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Microstructures and transformation characteristics of thin films of TiNiCu shape memory alloy ①

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[Abstract] Both sputtering conditions and crystallizing temperatures have great influence on the microstructures and phase transformation characteristics for $Ti_{51}Ni_{44}Cu_5$. By means of the resistance-temperature measurement, X-ray diffraction and atomic fore microscopic study, the results indicate that the transformation temperatures of the thin films increase and the "rock candy" martensitic relief is more easily obtained with promoting the sputtering Ar pressure, sputtering power, or crystallizing temperature. However, when sputtering Ar pressure, sputtering power, or crystallizing temperature are lower, a kind of "chrysanthemum" relief, which is related with Ti-rich GP zones, is much easier to be observed. The reason is that during crystallization process, both of the inherent compressive stresses introduced under the condition of higher sputtering pressure or higher crystallizing temperature are helpful to the transition from GP zones to $Ti_2(NiCu)$ precipitates and the increase of the transformation temperatures. The addition of copper to substitute for 5% nickel in mole fraction can reduce the transformation hysteresis width to about 10～ 15 ℃.

[Key words] shape memory alloys; thin films; TiNiCu; microstructures; phase transformation; sputtering
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1 INTRODUCTION

Over the past decade, TiNi-based shape memory alloy (SMA) thin films have been considered to be promising actuating materials for micro-actuators in micro-electromechanical systems (MEMS) and micro-optical-mechanical systems (MEOMS), because of their abilities to generate large forces with large power-to-weight ratio, high recoverable stress, low power consumption, long lifetime, and so forth[1～3]. Because the martensitic transformation temperatures of binary TiNi alloy are very sensitive to their compositions, it is difficult to seek the precise control of their transformation behaviors. This is unbeneficial to their applications. Nevertheless, many investigations have indicated that substituting Ni with 5%～15% Cu in normally equi- atomic TiNi system not only could reduce the sensitivity of transformation temperatures to compositions effectively, but also could decrease the transformation hysteresis width, resulting in higher response frequency in microactuators driven by TiNiCu thin films[4,5].

By now, the researches about TiNi-based thin films were mainly concentrated on binary TiNi thin films, and there have also been some reports about their application, such as micropumps[6,7], microvalves[8,9], micrografippers[1], and so on. To our knowledge, the researches on ternary TiNiCu thin films are fewer, and they are mainly about the study of copper concentration dependence of phase transformation[10,11]. In our research about TiNiCu thin films sputter-deposited, it was found that the microstructures and phase transformation characters of the films were related with sputtering conditions and crystallizing processes. Since the actuating performances of SMA films mainly depend on the phase transformation occurred in the films, the effects of sputtering conditions and crystallizing temperatures on the microstructures and transformation temperatures were analyzed and discussed in this paper.

2 EXPERIMENTAL

TiNiCu thin films were sputter-deposited on (100) single-crystal silicon substrates by r. f. magnetron sputtering in argon atmosphere. Since as-sputtered films were amorphous, all films were annealed at various temperatures for 30 min to crystallize and get shape memory effect. The specimen numbers and corresponding sputtering conditions, crystallizing temperatures are listed in Table 1.

The film thickness measured by surface profiler were about 5～6 μm, and the film average compositions in mole fraction measured with EPMA apparatus were approximately Ti∶Ni∶Cu= 51∶44∶5. The electrical resistance-temperature curves of all samples

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were measured by electrical resistivity measurement. The determination principle about the transformation temperatures of thin films is shown in Fig. 1 and all results measured are listed in Table 2. X-ray diffraction analyses were carried out to identify the phases formed in the films in D/max-IIIA. Surface microstructures were observed by optical microscope with large magnification and by Nanoscope IIIa atomic force microscope (AFM).

3 RESULTS AND DISCUSSION

3.1 Sputtering conditions dependence of microstructures and transformations

3.1.1 Effect of sputtering Ar pressure

On the condition of the same sputtering power (250W) and the same crystallizing temperature (550 ℃), e.g., Sample B3, B5-B7, the effect of sputtering Ar pressure on transformation temperatures in $Ti_{51}Ni_{44}Cu_5$ thin films is shown in Fig. 2.

