Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 428 (2005) 199–205
thermochimica acta
www.elsevier.com/locate/tca

Temperature memory effect in TiNi-based shape memory alloys

Z.G. Wang[a], X.T. Zu[a,*], Y.Q. Fu[b], L.M. Wang[c]

[a] Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, PR China
[b] Department of Engineering, University of Cambridge, Trumpington Street, Cambridge, CB2 1PZ, UK
[c] Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI 48109, USA

Received 26 August 2004; received in revised form 13 November 2004; accepted 16 November 2004
Available online 18 December 2004

Abstract

An incomplete thermal cycle upon heating of a shape memory alloy (arrested at a temperature between austenite transformation start and finish temperatures, A_s and A_f) induced a kinetic stop in the next complete thermal cycle. The kinetic stop temperature was closely related to the previous arrested temperature. This phenomenon is named temperature memory effect (TME). In this work, the TME induced by incomplete cycling in TiNi and TiNiCu ribbons, TiNiCu thin films and TiNiCu wire showing two-way shape memory effect was systematically investigated by performing either a single incomplete cycle, or a sequence of incomplete cycles with different arrested temperatures. Results showed that the TME is a common phenomenon in shape memory alloys, caused by a partial martensite to parent phase ($M \rightarrow P$) transformation. N points of temperatures could be memorized if N times of incomplete cycles on heating were performed with different arrested temperatures in a decreasing order. On the contrary, if a partial parent phase to martensite ($P \rightarrow M$) transformation was performed by an incomplete cycle on cooling, the next complete $P \rightarrow M$ transformation did show any evidence of TME. The incomplete cycle of parent phase to R-phase and R-phase to parent phase transformations did not show any evidence of TME. Results showed that the capability to memorize the temperature is a specific characteristic of the martensitic phase, and the decrease in microstrains and elastic energy after ICH procedure has significant contributions to the TME.

PACS: 73.61.At; 74.25.Fy; 81.40.Wx

Keywords: TiNi-based shape memory alloys; Temperature memory effect (TME); Incomplete transformation; Differential scanning calorimetry (DSC)

1. Introduction

TiNi-based alloys are well known for their unique shape memory effect (SME) and superelasticity (SE) behavior. The SME and SE have been extensively investigated in the past decades due to their potential use in many applications, especially for smart materials [1,2]. The unique SME and SE originate from martensitic transformation and its reverse transformation. They are first-order solid–solid diffusionless transformations which involve two different solid phases: the martensite (M, monoclinic, thermodynamically stable at low temperature) and the parent phase (P phase, B2 cubic, thermodynamically stable at higher temperature). The characteristic transformation temperatures are defined as follows:

- M_s: martensite start temperature upon cooling;
- M_f: martensite finish temperature upon cooling;
- A_s: reverse transformation start temperature upon heating;
- A_f: reverse transformation finish temperature upon heating.

Using the above terminology, SME can be defined as a phenomenon in which a plastic strain given at a temperature below M_f can be recovered by heating to a temperature above A_f, by virtue of the crystallographically reversible transfor-

* Corresponding author. Tel.: +86 28 83201939; fax: +86 28 83201939.
E-mail addresses: xiaotaozu@yahoo.com, xtzu@uestc.edu.cn (X.T. Zu).

0040-6031/$ – see front matter
doi:10.1016/j.tca.2004.11.018

mation. SE, which is a pseudoelasticity occurring at a temperature above A_f, is caused by a stress-induced martensitic transformation upon loading and a subsequent reverse transformation upon unloading.

Recently, Zheng et al. [3] defined a new phenomenon in shape memory alloys (SMAs), called temperature memory effect (TME). If a reverse transformation of an SMA is arrested at a temperature between A_s and A_f, a kinetic stop will appear in the next complete transformation cycle. The kinetic stop temperature is a "memory" of the previous arrested temperature. Previously this phenomenon was also named thermal arrest memory effect (TAME) [4] or step-wise martensite to austenite reversible transformation (SMART) [5,6]. The SMART was firstly reported in thermally induced phase transformation in TiNi alloys [7]. It is a consequence of a partial reverse M → P phase transformation due to an incomplete cycle on heating (ICH) with a low temperature limit below M_f and a high temperature limit between A_s and A_f. The arrested temperature can be defined as T_{ICH}. The ICH procedure induces a stop in the kinetics of the following complete M → P transformation at a temperature slightly higher than T_{ICH}. The TME can be wiped out: the next M → P complete transformation following the TME cycle will not show TME. The SMART phenomenon has also been found in stress-induced transformation [6]. However, the SMART in the stress-induced transformation cannot be erased by conducting complete mechanical-thermal cycles, but can be erased through an appropriate thermal treatment [6]. So far, the mechanism of the temperature memory effect is still unclear.

