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Effect of low temperature ageing on the transformation behaviour of near-equiatomic NiTi

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A unique three-stage transformation behaviour on cooling has been observed in a Ti–50.2 at % Ni alloy after a low temperature ageing treatment. The cooling transformation in the aged alloy occurred as a three-stage process of austenite-to-R phase transition followed by two separate martensitic transformations. The R phase transition developed during ageing with a clear second order nature initially and gradually evolved into a predominantly first order process. The occurrence of the R transition is not associated with a decrease in the martensitic transformation temperature during ageing. The reverse transformation to austenite occurred in one step, regardless of the nature of the forward transformation on cooling. An all-round shape memory effect was observed in aged samples. These experimental observations suggest that precipitation induced by the ageing treatment is responsible for the unusual transformation behaviour.

1. Introduction

An unusual multi-stage transformation behaviour has been observed in near-equiatomic NiTi alloys after low temperature ageing treatments [1–4]. The behaviour is characterized by a three-stage transformation on cooling and a two-stage transformation on heating. The experimental observations in preliminary studies seem to suggest two different transformation routes for the three-stage cooling transformation, although both involve only two product phases forming from the austenite; – the R phase and martensite. One transformation route, found in a Ti–50.5 at % Ni [2] alloy and a Ti–51.14 at % Ni alloy [4], involves an austenite-to-R phase transition (A → R) followed by two separate martensitic transformations from the R phase (R → M1 and R → M2). In another study of a Ti–50.2 at % Ni alloy under nearly identical ageing conditions to those reported by Favier *et al.* [2], it was found that the first stage involved only a partial A → R transformation and the following two transformations were R → M1 and A → M2 transformations, respectively [3]. In both cases two separate martensitic transformations have been observed without any differences in the product martensites of the two transformations being observed. In those investigations, the multi-stage transformation behaviour has been measured using different techniques including differential scanning calorimetry (DSC) and internal friction measurements [1, 4] and the effects of ageing time and previous heat treatment conditions have been studied [2, 3]. Several mechanisms for this unusual behaviour, including precipitation induced stress fields, compositional inhomogeneity [2, 3] and vacancy ordering during ageing [1, 4], have been suggested. However, as yet there is no direct experimental evidence which favours any of the proposed mechanisms. This paper reports the results of a further investigation of this phenomenon.

2. Experimental procedure

The material used in this study was a commercial Ti–50.2 at% Ni alloy. The as-received wires (1–1.5 mm in diameter) were initially annealed at 1173 K for 1.8 ks and quenched into water. Samples of the annealed wires were then aged at different temperatures ranging from 598 to 698 ± 0.1 K in sealed quartz tubes with a high purity argon atmosphere. The transformation behaviour of the samples after different stages of ageing was studied using a Perkin–Elmer DSC4 differential scanning calorimeter. The transformation temperatures reported here correspond to the temperature of maximum heat flow of a DSC measurement. A constrained ageing treatment was also conducted to investigate the "all-round shape memory" (ARSM) effect [5]. In this experiment the as-received wires were cold rolled to ribbons of 2 mm in width and 0.22 mm in thickness. Following annealing the ribbons were constrained within a circular steel mould of 22 mm radius during ageing.

3. Results

3.1. Effect of ageing time

Fig. 1(a and b) shows the DSC curves of a specimen aged at 598 K for different times. The transformation on cooling exhibited a change from a single step A → M transformation to a two step A → R → M

