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Crystallization of NiTi shape memory alloy sputtering-deposition film①

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Abstract: The crystallization of NiTi shape memory alloy sputter-deposition film in the course of sputtering-deposition and that after heat-treated were studied. The relationship between the process factors, such as substrate type, temperature, as well as the crystallization when heat treated after plating was investigated. The results show that a new phase precipitates during heat treatment after sputtering deposition and the degree of crystallization among different layers and the stress in grains are obviously different.

Key words: sputtering-deposition films; crystallization; shape memory alloys **Document code: A**

1 INTRODUCTION

The sputtering-deposition film of the shape memory alloy has unique function in the fields of micro-electronics and micro-machines[1]. In general, the film produced by ion sputtering, ion plating or ion injection is mostly amorphous without the effect of shape memory, and it must be crystallized. At present the film crystallization theory is believed to be an annealing recrystallization process[2,3]. However we believe that the crystallization should be a transformation process from amorphous to crystal. The Hollow Cathode Deposit (HCD) method was used to produce the film and study the effect of the factors on the film crystallization, such as substrate type, temperature and heat treatment after plating and profoundly study the differences of crystallization between the inner and surface layers, and put forward the crystallization mechanism and production method of NiTi shape memory alloy film.

2 EXPERIMENTAL

The NiTi memory alloy film was produced by HCD. The temperatures of furnace were 380, 400, 440 ℃ respectively. Three kinds of substrates (mica sheet, pure copper and glass) were placed into furnace No.1, and glass substrates into the other furnaces. The preparation process is listed in Table 1. The gauge of the samples was 16 mm × 10 mm × (6 ~ 15) μm. The compositions of NiTi film tested by EDXA (Energy Dispersive X-Ray Analysis) are listed in Table 2.

The substrate temperature during depositing for every furnace and the subsequent heat treatment process for furnaces No.2 ~ 4 are listed in Table 3. The heat treatment was carried out under a pressure of 1.13×10^{-2} Pa.

The crystallization temperature of the depositing amorphous film and the heat energy transformation were tested by the Differential Scaning Calorimetery (DSC). The phase structure of NiTi deposited film was determined by the X-ray diffraction D/max-TB and the small angle diffraction D/max-RB. JEM-200CX was used to observe and diffract the thinned samples by the double ion thinning instrument produced by the Gatam Co in order to study the morphology and structure.

3 RESULTS AND DISCUSSION

3.1 Behaviour of crystallization during deposition

When using HCD for deposition, for the pre-baked and thermal radiation effect by arcing, the temperature of the substrate will rise (350 ~ 480 ℃). When the particles of the vapouring source deposit to the substrate, much heat will be carried away, which makes the atoms deposited on the substrate diffuse easily, and makes it easy to crystallize during depositing: XRD indicates that the partial crystallization occurs during depositing.

3.1.1 Effect of substrate type on crystallization

The samples with nearly the same Ni and Ti compositions in furnace No.1 (Table 2) have different crystallization degrees, as shown by Fig.1. The pure copper and mica substrates have high crystallization degree, while the film on the glass substrate is amorphous. The pure copper and mica substrates can induce and promote the crystal formation and growth based on the "matching principle of structure similarity, size closeness"[4]. For instance, the crystal lattice of the pure copper substrates and that of the parent

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Table 1 Process parameters of deposition film

Pressure / Pa	Pressure of argon/ Pa	Voltage / V	Current / A	Crucible beam voltage/ V	Crucible beam current/ A	Bias voltage/ V	Bias current/ A
1.13×10^{-3}	0.113	40	170	1.8	0.5	20	4

Table 2 Compositions of NiTi alloy deposition film

Furnace No.	Substrate	x(Ni)/ %	x(Ti)/ %
	Mica sheet	50.00	50.00
1	Pure copper	48.95	51.05
	Glass	49.83	50.17
2	Glass	54.50	45.50
3	Glass	51.13	48.87
4	Glass	43.27	56.73
5	Glass	49.49	50.51

Table 3 Substrate temperature and subsequent heat treatment process

Furnace No.	Substrate temperature / ℃	Heating temperature / ℃	Holding time / min
1	380		
2	380	420, 420, 500	10, 30, 30
3	400	460, 500	30.30
4	440	420, 500	30
5	400		

phase (B_2) of crystallized NiTi film are similar, being cubic system, and their lattice constants are 0.361 nm and 0.302 nm, respectively, promoting the formation of crystal in the film. The mica substrate monoclinic system and that(martensite) of crystallized NiTi film are the same[5], which makes the crystallization of the film on the mica substrate better. The deposited film on the amorphous glass substrate is basically amorphous.