SMA thin film has been recognized as a promising material for application in micro-electro-mechanical-system (MEMS), due to its SME, large energy density, pseudoelasticity and high damping capacity. It is very interesting to study whether there is TME in SMA thin films.

In addition to the well known one-way shape memory effect upon heating, shape memory alloys may also exhibit a shape recovery upon cooling, i.e. two-way shape memory effect (TWSME), which is more suitable in the two-way actuation. As far as we know, there is no report whether the TME still exists in a shape memory alloy showing TWSME.

R-phase transformation in TiNi alloys is particularly important for many practical applications, as it exhibits small temperature hysteresis and less sensitivity to various physical factors [8,9]. R-phase transformation is martensitic and thermoelastic, and it also shows SME and SE [10–13]. However, there seems no report on the TME of the R-phase transformation in the literature.

In this study, the TME induced by incomplete cycling in TiNi and TiNiCu ribbons, TiNiCu thin films and TiNiCu wire showing TWSME, were systematically investigated by performing either a single incomplete cycle, or a sequence of incomplete cycles with different arrested temperatures, with an aim to compare TME of different TiNi-based materials and to clarify the origin of the TME.

2. Experimental

Commercial Ti–43 at.%Ni–7 at.%Cu ribbon with a thickness of 0.30 mm, provided by the Northwestern Institute of Non-Ferrous Metal of China, was annealed at 500 °C for 3 h in an evacuated silica tube followed by air-cooling. Samples with dimensions of 5 mm × 5 mm × 0.35 mm were used for differential scanning calorimetry (DSC) measurements.

Ti–41 at.%Ni–9 at.%Cu (TiNiCu9) and Ti–46 at.%Ni–4 at.%Cu (TiNiCu4) thin films were prepared by co-sputtering of a TiNi target and a Cu target on (1 0 0) silicon wafers using a magnetron sputter, Coaxial MSS3A, England [14]. Substrate temperature was 450 °C and substrate holder was rotated during deposition to achieve the uniform deposition. The base pressure of main chamber was 1×10^{-7} Torr. The argon pressure was 1.0 mTorr during deposition and the substrate-to-target distance was 100 mm. TiNiCu9 films peeled off from substrate were used for the temperature memory effect measurements. TiNiCu4 film on the Si substrate was also used to measure the TME with dimension of 5 mm × 5 mm, and a Si substrate with same dimension was used as a reference.

Ti–43 at.%Ni–7 at.%Cu wire with a diameter of 0.50 mm, provided by the Northwestern Institute of Non-Ferrous Metal of China, was used to train TWSME spring. The detailed training process of TWSME was described in reference [15] (as shown in Fig. 1). The TiNiCu wires were wound on a cylindrical jig, then annealed at 500 °C for 1 h followed by air-cooling. The mean diameter of the spring is 4.5 mm and the pitch of the spring is 0.1 mm after annealing. Then the springs were extended till the pitch reached 12 mm and constrained at the extension state and annealed at 550 °C for 1 h followed by air-cooling. The springs were thermal-mechanically trained for 150 cycles, and the elongation was about 60%. About 10 mg TiNiCu wire showing TWSME was used to do the DSC measurement.

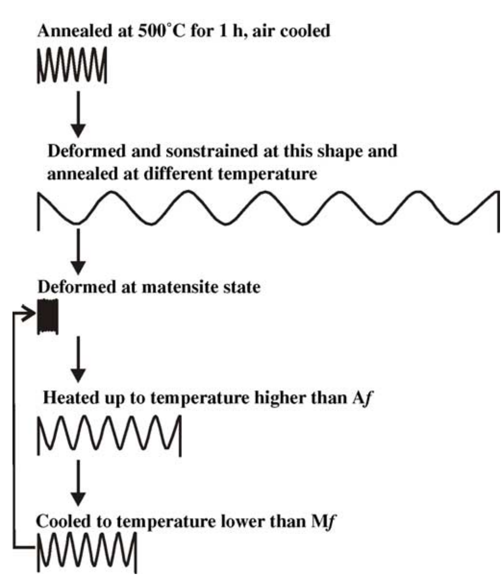

Fig. 1. The procedure of processing TWSME TiNi SMAs spring.

