Cyclic ageing of Ti–50.8 at.% Ni alloy

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Abstract

This study investigated the effects of cyclic ageing on the transformation behaviour of Ti–50.8 at.% Ni by means of differential scanning calorimetric analysis. It is found that cyclic ageing between two different temperatures causes reversible changes of the transformation behaviour and alternating increases and decreases of transformation temperatures. This is attributed to the temperature dependence of the phase equilibria between the B2 matrix and Ni-rich precipitates. Based on the experimental evidences, the solvus of the precipitates (Ti3Ni4) in B2–NiTi is estimated.

Keywords: B. Martensitic transformations; B. Shape-memory effects; C. Heat treatment; F. Calorimetry

1. Introduction

Near-equiaxial NiTi alloys are attractive functional shape memory alloys for a wide spectrum of innovative applications, largely owing to their novel properties of shape memory effect and pseudoelasticity. It is well known that the transformation behaviour and thermomechanical properties of NiTi alloys with excess Ni to the equiatomic stoichiometry are sensitive to ageing treatment due to the formation of Ni-rich precipitates [1,2]. Three types of Ni-rich precipitates have been observed, including TiNi3, Ti2Ni3 and Ti3Ni4 [1–7]. TiNi3 [4] and Ti2Ni3 [2,5] are incoherent in B2–NiTi, thus ineffective to the transformation behaviour of the B2 matrix. In comparison, Ti3Ni4 is more influential to the transformation behaviour and thermomechanical properties of NiTi, including the R-phase transformation [8,9], all-round shape memory effect [10] and multiple-stage transformation behaviour [11]. Ti3Ni4 has a hexagonal structure and is coherent with the B2-matrix [6,7].

Precipitation is a thermally reversible process. In 1988, Horikawa et al. [12] conducted a study of “short-time” cyclic anneals between 713 K and 783 K of a Ti–51 at.% Ni alloy. They observed an interesting up-and-down movement of the transformation temperatures with anneal cycles. Zhang et al. [13] later conducted a similar study with long-time ageing and observed the same reversible change of transformation temperatures with repeated ageing cycles. They explained the phenomenon in terms of phase equilibrium between the NiTi matrix and the metastable Ti3Ni4 precipitates at different ageing temperatures.

Whereas the concept of the equilibrium between B2-matrix and Ti3Ni4 has been reasonably well established, actual data on the position of the solvus [14] and cyclic variation of the transformation behaviour [13] have been scarce in the literature. This study investigated the effect of cyclic ageing on the transformation behaviour of a Ti–50.8 at.% Ni alloy. Based on the transformation temperatures determined, the solvus between Ti3Ni4 and the B2–TiNi matrix is estimated.

2. Experimental procedure

A commercial Ti–50.8 at.% Ni alloy wire of 1 mm in diameter was used in this study. Samples were solution treated...
in vacuum at 1273 K for 3.6 ks. Two solution treated samples were further heat treated following different ageing routines. Sample A was cyclically aged at 673 K for 126 ks and 753 K for 45 ks. Sample B was cyclically aged at 753 K for 45 ks and 833 K for 10.6 ks. The ageing treatment durations were chosen to be long enough for the respective ageing temperatures to ensure full precipitation. After each ageing treatment, the samples were slightly chemically etched to remove surface oxide layer using an aqueous solution of 40 vol.% HNO₃ and 10 vol.% HF. The transformation behaviour of the samples was characterized using a Perkin–Elmer Diamond Differential Scanning Calorimeter (DSC) with a heating and cooling rate of 20 K/min.

### 3. Results

Fig. 1 shows DSC measurements of the transformation behaviour of the Ti–50.8 at.% Ni alloy over three ageing cycles between 673 K and 753 K. Curve (a) was measured under the solution treated condition. The sample underwent a single-stage A ↔ M transformation, at 240 K and 276 K on cooling and on heating, respectively. Curve (b) was measured after ageing at 673 K for 126 ks. The sample developed two-stage transformations both on cooling and on heating, which are identified to be A ↔ R (1–1′) and A ↔ M (2–2′) transformations. It is necessary to clarify that these are two independent transformation streams. The occurrence of such separate transformation streams is indicative to microstructural inhomogeneity of the matrix [11]. The A ↔ M transformations occurred at significantly increased temperatures compared to the transformations in the solution treated sample, indicating depletion of Ni content in the B2 matrix due to formation of Ni-rich precipitates.

Curve (c) was measured after a second ageing treatment at 753 K, 80 K above the initial ageing temperature, for a further 45 ks. The sample exhibited a transformation sequence of A → R → M on cooling and M → A on heating. The critical temperatures of the transformations are obviously lower than those after the first ageing treatment. This is attributed to increase in the Ni content of the matrix caused by the dissolution of Ni-rich precipitates at higher temperatures [13]. Curve (d) was measured after a further ageing treatment at the same temperature as for curve (b), at 673 K for 126 ks. The sample exhibited a similar transformation sequence of A → R → M on cooling and M → A on heating as curve (c) but at similar temperatures as (b). Continued ageing cycles practically repeated the transformation behaviours shown in curves (c) and (d).