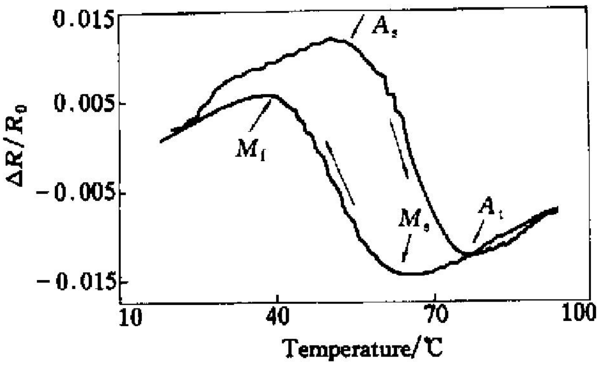

Fig. 1 Determination principle about transformation temperatures of TiNiCu thin films (e.g., sample B1)

The transformation temperatures of the thin films increase with promoting sputtering Ar pressure, especially increasing from 0.13 Pa to 0.53 Pa. The transformation hysteresis (H_{hys}) is about 10~ 13 ℃.

Table 1 Sputtering conditions and crystallizing processes of samples

Sample No.	Sputtering conditions				Crystallizing process
	Base pressure/Pa	Ar pressure/Pa	r.f. power/W	Deposition time/min	
B1-400	8.0×10^{-5}	0.13	150	60~ 120	400 ℃, 30min
B1-450		0.13	150		450 ℃, 30min
B1-550		0.13	150		550 ℃, 30min
B1-650		0.13	150		650 ℃, 30min
B2		0.13	200		550 ℃, 30min
B3		0.13	250		550 ℃, 30min
B4		0.16	300		550 ℃, 30min
B5		0.53	250		550 ℃, 30min
B6		1.06	250		550 ℃, 30min
B7		1.30	250		550 ℃, 30min

Table 2 Transformation temperatures of $Ti_{51}Ni_{44}Cu_5$ thin films (℃)

Sample No.	A_s	A_f	M_s	M_f	$A^* = (A_s + A_f)/2$	$M^* = (M_s + M_f)/2$	$H_{hys} = (A^* - M^*)$
B1-400	-	-	-	-	-	-	-
B1-450	-8.9	24.3	19.1	-12.3	7.7	3.4	4.3
B1-550	21.8	45.9	29.3	13.4	33.9	21.4	12.5
B1-650	55.7	71.9	61.8	45.6	63.8	53.7	10.1
B2	22.4	54.9	40.6	6.9	38.7	23.8	14.9
B3	27.5	48.2	36.5	17.6	37.9	27.1	10.8
B4	33.0	54.9	42.5	17.7	44.0	30.0	14.0
B5	31.5	62.5	48.3	19.9	47.0	34.1	12.9
B6	41.4	58.2	46.6	33.9	49.8	40.3	9.5
B7	39.9	58.2	45.6	28.8	49.1	37.2	11.9

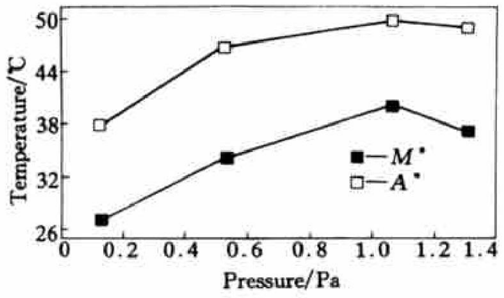

Fig. 2 Effect of sputtering Ar pressure on transformation temperatures in $Ti_{51}Ni_{44}Cu_5$ thin films (sputtering power, 250 W; crystallizing, 550 ℃)

1) $Ti_{51}Ni_{44}Cu_5$ thin films sputtered under lower Ar pressure

In all $Ti_{51}Ni_{44}Cu_5$ thin films sputtered under lower Ar pressure (e.g., 0.13~0.16 Pa), much "chrysanthemum" relief could be found at 12 ℃ by optical microscope or AFM, as shown in Fig. 3, and the quantity of "chrysanthemum" relief decreases with promoting sputtering power.

