Thermal Cycling Effects in an Aged Ni-rich Ti–Ni Shape Memory Alloy*

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Thermal cycling effects in an aged Ni-rich Ti–Ni shape memory alloy have been examined by means of differential scanning calorimetry (DSC) and transmission electron microscopy (TEM), changing aging temperature and time, temperature range for thermal cycling, and the number of thermal cycles up to $10^4$ times. Two kinds of thermal cycling termed “complete cycling” and “incomplete cycling” were adopted: The complete cycling caused the B2 matrix→rhombohedral intermediate (R phase)→monoclinic martensite (M) transformations in the appropriately aged alloy, and the incomplete cycling did only the first B2→R transformations. The DSC measurement revealed that the complete cycling significantly affected not only the R→M transformation temperature, $M^*$, but also the B2→R one, $T^*_R$, of the aged alloy, $M^*$ being lowered to a great extent whereas $T^*_R$ being raised up considerably. Meanwhile, the R→B2 reverse transformation temperature, $T^*_R$, was raised like wise with $T^*_R$, and the M→R reverse one, $A^*$, was lowered a little. On the other hand, the incomplete cycling brought about substantially no change in the transformation temperatures. The TEM observation on the aged alloy subjected to the complete cycling of $10^4$ times showed that the B2 matrix regions between the Ti$_3$Ni$_4$ precipitates were heavily roughened by some lattice defects. However, the TEM observation on the alloy subjected to the incomplete cycling showed no change. The observed decrease in $M^*$ and increase in $T^*_R$ are discussed standing on a point of view that stress fields around the precipitates formed during aging may be relaxed by the thermal cycling.

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I. Introduction

Nearly equiatomic Ti–Ni alloys are well-known as most excellent shape memory alloys for their out-standing shape memory characteristics. For the practical applications, however, thermal cycling effects in the alloys are an important factor to be explored. The thermal cycling effects have been extensively studied for several Cu-based and other shape memory alloys, but not so for the Ti–Ni alloys. Among the latter studies(1)-(6), the recent work by Miyazaki et al.(5) is to be noted: They extensively investigated the influence of Ni content, aging after solution-treatment and annealing after cold working on the thermal cycling effects. According to them, the shift of $M_s$, increases in electrical resistance prior to the martensitic transformation on cooling, and increases in $(M_s-M_f)$ were observed in all of the solution-treated alloys irrespective of Ni content, but not in aged Ni-rich alloys and in cold-worked Ni-poor ones annealed at a temperature lower than the recrystallization temperature. Meanwhile, the “premartensitic” transformation temperature, $T^*_R$(5), remained unchanged by thermal cycling. These results were, however, obtained under conditions of thermal cycling up to $10^2$ times at most. The effect of more thermal cycles up to $10^4$ times was examined by Tamura et al.(6) on a cold-worked and annealed Ti-50.2 at%Ni alloy under constraint. According to the examination, incomplete thermal cycling repeating solely the B2→R transformations† (widely called the R-phase transformation) brings about no

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† An incommensurate phase has been reported to exist between the B2 and R phases(7).
change on differential scanning calorimetry (DSC) curves. However, more Ni-rich Ti–Ni alloys, in which fine Ti$_3$Ni$_4$ precipitates have been reported to be formed during aging, have not been examined.

The aged Ni-rich alloys with the fine Ti$_3$Ni$_4$ precipitates\(^{(8)-(10)}\) exhibit notable mechanical properties such as transformation pseudo-elasticity as well as the shape memory effect in a wider temperature range, the slip deformation being inhibited\(^{(11)-(12)}\). Furthermore, the all round shape memory effect is realized when the aging is given under constraint\(^{(13)}\). Transmission electron microscopy (TEM) has revealed that a high density of dislocations is introduced in the matrix of as-solution-treated Ni-rich Ti–Ni alloys\(^{(4)}\), while no change in microstructure is substantially brought about in the aged ones\(^{(5)}\). However, it is not obvious whether this is the case for the more thorough thermal cycling despite its very important implication in the practical applications.