Fig. 2 shows the transformation peak temperatures as a function of the number of ageing cycles between 673 K and 753 K. The data points appearing at “half” cycles represent ageing at 673 K and those at “full” cycles represent ageing at 753 K. The two initial data at “0” cycle represent the as-solution treated condition. The occurrence of the A → R → M transformation on cooling suppressed the A → M transformation, thus direct measurement of the transformation is impossible. However, the temperature of the prohibited A → M transformation may be estimated based on thermodynamic principles as [15,16]:

\[
T_{A-M} = \frac{\Delta H_{A-M}}{\Delta H_{A-R} + \Delta H_{R-M}}
\]

where \(\Delta H\) are the transformation enthalpies, which can be determined experimentally from the DSC curves, and \(T_{A-R}\) and \(T_{R-M}\) are peak temperatures of the respective transformations. The \(T_{A-M}\) calculated using Eq. (1) is also shown in the figure, as the dashed curve. It is seen that \(T_{A-R}\), \(T_{R-M}\), \(T_{A-M}\) and \(T_{M-A}\) all show similar zig-zag patterns of increase and decrease in accord with the ageing temperatures. It is also noticed that there were slight increases of \(T_{M-A}\) and \(T_{R-M}\) (and \(T_{A-M}\)) with increasing ageing cycles for both ageing

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**Fig. 1.** Transformation behaviour of Ti–50.8 at.% Ni alloy after cyclic ageing at 673 K and 753 K.

**Fig. 2.** Effect of cyclic ageing at 673 K and 753 K on the transformation temperatures of Ti–50.8 at.% Ni alloy. The dashed curve indicates \(T_{A-M}\) calculated using Eq. (1).
temperatures. This is attributed to the incompleteness of the ageing process at the temperatures up to the ageing times. In contrast to the martensitic transformations, $T_{A \rightarrow R}$ showed little variation with ageing cycle, implying much weaker composition and precipitation dependences of $T_{A \rightarrow R}$ compared to the temperatures of the martensitic transformations [17].

Fig. 3 shows DSC measurements of the transformation behaviour of the alloy over two ageing cycles between 753 K and 833 K. After ageing at 753 K, the sample showed a two-stage $A \rightarrow R \rightarrow M$ transformation on cooling and a single-stage $M \rightarrow A$ transformation on heating, typical of fully aged condition (curve (b)). When the ageing temperature was raised to 833 K (curve (c)), the transformation behaviour was restored to becoming similar to that of the solution treated sample (curve (a)), i.e. a single-stage $A \rightarrow M$ transformation, implying a solutionised condition. It is also clear that repeating the alternative ageing process simply restored the transformation behaviour to those shown in curves (b) and (c) alternatively.

Fig. 4 shows the transformation temperatures as a function of the number of ageing cycles between 753 K and 833 K. The data points appearing at “half” cycles represent ageing at 753 K and those at “full” cycles represent ageing at 833 K. The sample showed no R-phase transformation after ageing at 833 K and in this case the $T_{A \rightarrow M}$ values were directly determined from the DSC measurements. When aged at 753 K, the sample exhibited a two-stage $A \rightarrow R \rightarrow M$ transformation on cooling. In this case $T_{A \rightarrow M}$ is calculated using Eq. (1). It is seen that the transformation temperatures of this sample exhibited similar alternating increases and decreases with cyclic ageing to the sample shown in Fig. 2.

Fig. 5 shows the dependences of $T_{A \rightarrow M}$ and $T_{M \rightarrow A}$ on ageing temperature. The data shown are collected from the last ageing cycle from each sample, because the ageing process is regarded the most complete in these cycles (refer to Fig. 1). The data for ageing temperature of 753 K are from the second sample (shown in Fig. 3). $T_{A \rightarrow M}$ values shown for ageing temperatures of 673 K and 753 K are calculated values from $T_{A \rightarrow R}$ and $T_{R \rightarrow M}$ using Eq. (1). The data at above 900 K are from two additional samples, whose transformation behaviours are shown in the inset. It is seen that the ageing temperature may be divided into two distinctive regions, as indicated in the figure. In region I, $T_{A \rightarrow M}$ and $T_{M \rightarrow A}$ decreased with increasing ageing temperature to 833 K. For higher ageing temperatures in region II, $T_{A \rightarrow M}$ and $T_{M \rightarrow A}$ remained unchanged, implying that the ageing temperature has reached above the solubility limit. This is consistent with the behaviour of single-stage $A \leftrightarrow M$ transformation observed, as shown in the inset.