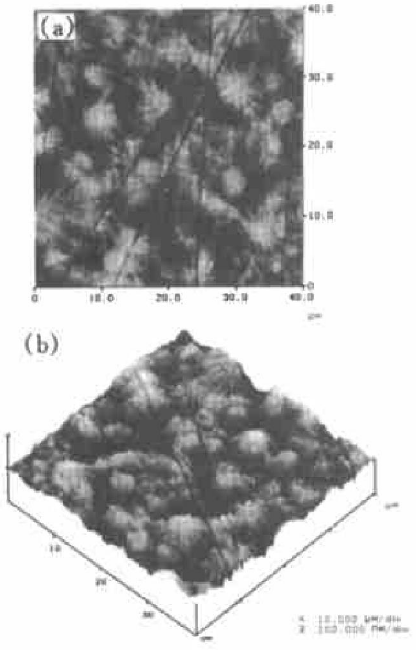

Fig. 3 AFM micrographs of $Ti_{51}Ni_{44}Cu_5$ thin film with "chrysanthemum" surface relief at 12 ℃
(Sample B4: sputtering, 0.16 Pa, 300 W; crystallizing, 550 ℃)
(a) —Planar micrograph; (b) —3D micrograph

In addition, these thin films were heated and cooled during 0~100 ℃ to generate the phase transformation between low-temperature martensite (M, or $B19'$) and high-temperature austenite (*A*, or *B*2). Differing from block martensitic relief, as discussed next, the "chrysanthemum" relief does not disappear and has not any change in its appearance during the thermal cycles. It may suggest that the "chrysanthemum" relief is a new kind of microstructure, which is different from either austenite or martensite.

In some researches[12~14] on Ti-rich TiNi thin films crystallized at lower temperature, similar "chrysanthemum" relief was also reported, and it is considered to be Ti-rich GP zone. Studied on microstructure of $Ti_{51.8}Ni_{48.2}$ thin films, Ishida[13] found that when amorphous Ti-rich thin films are crystallized and after B_2 phase have formed, the formation of Ti_2Ni precipitates undergoing some sequences as followed: disc shape Ti-rich GP zones lying on the {100} planes of B_2 phase → spherical Ti_2Ni precipitates. In a word, Ti-rich GP zone is a transitional nonequilibrium microstructure and its formation is extremely related with crystallizing process and Ti-rich compositions.

$Ti_{51}Ni_{44}Cu_5$ can be regarded as $Ti_{51}(NiCu)_{49}$, and its crystal lattice is similar to that of Ti-rich TiNi binary thin film in crystal lattice. So under certain crystallizing process, these Ti-rich GP zones with "chrysanthemum" shape as shown in Fig. 3 can be also formed in $Ti_{51}Ni_{44}Cu_5$ thin films. Since Ti-rich GP zones can be formed only above critical crystallization temperature (generally above 420 ℃), Ti-rich GP zones ("chrysanthemum" relief) are impossible to disappear during thermal cycles below critical crystallization temperature (e.g., 0~100 ℃).

According to the XRD analysis results, the main microstructure of sample B1-550 is martensite at 12 ℃ as shown in Fig. 4(a), but is austenite at 50 ℃ as shown in Fig. 4(b). Besides of these, there are Ti-rich GP zones in the thin film both at 12 ℃ and at 50 ℃. This result is in agreement with the measure-

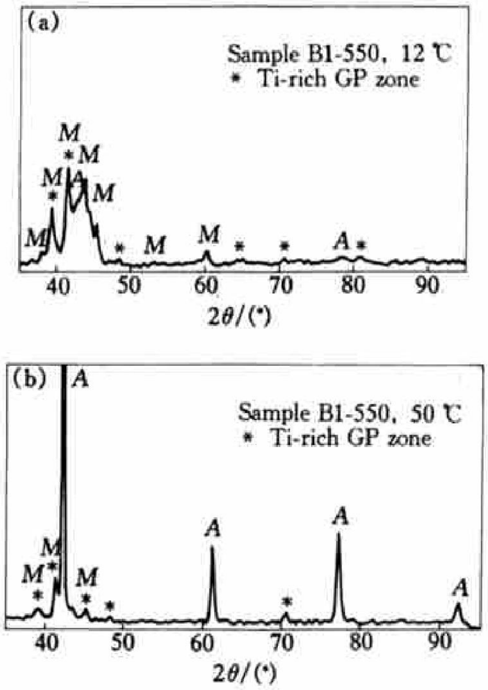

Fig. 4 X-ray diffraction patterns of sample B1-550
(sputtering: 0.13 Pa, 150 W; crystallizing, 550 ℃)
(a) —*t* = 12 ℃; (b) —*t* = 50 ℃

ment result of transformation temperature (sample B1-550: M_f = 13.4 ℃, A_f = 45.9 ℃). Since the compositions and lattice parameters of the Ti-rich GP zone may approach to those of $Ti_2(NiCu)$, its X-ray diffraction peaks are so close to those of $Ti_2(NiCu)$ that it is difficult to be distinguished.