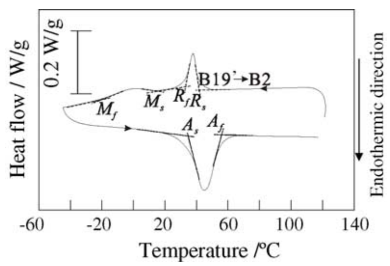

Fig. 2. Transformation behavior of a Ti–50.7at.%Ni SMA annealed at 450 °C for 1 h in an evacuated silica tube followed by air-cooling.

Ti–50.7 at.%Ni ribbon with a dimension 5 mm × 5 mm × 0.35 mm, provided by the Northwestern Institute of Non-Ferrous Metal of China, was annealed at 450 °C for 1 h in an evacuated silica tube followed by air-cooling. The transformation behavior of the TiNi ribbon is shown in Fig. 2. Upon cooling, two-step transformation among austenite, R-phase and martensite can be observed, while upon heating, only one-step transformation between martensite and austenite can be detected. This sample was used to study the temperature memory effect of the R-phase transformation in the temperature range between 10 and 85 °C.

The phase transformation behavior of the samples was studied using differential scanning calorimetry (DSC131, Setaram Company, France) with a scanning rate of 10 °C/min in nitrogen atmosphere.

3. Results

3.1. Temperature memory effect in TiNiCu ribbon

The DSC result of TiNiCu ribbons with a global transformation cycle is shown in Fig. 3(a). Those of TiNiCu ribbons with single incomplete cycle upon heating at T_{ICH} = 58.6, 61.1 and 64.3 °C, respectively, are shown in Fig. 3(b), (c) and (d), and the kinetic stops are clearly observed on the heat flow curves upon heating. Fig. 4(a) shows the DSC results of TiNiCu ribbon after performing three successive incomplete cycles upon heating at temperatures of 63.6, 61.3 and 58.3 °C, respectively (with decreasing order), and three kinetic stops can be clearly observed corresponding to the three arrested temperatures. Fig. 4(b) shows the DSC results of TiNiCu ribbon after performing three successive incomplete cycles upon heating at three arrested temperatures of T_{ICH} = 58.3, 61.3 and 63.3 °C but with increasing order. Only one kinetic stop can be observed as shown in Fig. 4(b), and the maximum temperature of T_{ICH} = 63.3 °C is memorized. The phenomenon shows that only the highest temperature of the three successive temperatures (with increasing order) is memorized implies that further heating to a temperature exceeding the previous stop temperature can wipe out the temperature memory effect caused by the previous stop temperature. The above results consist with those from previous reports [16]. If a number N of ICHs with different arrested temperatures is performed in a decreasing order, N interrup-

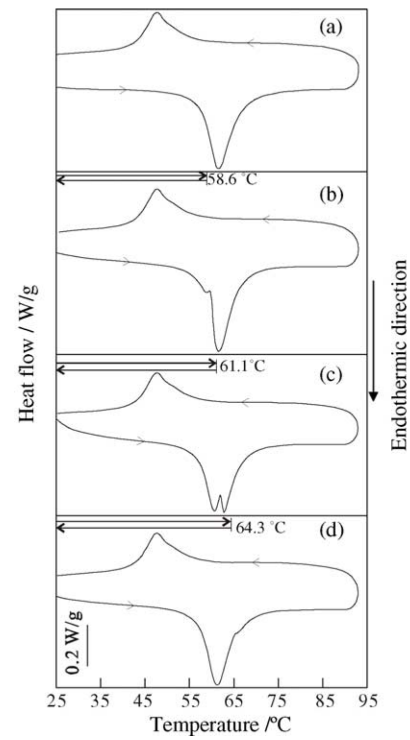

Fig. 3. DSC results of a TiNiCu ribbon (a) and the temperature memory effect of same sample with single incomplete cycle on heating at 58.6 (b), 61.1 (c) and 64.3 °C (d).

