Effect of incomplete transformation on the transformation behavior in TiNi shape memory alloys

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An incomplete transformation upon heating induces temperature memory effect (TME) in shape memory alloy (SMA) [1]. If a reverse transformation of a SMA is arrested at a temperature between reverse phase transformation start and finish temperatures (i.e., 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) [2] or step-wise martensite to austenite reversible transformation (SMART) [3]. An incomplete transformation upon cooling can induce splitting of the reverse transformation in a sample showing Rphase transformation [4]. In a sample showing R-phase transformation, when the stop temperature arrested in a value between $R_{\rm f}$ and $M_{\rm s}$, the heat flow detected upon following heating only shows one endothermic peak. With decreasing the arrested temperature to a temperature between M_s and M_f , two endothermic peaks (or peak splitting) can be observed upon the following heating.

The mechanism of the TME and peak splitting is still unknown. In this work, incomplete transformation upon heating and cooling is performed in TiNi shape memory alloys showing or without showing R-phase transformation. The purpose of this work is to discuss the mechanism of TME and peak splitting.

The investigations have been carried out on commercial Ti-49.8at.%Ni wire with a diameter of 0.55 mm, provided by the Northwestern Institute of Non-Ferrous Metal of China, was annealed at 400 °C and 550 °C for 1 hr followed by air-cooling. Samples with weight of 10 mg were used for differential scanning calorimetry (DSC) measurements. DSC tests (using an equipment of DSC131, Setaram company, France) were performed with a scanning rate of 10 °C/min in nitrogen atmosphere. The global transformation behavior of the above samples was measured firstly, and then the incomplete transformation behavior was recorded.

Fig. 1 shows the DSC results of TiNi wire annealed at 400 °C for 1 hr. The global transformation result (Fig. 1(a)) shows that 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. The DSC results with incomplete cycle upon heating at 68.6 and 69.1 °C are shown in Fig. 1(b) and (c) respectively, and the kinetic stops are clearly observed on the heat flow curves upon heating. Fig. 1(d) shows an arrested temperature (44 °C) lower than R_s but higher than M_s , the heat flow curve detected upon following heating shows one endothermic peak, and the peak emerges at the lower temperature side of that of the martensite to parent transformation in the global transformation. With decreasing the arrested temperature to a temperature 33 °C which is between M_s and M_f (Fig. 1(e)), two endothermic peaks can be observed upon the following heating. The second peak lies in the temperature range between A_s and A_f .

Fig. 2 shows the effect of incomplete transformation upon cooling on the transformation behavior after performing an incomplete transformation upon heating at an arrested temperature of 69.2 °C in a sample showing R-phase transformation. With an arrested temperature upon cooling lower than R_s but higher than M_s , the heat flow curve detected upon following heating shows two endothermic peaks, one is a new peak denoted by peak R, the other peak is M2. M1 does not occur. With decreasing the arrested temperature to a temperature between M_s and M_f , three endothermic peaks can be observed upon the following heating, i.e. the R, M1, and M2 peak. With further decreasing the arrested temperature lower than $M_{\rm f}$, the peak R disappears and only M1 and M2 occur successively. The decrease of latent heat of peak R and the increase of that of M1 with decreasing arrested temperature are shown in Fig. 3.

Fig. 4 shows the effect of incomplete transformation upon cooling on the transformation behavior after performing an incomplete transformation upon heating at an arrested temperature of 73.6 °C in a sample 550 °C for 1 hr. When the stop temperature arrested at a value higher than M_s , the heat flow detected upon following heating only shows one endothermic peak M2. With decreasing the arrested temperature to a value lower than M_s endothermic peaks M1 can be observed upon the following heating. Fig. 5 shows the increase of the latent heat of M1 with decreasing the arrested temperature.

Martensitic transformation in shape memory alloy occurs between austenite (A, a crystallographic more-ordered parent phase) and martensite (M, a



Figure 1 DSC results of TiNi wire annealed at 400 $^{\circ}$ C for 1 hr (a) global transformation and incomplete transformation at arrested temperature of (b) 68.6 $^{\circ}$ C, (c) 69.1 $^{\circ}$ C upon heating and incomplete transformation at arrested temperature of (d) 44 $^{\circ}$ C, (e) 33 $^{\circ}$ C upon cooling.

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 [5]. 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 called the habit planes. The coherent energy resulted from the lattice distortions at the coherent interfaces of the adjacent phases has a prominent effect on the transformation characteristics [6]. 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 [7].

In the TiNi samples showing R-phase transformation, after performing the incomplete transformation upon heating only M1 transforms into parent phase with the arrested temperature lying between R_s and M_s upon cooling, only the M1 transformed into R-phase, so only two peaks occur in the following heating process corresponding to the transformation of R-phase \rightarrow parent phase and M2 \rightarrow parent phase, respectively. With further decreasing the arrested temperature to a temperature lower than M_s and higher than $M_{\rm f}$, the parent phase transforms (M1) into R-phase completely, and only part of the R-phase transforms into the martensite, with the rest of the R-phase remaining. During the following heating process, the remained R-phase and martensite will transform into parent phase, contributing to the latent heat of the peak R and the peak M1, respectively, and peak M2 still oc-



Figure 2 Effect of incomplete transformation upon cooling on the DSC curves of a TiNi wire annealed at 400 °C for 1 hr after performing an incomplete transformation upon heating.



Figure 3 The decrease of latent heat of peak R and the increase of that of M1 with decreasing arrested temperature of the sample annealed at 400 °C for 1 hr.

curs. This may be caused by the less lattice movement and small transformation strain of R-phase transformation compared to those from martensitic transformation [8], thus less driving force is required to finish the R-phase to parent phase transformation than that of the martensite to parent phase transformation.



Figure 4 Effect of incomplete transformation upon cooling on the DSC curves of a TiNi wire annealed at $550 \,^{\circ}$ C for 1 hr after performing an incomplete transformation upon heating.



Figure 5 The increase of the latent heat of M1 with decreasing the arrested temperature of the sample annealed at 550 °C for 1 hr.

Therefore, the R-phase \rightarrow B2 transformation could occur at a low temperature, while the martensite \rightarrow B2 transformation could happen at high temperature. With further decreasing the arrested temperature lower than $M_{\rm f}$, the M1 transform into martensite completely, and M1 and M2 transform into parent phase successively. It is the same in the sample showing no R-phase transformation. After performing the incomplete transformation upon heating only M1 transforms into parent phase with arrested at a value higher than $M_{\rm s}$, there is no martensitic transformation. M1 is still parent phase, so only the M2 peaks occur during the following heating process. When the arrested temperature is lower than M_s , only part of the parent phase M1 transforms into the martensite, with the rest of the parent phase M1 remaining. Therefore, with the decreasing of arrested temperature, more martensite forms, which leads to the increase of the latent heat of transformation of M1.

In summary the incomplete transformation upon cooling after performing an incomplete transformation upon heating has a prominent effect on the transformation behavior. In a sample showing R-phase transformation, when the stop temperature arrested in a value between R_f and M_s , the heat flow detected upon following heating only shows two endothermic peaks corresponding to R-phase \rightarrow B2 and martensite \rightarrow B2 transformation. With decreasing the arrested temperature to a temperature between M_s and M_f , three endothermic peaks can be observed upon the following heating corresponding to R-phase \rightarrow B2 and two kinds of martensite \rightarrow B2 transformation. TME is originated from the relaxation of both the strain energy between martensites and coherent strain between parent phase and martensite.

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