Microstructure and Optical Properties of $\text{Ti}_{54.5}\text{Ni}_{45.5}$ Nanocrystalline Thin Film

Xin Zhang¹ · Jie-He Sui² · Yong-Chao Lei² · Wei Cai²

Received: 9 March 2017 / Revised: 17 April 2017 / Published online: 22 June 2017
© The Chinese Society for Metals and Springer-Verlag GmbH Germany 2017

Abstract Nanocrystalline $\text{Ti}_{54.5}\text{Ni}_{45.5}$ thin film was prepared by magnetron sputtering followed by rapid thermal annealing. The film displayed martensite structure and (001) compound twin substructure, and the transformation temperatures M_s and A_s are 313 and 365 K, respectively. The reflectivity for the wavelength from 200 to 800 nm at 298 and 393 K was investigated, and the results showed that the optical reflectivity contrast between martensite and austenite at 780, 650, 514 and 405 nm was 105.64, 170.83, 112.22 and 149.92%, respectively, which were larger than those of other reported optical recording materials.

KEY WORDS: Ti–Ni thin films; Sputtering; Shape memory alloys; Optical properties; Microstructure

1 Introduction

At present, the Ti–Ni-based alloy thin films are widely investigated as micro-driven material in micro-electro-mechanical system and biomedical micro-devices, owing to their excellent shape memory effect and biocompatibility [1–11]. It is well known that the martensite and austenite are the two kinds of phase states for Ti–Ni thin films at different temperatures, and their crystal structure difference leads to the large differences of physical properties such as optical performance. Wang [12] calculated the photoconductivity of martensite and austenite in Ti–Ni alloy for far infrared and

visible light band using the first principles. Tabib-Azar et al. [13] measured the reflectivity of martensite and austenite in the Ti–Ni thin film using home-made optical fibre reflectance measurement device. They all implied that the reflectivity of martensite and austenite for Ti–Ni thin film is different. However, the optical properties of Ti–Ni thin films have not yet been researched systematically. In this work, a $\text{Ti}_{54.5}\text{Ni}_{45.5}$ nanocrystalline thin film is prepared by magnetron sputtering and RTA, and the grain size, microstructure, martensitic transformation temperatures and optical properties are investigated.

2 Experimental

Amorphous $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film with the thickness of 90 nm was deposited on silicon (100) substrates by high vacuum direct current (DC) magnetron sputtering system for 5 min, and the Ar gas pressure and DC powers were 0.6 Pa and 100 W, respectively. After sputtering, the deposited film was annealed at 873 K for 60 min in a vacuum RTA furnace with Ar gas protection to induce crystallization and then cooled to room temperature in the furnace. The heating rate of RTA was 1200 K/min.

Available online at <http://link.springer.com/journal/40195>

✉ Jie-He Sui
suijiehe@hit.edu.cn

✉ Wei Cai
weicai@hit.edu.cn

¹ School of Materials Science and Engineering, Tianjin University of Technology, 300384 Tianjin, China

² National Key Laboratory Precision Hot Processing of Metals, Harbin Institute of Technology, 150001 Harbin, China

XRD measurements were taken by Rigaku D/max-rB with CuK_α radiation. The microstructures were observed by transmission electron microscopy (TEM) using a PHILIPS CM-12 TEM/STEM instrument at an operating voltage of 120 kV. Thin foils for TEM observation were prepared by double-jet electropolishing in an electrolyte solution consisting of 95% acetic acid and 5% perchloric acid by volume. The martensitic transformation temperatures were determined by a home-made electrical resistance instrument with system error of $\pm 2 \text{ k}\Omega$, and the size of the sample was $10 \text{ mm} \times 10 \text{ mm}$. The reflectivity was measured by PerkinElmer Lambda spectrophotometer with a heating stage. The scan rate and measurement wavelength range were 750 nm/min and $200\text{--}800 \text{ nm}$, respectively.

3 Results and Discussion

Figure 1 shows the XRD pattern of $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film after RTA and the standard XRD pattern of martensite for Ti–Ni alloy. As shown in Fig. 1, the structure of annealed $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film at room temperature is

Fig. 1 XRD pattern of annealed $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film at room temperature **a** and standard XRD pattern of martensite for Ti–Ni alloy **b** (M: martensite)

indexed as martensite, and its grain size D can be calculated by Scherrer formula:

$$D = K\gamma/\beta \cos \theta, \quad (1)$$

where K is the Scherrer constant, β is the half peak width, θ is diffraction angle, γ is the wavelength of X-ray (0.154056 nm). The average grain size of 50 nm is calculated by the diffraction peak of $(012)_M$.

Generally, the precipitate phase Ti_2Ni is often observed in the coarse grain films [14] and bulk materials [15] of Ti–rich Ti–Ni alloys. However, our $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film displays single phase of martensite. It had been proved that the nucleation barrier of precipitated phase is increased with decreasing the grain size of parent phase [16]. When the grain size is smaller than a critical size, the formation of precipitated phase will be prohibited completely. Thus, it can be understood that there is no precipitated phase in nanosized $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film.

