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Grain size and its distribution in NiTi thin films sputter-deposited on heated substrates*

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Grain size and its distribution in NiTi thin films sputter-deposited on a heated substrate have been investigated using the small angle x-ray scattering technique. The crystalline particles have a small size and are distributed over a small range of sizes for the films grown at substrate temperatures 370 and 420°C. The results show that the sizes of crystalline particles are about the same. From the x-ray diffraction profiles, the sizes of crystalline particles obtained were 2.40nm and 2.81nm at substrate temperatures of 350 and 420°C, respectively. The morphology of NiTi thin films deposited at different substrate temperatures has been studied by atomic force microscopy. The root mean square roughness calculated for the film deposited at ambient temperature and 420°C are 1.42 and 2.75nm, respectively.

Keywords: NiTi thin film, substrate temperature, crystalline particle size
PACC: 6110, 6480G

1. Introduction

Recently, shape memory alloys (SMAs) have attracted great research attention and their properties have been extensively studied to meet the increased demands for microactuators. NiTi is recognized as one of the most promising SMAs due to its fascinating properties such as larger deformation, large recovery force, high corrosion resistance, and excellent fatigue behaviour.[1,2] Several NiTi thin film micropumps and microvalves have been reported.[3] The martensitic transformation temperatures of NiTi SMAs are very sensitive to the composition, the size of crystalline particle, sputtering condition and heat-treatment condition.[4−9] The physical and chemical properties of NiTi thin films are found to have a close relationship with particle sizes and their size distribution.[4] However, to our knowledge, there is still no such report on NiTi film. In this work, the formation and growth of crystalline particles in NiTi thin films sputter-deposited on heated substrates are investigated using the small angle x-ray scattering (SAXS) technique and atomic force microscopy (AFM). The distribution of grain sizes in NiTi films is determined.

2. Experimental details

The NiTi thin films were deposited on mica and Si (111) substrates by DC magnetron sputtering in an argon discharge. The sputtering target was an equiatomic NiTi alloy, and substrate-to-target distance was 65mm. The sputtering conditions were as follows: base pressure, 1.0×10^{-3}Pa; argon pressure, 4×10^{-2}Pa; sputtering power, 280W; deposition rate, 15nm/min; the films were deposited on substrates heated at various temperatures between room temperature (RT) and 420°C.

The NiTi films on mica substrates with a thickness of about 2μm were characterized using SAXS and x-ray diffraction (XRD), and the morphology of NiTi films on silicon (111) was examined using AFM. The film composition was determined by energy dispersive x-ray spectroscopy, which showed that the film was Ti–51.45 at.% Ni. The SAXS experiments were carried out using a diffractometer with a four-slit system (RIGAKU D/max-rA). The widths of collimation slits were 0.04, 0.03 and 0.05mm, respectively, and the width of the detector slit was 0.1mm. Cu$K\alpha$

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radiation emitted from an x-ray tube with a current of 150mA and a voltage of 50kV was filtered by Ni foils, with the background intensity subtracted. XRD experiments were carried out using a diffractometer (D8 GADDS). AFM measurements were performed using commercial instruments (Digital Instruments, Nanoscope IIIA) with Si cantilevers. The AFM images were taken in tapping mode in air.

3. Results and discussion

The XRD results of the films deposited on mica substrates at RT, 350 and 420°C are shown in Figs.1 and 2.

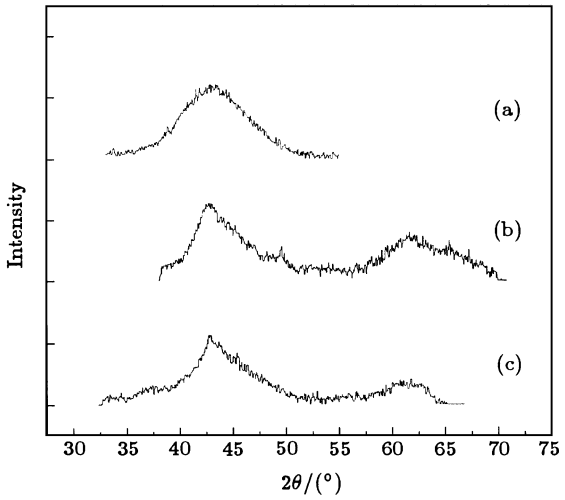


Fig.1. XRD profiles of the NiTi films deposited on (a) substrate at ambient temperature; (b) substrate at 350°C; (c) substrate at 420°C.