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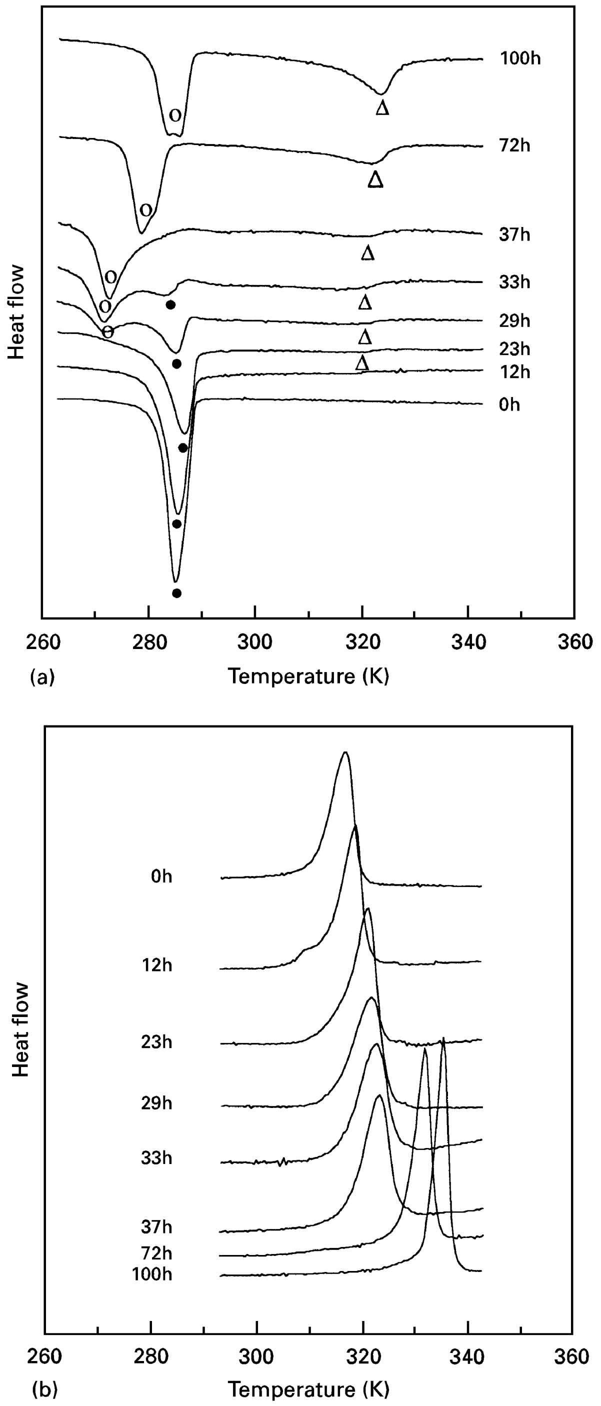

Figure 1 Effect of ageing on transformation behaviour: (a) Exothermic transformations on cooling, Key: (●) M1 (A – M); (○) M2 (R – M) and (△) R (A – R) (b) Endothermic transformation on heating.

transformation with increasing ageing time. For intermediate ageing times, two separate martensitic transformations were observed, with the DSC peak weight of the second martensitic transformation (M2) increasing at the expense of that of the first (M1). The occurrence of the second martensitic transformation appeared to coincide with the occurrence of the R phase transition. The R phase transition appeared to start with a second-order transition nature and gradually developed into a first order transformation. The heating transformation, as shown in Fig. 1b, exhibited a single stage transformation, regardless of the sequence of the cooling transformation.

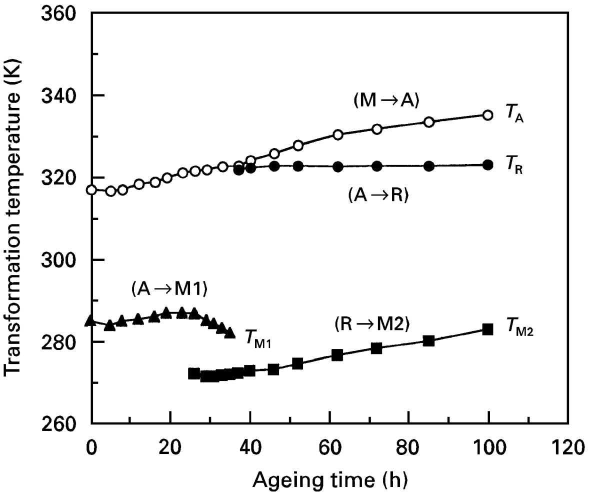

Figure 2 Effect of ageing time on the transformation temperatures.

