Effect of ageing treatment on the transformation behaviour of Ti–50.9 at.% Ni alloy

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Abstract

This study investigated the effect of ageing on the transformation behaviour of a Ti–50.9 at.% Ni alloy. Ageing at below 573 K was found to suppress the original A ↔ M transformation. This phenomenon has not been recognized in the literature. The effect is ascribed to the lowering of B2 ordering of the matrix caused by the formation of GP zones as a pre-phenomenon for precipitation. Ageing at between 573 and 813 K resulted in complex multiple-stream transformations. These complex transformation behaviours are attributed to long-range heterogeneity of precipitation structure between grain boundaries and grain interior, and short-range heterogeneity caused by partial dissolution of coherent precipitates and formation of incoherent precipitates. Ageing at above 833 K led to a single-stage A ↔ M transformation, which indicates total dissolution of coherent Ti₃Ni₄.

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1. Introduction

Near-equiatomic NiTi shape memory alloys are known to exhibit three different phases: the B2 austenite (A), the monoclinic B19′ martensite (M) and the trigonal R-phase (R) [1]. Under solution-treated conditions, near-equiatomic NiTi alloys, typically containing 49–51 at.% Ni, exhibit a single-stage transformation between the B2 austenite and the B19′ martensite [2–5]. Under certain conditions, including thermal cycling, cold working, partial annealing and ageing, the R phase may appear between the austenite and the martensite. Among these three phases, several transformation sequences are possible, stemming from various combinations of the A ↔ R, A ↔ M and R ↔ M transformations [6,7]. All these transformations are martensitic in nature.

It is known that ageing treatment causes complex transformation behaviour in near-equiatomic NiTi shape memory alloys [8–12]. The austenite has an ordered B2 structure, thus its stoichiometry is Ti–50.0 at.% Ni. In this regard, non-equiatomic NiTi alloys containing an excess of Ni are subjective to precipitation upon ageing [8–14]. At the same time, the martensitic transformations in NiTi are also processes of microscopic lattice distortions as well as phase transformation processes. Therefore, they are sensitive to variations in mechanical conditions [15,16], chemical conditions [17] and level of ordering. Ageing of Ni-rich NiTi alloys causes variations in both the internal stress state and the chemical composition with the formation of various Ni-rich precipitates. In addition, the depletion of Ni content due to the formation of Ni-rich precipitates restores the alloy composition towards NiTi stoichiometry, enhancing the level of B2
ordering. Because of these effects, various ageing-induced complex transformation behaviour have been observed for Ni-rich NiTi alloys [2–14].

The effects of ageing on the transformation and deformation behaviour of Ni-rich NiTi shape memory alloys have raised research interests in the past two decades. A milestone work was published by Nishida and co-workers on the ageing temperature–time diagram for the formation of various Ni-rich precipitates [18]. Other early works, represented by Otsuka and Miyazaki, were focused on establishing the effective ageing conditions for optimum mechanical properties, in particular the pseudoelastic properties of the alloys [19]. Adequate empirical data have been generated to guide effective industrial production of pseudoelastic NiTi materials and products. In more recent years, extensive research has been carried out to characterize complex ageing-induced multiple-stage transformation behaviour [20–22]. Another important aspect is the effect of ageing under the influence of bias stresses, a condition commonly encountered in shape memory product fabrication. The main findings of these studies may be summarized as follows:

1. Solution treatment at elevated temperatures induces single stage A ↔ M transformation. The transformation latent heat and critical temperatures decrease with increasing Ni content at above 50.0 at.%. 
2. Ageing of Ni-rich NiTi alloys leads to the progressive precipitation of Ti$_3$Ni$_4$, Ti$_2$Ni$_3$ and TiNi$_3$ precipitates in order with increasing ageing time, temperature and Ni content [18]. Ti$_3$Ni$_4$ is coherent with the matrix [23–27] and is most influential in affecting the transformation behaviour and mechanical properties of the alloys [27,28].
3. Ageing at 673–723 K of Ti–50.8 at.% Ni for 1.8–3.6 ks appears to be the optimum conditions for obtaining pseudoelasticity [18].
4. Ageing at low temperatures (typically below 723 K) results in multiple-stage transformation sequences, involving double-stage A → R transformations [5,17] or double-stage R → M transformations [8,9]. The mechanisms causing the split of the same transformation into multiple stages have been a focus of discussion in the recent literature. Whereas various hypotheses have been proposed, including microscopic composition variation [23] and microscopic stress heterogeneity [25,29,30], the most credible argument appears to be the inhomogeneous distribution of Ti$_3$Ni$_4$ precipitates between grain boundary regions and grain interior regions [22,31].
5. Overageing (higher temperatures or prolonged times) generally results in the single transformation of M ↔ A. It is also found that the latent heat of the transformation is larger than those measured under solution-treated or peak aged conditions [32]. This is obviously related to the formation of non-coherent precipitates and the reduction in the Ni content in the matrix caused by the extensive precipitation of Ni-rich precipitates, consistent with the findings described in point (1) above.
6. Ageing under the influence of bias stresses is able to create aligned Ti$_3$Ni$_4$ precipitates [27,33], which in turn creates anisotropic internal stress fields and leads to the occurrence of an “all round shape memory effect” [34,35].

In review of the literature, the following statements may be reached:

1. The original work published by Nishida et al. [18] appears to be the only systematic study of the effect of ageing conditions on NiTi. This work is on a Ti–52.0 at.% Ni alloy and is concerned with the effect of ageing temperature and time on the formation of precipitate phases of binary Ni–Ti [18]. This work does not provide information on the functional properties of NiTi, such as transformation behaviour and deformation properties. In addition, Ni–Ti alloys of this composition generally do not exhibit the B2–B19 martensitic transformation, and thus no shape memory effect. Practical Ni–Ti shape memory alloys generally contain <51.0 at.% Ni. In this regard, despite the wide reference by numerous publications, this study does not provide direct guidance to the study or production of practical NiTi shape memory alloys.

2. Despite the intensive recent interest and the publication of a number of highly credible studies on the possible mechanisms for ageing-induced multiple-stage transformation behaviour [20–22], comprehensive knowledge of the effects of ageing conditions on the transformation and mechanical properties is lacking, largely owing to the complexity of the issue itself. Ageing involves three independent parameters, i.e. temperature, time and alloy composition. The lack of an adequate database hinders the design and production of NiTi alloys and components for innovative applications beyond the common practice of 673–723 K ageing for 1.8 ks for optimum pseudoelasticity adopted in the industry.

In this regard, comprehensive knowledge of the effects of ageing on the transformation and mechanical behaviour of Ni–Ti alloys is yet to be established. Such information is essential for the processing of NiTi alloys and design of NiTi apparatuses. This work was conducted as part of the effort to establish such a knowledge base, with particular reference to ageing under stress-free conditions.

2. Experimental details

A commercial Ti–50.9 at.% Ni alloy in wire form was used. The wire was solution-treated in vacuum at 1073 K for 3.6 ks followed by quenching into water. The
solution-treated specimens were then aged in vacuum for 1.8 ks at various temperatures between 473 and 873 K and for various time intervals up to 57.6 ks (16 h). After the ageing treatment, the specimens were slightly chemically etched to remove the surface oxide layer. The etching agent was an aqueous solution of 40 vol.% HNO₃ and 10 vol.% HF.

The transformation behaviour of the specimens was characterized using a Perkin-Elmer Diamond differential scanning calorimeter (DSC) with a heating and cooling rate of 20 K min⁻¹. The phase formation of the samples was analyzed by means of X-ray diffraction (XRD) at ambient temperature using a Philips X’Pert Pro diffractometer with Cu Kα radiation.