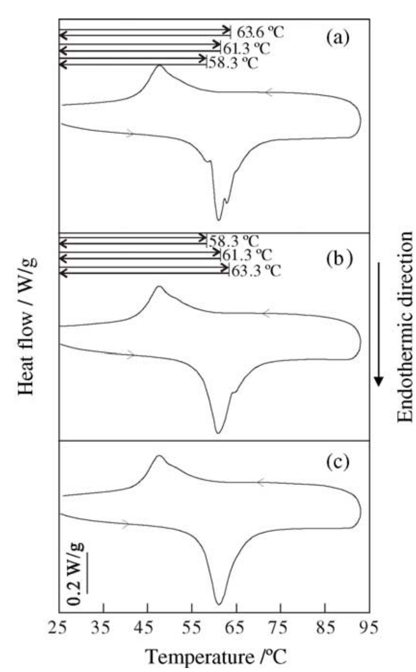

Fig. 4. DSC results showing the temperature memory effect of TiNiCu ribbon with three single stops at T_{ICH} = 63.6, 61.3 and 58.3 °C with decreasing order (a), T_{ICH} = 58.3, 61.3 and 63.3 °C with increasing order (b) and subsequent global transformation (c).

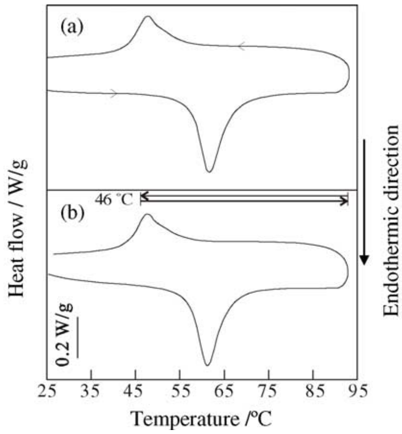

Fig. 5. An incomplete cycle on cooling does not show any temperature memory effect of TiNiCu ribbon.

tions can be found. The TME is a reversible process, and from Fig. 4(c) it can be noticed that the transformation kinetics of the global transformation (Fig. 3(a)) is completely recovered in the following complete cycle.

Fig. 5(a) shows global transformation of the TiNiCu ribbon and (b) shows DSC results of the TiNiCu ribbon after performing an incomplete cycle upon cooling, with an arrested temperature of 46 °C. In this case, only part of austenite transforms into martensite phase, and the rest of the austenite remains. The transformed martensite can change to austenite again with further increasing temperature above A_f. However, results showed that the next complete P → M transformation does not show any evidence of kinetic interruption, which can support the previous findings in Ref. [17].

For practical applications, shape memory alloys are often used in many thermal cycles. It is interesting to study the repeatability of TME after many cycles. We define one incomplete thermal cycle upon heating and subsequent global transformation cycle as one working cycle. Fig. 6 shows the first working cycle and 30th working cycle of a TiNiCu ribbon. We can see that there is perfect repeatability for the TME for the TiNiCu ribbon.

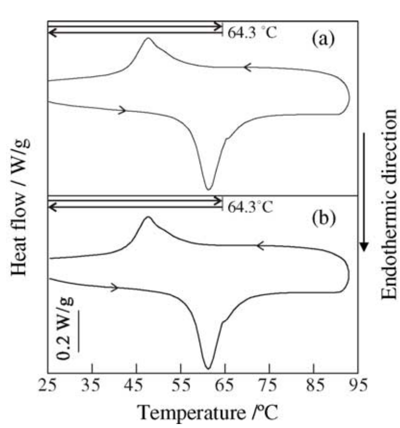

Fig. 6. The first cycle (a) and 30th working cycles (b) of the temperature memory effect of a TiNiCu ribbon.

3.2. *Temperature memory effect in TiNiCu thin films*

Fig. 7(a) shows the DSC results of the TiNiCu4 film attached on a Si substrate. Upon heating and cooling, there is only one peak observed, corresponding to transformation between austenite and martensite. Fig. 7(b), (c) and (d) show the temperature memory effects of the TiNiCu4 thin film attached on a Si substrate in one single incomplete cycle upon heating at the arrested temperatures of 75.2, 76.7 and 78.2°C, respectively. Clearly one kinetic stop temperature, corresponding to the arrested temperatures can be clearly observed for each DSC curves. Fig. 7(e) shows the DSC results of TiNiCu4 film performed with three successive stops at T_{ICH} = 78.2, 76.7 and 75.2°C with decreasing order, and three kinetic stop temperatures can be observed in the curve. For all the above results, the kinetic stop temperature is slightly higher than the arrested temperature. The temperature memory effect can be easily wiped out by the following complete thermal cycle as revealed from Fig. 7(f).

