun ribbons and mechanical-alloyed powders have been reported in several papers, the crystallization behavior of sputter-deposited Ti-Ni thin films has been rarely investigated. In this study, the crystallization process of Ti-Ni amorphous thin films fabricated by a r.f. magnetron sputter-deposition method was investigated. The critical temperature and activation energy for crystallization were systematically investigated as a function of alloy composition. The variation of microstructure during crystallization was also discussed.

2. EXPRIMENTAL

Ti-Ni thin films were fabricated by a r.f. magnetron sputter-deposition method. The films were deposited on a Cu substrate in Ar atmosphere. The alloy compositions of the targets used were Ti-50.0at%Ni and Ti-60at%Ni, and small Ti plates were placed on either of the target in order to control the composition of the deposited thin films. The composition of the thin films was determined by the electron probe microanalysis (EPMA). The composition of the Ti-Ni thin films were controlled to Ti-36.9 ~ 73.9at%Ni. Crystallization temperatures of amorphous thin films were measured by a differential scanning calorimeter (DSC) with various heating rates of 5, 10, 20 and 30K/min. The activation energy for crystallization of amorphous Ti-Ni thin films was calculated by Kissinger method [10]. The structures and precipitates of as-sputtered and heat-treated thin films were determined by the X-ray diffraction (XRD).

3. RESULTS AND DISSCUSION

3.1 XRD analysis of as-sputtered films

In order to identify the phase of as-sputtered Ti-Ni films, XRD measurements were carried out. Fig.1 shows the XRD profiles of Ti-49:9~73.4at%Ni as-sputtered thin films. The small peak at $2\theta = 43.4°$ corresponds to the diffraction from the Cu sample holder used. An amorphous mound was observed in the profiles of Ti-49.9, 64.7 and 67.6at%Ni films. The amorphous mound was not observed in as-sputter-deposited films with Ni-content more than 68.3at%, while a diffraction peak corresponding to $TiNi_3$ was observed in the films with Ni-content more than 67.6at%. Furthermore diffraction peaks of Ti_2Ni_3 precipitates were also observed in the 73.9at%Ni thin film. This result indicates that the thin films more than 67.6at%Ni were crystallized to $TiNi_3$ during sputtering.

3.2 Crystallization temperature and activation energy

Fig.2 shows typical DSC curves of the amorphous Ti-49.9at%Ni thin films measured at various heating rates of 5-30 K/min. Each peak during continuous heating corresponds to the crystallization temperature. The peak shifted to higher temperature with increasing heating rate. The activation energy of crystallization of this thin film was estimated by the following Kissinger

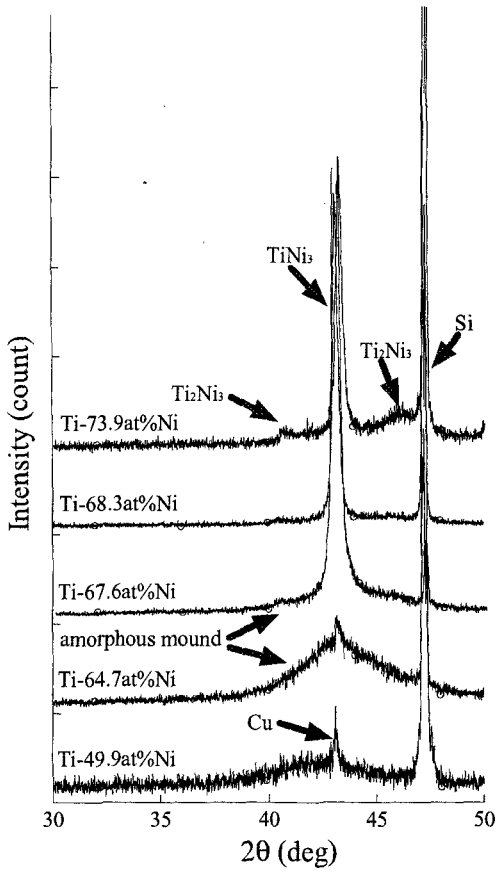

Fig.1 The XRD patterns for Ti-49.9~73.9at%Ni as-sputtered thin films

equation;

$$\ln(\alpha / T_p^2) = C - Q / RT_p \qquad \cdots(1)$$

where α is the heating rate, T_p the peak temperature of the DSC curve, C a constant, and Q the activation energy. The activation energy of crystallization of the Ti-49.9at%Ni was determined to be 254 kJ/mol. The activation energies of crystallization of Ti-Ni amorphous thin films with various compositions were determined in the same way.