3. Results

Fig. 1 shows DSC measurements of the transformation behaviour of the Ti₄₉.₁Ni₅₀.₉ alloy after ageing for 1.8 ks at different temperatures. The solution-treated sample (1073 K for 3.6 ks) underwent a single-stage A ↔ M transformation with a hysteresis of 42 K. The latent heats of the A → M and the M → A transformations were 16.8 and 20.0 J g⁻¹, respectively. Ageing at between 473 and 533 K suppressed the martensitic transformation, as evidenced by the reduced peak of the transformations. These transformations are denoted A ↔ M₀, signifying that it is the original martensitic transformation from the solutionized B₂ matrix. Ageing at 583 K led to the appearance of the A ↔ R transformation at a higher temperature. Increasing the ageing temperature to 623 K resulted in the appearance of another peak below the R → A transformation on heating, apparently of an M → R reverse transformation of the martensite formed on cooling from the R phase. The same behaviour became more obvious in the sample aged at 653 K.

Samples aged at 673 and 703 K developed an apparent one-stage A → R transformation on cooling and two-stage M → R → A transformation on heating. The combined heat of the reverse transformations was 10.8 J g⁻¹ whereas that for the forward transformation was 6.9 J g⁻¹, implying some “invisible” transformation after A → R on cooling. Increasing the ageing temperature to 733 K revealed R → M₁ transformation at low temperature. The transformation is marked M₁ to indicate that it is from the R phase instead of the original A. Ageing at 763 K led to the appearance of A → M₂ between A → R and R → M₁. The identification of this new A → M₂ transformation is presented in Fig. 4. After ageing at 793 K, R → M₁ continued to shift to a higher temperature whilst A → M₂ decreased in temperature, exchanging their relative positions. At the same time, the heat intensity of A → M₂ intensified whilst that of R → M₁ diminished. During this process, the two heating transformation peaks merged to form a single peak. The latent heat of the reverse transformation, as determined from the sample aged at 793 K, was 19.4 J g⁻¹. After ageing at 813 K, A → M₂ prevailed whereas R → M₁ disappeared. At the same time, the temperature of A → R continued to decrease to become sufficiently low compared with the reverse M → A transformation, resulting in the appearance of the R → A transformation on heating prior to M → A.

Samples aged at above 833 K underwent a single-stage A ↔ M transformation. The peak temperatures for the transformations were $T_{A-M} = 223$ K and $T_{M-A} = 258$ K, as determined from the sample aged at 833 K. Latent heats were measured to be $\Delta H_{A-M} = 18.7$ J g⁻¹ and $\Delta H_{M-A} = 20.0$ J g⁻¹. There appeared to be a slight general decrease in the transformation temperatures with increasing ageing temperature.

In order to identify the various transformation peaks, five representative samples aged at different temperatures were selected for further analysis. It is seen in Fig. 1 that ageing at 533 K after the solution treatment suppressed the A ↔ M transformation. It needs to be clarified whether this effect is time dependent. Fig. 2 shows the effect of ageing time at 533 K on the transformation behaviour of the
ally. It is seen that short-time ageing suppressed the A→M transformation progressively and then with prolonged ageing the A→R transformation emerged at a higher temperature. The DSC curve of the specimen aged at 583 K for 1.8 ks is also shown in the figure for comparison. It is evident that the transformation behaviour after prolonged ageing at 533 K is similar to that after ageing at 583 K, suggesting that the effect is time dependent.

Fig. 3 shows partial transformation cycle measurement of the sample aged at 703 K. This sample is of interest because it exhibits an apparent two-stage transformation on heating and a single-stage transformation on cooling. An abnormal behaviour contrary to the usual observation of A→R transformation on cooling and M→A on heating, because it exhibits an apparent two-stage transformation of the sample aged at 763 K. This sample is of interest for a full M→R→A, possibly indicating that the R→M transformation was incomplete to the minimum temperature reached during the measurement. In summary, the transformation sequence of this sample is A→R→M on cooling and M→R→A on heating.