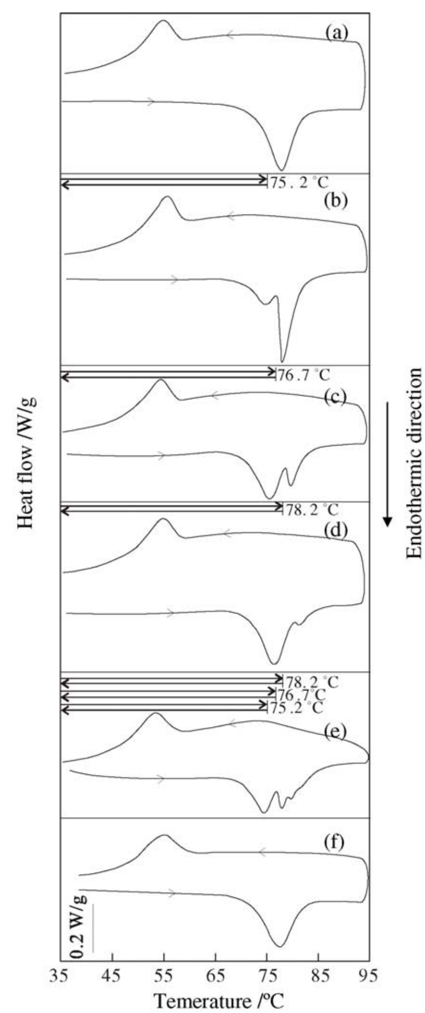

Fig. 7. DSC results of a TiNiCu4 thin film (a) and the temperature memory effect of same sample with single incomplete cycle on heating at 75.2 (b), 76.7 (c), 78.2 °C (d), three single stops at T_{ICH} = 78.2, 76.7 and 75.2 °C with decreasing order (e) and subsequent global transformation (f).

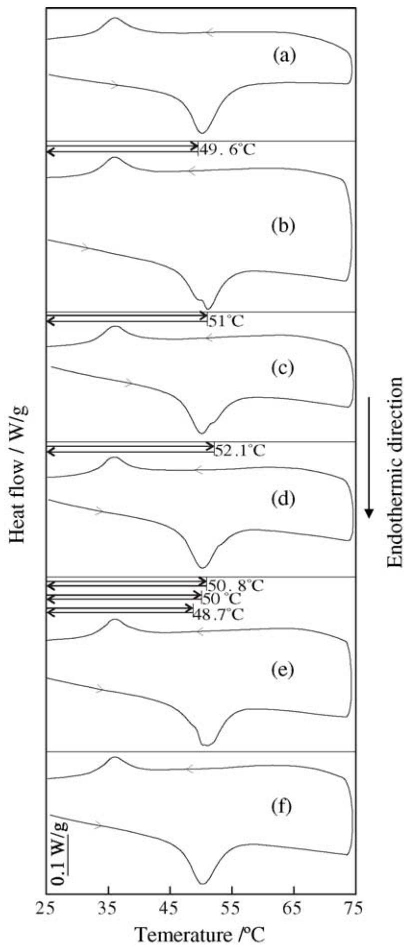

Fig. 8. DSC results of a TiNiCu9 thin film (a) and the temperature memory effect of same sample with single incomplete cycle on heating at 49.6 (b), 51 (c), 52.1 °C (d), three single stops at T_{ICH} = 50.8, 50 and 48.7 °C with decreasing order (e) and subsequent global transformation (f).

Fig. 8(a) shows the DSC results of the free-standing TiNiCu9 films (peeled from the Si substrate). Upon heating and cooling, there is only one peak observed, corresponding to transformation between austenite and martensite. Fig. 8(b), (c) and (d) shows the temperature memory effects of the TiNiCu9 thin film in one single incomplete cycle upon heating stopping at arrested temperatures of 49.6, 51 and 52.1°C, respectively. Clearly one kinetic stop temperature can be observed in each test. Fig. 8(e) shows the DSC results of TiNiCu9 film performed with three successive stops at T_{ICH} of 50.8, 50 and 48.7°C with decreasing order, and three kinetic stop temperatures can be clearly observed in the curve. The temperature memory effect can also be easily wiped out by the following complete thermal cycle as shown in Fig. 8(f). Compared the results from Figs. 7 and 8, it can be concluded that the substrate has no effect on the temperature memory effect.