In order to further confirm the grain size and microstructure of $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film, the TEM observation is carried out. Figure 2 shows the TEM images of $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film and the corresponding diffraction patterns. It can be found from Fig. 2a, b that the grain size is ranged from 20 to 50 nm , which is consistent with XRD results. The diffraction rings (inset) are indexed as martensite. The martensitic variants within the grains are obviously observed (Fig. 2c), and the interfaces among variants are straight and well defined.

As seen in Fig. 2d, the electron diffraction pattern (EDP) contains two sets of martensitic spots, proving that the substructure of martensite is (001) compound twins. M1 and M2 in Fig. 2e are martensitic variants of (001) compound twins, and their interface is straight, well defined and non-distorted, which implies high atomic coherency. The width of (001) compound twin variant is about 2.4 nm , the same as that of Ti–Ni bulk materials prepared by high-pressure torsion [17], but far less than that of reported Ti–Ni film [18, 19] (dozens to 100 of nanometres) and melted Ti–Ni bulk materials [20–22] (100 of nanometres to several micrometres).

Figure 3 shows the electrical resistance–temperature curves of $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film. $\text{Ti}_{54.5}\text{Ni}_{45.5}$ thin film exhibits the typical one-step thermoelastic martensitic transformation, which is similar to the Ti–Ni bulk materials. With the heating temperature increasing, the electrical resistance increases until the temperature is 365 K and then decreases monotonically. Similarly, when the temperature is decreased, the electrical resistance is increased at first and then decreased. The temperatures corresponding to the two maximum represent the martensitic transformation starting temperature ($M_s = 313 \text{ K}$) and austenitic transformation starting temperature ($A_s = 365 \text{ K}$), respectively.

Fig. 2 TEM images of $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film and corresponding diffraction patterns: **a** bright field image; **b** enlarged image of Fig. 2a; **c** bright field image of (001) compound twinned thermal martensite; **d** diffraction pattern of (001)_M zone taken from Fig. 2c; **e** bright field image of (001) compound twinned thermal martensite

Fig. 3 Electrical resistance–temperature curves of $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film

Figure 4a represents the reflectance spectrum curves of $\text{Ti}_{54.5}\text{Ni}_{45.5}$ thin film with the states of martensite and austenite. It can be seen that the reflectivity of martensite at 298 K (R_M) is reduced after rising first with the wavelength increasing and then continues to rise. Two peaks and one trough can be seen in the curve of austenitic reflectivity at 393 K (R_A). Comparing with the R_M , the wavelength corresponding to minimum and maximum positions of R_A

is increased. At the wavelength of Blu-ray storage band (405 nm), the reflectivity difference ($\Delta R = |R_A - R_M|$) value between martensite and austenite is up to 34%. When the wavelength is more than 477 nm, R_A is lower than R_M .

If the Ti–Ni thin films are used as an optical recording material, their storage must be based on the difference of reflectivity between martensite and austenite. Meanwhile, for practical applications, a recordable or rewritable material should possess a high carrier-to-noise ratio (CNR) more than 40 dB before and after writing or erasing at the working wavelength. This can be translated into a high reflectivity contrast (C), which is defined as follows:

$$C = 2 \times \Delta R / (R_M + R_A) \times 100\%; \quad (2)$$

hence the reflectivity contrast of recording material should be larger than 15%.

Figure 4b exhibits the reflectivity contrast of $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film, and the reflectivity contrast of 780, 650, 514 and 405 nm is 105.64, 170.83, 112.22 and 149.92%, respectively. It is well known that 780 and 650 nm are the application of laser wavelength of compact disc (CD) and digital video disc (DVD), respectively. 514 nm is in the blue–green short wavelength band, which can further improve the recording density. The reflectivity contrast of $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film is far larger than those of other

Fig. 4 Reflectivity spectrum **a** and reflectivity contrast **b** of $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film

reported optical recording materials [23], which are listed in Table 1. All the C values at commonly used wavelengths are higher than 100%. Thus, it can be concluded that $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film is a kind of excellent optical recording medium due to its large reflectivity difference

Table 1 Reflectivity contrast of different optical recording medium at commonly used wavelengths

Material	Reflectivity contrast
$\text{Ge}_2\text{Sb}_2\text{Te}_5$ [23]	≤ 42
$\text{Ag}_8\text{In}_{14}\text{Sb}_{55}\text{Te}_{23}$ [24]	≤ 70
AgInTeSbGe [25]	≤ 65
Al_xGST [26]	≤ 30
Si:SbO_x [27]	≤ 36
Mo/Si bilayer [28]	25.8 (405 nm)
Metal(II) hydrazone complexes [29]	≤ 45
Our work	≥ 100

and high reflectivity contrast between martensite and austenite.