Fig. 4 shows the partial transformation cycle measurement of the sample aged at 763 K. This sample exhibited an apparent three-stage transformation on cooling and a single-stage transformation on heating. The first peak (peak 1) on cooling is the A→R transformation. Partial cycle (1) revealed the reverse R→A transformation (peak 4), which appeared inside the main reverse transformation peak. The latent heats of the A→R transformations were \( \Delta H_{A \rightarrow R} = 5.2 \text{ J g}^{-1} \) and \( \Delta H_{R \rightarrow A} = 5.4 \text{ J g}^{-1} \). Continuing cooling to beyond the second forward transformation (peak 2) resulted in the appearance of a small peak (peak 5) on the right side of the R→A peak (peak 4) on heating, implying that peaks 2 and 5 are the forward and reverse processes of the same transformation. It is also noted that the reverse R→A transformation remains practically unchanged in size to that observed in the first partial cycle. This implies that the 2→5 transformation is independent of the A→R transformation. This pair is identified as A→M2 transformation. The A→M2 transformation has a large hysteresis of 34 K, typical of A→M transformations. Continuing cooling to beyond the third forward transformation (peak 3) resulted in the appearance of the major reverse transformation peak (peak 6). A shoulder on the high temperature side is recognizable, corresponding to the M2→A transformation. The temperature difference between peak 3 and peak 6 is 66 K and the latent heat of
peak 3 is $9.3 \text{ J g}^{-1}$. Peak 3 is the $R \rightarrow M_1$ transformation and peak 6 is the reverse $(M_1 + M_2) \rightarrow A$. The combined latent heat of $(M_1 + M_2) \rightarrow A$ is $19.1 \text{ J g}^{-1}$. It is to be noted that the temperature difference between $R \rightarrow M_1$ and $M_1 \rightarrow A$ is not a transformation hysteresis, because the forward and reverse transformations are not reciprocal transformations. According to thermodynamic principles, this temperature difference is smaller than the hysteresis of the $R \leftrightarrow M_1$ transformation and larger than the hysteresis of the $A \leftrightarrow M_1$ transformation [7]. In summary, the transformation of this sample occurs in two separate streams: $A \rightarrow R \rightarrow M_1$ on cooling and $M_1 \rightarrow A$ on heating in stream 1, and $A \leftrightarrow M_2$ in stream 2. In comparison with the transformation behaviour of the sample shown in Fig. 3, it is obvious that the $R \rightarrow M_1$ transformation is intensified and shifted to higher temperatures with increasing ageing temperature.

Fig. 5 shows the partial transformation cycle measurement of the sample aged at 793 K. This sample exhibited transformation behaviour similar to that of the sample shown in Fig. 4, with three separate transformations on cooling and two overlapping transformations in one peak on heating. However, the partial cycle measurements suggest that this sample exhibited a different transformation sequence. Partial cycle (1) revealed the $R \rightarrow A$ transformation. The small shoulder (peak 5) to the right of the $R \rightarrow A$ transformation peak apparently corresponds to the early fraction of the second transformation peak (peak 2) on cooling. Partial cycle 2, cooled to after the completion of the second transformation peak on cooling, resulted in peak 5 becoming the major reverse transformation. It is important to note that there is almost no reverse $R \rightarrow A$ transformation in this cycle, implying that the $R$ phase formed in peak 1 had been completely consumed in the transformation to martensite in peak 2, i.e. $R \rightarrow M_1$. This implies that the third peak on cooling (peak 3) is a separate martensitic transformation from the parent phase, i.e. $A \rightarrow M_2$. This transformation corresponds to the second transformation shown in Fig. 4. The full transformation cycle demonstrates that the reverse transformation peak is a compound peak of $M_2 \rightarrow A$ and $M_1 \rightarrow A$. Summarizing the analysis above, this sample exhibited a transformation sequence of $A \rightarrow R \rightarrow M_1$ and $A \rightarrow M_2$ on cooling and $M_2 \rightarrow A$ and $M_1 \rightarrow A$ on heating. This transformation sequence identification is more clearly seen in Fig. 7, which shows the evolution of the various transformations with ageing temperature. Obviously, this transformation sequence is different from that of the sample aged at 763 K.