Measurements of the effect of ageing time on transformation temperatures are shown in Fig. 2. It is seen that the temperature of the reverse transformation, T_A, increased monotonously during the course of ageing, by nearly 20 K after 100 h. The R phase transition emerged at ~321 K after ~23 h of ageing, which was 34 K above the temperature of the M1 transformation, T_{M1}, or 36 K above the T_{M1} at the start of ageing. The R phase transition temperature remained constant throughout the ageing process. It is of interest to note that at the onset of the R phase transition, its temperature is equal to T_A. T_{M1} did not vary significantly with ageing time until the onset of the R phase transition, when it started to decrease. The onset of the M2 transformation coincided with the R phase transition, with T_{M2} being approximately 15 K less than T_{M1}. T_{M2} increased with ageing time to approximately the same level as the initial value of T_{M1} after ageing for 100 h.

Measurements of the transformation heat are shown in Fig. 3. The two separate martensitic transformations on cooling were combined together for the measurement, due to the partial overlapping of the two peaks. The R phase transition evolved gradually from a second order process to a first order process during ageing, as evident in Fig. 1(a and b), making the measurement of transformation heat very difficult. At early stages of ageing, when the first order nature of the R transition was not fully developed, the heat of the transition was estimated by integrating the area between the "step" and a line joining the baselines on two sides of the step. Consequently, the measurements have an inherently low accuracy. It is seen from Fig. 3 that the latent heat of the reverse transformation remained unchanged with increasing ageing time, at ~20 J g^{-1}. The latent heat of the martensitic transformation (M1) on cooling decreased rapidly during the initial stages of ageing prior to the appearance of the R phase transition and the second martensitic transformation, resulting in a significant increase in the net heat loss for a complete transformation cycle. The latent heat of the M2 transformation remained unaffected by further ageing once the M1

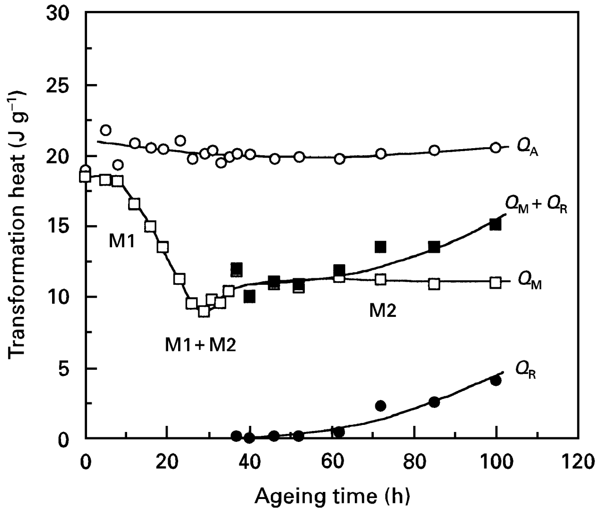

Figure 3 Effect of ageing time on the transformation heat.

transformation had disappeared. The latent heat of the R phase transition increased progressively, as its first order nature developed during ageing.