2.1.2 Effect of substrate temperature on crystallization behaviour

The substrate temperature can affect several parameters of the film, such as adhesion coefficient and surface moving rate[6]. Fig.2 shows when the substrate temperature is lower, the film is amorphous (Fig.2(a)), and it is difficult for Ni and Ti atoms to diffuse, which makes it difficult for atoms to rearrange and to form long distance order. When the substrate temperature is higher, the diffraction peak will become narrower (Fig.2(b)), i.e. it is easy for atoms to migrate and diffuse. When the temperature rises more higher, the diffraction peak becomes sharp (Fig.2(c)), at the same time, the number of peaks increases.

3.2 Effect of heat treatment on film crystallization

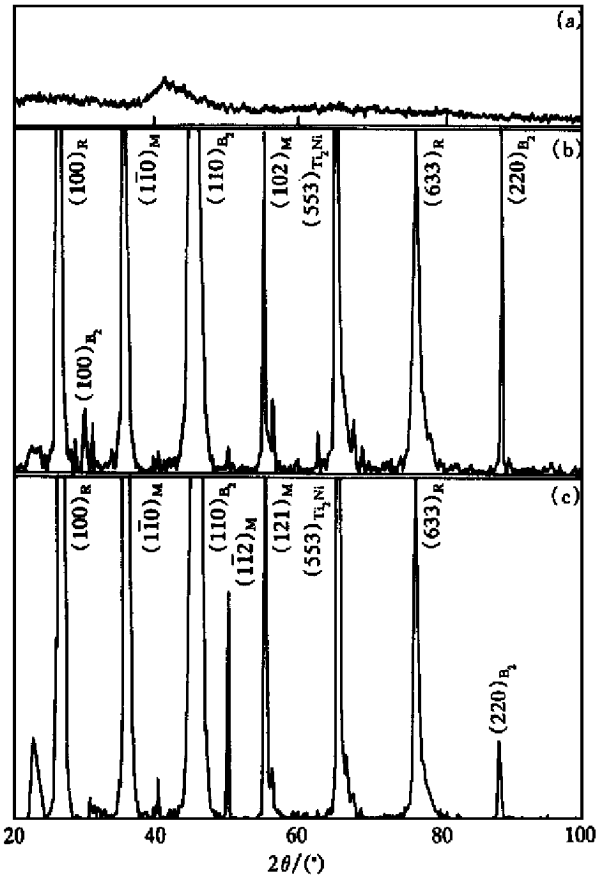

Fig.1 XRD patterns of film on various substrates in furnace No.1
(a) —Glass substrate; (b) —Mica substrate; (c) —Pure copper substrate

The amorphous film in non-equilibrium state possesses higher energy. Its structure will change and release energy, transforming into crystalline under the conditions of heat treatment and other effects[7].

3.2.1 Crystallization during heating process

The sample DSC analyses during heating process (heating rate 10 ℃/ min) for furnace No.2 and No.5 is shown in Fig.3.

With increasing temperature, there occur heat release peaks in the patterns of the samples of furnace No.2, among which three peaks are larger at 398, 409 and 419 ℃, with enthalpies -0.582, -1.079 and -0.237 J/g, respectively. The consumed energy is much less than that needed by the phase change among the parent phase, R phase and martensite[8]. These heat release peaks are neither induced by the phase transformation nor by the film crystallization, because the starting temperature for crystallization of the film is about 460 ℃[6]. When these heat release peaks occur, the temperature is not high enough to