Fig. 6 shows the effect of ageing temperature on the evolution of transformation (peak) temperatures. The range of ageing temperature may be roughly divided into five regions, as indicated in the figure. In region I, the transformation event was the $A \leftrightarrow M_0$ transformation, inherited from the solution-treated condition. The transformation temperatures appeared to decrease with increasing ageing temperature. In region II the transformation event was $M_0 \rightarrow A$. There was no sign of a martensitic transformation, from either the original B2 parent phase or the newly developed R phase. The critical temperatures of the transformations, $T^{R\rightarrow A}$ and $T^{A\rightarrow R}$, increased with increasing ageing temperature. In region III the $R \leftrightarrow M_1$ transformation...
emerged. However, in the early stage (low ageing temperatures) the forward R → M1 transformation was too broad and too weak in heat intensity to be directly detected by DSC. The occurrence of this transformation is demonstrated by the reverse M1 → R transformation and the partial cycle measurements shown in Fig. 3. In this region, \( T^{A-R} \) continued the incremental trend in region II to reach a maximum at 673 K ageing temperature, then started to decrease with further increasing ageing temperature. \( T^{M1-R} \) increased with ageing temperature in a trend similar to that of \( T^{A-R} \).

In region IV, complex transformation behaviour developed. In this region, the forward R → M1 transformation became more detectable and its temperature increased rapidly with increasing ageing temperature. In addition to the A → R → M1 transformations, the separate A → M2 transformation emerged on cooling at a point between the A → R and the R → M1 transformations. The temperature of this transformation, \( T^{A-M2} \), was 263 K when it first emerged. This temperature is 40 K above that of the solution-treated sample, implying that it is a new A → M transformation resulting from the ageing treatment. \( T^{A-M2} \) decreased with increasing ageing temperature. In this region, the A → R transformation shifted progressively to lower temperatures with increasing ageing temperature. During the entire history, the A → R transformation exhibited a constant temperature hysteresis of ~6 K.

In region V, the alloy exhibited a simple transformation of A → M, without the R-phase transformation. It is obvious that the A → M is a continuation of the A → M2 transformation identified in region IV. The critical temperatures of the A → M2 transformation, \( T^{A-M2} \) and \( T^{M2-A} \), were above their respective counterparts for the solution-treated condition when they first emerged and decreased progressively with increasing ageing temperature. Their final values approached those of the solution-treated samples, as indicated by the two horizontal dashed lines, marked \( T^{A-M} = 210 \text{ K} \) and \( T^{M-A} = 256 \text{ K} \).

Fig. 7 shows the effect of ageing temperature on transformation heats. The latent heats marked for individual transformations are estimated from the corresponding transformation peaks. The latent heat curve marked \( \Delta H_0 \) indicates the combined latent heat of all the reverse transformations on heating. The latent heat curve marked \( \Delta H_c \) indicates the combined latent heat of all the forward transformations on cooling. The range of ageing temperature is divided into the same five regions as in Fig. 6.

Region I is for the original A → M0 transformation. The latent heat of the A → M0 transformation decreased rapidly with ageing. In region II the A → R transformation evolved gradually. Its latent heat increased with increasing ageing temperature, to \( \sim 2.5 \text{ J g}^{-1} \), which is below what may be expected for a complete A → R transformation. In region III the R → M1 transformation emerged, whilst the A → R transformation continued to evolve in strength (latent heat), reaching a maximum of \( 6.9 \text{ J g}^{-1} \) at 703 K. This value corresponds well to those reported in the literature for the A → R transformation [18], implying that the A → R transformation at this ageing temperature was practically a complete transformation, i.e. there was no residual austenite at the completion of the transformation (peak 1 in Fig. 3). The latent heat of the R → M1 transformation evolved in a bell shape, exhibiting a maximum of \( 8.7 \text{ J g}^{-1} \) at 763 K of ageing. The dashed section of the curve is an extrapolation of the experimental curve. Due to the extremely low temperature and the low heat flow intensity, reliable measurement of the latent heat in this range is impossible. The tentative position of this curve is supported by the measurement of the \( \Delta H_0 \), which is in principle equal to the summation of the latent heats of the A → R and R → M1 transformations.