4. Discussion

4.1. Effects of matrix composition and internal stresses

Ageing of Ni-rich B2–NiTi alloys causes complex variations to the transformation behaviour, as evident in this study
as well as being well documented in the literature [18,19]. These effects have been traditionally attributed to variations in the chemical composition of the B2 matrix and the influences of internal stresses associated with precipitates, in particular coherent Ti3Ni4 [20]. It is our view that claims of the effect of internal stresses on transformation temperatures are incorrect. The common perception of the effect of internal stresses on transformation temperatures is based on the well-established understanding of the effect of applied constant stresses on transformation temperatures, as expressed in the Clausius–Clapeyron relation [21]. The analogy of internal stress to applied stress is inappropriate. In the case of a constant applied stress, the stress remains effective throughout the process of the transformation. In the case of local internal stresses, which are contained in the form of elastic strains, the stresses are relaxed immediately with the nucleation of martensite, due to the fact that the first martensite variant is formed ‘into’ the stress field, thus are ineffective to the bulk of the process of the transformation. In this regard, we consider that the transformation temperatures are mainly affected by the variations of the matrix composition and that the effect of Ti3Ni4 is mainly to facilitate the nucleation of the R-phase [22].

Fig. 6 shows the Ni-content dependences of $T_{A\rightarrow M}$ and $T_{M\rightarrow A}$ using data from this study as well as from the literature [23,24], as under solution treated condition. The slopes are determined to be 106 K/(at.% Ni) and 101 K/(at.% Ni) for $T_{A\rightarrow M}$ and $T_{M\rightarrow A}$, respectively. Based on these dependences, Ni content of the matrix after ageing may be estimated using the transformation temperatures experimentally measured. Using the $T_{M\rightarrow A}$ values shown in Fig. 5, which are less affected by the occurrence of the A $\rightarrow$ R transformation (as compared to $T_{A\rightarrow M}$), the Ni contents of the matrix after ageing at the three different temperatures are estimated to be 50.11 at.% , 50.34 at.% and 50.76 at.%, as indicated in Fig. 6.

4.2. Solubility of Ni in B2$\rightarrow$NiTi

Using the Ni content determined in Fig. 6, the solvus of Ti$_3$Ni$_4$ in B2$\rightarrow$NiTi is estimated as shown in Fig. 7. For the Ti$-50.8$ at.% Ni alloy, the dissolution temperature for Ti$_3$Ni$_4$ is estimated to be 833 K, which is consistent with that reported by Zhang [13]. The data points of the samples heat treated at 903 K and 933 K clearly indicate that they are above the solvus of Ti$_3$Ni$_4$, i.e. correspond to the “solutionised” condition.

Also shown in the figure are the tentative positions of the solvuses of Ti$_2$Ni$_3$ and TiNi$_3$ in B2$\rightarrow$NiTi (the solvus of TiNi$_3$ is defined in the equilibrium Ni$\rightarrow$Ti phase diagram). This implies that for a given alloy composition, different solution treatment temperatures exist for the three different precipitates, as indicated by $T_1$, $T_2$ and $T_3$. In this regard, the condition of the two samples heat treated at 903 and 933 K is more appropriately regarded as “solutionised” for Ti$_3$Ni$_4$. The fact that the matrix composition of these two samples is slightly lower than the original (the $T_{M\rightarrow A}$ temperature is slightly higher than the original value before ageing) implies that there may still exist some stable precipitates (TiNi$_3$) at this temperature.

4.3. Mechanism of the effects of cyclic ageing

This study is a continuation of the early works by Horikawa et al. [11] and Zhang et al. [13]. There have been discussions of the mechanism of this reversible movement of transformation temperatures with cyclic ageing, being either the reversal of unstable Ni-rich GP zones [11] or dissolution of metastable Ti$_3$Ni$_4$. In our opinion, the two hypotheses have no real contradiction in the principle of reversible change of the matrix Ni content, differing only on the aspect of which Ni-rich “phase” is formed and dissolved at different temperatures. This clarification is fundamentally necessary because Ni-rich near equiatomic NiTi alloys are known to develop several precipitates [1,3]. For each of these precipitates
(and GP zones), similar alternating cycles of formation and dissolution may occur. In this regard, the alternating variations of the transformation temperatures and sequences with alternating ageing treatment are intrinsic property of the alloys due to the varying solvuses of the precipitates.

5. Conclusions

1. Cyclic ageing at alternating temperatures within the range of 673–833 K causes reversible cyclic variations of transformation sequences and temperatures of Ti–50.8 at.% Ni alloy. $T_{A\rightarrow M}$ and $T_{M\rightarrow A}$ temperatures increase with lowering ageing temperature and decrease with increasing ageing temperature reversibly. The R-phase transformation appears with lowering ageing temperature and disappears with increasing ageing temperature reversibly.

2. This reversible ageing effect is attributed to equilibrium between the $B2\rightarrow NiTi$ matrix and Ni-rich precipitates. Higher Ni content in the $B2\rightarrow NiTi$ matrix results in lower temperatures for the martensitic transformations in NiTi and vice versa. The presence of Ti$_3$Ni$_4$ is attributed to the cause of the appearance of the R-phase transformation.

3. The solvus of Ti$_3$Ni$_4$ in $B2\rightarrow NiTi$ is estimated based on transformation temperature measurement. The solvus of Ti$_3$Ni$_4$ in $B2\rightarrow NiTi$ for the Ti–50.8 at.% Ni alloy is estimated to be at 833 K.

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