3.2. Effect of ageing temperature

The effect of ageing temperature was investigated at five different temperatures between 598–698 K, at 25 K intervals. It was observed that increasing ageing temperature accelerated the ageing process. With exactly the same trend as that shown in Fig. 1(a and b), the M2 transformation always appeared together with the R phase transition, which developed progressively from a pure second order nature to a transition with a dominant first order characteristic. A transition from the M1 to M2 transformation was observed over the entire ageing temperature range studied. The critical times for the appearance of M2 and the disappearance of M1 transformations decreased with increasing ageing temperature. The ageing time range within which the M1 and M2 transformations co-existed also decreased with increasing ageing temperature, resulting in the M1 and M2 transformations being observed to co-exist only at ageing temperatures below 648 K. The transformation behaviour of the alloy during cooling is summarized in an ageing time–temperature chart shown in Fig. 4. It is seen that there exist three regions on the chart. In region I the alloy transformed from austenite to martensite in one step. In region III the cooling transformation took two steps from austenite to the R phase and then the R phase transformed to martensite. Region II is where the two martensitic transformations co-existed. In this region the R phase was not fully developed as a first order transition. Region II contracts with increasing ageing temperature and vanishes at ~680 K.

Fig. 5 shows the measurements of T_A and T_{M2} temperatures for specimens aged at different temperatures. It is seen that both T_A and T_{M2} increased with ageing time at all ageing temperatures. For ageing temperatures ⩾648 K, transformation temperatures appeared to reach saturation after certain stages of ageing, suggesting completion of the ageing process. Increasing the ageing temperature in this range seemed to decrease the saturation levels of the transformation temperatures as well as the necessary ageing time required for the transformation temperatures to reach saturation. For lower ageing temperatures, i.e., 598 and 623 K, the transformation temperatures did not reach saturation at the end of the ageing treatment. At 100 h when the ageing treatment was terminated, both T_A and T_{M2} were measured to be higher for the specimen aged at 623 K than for the specimen aged at 598 K. It is expected that the transformation temperatures would be further increased if the specimens had been allowed to reach completion of the ageing process.

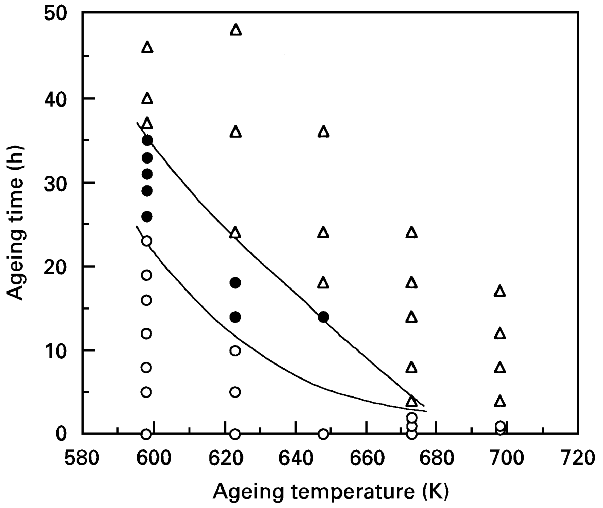

Figure 4 Effect of ageing on the transformation behaviour during cooling. Key: (○) A − M1; (●) A − R − M1 + M2 and (△) A − R − M2.

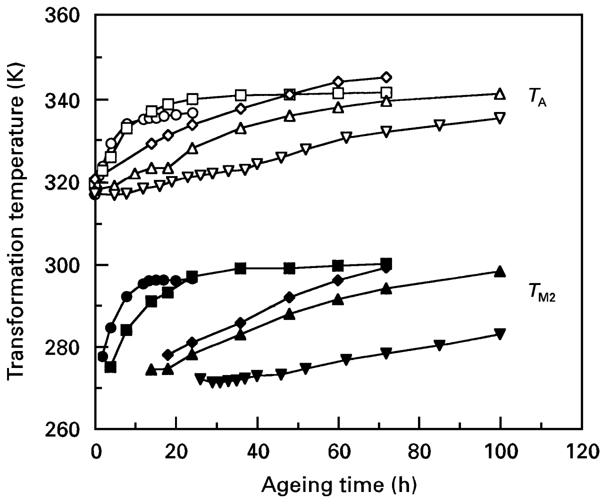

Figure 5 Effect of ageing temperature on transformation temperatures. Key: measurement temperatures of: (▽, ▼) 598 K, (△, ▲) 623 K, (◇, ◆) 648 K, (□, ■) 673 K and (○, ●) 698 K.