Therefore, the present study has been conducted to examine thermal cycling effects in an aged Ti–51.0 at%Ni alloy by means of DSC and TEM, extending the number of thermal cycles up to $10^4$ times. As a result, significant changes in transformation temperature and microstructure were observed even in the aged alloy when thermal cycling was extended to roughly more than $10^3$ times. In this paper the origin of thermal cycling effects in the aged Ni-rich Ti–Ni alloys is mainly discussed.

II. Experimental Procedure

A Ti–51.0 at%Ni alloy sheet 0.25 mm thick was supplied by Tokin Corporation. Disks 3 mm in diameter were cut from the sheet by a spark cutting machine, and then solution-treated at 1273 K for 3.6 ks in evacuated quartz tubes, followed by quenching into iced water. Subsequently, the specimens were aged at 773 or 723 K for various periods up to 540 ks in order to change the size of precipitates.

Two kinds of thermal cycling were undertaken: One was done in the temperature range between 77 and 333 K, so that successive B2⇒R⇒M transformations took place, and the other in the range between 253 and 333 K, so that only the B2⇒R transformations took place. The former thermal cycling will be called “complete cycling” and the latter one “incomplete cycling” here.

Transformation temperatures of the aged specimens and their variations with thermal cycling have been examined by the DSC measurement, using a Rigaku DSC-8230B type equipment operating at a cooling/heating rate of 0.17 K/s. For simplicity, the temperatures where DSC peaks appeared were regarded as the transformation temperatures of the corresponding phase transformations, and they are designated by $T^*_R$ and $T^*_R$ for the R-phase transformation and its reversion, respectively, and by $M^*$ and $A^*$ for the martensitic transformation and its reversion, respectively.

Microstructural changes associated with the aging and thermal cycling of the B2 matrix have been examined by TEM observation. The electron microscope used was a H-700SS type one operating at 200 kV.

III. Results

Figure 1 shows DSC curves for an identical specimen subjected to the complete cycling of $0, 3 \times 10^3$ and $10^4$ times after aging at 773 K for 3.6 ks. Here, it is to be noted that $M^*$ decreases to a great extent while $T^*_R$ increases considerably with increasing thermal cycle.

Fig. 1 DSC curves upon cooling and heating an identical specimen aged at 773 K for 3.6 ks, which were plotted as a function of the number of complete cycling.
The reason for the opposite effect of thermal cycling on the martensitic and R-phase transformations will be discussed in the next section.

In Fig. 2, $M^*$ and $A^*$ in the specimens aged at 773 K for various periods are shown as a function of the number of thermal cycles. Although the values of $M^*$ and $A^*$ before the thermal cycling are different according to the aging treatments, the variations are almost parallel in the three kinds of aged specimens. That is, $M^*$ initially decreases rather drastically with increasing thermal cycle, but gradually levels off. The amount of the decreases, $\Delta M^*$, reached about 25 K to the largest after the thermal cycling of $10^4$ times. Meanwhile, $A^*$ decreases a little with increasing thermal cycle in all the specimens. The amount of the decrease, $\Delta A^*$, was only about 5 K after the thermal cycling of $10^4$ times. Such variations in transformation temperatures suggest that the thermal cycling influences the formation of martensites more effectively, rather than its reversion.

The difference in $M^*$ and $A^*$ before thermal cycling may be due to that in aging treatment, and accounted for by the depletion of solute atoms in the matrix phase, accompanying the growth of the precipitates with increasing aging time. However, the increase in $M^*$ with increasing aging time is much larger than that in $A^*$. In other words, the temperature hysteresis in the $R \leftrightarrow M$ transformations becomes smaller with increasing aging time. This is probably because the largely grown precipitates may no longer act effectively as obstacles impeding the movement of $R/M$ interfaces.