In addition, it can be assumed that the grain size of Ti–Ni alloy thin film is 50 nm, and each grain with the square shape (50 nm $\times$ 50 nm) should be corresponded to one data point. The outer diameter and inner diameter of common disc are 120 and 15 mm. Thus, the storage area of each disc is $111.27375 \times 10^{14} \text{ nm}^2$. It can be calculated that the number of data points is 4.45095×10^{12} in the ideal conditions, compared with the storage of 500 GB.

4 Conclusion

The $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film with nanocrystalline is prepared by magnetron sputtering and RTA. The structure and substructure of this thin film are martensite and (001) compound twins. $\text{Ti}_{54.5}\text{Ni}_{45.5}$ alloy thin film exhibits excellent optical functional characteristics at the commonly used wavelengths of disc such as 780, 650, 514 and 405 nm.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Nos. 51471061 and 51601126) and the Program for New Century Excellent Talents in University of Ministry of Education of China (No. NCET-12-0160).

References

- [1] J.D. Busch, A.D. Johnson, *J. Appl. Phys.* **68**, 6224 (1990)
- [2] A.D. Johnson, *J. Micromech. Microeng.* **1**, 34 (1991)
- [3] A.P. Jardine, G. Baure, A.N. Le, G.P. Carman, in *Proceedings of the Materials & Processes for Medical Devices Conference* (ASM International, Materials Park, 2004), pp. 112–115
- [4] J. Ye, R.K. Mishra, A.R. Pelton, A.M. Minor, *Acta Mater.* **58**, 490 (2010)
- [5] X.L. Meng, M. Sato, A. Ishida, *Acta Mater.* **59**, 2535 (2011)
- [6] M. Tomozawa, H.Y. Kim, A. Yamamoto, S. Hiromoto, S. Miyazaki, *Acta Mater.* **58**, 6064 (2010)
- [7] A. Ishida, M. Sato, Z.Y. Gao, *Acta Mater.* **69**, 292 (2014)
- [8] M. Kabla, H. Seiner, M. Musilov, M. Landa, D. Shilo, *Acta Mater.* **70**, 79 (2014)
- [9] D. Koenig, P.J.S. Buenconsejo, D. Grochla, S. Hamann, J. Pfetzing-Micklich, A. Ludwig, *Acta Mater.* **60**, 306 (2012)
- [10] M. Krishnan, J.B. Singh, *Acta Mater.* **48**, 1325 (2000)
- [11] M. Krishnan, *Acta Mater.* **46**, 1439 (1998)
- [12] X.D. Wang, *Phys. Rev. B* **58**, 2964 (1998)
- [13] M. Tabi-Azar, B. Sutapun, M. Huff, *Sens. Actuator A* **77**, 34 (1999)
- [14] A. Ishida, K. Ogawa, M. Sato, S. Miyazaki, *Metall. Mater. Trans. A* **28**, 1985 (1997)
- [15] L. Zhang, C.Y. Xie, J.S. Wu, *Mater. Sci. Eng. A* **438–440**, 905 (2006)
- [16] S.Q. Xu, Z.H. Guo, T.Y. Hsu, *Mater. Sci. Forum* **475–479**, 3463 (2005)
- [17] T. Waitz, H.P. Karnthaler, *Acta Mater.* **52**, 5461 (2004)
- [18] X.L. Meng, M. Sato, A. Ishida, *Acta Mater.* **56**, 3394 (2008)
- [19] J.X. Zhang, M. Sato, A. Ishida, *Acta Mater.* **54**, 1185 (2006)

- [20] T. Saburi, S. Nenno, T. Fukuda, *J. Less Common Met.* **125**, 157 (1986)
- [21] W.J. Moberly, J.L. Proft, T.W. Duerig, R. Sinclair, *Acta Metall. Mater.* **38**, 2601 (1990)
- [22] W.J. Moberly, *Ultramicroscopy* **30**, 395 (1989)
- [23] F.X. Gan, L.S. Hou, G.B. Wang, H.Y. Liu, J. Li, *Mater. Sci. Eng. B* **76**, 63 (2000)
- [24] J.Y. Li, F.X. Gan, *Thin Solid Films* **402**, 232 (2002)
- [25] B. Liu, F.X. Gan, *Appl. Phys. A* **77**, 905 (2003)
- [26] S.J. Wei, J. Li, X. Wu, P. Zhou, S.Y. Wang, Y.X. Zheng, L.Y. Chen, F.X. Gan, X. Zhang, G. Li, *Opt. Express* **15**, 10584 (2007)
- [27] Y. Zhou, Y.Y. Geng, D.H. Gu, Q. Zhu, Z. Jiang, *Appl. Surf. Sci.* **254**, 1369 (2007)
- [28] S.L. Ou, K.S. Kao, H.F. Chang, T.S. Ko, C.Y. Yeh, *J. Nanomater.* **2014**, 1 (2014)
- [29] Z.M. Chen, Y.Q. Wu, C.Y. He, B. Wang, D.H. Gu, F.X. Gan, *Synth. Met.* **160**, 2581 (2010)