In region IV, the A → M2 transformation emerged at above 763 K of ageing, as described in Fig. 6. Its latent heat increased rapidly with increasing ageing temperature. Accompanying the rapid increase of the latent heat of A → M2, the latent heats of A → R and R → M1 decreased sharply, implying a process of the A → M2 transformation stream gradually replacing the A → R → M1 transformation stream. In region V only the A → M2 transformation prevailed. The latent heat of the A → M2 transformation increased moderately with increasing ageing temperature. The final values were \( \Delta H^{A-M} = 19.5 \text{ J g}^{-1} \) and \( \Delta H^{M-A} = 21.0 \text{ J g}^{-1} \) after ageing at 873 K. These values are above those of the solution-treated sample.

Fig. 8 shows a “TTT” diagram summarizing the effects of ageing time, temperature and time on the transformation behaviour of the Ti–50.9 at.% Ni alloy after solution treatment at 1073 K. The chart is divided into five regions, corresponding to those presented in Figs. 6 and 7. Among the various transformations, it needs to be clarified that there are three distinctive processes of the martensitic transformation in this presentation: M0, denoting the martensite formed from the original solutionized B2 phase; M1, being the martensite formed from the R phase; and M2, being the martensite formed from the aged and precipitated B2 matrix.

![Fig. 8. Effect of ageing time temperature and time on the transformation behaviour of Ti–51.0 at.% Ni alloy after solution treatment at 1073 K in vacuum.](image-url)
Fig. 9 shows XRD spectra of several samples. All the samples showed a B2 matrix, and the figure shows only the 2θ range revealing the main (110) diffraction peak of the B2 phase. It is clear that the solution-treated sample contained a pure B2 phase. After ageing at 763 K for 1.8 ks, a small diffraction peak appeared at ~43.3°. This peak may be indexed to Ti2Ni3 [012], 43.27°; TiNi2 [021], 43.50°; or TiNi3 phase [004], 43.55°. With reference to the evidences of the transformation behaviour measured, this peak is identified to be from Ti2Ni4 for the samples aged at 763 and 793 K. When the ageing temperature was increased to 813 K, this peak disappeared. Further increasing the ageing temperature to above 833 K led to the reappearance of the diffraction peak. With reference to the single stage A → M transformation behaviour of this sample shown in Fig. 1, this peak is attributed to Ti2Ni3 precipitate. The inset shows the effect of ageing temperature on d-spacing of the (110)B2 planes, as determined from the peak shift of the (110)B2 diffraction. It has been reported in the literature that the lattice parameter of the B2 phase decreases with increasing Ni content. In addition, the lattice parameter is also found to increase with the formation of Ti2Ni3 [36], apparently due to the depletion of Ni from the B2 matrix. In this work, d110(B2) is found to increase with increasing ageing temperature from 763 to 833 K. This is attributed to the progressive depletion of the Ni content of the B2 matrix with increased Ni-rich precipitation.

4. Discussion

4.1. Effect of ageing on transformation behaviour

Ageing at different temperatures are found to cause different variations to the transformation behaviour of Ti–50.9 at.% Ni. Ageing at low temperatures below 600 K in region I suppresses the original A ↔ M transformation, both in terms of transformation temperature and volume of the latent heat. The suppression of the A ↔ M transformation by low-temperature ageing has not been recognized in the literature. This effect is attributed to atomic rearrangement as a precursor phenomenon for precipitation. Such atomic rearrangement upsets the level of ordering of the B2 matrix, causing the decreases in temperature and latent heat of the martensitic transformation. This hypothesis clearly requires further experimental verification.

Favier et al. studied the effect of ageing on the transformation behaviour of Ti–50.5 at.% Ni and reported a novel multiple-stage transformation behaviour involving two separate R → M transformations [8]. Kim et al. later studied the effect of long-time ageing in the temperature range of 470–600 K and found multiple-stage transformation behaviour involving two separate A → R transformations [5]. Zhou et al. also observed multistage R → M transformations in Ti–50.6 at.% Ni aged at 533 K [17]. These observations indicate that the suppression of the A ↔ M transformation prior to the appearance of the A → R transformation observed in this study is a short-time ageing phenomenon, as evident in Fig. 2. This is consistent with the hypothesis that it is a precursor process prior to precipitation.