Fig.3 shows the relationship between the crystallization peak temperature and composition of amorphous Ti-Ni thin films, the heating rate being 10K/min. The peak temperature became the minimum value at the near-equiatomic composition, and increased with increasing both Ni- and Ti-contents. The peak temperature in the Ni-rich region increased more steeply than that in the Ti-rich region. The peak was not observed in DSC curves of thin films with Ni-content more than 67.6at% because they were already crystallized to $TiNi_3$ and/or Ti_2Ni_3 during sputtering. Fig.4 shows the activation energy for crystallization as a function of Ni-content. Buschow [9] and Chen and Wu [11] have measured the activation energy of binary Ti-Ni bulk and thin film amorphous alloys by DSC using the Kissinger method. In this study, the peak temperature and activation energy became minimum at

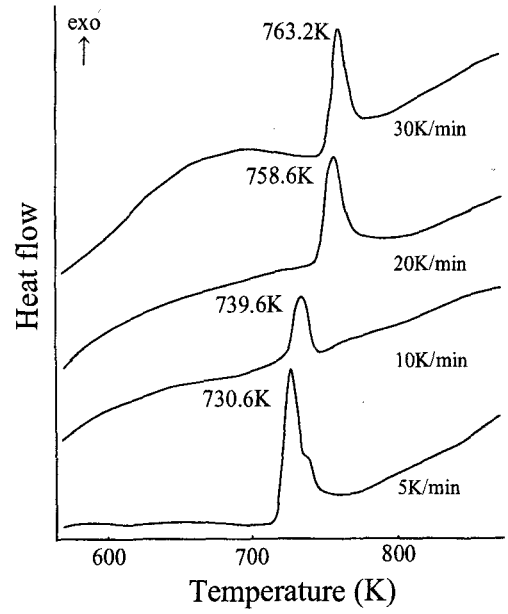

Fig.2 DSC curves with different heating rates for the Ti-49.9at%Ni thin film.

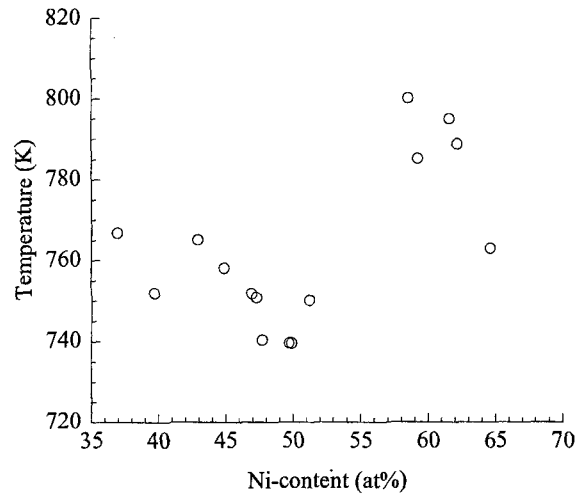

Fig.3 Relationship between the DSC peak temperature of crystallization obtained at 10K/min and Ni-content

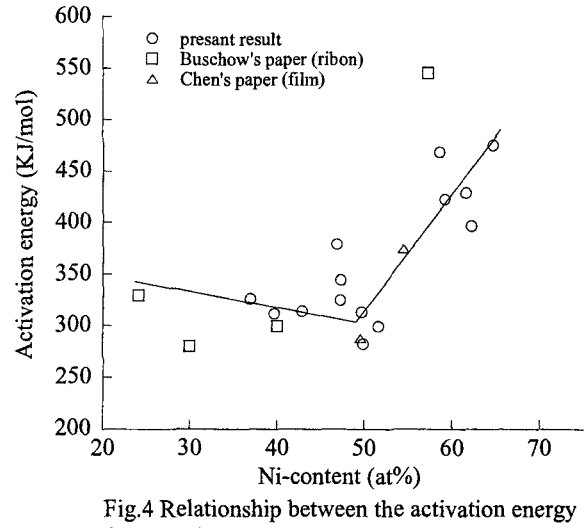

Fig.4 Relationship between the activation energy for crystallization and Ni-content

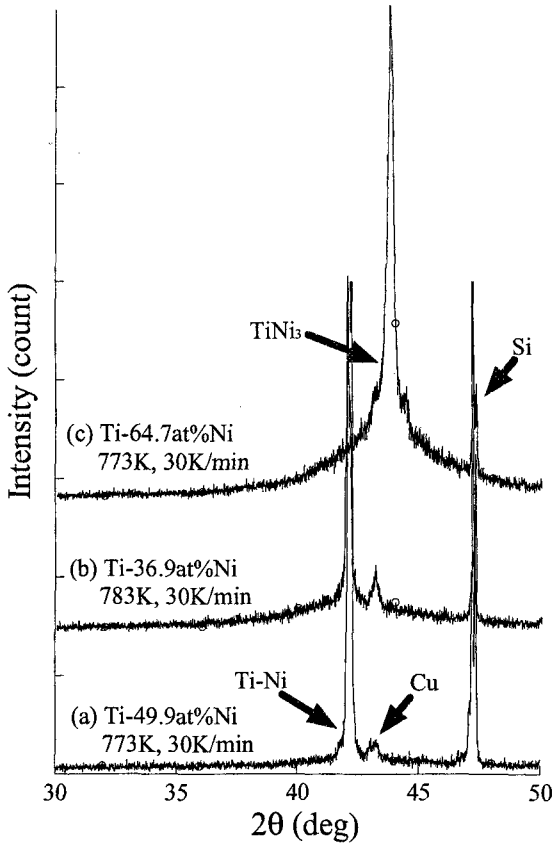

Fig.5 XRD patterns of (a) Ti-49.9at%Ni, (b) Ti-36.9at%Ni and (c) Ti-64.7at%Ni thin films.