Variations in $T^*_R$ and $T^*_{R'}$ by thermal cycling are shown in Fig. 3 for the differently aged specimens. $T^*_R$ and $T^*_{R'}$ in all the specimens increase similarly with increasing thermal cycle. The amounts of the increases, $\Delta T^*_R$ and $\Delta T^*_{R'}$, are equally about 10 K after the thermal cycling of $10^4$ times. It is interesting to note that $T^*_R$ and $T^*_{R'}$ are not much affected by aging time within the range of time indicated in Fig. 3, compared with $M^*$ and $A^*$. The reason for this, however, is not clear.

In Fig. 3, $T^*_{R'}$ of the specimen aged for 540 ks is not shown for thermal cycling less than $5 \times 10^3$ times. This is because the $R \leftrightarrow B2$ reverse transformation did not occur in the specimen upon heating, instead the direct $M \leftrightarrow B2$ reverse transformation took place. DSC curves indicating such the direct transformation are shown in Fig. 4. Before thermal cycling, two exothermic peaks appear upon cooling, but only one endothermic peak does upon heating. By the way, as seen from Fig. 1, the temperature hysteresis in the $B2 \leftrightarrow R$ transformations is as small as a few degrees, while that in the $R \leftrightarrow M$ ones is as large as several ten degrees or more. Therefore, an endothermic peak corresponding to the $R \leftrightarrow B2$ transformation, if any,

![Fig. 2 Martensitic transformation temperatures, $M^*$, and reverse ones, $A^*$, as a function of the number of complete cycling.](image1)

![Fig. 3 R-phase transformation temperatures, $T^*_R$, and reverse ones, $T^*_{R'}$, as a function of the number of complete cycling.](image2)
should appear upon heating before the existing large endothermic peak does. Thus, the peak appearing around 300 K is considered to be due to the direct $M \rightarrow B_2$ reverse transformation. However, splitting of the single endothermic peak takes place gradually with increasing thermal cycle, as seen in Fig. 4. For example, a doublet peak is seen in the DSC curve obtained upon heating after the thermal cycling of $10^4$ times. The shoulder peak at higher temperature side is considered to be due to the $R \rightarrow B_2$ reverse transformation, taking account of the small hysteresis of the $B_2 \rightarrow R$ transformations, and thus the main peak should be due to the $M \rightarrow R$ reverse transformation. In the specimen aged for 540 ks, therefore, the transformation occurs in the following way when the thermal cycling is less than $5 \times 10^3$ times: $B_2 \rightarrow R \rightarrow M$ on cooling and $M \rightarrow B_2$ on heating. Similar transformation sequences have also been reported by Todoroki et al. in Ti–Ni alloys annealed after cold working. The variation of DSC curves for the specimens subjected to the thermal cycling after aging at 723 K for 3.6 ks was quite similar to that shown in Fig. 1. It is thus concluded that the complete cycling in the aged Ni-rich Ti–Ni alloys generally results in a decrease of $M^*$ and increases of $R^*$ and $A^*$, leaving $A^*$ almost constant.

Figure 5 shows DSC curves before and after the incomplete cycling of $10^4$ times in a specimen aged at 773 K for 3.6 ks. It is evident that the incomplete cycling produces a very little change (a few degrees) in $M^*$ and $A^*$, and substantially no change in $R^*$ and $A^*$. This result is consistent with that of a previous study by Tamura et al., where a Ti–50.2 at%Ni alloy annealed after cold working was subjected to the incomplete cycling up to $10^4$ times under constraint, but no deterioration as to recovery forces was observed.

Microstructural changes accompanied with the complete cycling have been examined by TEM observation. The results are shown in Fig. 6, (a) and (b) being taken from the specimens aged at 773 K for 3.6 ks before and after the thermal cycling of $10^4$ times, respectively. The lenticular precipitates seen in (a) are those having rhombohedral structure and the composition of Ti$_3$Ni$_4$, as identified previously. The matrix regions between the precipitates are smooth in (a), but are heavily roughened in (b). Dislocation contrasts are not necessarily clear in (b), but the matrix lattice is disturbed by the existence of some kinds of defects. Meanwhile, (c) and (d) were obtained from the specimens aged at 773 K for 540 ks before and after the thermal cycling of $10^4$ times, respectively. Coarsening of the precipitates is evident in (c) and dislocation like contrasts are visible here and there in (d). As a whole, however, the substructure of the
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The matrix phase after the thermal cycling appears to be somewhat different from those of tangled dislocations, as observed in the solution-treated alloys after thermal cycling (4)(5). The nature of the defective substructure of the aged alloy after thermal cycling is now being studied. On the other hand, the TEM observation on the aged specimens subjected to the incomplete thermal cycling revealed no change, in contrast with the case of complete cycling.