2) $Ti_{51}Ni_{44}Cu_5$ thin films Sputtered under higher Ar pressure

From Fig. 2, it can also be found that the transformation temperatures of the thin films formed under higher Ar pressure (e. g., not less than 0.53 Pa; sample B5-B7) are higher than those of the thin film formed under lower Ar pressure (e. g., 0.13 Pa; sample B3), and are generally above room temperature.

At 12 ℃, in all of $Ti_{51}Ni_{44}Cu_5$ thin films sputtered under higher Ar pressure (not less than 0.53 Pa), a lot of block surface relief was found with optical microscope, or much "rock candy" surface relief was observed with AFM shown in Fig. 5.

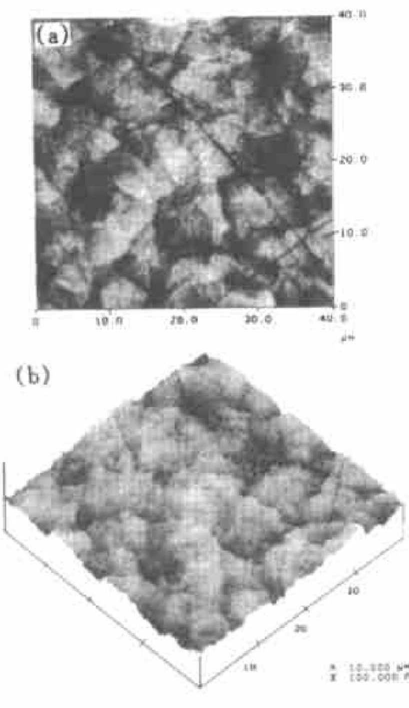

Fig. 5 AFM micrographs of $Ti_{51}Ni_{44}Cu_5$ thin film with "rock candy" surface relief at 12 ℃
(Sample B7: sputtering, 1.3 Pa, 250 W; crystallizing, 550 ℃)
(a) —Planar micrograph; (b) —3D micrograph

But there is no any "chrysanthemum" surface relief could be observed. Additionally, during thermal cycles during 0 ~ 100 ℃, block martensitic relief gradually disappears and the surface tends to smooth gradually due to the $M \rightarrow A$ transition upon heating, but these block martensitic relief gradually appear due to the $A \rightarrow M$ transition upon cooling. During the thermal cycles no "chrysanthemum" relief could be found all the time. It may refer that there is almost no Ti-rich GP zone in these thin films.

Analyzing the XRD patterns of sample B7 at 12 ℃ and at 50 ℃, as shown in Fig. 6(a) and (b) respectively, it could be found that the phases of sample B7 are martensite and $Ti_2(NiCu)$ at 12 ℃, but are austenite, $Ti_2(NiCu)$ and few martensite at 50 ℃. This result is also in accordance with the measurement result of transformation temperatures (sample B7: M_f= 28.8 ℃, A_f= 58.2 ℃).

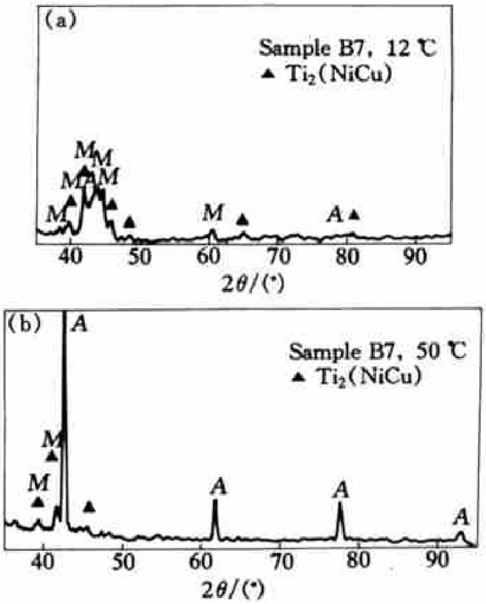

Fig. 6 X-ray diffraction patterns of sample B7
(sputtering: 1.3 Pa, 250 W; crystallizing, 550 ℃)
(a) —t= 12 ℃; (b) —t= 50 ℃

