

# Temperature memory effect in TiNi-based shape memory alloys

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## 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.

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## 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-

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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  $M \rightarrow P$  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  $M \rightarrow P$  transformation at a temperature slightly higher than  $T_{ICH}$ . The TME can be wiped out: the next  $M \rightarrow P$  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  $1 \times 10^{-7}$  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.

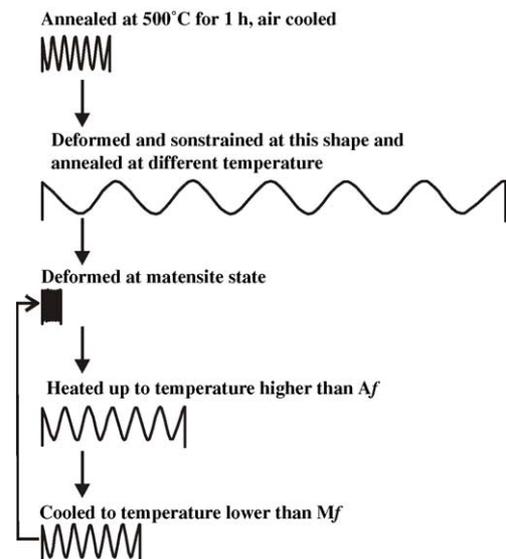


Fig. 1. The procedure of processing TWSME TiNi SMAs spring.

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