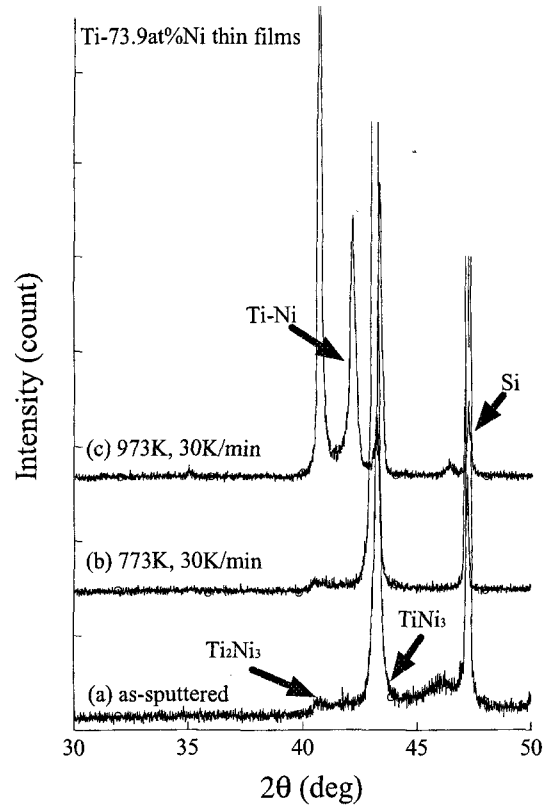

Fig.6 XRD patterns of Ti-73.9at%Ni thin films: (a) as-sputtered, (b) heated up to 773K and (c) heated up to 973K at 30K/min .

the near-equiatomic composition. Buschow reported that the minimum activation energy value appeared at a near-30at%Ni composition. In the present study, the amorphous Ti-Ni samples were fabricated by the sputtering method, while Buschow fabricated these amorphous Ti-Ni samples by melt-spinning. Although the fabrication process is different, Fig.4 including the present data and the past ones shows that the minimum value of activation energy appears at the equiatomic composition. The activation energy also shows a strong dependence on Ni-content in the Ni-rich region, while it shows a weak dependence in the Ni-poor region.

3.3 Crystallization behavior

Fig.5 shows the XRD profiles of Ti-36.9, 49.9 and 64.7at%Ni thin films heated up to each crystallization peak temperature obtained by DSC at 30K/min. The peak corresponded to Ti-Ni diffraction was observed in the 36.9 and 49.9at%Ni thin films. The peak corresponded to $TiNi_3$ diffraction was observed only for 64.7at%Ni thin film. Therefore, the peak temperature and activation energy of 64.7at%Ni correspond to the crystallization of $TiNi_3$. The peak corresponded to $TiNi_3$ was not observed in the diffraction profiles of 62.2 and 61.6at%Ni thin films heat treated up to each peak temperature. The composition near 64.7at%Ni, therefore, was considered to be boundary line of crystallization between TiNi and $TiNi_3$.

The peak temperature of crystallization was not observed in thin films with Ni-content more than 64.7at%. But the microstructure was changed by heat-treatment. Fig.6 shows the XRD profiles of as-sputtered 73.9at%Ni thin film. The XRD profiles after heated up to 773Kand 973K at 30K/min are also shown in Fig.6. There were peaks corresponding to $TiNi_3$ and. Ti_2Ni_3 in both the as-sputtered film and the film heated up to 773K. A diffraction peak from Ti-Ni was observed only in the specimens heated up to 973K in addition to those from $TiNi_3$ and Ti_2Ni_3.

The activation energy of crystallization to Ti-Ni in Fig.4 exhibited the minimum value at the equiatomic composition, and increased with increasing Ni- or Ti-content within the range of Ni-content less than 64.7at%. However, in the region of Ni-content more than 64.7at%Ni, the activation energy of crystallization to Ti-Ni is higher than the activation energy of crystallization to $TiNi_3$ and the activation energy of crystallization to $TiNi_3$ decreases with further increasing Ni-content. Thus the activation energy of crystallization to $TiNi_3$ became low enough to crystallize the Ti-Ni films with Ni-content more than 67.6at%Ni during sputtering.

4. CONCLUSION

(1) Ti-(36.9~64.7)at%Ni thin films were amorphous in as-sputtered condition, whereas, Ti-(67.6 ~ 73.9)at%Ni thin films were crystallized to $TiNi_3$ during sputtering.

(2) Ti-(36.9~62.2)at%Ni thin films were crystallized to Ti-Ni phase by heating. The crystallization temperature and activation energy became the minimum value at the equiatomic composition, and increased with increasing Ni- or Ti-content.

(3) Crystallization temperature and activation energy for crystallization of $TiNi_3$ are less than those for formation of Ti-Ni in Ti-Ni amorphous thin films with Ni-content more than 64.7at%Ni.

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