3.1.2 Effect of sputtering power

Distinct thin films formed under different sputtering powers, but under same lower Ar pressure (0.13~ 0.16 Pa) and at same crystallizing temperature (550 ℃), e. g., sample B1-550, B2~ B4, were obtained. In these films much "chrysanthemum" relief could be found, and the "chrysanthemum" quantity decreases but transformation temperatures increase with promoting sputtering power, as shown in Fig. 7. Compared Fig. 7 with Fig. 2, it could also found that the effects of sputtering power on microstructures and transformation temperatures are less

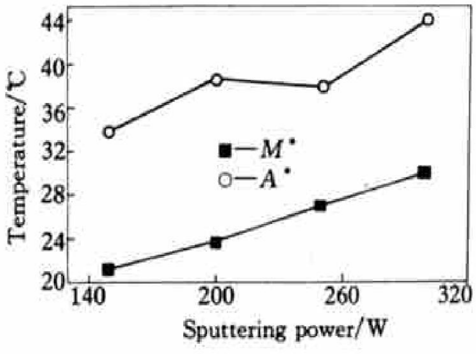

Fig. 7 Effect of sputtering power on transformation temperatures in $Ti_{51}Ni_{44}Cu_5$ thin films
(sputtering pressure, 0.13~ 0.16 Pa; crystallizing, 550 ℃)

obvious than those of sputtering Ar pressure. The transformation hysteresis (H_{hys}) are about 10 ~ 16 ℃.

3.1.3 Discussion abut effect of sputtering conditions

Based on the analyses about Ti51Ni44Cu5 thin films above, it could be concluded that Ti-rich GP zones are easily formed in the films sputtered under lower Ar pressure (0.13 ~ 0.16 Pa) or under lower power, but $Ti_2(NiCu)$ precipitates are easily formed in the films sputtered under higher Ar pressure (not less than 0.53 Pa). At the same time it can be also found that the transformation temperatures of the former are obviously lower than those of the latter. It refers that there is a certain relationship between Ti-rich GP zones and transformation temperatures. Additionally, the sputtering Ar pressure and the sputtering power, especially the former, have significantly effect on the microstructures and transformation temperatures of the films.

In general, increasing the sputtering Ar pressure can obviously raise the inherent compressive stress in the as-sputtered amorphous thin film[15]. During the crystallization of the amorphous thin film, the amorphous-to-crystalline transformation tends to reduce the volume[16]. The compressive stress introduced under higher Ar pressure is helpful to decrease the crystallized volume and is favorable for crystallizing. In other words, the activation energy of the amorphous-to-crystalline transition (namely, critical crystallization temperature) of the thin films sputtered under higher Ar pressure is lower than those of the thin films sputtered under lower Ar pressure.

Moreover, During the crystallization process of Ti-rich TiNiCu ternary thin films, the formations of Ti-rich GP zones or $Ti_2(NiCu)$ precipitates can only begin after the formation of B2 phase, e.g., amorphous-to-crystalline transition. It refers that the formation of Ti-rich GP zones and $Ti_2(NiCu)$ precipitates is related with crystallization temperature. On the one hand, for the Ti-rich TiNiCu thin films sputter-deposited under lower Ar pressure, since the critical crystallization temperatures is relatively higher, as discussed above, Ti-rich GP zones just have formed but $Ti_2(NiCu)$ phase still have no time to precipitate after the formation of $B2$ phase. So there are many "chrysanthemum" GP zones to be remained in these thin films. On the other hand, for the Ti-rich TiNiCu thin films sputter-deposited under higher Ar pressure, after formed of $B2$ phase and GP zones, $Ti_2(NiCu)$ particles can entirely precipitate from GP zones in time, due to the lower critical crystallization temperatures of the films. Thus, no "chrysanthemum" GP zone is observed in the thin films formed under higher Ar pressure.