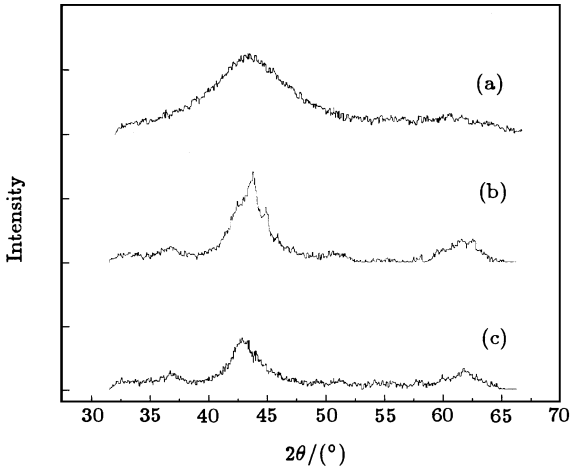


Fig.2. XRD profiles of the NiTi films annealed at 450°C for 2h for the films grown on (a) substrate at ambient temperature; (b) substrate at 350°C; (c) substrate at 420°C.

From Fig.1, the results reveal that the films deposited at RT are amorphous. The films deposited at substrate temperatures of 350 and 420°C are partly crystallized with B2 austenite structure. The peaks observed at 42.7° and 62.2° correspond to the B2(110) plane and B2(200) plane, respectively. The average grain sizes are obtained by the SAXS and XRD profiles.[10−12] Figure 2 shows the XRD results for the films annealed at 450°C for 2h. It is shown that the film deposited at RT is still amorphous even after annealing at 450°C. The nanocrystalline particles obtained at substrate temperatures of 350 and 420°C have gradually grown up. The sizes of crystalline particles obtained for the NiTi films deposited at 350 and 420°C are calculated to be 2.40 and 2.81nm, respectively. After annealing at 450°C for 2h, the grain sizes are about 3.95 and 4.80nm, respectively. The error of the calculated values is about ±0.05nm.

For an ideal two-phase structure having sharply defined phase boundaries, the asymptotic behaviour of the intensity curve is found to obey Porod's law,[13−17]

$$\lim_{S\to S_{\max}} [s^3 J(s)] = K'_{\mathrm{p}}, \qquad (1)$$

where $s = 2\sin\theta/\lambda$, 2θ is the scattering angle, λ is the wavelength of x-rays, K'_{p} is Porod's constant, and $J(s)$ is the SAXS intensity with the background intensity extracted. Equation (1) shows that the value of $s^3 J(s)$ approaches a constant as s increases to a large value. In SAXS experiments, background correction is important because the validity of Porod's law is sensitively affected by the background error. In the background correction, the x-ray intensity recorded when the sample is placed in front of the first slit is taken as the background scattering of the sample. From Fig.3, Porod's law is not satisfied for an amorphous NiTi film deposited at ambient temperature. There is a positive slope of the plots of $s^3 J(s)$ versus s. In this case, Koberstein *et al*,[18] Meng *et al*[19] and Li *et al*[20] considered that there is a micro-fluctuation of density with the size smaller than 1nm. Instead, Porod's law is satisfied for the films deposited on heated substrates. Chou and Turnbull[21] investigated the gradient of the concentration at the interface by using Porod's law, and found that the value of $s^3 J(s)$ should be constant at large s, if there was a sharp interface. According to this investigation, we believe that the NiTi films deposited on heated substrates should have a sharp interface between the crystallized and amorphous phases. The films deposited on substrates kept at 350, 370 and 420°C are crystallized ones. The in-

variant Q_s is calculated as described in Ref.[22]:

$$Q_s = \int_0^\infty sJ(s)\mathrm{d}s = \int_0^{s_1} sJ(s)\mathrm{d}s + \int_{s_1}^{s_2} sJ(s)\mathrm{d}s + \int_{s_2}^\infty sJ(s)\mathrm{d}s, \quad (2)$$

where s_1 to s_2 is the range of s in which the scattering intensities can be obtained immediately from experiment; 0 to s_1 is the range of s in which the scattering intensities can be obtained by extrapolation of the values of $J(s)$ which lie in the range from s_1 to s_2, and s_2 to ∞ is the range in which $s^3J(s)$ keeps constant. Hence, from Eq.(1) $\int_{s_2}^\infty sJ(s)\mathrm{d}s$ can be written as follows:

$$\int_{s_2}^\infty sJ(s)\mathrm{d}s = K'_\mathrm{p}/s_2, \quad (3)$$

The size distribution of the crystalline particles is calculated by log-normal distribution theory:[23,24]

$$P(R) = 1/[(2\pi)^{1/2}R\ln\sigma] \times \exp\{-[(\ln R - \ln\mu)/(2^{1/2}\ln\sigma)]^2\}, \quad (4)$$

where R is the radius of the crystallized particles, μ is the geometric mean of the distribution and σ is the square root of the variance of the distribution. The values μ and σ are determined by the following equations:

$$R_\mathrm{G} = \exp(\ln\mu + 6\ln^2\sigma), \quad (5)$$

$$R_\mathrm{P} = \exp(\ln\mu + 2.5\ln^2\sigma), \quad (6)$$

where R_G and R_p are the gyration radius and Porod's radius of the crystalline particles, respectively. The value of R_G is obtained from the slope of the $\ln J(h)$–h^2 plot at the low angle,[11] where $h = 4\pi\sin\theta/\lambda$. According to SAXS theory,[12] the average radius (R) of the crystalline particles is obtained by

$$R = \sqrt{\frac{5}{3}}R_\mathrm{G}. \quad (7)$$

The value of R_p[24,25] is obtained by

$$R_\mathrm{p} = 3Q_s/(8\pi K'_\mathrm{p}). \quad (8)$$

K'_p and Q_s can be obtained from Eqs.(1) and (2). In Fig.4, the size distribution curve, $P(R)$–R, is shown. One can see that the crystalline particles obtained at substrate temperatures of 370 and 420°C have small sizes and are distributed over a small range of size. These results show that the sizes of crystalline particles are about the same for the same substrate temperature. Kikuchi *et al*[26] also obtained the sizes of nanocrystals which were formed as the amorphous Ti-rich NiTi thin films were heated at 414°C, by high-resolution electron microscopy. The sizes of nanocrystals were about the same.

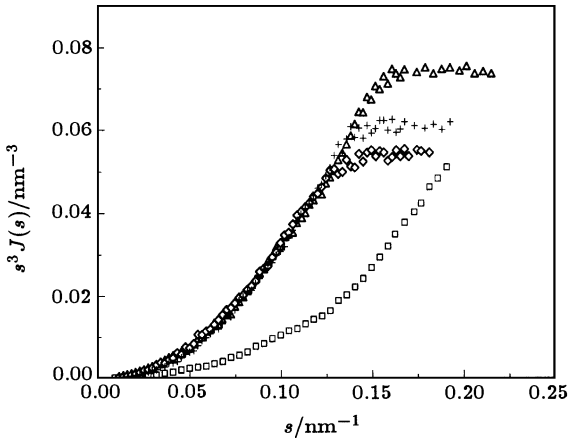


Fig.3. $s^3J(s)$–s plots for the NiTi films deposited on substrate at (□) ambient temperature; (△) 350°C; (+) 370°C; (◇) 420°C.