Figs. 9 and 10 show the DSC results of TiNiCu4 and TiNiCu9 films after performing an incomplete cycle at a temperature between M_s and M_f upon cooling. For all

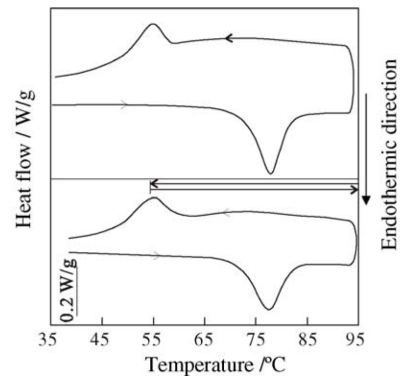

Fig. 9. An incomplete cycle on cooling does not show any temperature memory effect of a TiNiCu4 thin film.

the testing results, theirs is no evidence of kinetic interruption for the next complete P → M transformation. Results confirmed that the temperature memory effect of the TiNiCu film is identical to that of the TiNiCu bulk material.

3.3. Temperature memory effect in TiNiCu wire with TWSME

Fig. 11(a) shows the DSC results of TiNiCu wire with TWSME, revealing the one-stage transformation between austenite and martensite. Fig. 11(b) and (c) shows the temperature memory effect of TiNiCu wire with the arrested temperature of 62.5 and 41 °C upon either heating or cooling process. The kinetic stop temperature can be observed clearly in the incomplete cycle during heating but cannot be observed for the incomplete cycle during cooling. Results confirmed that the TME of the TiNiCu wire with TWSME are identical to those with only one-way shape memory effect.

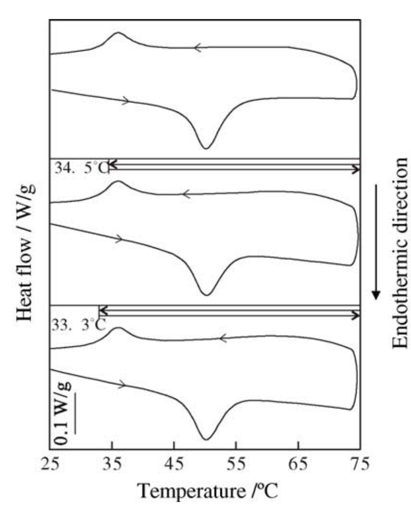

Fig. 10. An incomplete cycle on cooling does not show any temperature memory effect of a TiNiCu9 thin film.

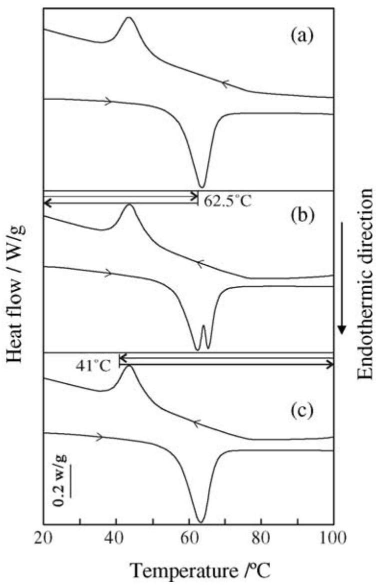

Fig. 11. DSC results of a TiNiCu wire with two-way shape memory effect (a), the temperature memory effect of same sample with single incomplete cycle on heating at 62.5 (b) and an incomplete cycle on cooling does not show any temperature memory effect (c).

3.4. Temperature memory effect of R-phase transformation in TiNi ribbon

Fig. 12(a) shows DSC result of the transformation between R-phase and parent phase. Fig. 12(b) and (c) are the DSC results of the TiNi ribbon after performing incomplete cycles on heating at the arrested temperatures of 40.5 and 42.5 °C, respectively. There is no apparent evidence of kinetic interruptions for the R-phase to B2 phase transformation, indicating no TME.