The R transition temperature was independent of the ageing time at all ageing temperatures, as seen in Fig. 2. However, the ageing temperature was found to have influenced the R phase transition temperature, T_R. Measurements of T_R at the end of the ageing procedures are shown in Fig. 6 as a function of ageing

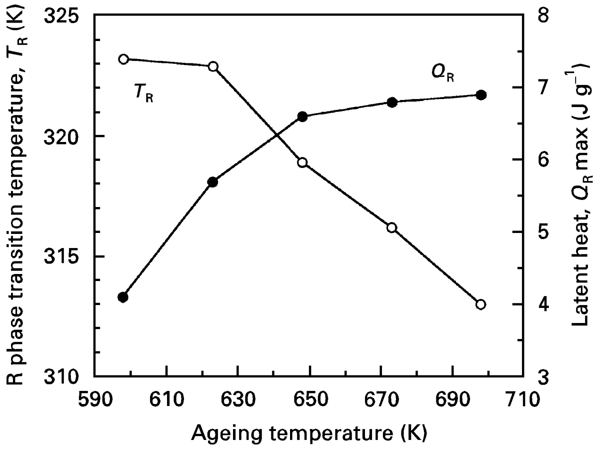

Figure 6 Effect of ageing temperature on the R phase transition.

temperature. It is seen that T_R decreased progressively with increasing ageing temperature. The R phase transition, as mentioned earlier, emerged as a second order transition initially and gradually developed into a transition with a dominant first order character. The latent heat associated with the first order process of the R transition thus increased with ageing time. Measurements of the maximum value of the latent heat for the R phase transition at the end of each ageing treatment, Q_R, are also shown in Fig. 6 as a function of ageing temperature. The latent heat of the R phase transition was found to increase with ageing temperature, with a maximum value of $\sim 7\,\mathrm{J\,g^{-1}}$ being measured after ageing at 698 K. The decreased values of the Q_R at low ageing temperatures are indicative of a partial A → R transition. It is interesting to note that for the three highest ageing temperatures at which the ageing process was complete Q_R varied only slightly whilst the value of T_R decreased significantly.

3.3. Constrained ageing

A constrained ageing treatment was carried out to clarify the possible mechanisms of the multi-stage transformation behaviour induced by ageing. After the constrained ageing treatment, specimens were found to exhibit a certain degree of the ARSM effect, similar to that reported by Nishida and Honma [5]. Fig. 7(a and b) shows video photographs of the two extreme positions of a ribbon after ageing at 623 K for 24 h in a constraint of 1/22 mm curvature (corresponding to a tensile strain of 0.99% at the outer surface). With no applied force the specimen in shape (a) changed to shape (b) upon cooling from 357 to 276 K and returned to shape (a) upon re-heating to 357 K. The tensile strain at the outer surface of the ribbon was calculated by measuring the curvature of the images recorded in video photographs. The results are shown in Fig. 8 as a function of temperature. It is seen that the maximum ARSM strain, as measured as a tensile strain at the outer surface of the ribbon, was 0.25%, corresponding to 25% of the constrained strain of ageing, and that a thermal hysteresis of ~12 K was exhibited by the ARSM effect.