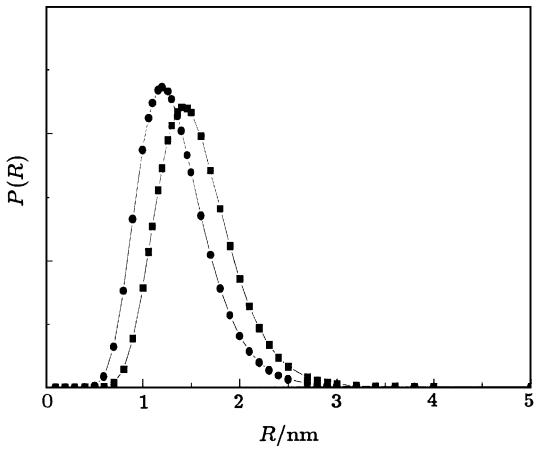


Fig.4. $P(R)$–R plots for the films deposited at substrate temperature (●)370°C; (■) 420°C.

Figure 5 shows the AFM images of the as-deposited films deposited on silicon (111) substrates at ambient temperature and 420°C with a thickness of several nanometres. It is found that in the initial deposition stage, the sputtered atoms are dispersed on the cold substrate, whereas the deposited atoms are accumulated on a heated substrate. It is possible that local heating created by metal atoms colliding with the surface provides the additional heat needed to reach the crystallization temperature. The AFM images of the films deposited on silicon substrate at ambient temperature and 420°C with a thickness of several hundred nanometres are shown in Fig.6. The film deposited on a substrate at ambient temperature has a smooth surface with a root mean square (rms) roughness of 1.42nm. The rms roughness calculated

for the film deposited at 420°C is 2.75nm. Similar images are also found in different scan areas. Santucci *et al*[27] observed the surface images of TiN/Ti/Si thin films after annealing at temperatures from 710 to 850°C. The higher annealing temperature led to an increase of the average protrusion size and a broadening of their size distribution. The formation and variation of the protrusions seem related to the transition from amorphous to crystalline state and to the growth of crystalline particles. The films deposited on a heated substrate are crystallized during deposition.

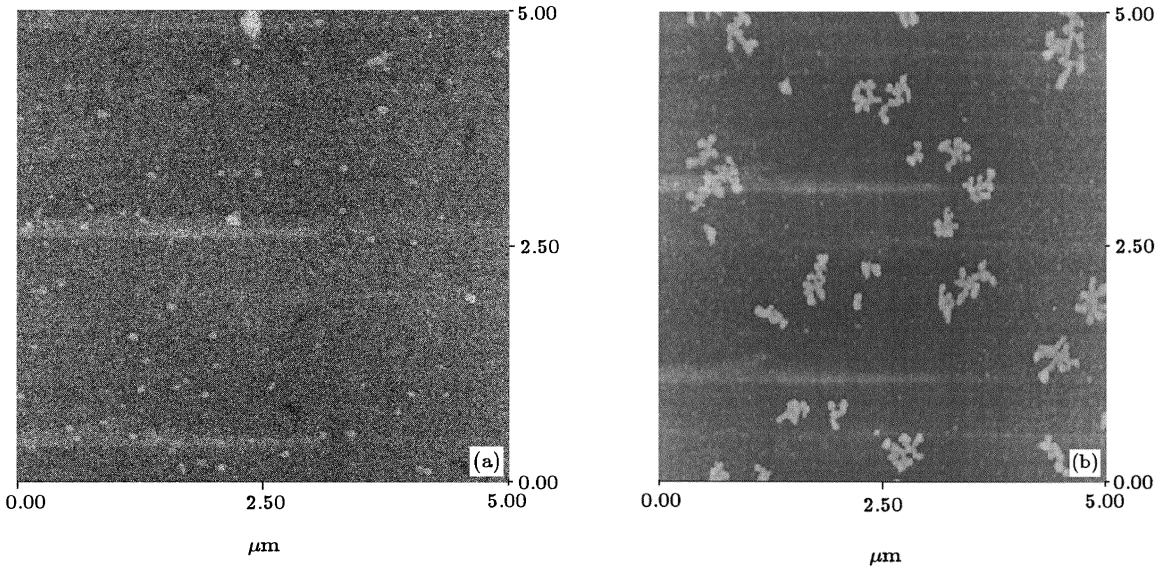


Fig.5. AFM images of NiTi films with a thickness of several nanometres obtained at substrate temperature (a) ambient; (b) 420°C.