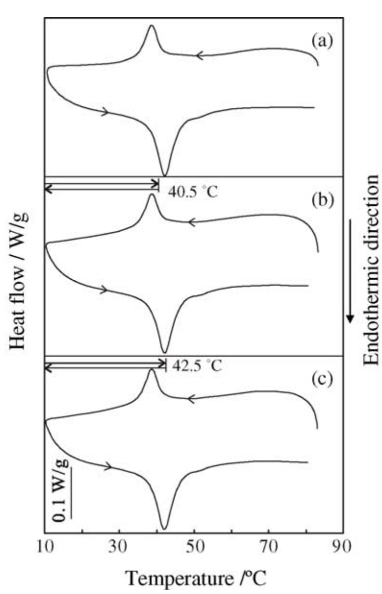

Fig. 12. DSC results of the transformation between R-phase and B2 phase for a TiNi ribbon (a) and after performing the single stops at T_{ICH} = 40.5 (b) and 42.5 °C (c). There is no evidence of kinetic interruptions for the R-phase → B2 phase transformation after the single stops.

4. Discussion

The temperature memory effect performed on four types of TiNi-based materials revealed clearly that TME is a common phenomenon in shape memory alloys, which is induced by a partial reverse M → P transformation. If a number *N* of ICHs with different arrested temperatures is performed with decreasing order, *N* temperatures can be memorized. On the contrary, if a partial P → M transformation is performed by an incomplete cycle on cooling, the next complete P → M transformation does not show any evidence of temperature memory effect. The partial P → R-phase and R-phase → P transformations do not show any evidence of temperature memory effect. Results indicate that the capability to memorize the arrested temperature is a special characteristic related to the martensite in TiNi alloys.

During the partial reverse M → P transformation, the martensite to austenite transformation is stopped at a certain temperature between A_s and A_f, and only part of the martensite transforms into the parent phase, with the rest of the martensite remaining. Here the remaining martensite is called M1. With further decreasing the temperature below M_f, the parent phase transforms back to martensite, and the newly formed martensite is called M2. During the following heating process, M2 and M1 transform into the parent phase sequentially, causing a kinetic stop between these transformations. Several researchers explained the temperature memory effect using the release of elastic strain energy, which serves as driving force during the reverse transformation [18]. However, the proposed mechanisms are quite controversial between each other. Madangopal et al. [4] proposed that M2 could store more elastic strain energy than M1 in a global transformation, therefore the reverse transformation of M2 could be somehow pre-positioned. Airoldi et al. [6] explained the temperature memory effect using the lack of elastic strain energy in M2, therefore a higher temperature is necessary to start the transformation of M1, after the transformation of M2 finishes.

Martensitic transformation in shape memory alloys occurs between austenite (A, a crystallographic more-ordered parent phase) and martensite (M, a crystallographic less-ordered product phase). Upon cooling, the atoms will arrange themselves in twinning structure with periodic stacking order structure, and 24 variants of the martensites could exist [19]. During the transformation from austenite (B2) to martensite, some elastic strain energy is stored in the thermoelastic martensite variants. The interphase boundaries between the martensites and the parent phase are coherent phase boundaries. The coherent energy resulted from the lattice distortions at the coherent interfaces of the adjacent phases has a prominent effect on the transformation characteristics [20]. The TME should not be only attributed to the release of the elastic strain energy stored in the martensite variants, and the coherent energy of the adjacent phases also contributes to the TME.

Results from Zheng et al. [3] showed that the formation of M2 is the result of the nucleation and growth of martensite nuclei in the parent phase, but not the growth of the already existing M1 martensite, otherwise M2 would have the same oriented structure as M1. When the martensite to austenite transformation is stopped at a certain temperature T_{ICH}, only part of the martensite transforms into the parent phase, there are coherent strain existed resulted from the lattice distortions at the coherent interfaces of the parent phase and martensite with the temperature decreased below M_f, the parent phase transforms back to martensite. The nucleation and growth of the preferential martensite variants are favored by the relaxation of the coherent strain. Therefore, the M1 and M2 have different orientation structures and different elastic energies between martensitic variants, which cause the different transformation temperatures of M1 and M2 into austenite during the next heating process. However, the X-ray diffraction and electrical resistance results clearly show that the martensite has the same orientation structure before and after ICH procedure, with a narrowing of diffraction peaks and a decrease of electrical resistance [17,21,22]. So the decrease in microstrains and elastic energy after ICH procedure has significant contributions to the TME.