It is apparent from Fig. 1 as well as Figs. 4 and 5 that the DSC peak for the R→M transformation is somewhat smaller than that for the reversion. Nominal values of the latent heat of those transformations obtained by integrating peak areas are shown in Table 1 for the specimen aged 773 K for 3.6 ks. Then, it is evident that the latent heat of the forward transformation, $\Delta H^{R\rightarrow M}$, is always smaller than that of the reversion, $\Delta H^{M\rightarrow R}$. Furthermore, it is seen that $\Delta H^{R\rightarrow M}$ decreases with increasing thermal cycle. These points will be discussed thermodynamically in the next section.

IV. Discussion

It has been found in the present study that even in the aged Ni-rich Ti-Ni alloy, $T^{\#}_R$ as well as $M^\#$ are significantly changed by thermal cycling when the cycling is extended roughly more than $10^3$ times. It is interesting to note that $M^\#$ is lowered while $T^{\#}_R$ is raised up by such a thermal cycling. That is, the influence of thermal cycling on $M^\#$ and $T^{\#}_R$ is opposite in sense. Such thermal cycling effects may be qualitatively accounted for from a point of view that stress fields around the precipitates formed during aging are relaxed by thermal cycling, as follows:

The detailed crystallographic analysis on the
Table 1  Changes in transformation temperatures and heats by thermal cycling in a Ti-51.0 at%Ni alloy aged at 773 K for 3.6 ks.

| Cycles (×10^2) | A*(K) | M*(K) | A*-M*(K) | ΔH^M-R (J/mol) | ΔH^R-M (J/mol) | ΔH^M-R-ΔH^R-M (J/mol) | ΔH^M-R-ΔH^R-M/A*-M* |
|---------------|-------|-------|----------|----------------|----------------|-----------------------|---------------------|
| 0             | 282   | 217   | 65       | 438            | 312            | 126                   | 1.9                 |
| 1             | 281   | 209   | 72       | 458            | 296            | 162                   | 2.2                 |
| 3             | 280   | 201   | 79       | 453            | 266            | 187                   | 2.4                 |
| 5             | 280   | 198   | 82       | 449            | 257            | 192                   | 2.3                 |
| 7             | 279   | 193   | 86       | 427            | 222            | 205                   | 2.4                 |
| 10            | 278   | 188   | 90       | 423            | 242            | 181                   | 2.0                 |

Very recently, an increase of \( T_R^* \) by thermal cycling under constraint was also found by Tamura et al.\(^{(16)} \) in a Ti-50.2 at%Ni alloy annealed after cold-working. However, whether or not the precipitation occurs in Ni-rich Ti-Ni alloys depends critically on Ni content, especially less than 51 at%Ni\(^{(11)(12)} \), and it was not directly examined in the Ti-50.2 at%Ni alloy. Thus, the origin of the increase of \( T_R^* \) observed by Tamura et al. is not clear at present.

In contrast with the prominent changes of transformation temperatures by the complete cycling, little change was brought about by the incomplete cycling, as shown in Fig. 5. This fact is quite reasonable when the shape strains accompanying the R-phase and the martensitic transformations are taken into account. The R-phase transformation is accomplished by a very small lattice distortion, the volume change being only of the order of \( 10^{-4} \). The shape strain, which is solely the volume change upon transformation, can thus be perfectly accommodated elastically, and no irreversible process such as generation of dislocations will not be involved in the transformation. Meanwhile, the shape strain associated with the martensitic transformation is 0.13, and the volume change is \( 3 \times 10^{-3} \), both being comparable to those for the martensitic transformations in other shape memory alloys such as Cu-Al-Ni ones\(^{(19)} \). The shear component of shape strain can be perfectly accommodated by grouping of proper variants of martensite plates\(^{(20)} \), but the dilatational component can not by any means. Then, the martensitic transformation accompanied by large volume changes must involve some irreversible processes. Therefore, large volume changes are considered to be one of the important causes...
for the generation of dislocations during thermal cycling\(^{(21)}\). Moreover, in practice incomplete accommodation of the shear component of shape strain by grouping of martensite variants may occur locally, resulting in the generation of dislocations. The roughening in the matrix as shown in Fig. 6 may be due to such plastic accommodations of the shape strain.