Since GP zones are coherent with the matrix, they could produce larger compressive stress fields around them to bring about high resistance to plastic deformation[14, 15]. Comparatively, the $Ti_2(NiCu)$ precipitates have partial coherency with the matrix and the misfit is considerably relaxed, the strengthening effect on the matrix seems to be lower than that of GP zones[14, 15]. Therefore, the suppress effect of GP zones on transformation temperatures are more remarkable than that of $Ti_2(NiCu)$ precipitates. It may be the reason that transformation temperatures of the thin films sputtered under lower Ar pressure are lower than those of the thin films sputtered under higher Ar pressure.

Additionally, the inherent sputtering compressive stress in the amorphous films can increase slightly with promoting sputtering power[16]. Based on the analysis about the inherent compressive stress dependence of microstructure, Ti-rich GP zone quantity should be decreased and transformation temperatures should be increased slightly with the increase of sputtering power. This conclusion is accordance with the analysis result of sputtering power dependence of "chrysanthemum" quantity and transformation temperatures as mentioned in section 3.1.2.

3.2 Crystallization temperature dependence of microstructures and transformations

Through analysis and discussion about Ti-rich TiNiCu thin films above, it seems that although the formation of GP zones can be avoided and transformation temperatures can be raised through increasing sputtering Ar pressure. However, that these thin films sputtered under higher Ar pressure easily exhibit porous and columnar structure is very harmful to actual application as microactuators. Hence, in order to get flat and compact as-sputtered thin films, it is still necessary to sputter the thin films under lower Ar pressure. According to the formation mechanism of GP zones and $Ti_2(NiCu)$ precipitates, the formation of GP zones in the thin films sputtered under lower Ar pressure can be also avoided and the transformation temperatures can be also increased through properly increasing annealing temperature or prolonging annealing time. So in our research the thin films sputtered under lower Ar pressure and lower power (e.g.: 0.13 Pa, 150 W) were crystallized at various temperature for 30 min, such as 400 ℃, 450 ℃, 550 ℃, 650 ℃, to explore the effect of crystallizing temperature on the microstructures and transformation temperatures.

Except that the thin film crystallized at 400 ℃ (sample B1-400) is amorphous due to the lower crystallizing temperature, the others crystallized at other temperature have been crystallized, as listed in Table 2. The "chrysanthemum" relief (Ti-rich GP zone) was also found in the thin films crystallized at 450 ℃ and 550 ℃, but the "rock candy" relief (block martensite) was found in the thin films crystallized at 650 ℃. With increasing crystallizing temperature, the "chrysanthemum" relief is fainter, but the "rock candy" is clearer. Additionally, the effect of crystallizing temperature on transformation temperatures is shown in Fig. 8. The transformation temperatures increase obviously with promoting the crystallizing temperature.

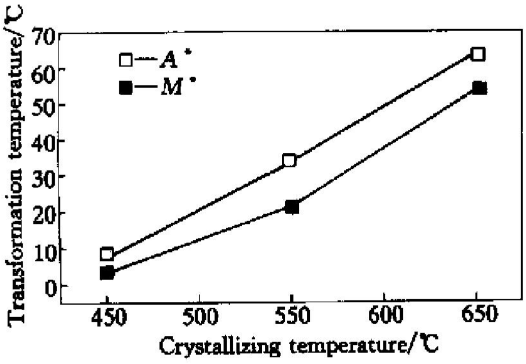

Fig. 8 Effect of crystallizing temperature on transformation temperatures of $Ti_{51}Ni_{44}Cu_5$ thin films (sputtering, 0.13 Pa, 150 W)

In conclusion, for Ti-rich TiNiCu thin films the transformation temperature could be promoted and the block martensite could be obtained easily through properly increasing crystallizing temperature.

4 CONCLUSIONS

1) With promoting the sputtering Ar pressure, sputtering power, or crystallizing temperature, the transformation temperatures of the thin films increase and the "rock candy" martensite relief is more easily obtained.

2) Lower sputtering Ar pressure, lower sputtering power, and lower crystallizing temperature are all helpful to the formation of "chrysanthemum" relief on the surface, which is related to Ti-rich GP zones.

3) The inherent compressive stress, which is introduced under the condition of higher sputtering pressure or higher sputtering power, is favorable to the transition from GP zones to $Ti_2(NiCu)$ precipitates and the increase of the transformation temperatures.

4) For $Ti_{51}Ni_{44}Cu_5$ thin films, the addition of copper to substitute for about 5% nickel can reduce the transformation hysteresis width to about 10 ~ 15 ℃.

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