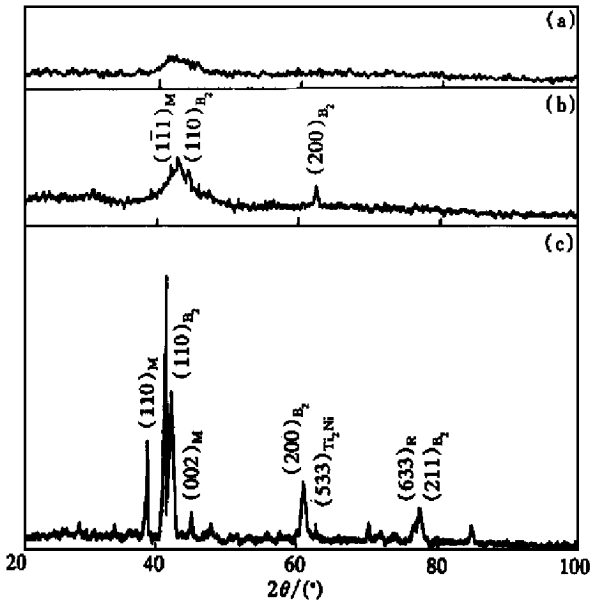

Fig.2 Thin film XRD patterns under different substrate temperatures
(a) —Sample No.2 (380 ℃); (b) —Sample No.3 (400 ℃); (c) —Sample No.4 (440 ℃)

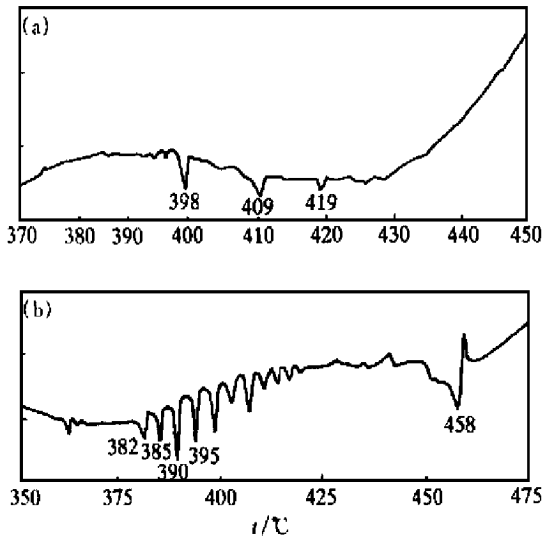

Fig.3 DSC patterns heating process of sample in different furnaces
(a) —No.2; (b) —No.5

cause the base crystallization. These peaks are the result of energy release during the formation of phase separation. The discontinuity of heat release peaks results from the discontinuity of the phase separation process. Only when energy fluctuation, structure fluctuation and concentration fluctuation meet the demand, can this process occur[9]. It has been verified by the TEM diffraction image and electron diffraction (Fig.4) of the samples of furnace No.2, which were heated to 420 ℃ and held for 30 min.

The wide and blurred diffraction ring in Fig.4 shows the base is amorphous[3]. The corresponding

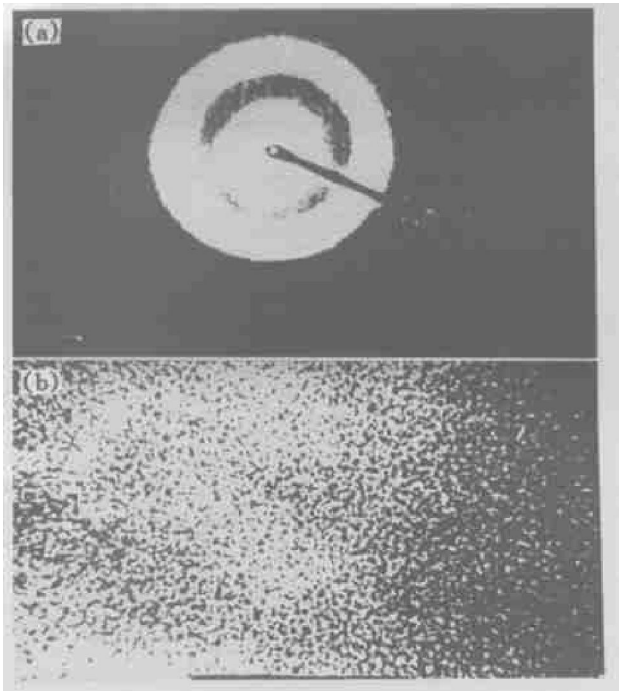

Fig.4 TEM diffraction images of sample after heated at 410 ℃ for 30 min in furnace No.2
(a) —Electron diffraction; (b) —Diffraction image

diffraction image indicates that an amorphous film disperses a few small particles. The experimental result is consistent with that of DSC.

Fig.3(b) shows that the crystallization of the base should be conducted at higher temperature. The deposition process also occurs in sample No.5 before the base crystallization with many heat release peaks and small temperature interval, which indicates that the deposition of this sample is easier than that of the sample in furnace No.2, which is related to the temperature of the substrate in furnace No.5 being higher than that during depositing. The heat release peaks mostly occur during 375 ~ 425 ℃. There is the greatest heat release peak at 458 ℃, whose enthalpy is -18.252 J/g. This is just the peak of base crystallization, and its enthapy is lower than the enthalpy of transforming among martensite, *R* and parent phase, but is higher than that of deposition.