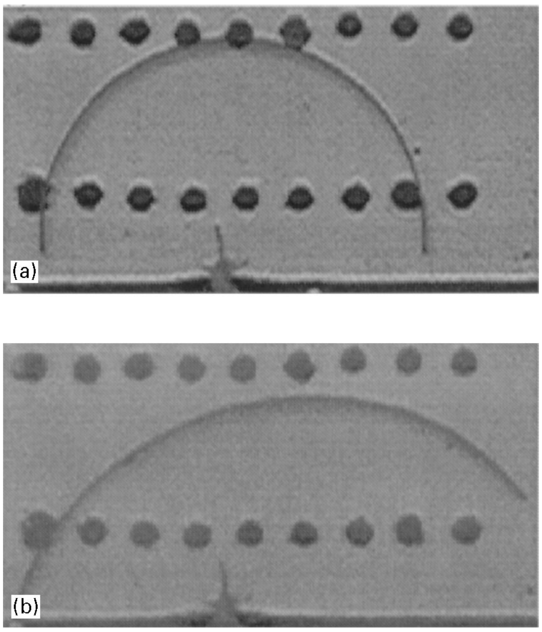

Figure 7 All-round shape memory effect after constrained ageing at 623 K for 24 h (a) at 357 K and (b) at 276 K.

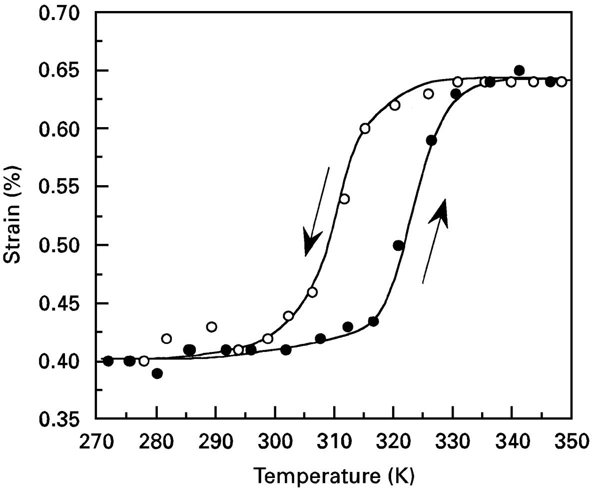

Figure 8 All-round shape memory strain as function of temperature.

4. Discussion

4.1. Two-stage martensitic transformation

It is evident in Fig. 1 (a and b) that the appearance of the M2 transformation is associated with the occurrence of the R phase transition. The DSC peak intensity of the M2 transformation increased with ageing time together with the development of the R phase transition at the expense of that of the M1 transformation. The evolution of T_{M1} was continuous at the occurrence of the R phase transition during ageing, indicating that the appearance of the R phase transition at a higher temperature had not affected the M1 transformation. The M2 transformation occurred at a temperature 15 K below that of the M1 transformation. This is consistent with the expected decrease in the martensitic transformation temperature accompanying the change of transformation from A → M to R → M [6, 7]. All these observations suggest that the M1 transformation was an A → M transformation and the M2 transformation was an R → M transformation, as previously reported by McCormick *et al.* [3]. Despite the complications to the forward transformation on cooling, the reverse transformation occurred in one step to austenite (Fig. 1b), indicating that the martensites formed by the two different transformations were of the same free energy. The co-existence of these two separate martensitic transformations implies that for these ageing conditions the R phase transition was incomplete.

4.2. Changes caused by ageing

The evolution of transformation behaviour during ageing suggests microstructural changes. However, there is no direct evidence in this study of the nature of the changes in the matrix caused by ageing. Similar studies have suggested two mechanisms, precipitation [2, 3] and ordering of vacancies [1]. Whilst the vacancy ordering hypothesis cannot be excluded as being responsible for the partial R phase transition, the precipitation mechanism certainly remains as a possibility due to the metastability of the B2 phase of NiTi alloys at temperatures below 900 K [8]. It has been clearly established that directional stress fields associated with Ni-rich precipitates are responsible for the all-round shape memory effect developed during constraint ageing treatment of NiTi alloys [5]. The occurrence of an all-round shape memory effect after constraint ageing under the same thermal conditions observed in this study suggests that precipitation had occurred in the specimens. This suggestion is consistent with the fact that the ageing process developed with ageing time and accelerated with increasing ageing temperature. The maximum tensile/compressive strain associated with the all-round shape memory effect was measured to be 0.25%. The low strain associated with the all-round shape memory effect is probably due to the relatively low Ni content of the alloy and low ageing temperature.