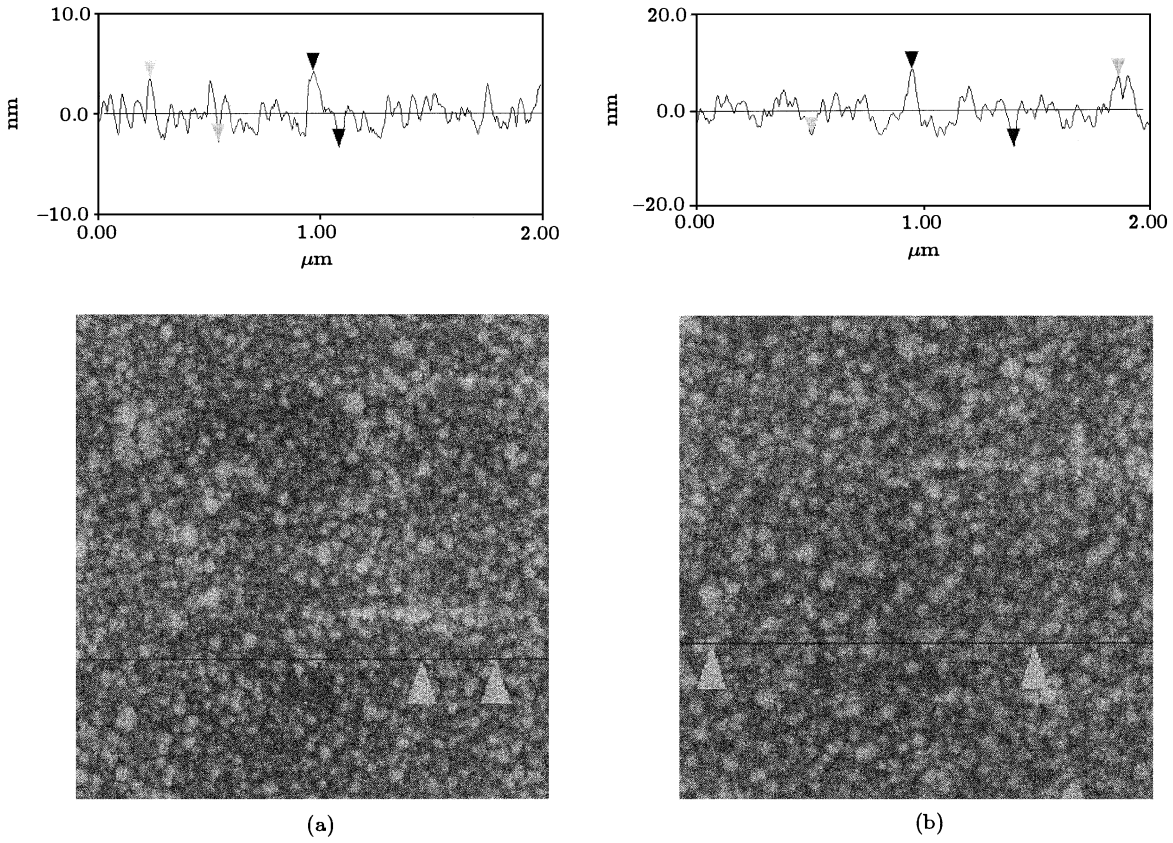


Fig.6. AFM images of NiTi films with a thickness of several hundred nanometres obtained at substrate temperature (a) ambient; (b) 420°C.

4. Conclusions

The film deposited at ambient temperature may have a micro-fluctuation of density with the size smaller than 1nm. The NiTi films deposited on a heated substrate at 350–420°C are crystallized during deposition with a B2 austenite structure. The crystalline particles have a small size and are distributed over a small range of size for the films grown at substrate temperatures of 370 and 420°C. The results show that the sizes of crystalline particles are about the same. The sputtered NiTi atoms are dispersed on a cold substrate. Instead, the deposited atoms will accumulate on a heated substrate. Increasing with the thickness of deposited film, the NiTi film deposited on a cold substrate has a much smoother surface than the film deposited on a hot substrate does. The surface roughnesses for the films grown on cold and heated substrates are 1.424 and 2.748nm, respectively.

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