It is still unclear why the TME related to the martensite and R-phase show different results. This may be caused by the less lattice movement and small transformation strain of R-phase transformation compared to those from martensitic transformation [23]. Therefore, the coherent stress has little effect on the orientation structure of the M2 phase.

5. Conclusions

In this work, the TME induced by incomplete cycling in TiNi and TiNiCu ribbons, TiNiCu thin films, and TiNiCu wire showing two-way shape memory effect, was investigated by performing either a single incomplete cycle, or a sequence of incomplete cycles with different arrested temperatures. The results showed that TME is common phenomenon in shape memory alloys, which is induced by a partial reverse $M \rightarrow P$ transformation. N points of temperatures can be memorized if a number N of incomplete cycles on heating with different arrested temperatures with decreasing order is performed. On the contrary, if a partial $P \rightarrow M$ transformation is performed by an incomplete cycle during cooling, the next complete $P \rightarrow M$ transformation does not show any evidence of temperature memory effect. The partial $P \rightarrow$ R-phase and R-phase $\rightarrow P$ transformation did not show any evidence of temperature memory effect. The decrease in microstrains and elastic energy after ICH procedure has significant contributions to the TME.

Acknowledgments

This study was financially supported by the National Natural Science Foundation of China (10175042) and by the Sichuan Young Scientists Foundation (03ZQ026-059) and by the Project-sponsored by SRF for ROCS, SEM.

References

[1] Z.G. Wei, R. Sandstrom, J. Mater. Sci. 33 (1998) 3743.
[2] Z.G. Wei, R. Sandstrom, S. Miyazaki, J. Mater. Sci. 33 (1998) 3763.
[3] Y.J. Zheng, L.S. Cui, J. Schrooten, Appl. Phys. Lett. 84 (2004) 31.
[4] K. Madangopal, S. Banerjee, S. Lele, Acta Metall. Mater. 42 (1994) 1875.
[5] G. Airoldi, A. Corsi, G. Riva, Scr. Materialia 36 (1997) 1273.
[6] G. Airoldi, A. Corsi, R. Riva, Mater. Sci. Eng. A 241 (1998) 233.
[7] W.A. Johnson, J.A. Domingue, S.H. Reichman, J. Phys. 43 (1982) 285.
[8] I. Ohkata, H. Tamura, Proceedings of the 1996 MRS Fall Symposium, Boston, MA, USA, 1996, p. 1202.
[9] Z.G. Wang, X.T. Zu, X.D. Feng, J.Y. Dai, Mater. Lett. 54 (2002) 55.
[10] H.C. Ling, R. Kaplow, Mater. Sci. Eng. A 11 (1981) 193.
[11] S. Miyazaki, K. Otsuka, Metall. Trans. A 17 (1986) 53.
[12] S. Miyazaki, K. Otsuka, Philos. Mag. A 50 (1984) 393.
[13] G.B. Stachowiak, P.G. MoCormick, Acta Metall. 36 (1988) 291.
[14] H.J. Du, Y.Q. Fu, Surf. Coat. Technol. 176 (2004) 182.
[15] Z.G. Wang, X.T. Zu, X.D. Feng, L.B. Lin, S. Zhu, L.P. You, L.M. Wang, Mater. Sci. Eng. A 345 (2003) 249.
[16] G. Airodi, G. Riva, in: E. Hornbogen, N. Jost (Eds.), The Martensitic Transformation in Science and Technology, DGM, Oberursel, Germany, 1989, p. 305.
[17] G. Airodi, S. Besseghini, G. Riva, Proceedings of the International Conference on Martensitic Transformation, ICOMAT-92, 1993, p. 959.
[18] Z.Y. Xu, Martensite and Matensite Transformation, Science Press, China, 1999, p. 59 (in Chinese).
[19] K. Otsuka, C.M. Wayman, Shape Memory Materials, Cambridge University Press, Cambridge, 1998, p. 2.
[20] Y. Huo, X. Zu, Continuum Mech. Thermodyn. 10 (1998) 179.
[21] G. Riva, G. Airoldi, S. Besseghini, Meccanica 30 (1995) 495.
[22] G. Airoldi, G. Carcano, G. Riva, J. Phys IV C4 (1991) 277.
[23] X. Ren, N. Miura, J. Zhang, K. Otsuka, K. Tanaka, M. Koiwa, S. Suzuki, Y.I. Chumlyakov, Mater. Sci. Eng. A 312 (2001) 196.