As shown in Table 1, the latent heat of the martensitic transformation, \(\Delta H^{R \rightarrow M}\), is certainly smaller than that of the reverse one, \(\Delta H^{M \rightarrow R}\). In general, the latent heat of a transformation under constant pressure is equal to the enthalpy change of the transformation. Assuming that the specific heats of the low and high temperature phases, \(c_p^{L}\) and \(c_p^{H}\), respectively, are independent of temperature, the enthalpy change at temperature \(T\) can be expressed as

\[
\Delta H(T) = -(T_0 - T)(c_p^{H} - c_p^{L}) + \Delta S(T_0) \cdot T_0,
\]

where \(T_0\) represents the temperature at which the Gibbs chemical free energies of the two phases are equal, and \(\Delta S\) the entropy change. Letting \(T_1\) and \(T_2\) be the temperatures of the onsets of the forward and the reverse transformations, respectively,

\[
\Delta H(T_2) - \Delta H(T_1) = (T_2 - T_1)(c_p^{H} - c_p^{L}).
\]

However, the martensitic transformation and the reversion do not take place instantaneously at those temperatures, but progress gradually over a certain temperature range. Then, for simplicity, it is assumed here that \(T_1\) and \(T_2\) can be replaced by \(M^*\) and \(A^*\), respectively, and that \(\Delta H(T_1)\) and \(\Delta H(T_2)\) can be replaced by \(\Delta H^{R \rightarrow M}\) and \(\Delta H^{M \rightarrow R}\), respectively. Then, the following equation is obtained:

\[
\Delta H^{M \rightarrow R} - \Delta H^{R \rightarrow M} = (A^* - M^*)(c_p^{R} - c_p^{M}),
\]

where \(c_p^{R}\) and \(c_p^{M}\) represent the specific heats of the R-phase and the martensite phase, respectively. The specific heats of both phases were obtained for a Ti-Ni-Fe alloy by Matsumoto and Honma\(^{(22)}\). According to them, \(c_p^{R}\) is larger than \(c_p^{M}\) by about 6 J/mol·deg. If this is the case for the present alloy, then we obtain the following relation:

\[
\Delta H^{M \rightarrow R} > \Delta H^{R \rightarrow M},
\]

which is indeed consistent with the present experimental results. The relation (4) is schematically illustrated in Fig. 7. As seen in Table 1, \(\Delta H^{R \rightarrow M}\) certainly decreases with increasing thermal cycle. This can be qualitatively understood from Fig. 7, because with increasing thermal cycle \(M^*\) is lowered and thus \(\Delta H^{R \rightarrow M}(M^*)\) is expected to become smaller. Similar results have been obtained experimentally for the direct B2 \(\rightarrow\) M transformations in Ti-Ni alloys by Airoldi et al.\(^{(23)}\).

It is seen in Table 1 that \(\Delta H^{M \rightarrow R} - \Delta H^{R \rightarrow M}\) increases with increasing \(A^* - M^*\). The last column in Table 1 shows the ratio, \(\Delta H^{M \rightarrow R} - \Delta H^{R \rightarrow M})/(A^* - M^*)\), which is seen to hardly change with thermal cycling. Equation (3) indicates that the ratio corresponds to the difference in specific heat between the two phases. The difference in specific heat thus obtained is about 2 J/mol·deg, and is much smaller than that in the above Ti-Ni-Fe alloy.

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