Ageing in temperature region II results in the disappearance of the original A ↔ M0 transformation and the appearance of the new A ↔ R transformation. The appearance of the A ↔ R transformation is indicative of the formation of Ti2Ni4 precipitates. Considering the transition of the transformation behaviour from A ↔ M in region I to A ↔ R in region II, it is natural to expect a transient window with ageing time and temperature in which both transformations occur concurrently. Such a condition implies a condition of microstructural inhomogeneity [23,25,29]. Such microstructural inhomogeneity, in the form of non-uniform distribution of precipitates between grain boundary regions and grain interior regions, as reported by Eggeler et al. [22,31], is long-range inhomogeneity.

It is also seen that in the early stage of the appearance of the A → R transformation the subsequent R → M transformation is absent. The R → M transformation appears only after increasing the ageing temperature to a level within stage III. The absence of the R → M transformation in the early stage (II) is consistent with the expectation for an atomically upset B2 matrix remnant from stage I, and the appearance and evolution of the R → M transformation are indicative of a gradual recovery of ordering of the B2 matrix with the progress of precipitation, consistent with the precipitation process.

In stage IV multiple transformations occur. The multiple-stage transformation behaviour is in two independent streams, A → R → M and A ↔ M. The newly appeared A → M is clearly from a different matrix compared with the original solutionized matrix, or more specifically from a B2 matrix of lower Ni content, as indicated by its higher temperatures. This is consistent with the expectation of Ni content depletion in the matrix as Ni-rich precipitation progresses. The co-occurrence of the two transformation streams is indicative of a heterogeneous matrix. However, considering the numerous experimental evidences reported.

Fig. 9. XRD spectra of Ti–51.0 at.% Ni after ageing at different temperatures.
in the literature revealing spatial uniformity of the distribution of precipitates [16,25,27,37,38], this microstructural heterogeneity is expected to be short-range, local and microscopic, between regions near coherent precipitate particles and regions away from them.

In stage V, the $A \leftrightarrow R \leftrightarrow M$ transformation stream disappears and the $A \leftrightarrow M$ transformation stream prevails. The disappearance of the R-phase transformation is indicative of the elimination of coherent Ti$_3$Ni$_4$. The occurrence of the single-stream $A \leftrightarrow M$ transformation is indicative of the uniformity of the matrix and the ineffectiveness of the existing precipitates. Such a condition is attributed to the formation of large incoherent precipitates, which are ineffective in influencing the transformation of the Ni-depleted matrix.

4.2. Mechanisms of the effects of ageing

The above discussion is illustrated schematically in Fig. 10. In the figure, the arrow to the right indicates the increase in the degree of ageing, mostly by increasing temperature. The shaded patches in (a) indicate segregation caused by atomic shuffling, possibly GP zones. Drawing (b) expresses the long-range precipitation inhomogeneity between grain boundary regions and grain interior regions occurring in the early stages of ageing. Drawing (d) expresses a mixed structure of two populations of precipitates, exhibiting local and short-range inhomogeneity. In this stage, the early-formed coherent precipitates (Ti$_3$Ni$_4$) have partially dissolved and new incoherent precipitates (Ti$_2$Ni$_3$) are emerging. These discussions of the evolution of the microstructure and the development of transformation behaviour are summarized in Table 1.