Both T_A and T_{M2} increased progressively during ageing, with the difference between the two temperatures, although not a true measure of transformation hysteresis [6], being approximately constant. This also can be rationalized by the development of elastic stress fields in the matrix such as those associated with the formation of precipitates. It is generally regarded that internal elastic stress fields cause shifts of transformation temperatures but does not affect the hysteresis.

4.3. R phase transition

The R phase transition developed progressively during ageing, giving rise to the co-existence of the two separate martensitic transformations. This incomplete nature of the R phase transition was not due to the interference of the martensitic transformation from austenite. As can be seen in Fig. 1a, the temperature difference between T_R and T_{M1} is approximately 40 K, much larger than the temperature interval required for the R phase transition to complete.

It has been clearly established that the R phase transition involves two second order events, the austenite-to-incommensurate transition prior to the rhombohedral lattice distortion [9, 10] and the continuous decrease of the rhombohedral angle of the R phase with decreasing temperature after the lattice distortion [11–13]. It is possible that the second order process observed in this study at the intermediate stages of ageing corresponds to the austenite-to-incommensurate transition and thus the M2 transformation is an incommensurate-to-martensite transformation. For the austenite-to-incommensurate transition, there has not been any experimental observation that it may occur without proceeding to the incommensurate-to-commensurate transformation. The present observation seems to suggest that the incommensurate structure can transform directly to martensite. This suggestion is obviously speculative and needs to be confirmed by transmission electron microscopy (TEM) investigations.

It has been suggested in the literature that "$M_S < T_R$" is the criterion for the appearance of the R phase transition prior to the martensitic transformation on cooling [14, 15]. Numerous studies have shown that factors that lead to a decrease in M_S, e.g., plastic deformation and thermal cycling, result in the occurrence of the R phase transition when M_S is lowered to below T_R. In this study, however, it was observed that the R phase transition developed during ageing at a temperature 26–37 K above T_{M1}. There is no evidence that ageing caused T_R to increase from below T_{M1} or T_{M1} to decrease from a value above T_R. This suggests that the occurrence of the R phase transition prior to martensite on cooling is not necessarily a consequence of the decrease of T_M, although $T_M < T_R$ still remains an essential condition.

There is little information in the literature on the factors affecting the R phase transition temperature. The only clearly established experimental evidence is that the R phase transition temperature has a small stress dependence [16, 17] due to its small lattice distortion [13]. This is consistent with the observation that T_R remained virtually constant during ageing whilst T_A and T_{M2} showed continuous changes due to the establishment of internal elastic stress fields. Other factors affecting the T_R temperature may include the chemical compositional changes in the matrix, which affects the relative free energies of the transforming phases, and the existence of precipitates, which affects the nucleation kinetics of the R phase [18]. However, whether these factors are responsible for the decrease of T_R at high ageing temperatures is yet to be clarified.

5. Conclusions

Unusual multi-stage transformation behaviour is observed in near-equiatomic NiTi alloys after appropriate ageing treatment. Although the mechanisms of this phenomenon are not understood, some conclusions can be drawn from the experimental observations of this study.

(1) The three-stage transformation behaviour can be induced in annealed near-equiatomic NiTi alloys by ageing for appropriate periods of time at temperatures between 590 and 650 K. Increasing the ageing

temperature results in acceleration of the ageing process.

(2) The product martensites of the two separate martensitic transformations on cooling appear to exhibit no thermodynamic difference.

(3) A decrease in the M_S temperature to below the T_R temperature is not a prerequisite for the occurrence of the R phase transition prior to the martensitic transformation, although that $M_S < T_R$ is still held to be a valid criterion.

(4) The R phase transition is observed to exhibit a second order nature during the intial stages of ageing. This second order "R" phase is capable of proceeding directly to martensite without completing the first order rhombohedral lattice distortion. The nature of this second order transition has yet to be clarified.

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