3.2.2 Effect of heat treatment on crystallization

The amorphous NiTi film crystallized after heated under vacuum and held for certain time, as shown in Fig.5.

In order to study the crystallization of the film with various depths, the samples heated at 500 ℃ for 30 min are diffracted with small angles 3° and 8°, respectively (Fig.5(d) and Fig.5(e)). Fig.5(d) is the film surface diffraction pattern and Fig.5(e) is the diffraction pattern from middle to surface layers. From Figs.5(d) and (e), it is known that the crystallization in the middle layer is better than that on surface. The *d* values of Fig.5(d) and (e) are 0.215

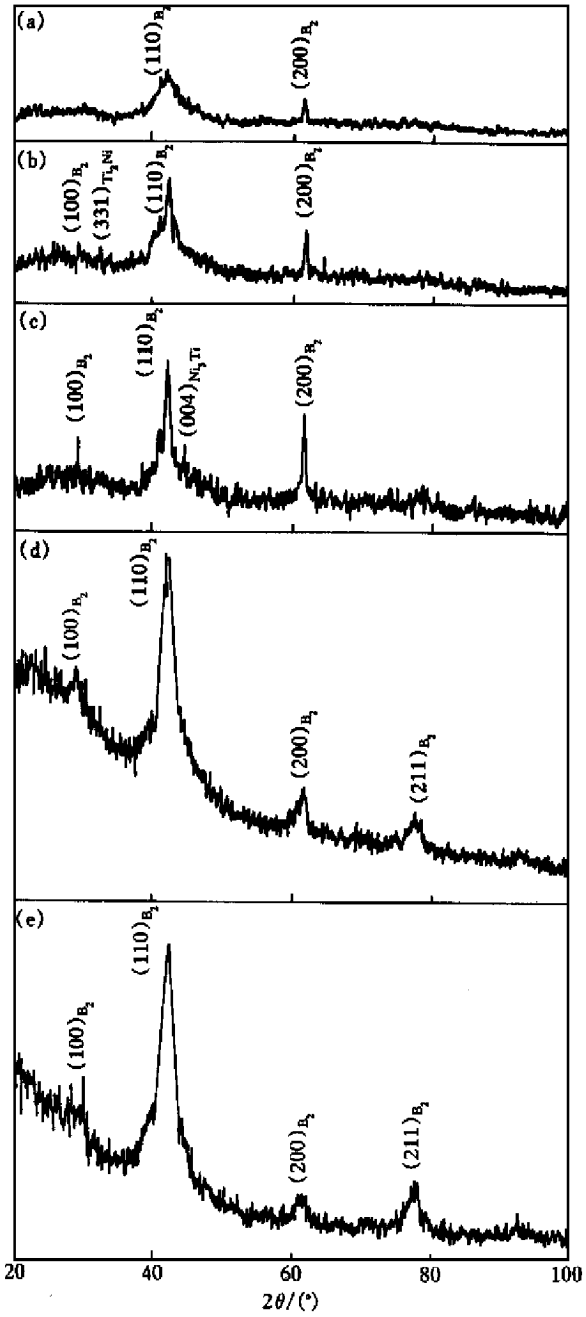

Fig.5 XRD patterns of samples of furnace No.3

(a) — Without heat treatment sample;
(b) —Sample heated at 460 ℃ for 30 min;
(c) —Sample heated at 500 ℃ for 30 min;
(d), (e) —Samples heated at 500 ℃ for 30 min, with diffraction angle 3° and 8°, respectively

nm and 0.219 nm, respectively, which result from macro-stress in the film[10].

4 CONCLUSIONS

1) During depositing, the substrate type has great effect on the crystallization. Pure copper and mica substrates promote the crystallization of deposition film, but the glass substrates are unfavourable to the crystallization of deposition film.

2) During depositing, the higher temperature of substrate is favourable to the crystallization of deposition film.

3) In the heating process of amorphous film, at first, the discontinuous phase is deposited with small enthalpy, then the base crystallizes with higher enthalpy.

4) The amorphous NiTi film can be crystallized by heat treatment. Under certain heat treatment conditions, the crystallization on surface is less than that in the middle layer and with higher tensile stress.

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