The multiple-stage transformation behaviour has attracted much attention in recent years [20–22]. Whereas several hypotheses have been proposed for the mechanisms of the phenomenon [23,25,29,31], the most credible appears to be microstructural heterogeneity in the form of non-uniform distribution of Ti$_3$Ni$_4$ precipitates [8]. Some reservations about this hypothesis include the inconsistency between the observations that the Ti$_3$Ni$_4$ distribution heterogeneity is generally observed at relatively early stages of ageing whereas the multiple transformation behaviour occurs in much later stages of ageing and is observed when spatially uniform distribution of the precipitates [5]. The heterogeneous distribution of Ti$_3$Ni$_4$ precipitates reported by Khalil-Allafi et al. [27] appears to correspond to the early stage long-range heterogeneous condition expressed in Fig. 10b. Under this condition, the grain boundary regions, which is scattered with fine coherent Ti$_3$Ni$_4$ precipitates, undergoes $A \leftrightarrow R \leftrightarrow M$ transformation. The interior of the grains, depending on the level of disordering of the matrix, may exhibit suppressed $A \leftrightarrow M$ transformation or no transformation. In the present study, the occurrence of the multistage transformation observed in stage IV is attributed to microscopic heterogeneity of the matrix, which is of a different mechanism from that reported by Khalil-Allafi et al. [27]. This hypothesis requires future experimental verification, possibly by means of transmission electron microscopy (TEM) and XRD.

In this regard, the suggestion of local short-range inhomogeneity caused by different types of precipitates, as expressed in Fig. 10d, is a new concept. The key to this suggestion is the switching over from the precipitation of coherent Ti$_3$Ni$_4$ to an incoherent precipitation (possibly of Ti$_2$Ni$_3$). Such a principle is well established [39,40], and supported directly by the XRD evidence shown in Fig. 9. Clearly, final confirmation of the hypothesis may be achieved by TEM observations.

4.3. Dissolution of Ti$_3$Ni$_4$

The development of the single-stage $A \leftrightarrow M$ transformation in stage V is indicative of the disappearance of coherent Ti$_3$Ni$_4$. This implies that Ti$_3$Ni$_4$ dissolves at 833 K (for 1.8 ks) for the alloy used in this study (Ti-50.9 at.% Ni). However, it is also evident, as seen in Figs. 6 and 7, that the temperatures of the $A \leftrightarrow M$ transformation continue to decrease and the latent heats continue to increase with increasing ageing temperature in stage V.

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**Fig. 10.** Mechanisms of the evolution of transformation behaviour of NiTi during ageing.
IV Formation of more stable incoherent precipitates (possibly Ti$_2$Ni$_3$);

V Large incoherent precipitates (possibly Ti$_2$Ni$_3$), uniformly distributed;

III Formation of uniformly distributed coherent Ti$_3$Ni$_4$ A

These variations are consistent with those expected for an increased Ni content of the matrix. This implies that there still exist some precipitates and the precipitates continue to dissolve into the matrix with increasing ageing temperature. This precipitate, apparently without effect on the transformation behaviour and apparently more stable than Ti$_3$Ni$_4$, is possibly Ti$_2$Ni$_3$. In this regard, the solvus of transformation behaviour and apparently more stable than Ti$_3$Ni$_4$, is possibly Ti$_2$Ni$_3$. In this regard, the solvus of Ti$_3$Ni$_4$ in B2-NiTi at 833 K corresponds to the solvus not of the original matrix composition of 50.9 at.% Ni, but of a matrix with a reduced Ni-content. This also implies that the total solution of aged Ti–50.9 at.% Ni may occur in different stages, corresponding to different precipitates.

5. Conclusions

The main experimental findings and analyses of this study may be summarized as follows:

(1) Ageing of Ti–50.9 at.% Ni within 473–900 K causes a progressive evolution of the transformation behaviour of the alloy. The evolution may be divided into five stages with respect to ageing temperature. The evolution process is (I) A $\leftrightarrow$ M transformation at higher ageing temperatures. This behaviour is attributed to the short-range heterogeneity of the microstructure.

(4) The occurrence of the final single stage A $\leftrightarrow$ M transformation is accompanied by long-range microstructural heterogeneity. Ageing in stage IV is accompanied by short-range microstructural heterogeneity. Ageing in stage V is accompanied by the dissolution of Ti$_3$Ni$_4$ and the formation of more stable Ni-rich precipitates.

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References