The Nature of Reversible Change in M_s Temperatures of Ti-Ni Alloys with Alternating Aging

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Ni-rich Ti-Ni alloys were aged alternately between 713 K and 823 K. The transformation temperatures and the microstructures of samples after the alternating aging treatments were systematically investigated by DSC and TEM. The transformation temperatures (R_s , M_s , A_f) showed nearly reversible changes, corresponding to the two aging temperatures; aging at 713 K (low temperature) leads to higher transformation temperatures and aging at 823 K (high temperature) leads to lower transformation temperatures. Meanwhile, some irreversible features were also found in this experiment, such as the dependence of martensitic transformation temperatures on the aging time and the number of alternating aging cycles. The nature of this interesting behavior (the reversible change and irreversible features) for Ni-rich Ti-Ni alloys found a simple explanation by considering the temperature dependence of the solubility of Ni in TiNi matrix, which is in equilibrium with the metastable Ti_3Ni_4 precipitates, as well as the effect of Ti_3Ni_4 precipitate size.

(Received August 6, 1999; In Final Form October 4, 1999)

Keywords: martensitic transformation, R-phase transformation, transformation temperature, control of transformation temperature, reversible change, titanium-nickel alloy, shape memory alloy, aging

I. Introduction

The Ti-Ni shape memory alloy is an important alloy, which exhibits the interesting shape memory effect and superelasticity. In fact it is the only alloy that has found wide applications in actuators, couplings, and medical uses⁽¹⁾. Since the shape memory effect and superelasticity are inherently due to the martensitic or R-phase transformations, the transformation temperature control becomes very important for practical applications. There are many factors, which greatly influence the transformation temperature, and considerable work has been done in this area such as: (1) the composition⁽²⁾⁻⁽⁴⁾; (2) aging after solution heat treatment⁽⁵⁾⁻⁽⁷⁾; (3) thermo-mechanical treatment⁽⁵⁾⁽⁶⁾⁽⁸⁾⁻⁽¹¹⁾; (4) addition of ternary elements⁽²⁾⁽⁶⁾⁽¹²⁾⁻⁽¹⁶⁾. Among these factors, aging treatment is widely used for controlling the shape memory behavior. It is well known that aging treatment can produce precipitates as a second phase from the super-saturated solid solution obtained by quench. These precipitates can affect the transformation behavior and the mechanical properties, *i.e.*, age-hardening. On the other hand, aging treatment is directly controlled by the phase diagram, which gives important information for considering a suitable heat-treatment in practical applications. Many investigations were made on the phase diagram of the Ti-Ni alloy system⁽¹⁷⁾⁻⁽²³⁾, their interests were especially focused on the intermetallic compound TiNi with B2 structure. The main results on the single phase "TiNi" (B2 type ordered phase) can be concluded as follows: (1) the single phase region in the phase diagram is very nar-

row at temperatures below 923 K⁽¹⁹⁾⁽²¹⁾⁽²³⁾ and below this temperature the TiNi matrix region exists only between 50.0 and 50.5 at%Ni; (2) Ni-rich Ti-Ni alloys, exceeding 50.5 at%Ni, produce precipitates upon aging treatment, and the final product is a mixture of the $TiNi_3$ and TiNi matrix; (3) There are three kinds of precipitates, Ti_3Ni_4 , Ti_2Ni_3 , $TiNi_3$ formed by appropriate aging treatments. The precipitation process occurring in the Ni-rich Ti-Ni alloys was studied in detail by Nishida *et al.*⁽²⁴⁾ According to their results, the precipitates Ti_3Ni_4 and Ti_2Ni_3 are metastable. In other words, the precipitation process occurs in the following order with aging time; change from a metastable Ti_3Ni_4 precipitate to another metastable Ti_2Ni_3 precipitate, and finally to a stable $TiNi_3$ precipitate. Based on the above results, a recent phase diagram of Ti-Ni alloy system was proposed by Massalski *et al.*⁽²⁵⁾, and a slight modification was added to it; there exists a BCC-B2 transition at 1363 K, proposed by Honma *et al.*⁽²⁶⁾ However, there still exists an important problem, that is, the phase diagram of Ti-Ni alloy were determined only above 923 K, and no detailed information was obtained below this temperature. Furthermore, it is important to note that the equilibrium phase diagram gives only the equilibrium relationship between TiNi and $TiNi_3$ precipitate. This reaction is of little use for practical purpose due to the coarse $TiNi_3$ precipitates. In order to avoid the precipitation of $TiNi_3$, aging treatment is usually carried out at lower temperature; the precipitation product is finely dispersed Ti_3Ni_4 . This precipitation reaction is important for improving the shape memory characteristics due to the hardening of the parent phase⁽⁵⁾⁽⁷⁾, and is responsible for all-round

shape memory effect⁽⁴⁾. Though the fine Ti_3Ni_4 precipitates coarsen with increasing aging time, they are stable over extremely long time. Thus for practical applications, it is necessary to consider the metastable equilibrium between the TiNi matrix and Ti_3Ni_4 precipitates. In this paper, we will show that the metastable equilibrium between the TiNi matrix and Ti_3Ni_4 precipitates can produce some interesting and important effect.

Horikawa *et al.*⁽²⁷⁾ reported that there existed a reversible change in the transformation temperatures of a Ti-51 at%Ni alloy by “short-time” alternating aging between 713 K and 823 K. Furthermore, they found that Ti-50 at%Ni alloy did not show such an effect; this indicated that this phenomenon was possibly due to a kind of precipitation process in the Ni-rich Ti-Ni alloy. They tentatively ascribed the effect due to “reversion”, which results from the dissolution of unstable GP-zones, as found in aged Al-Cu alloys⁽²⁸⁾. However, if reversion is responsible for such effect, this effect is expected to appear only by short-time aging, because long-time aging would lead to the formation of more stable precipitates and make the process irreversible. In a preliminary report⁽²⁹⁾, we showed that the phenomenon still existed even by long-time aging. This suggests that this phenomenon is not due to reversion. We proposed that the essential feature of alternating aging (*i.e.*, the reversible change in the transformation temperatures) is probably related to the phase equilibrium between the TiNi matrix and metastable Ti_3Ni_4 precipitates at different aging temperatures. However, we also found some “irreversible features”; the slight cycle dependence and aging-time dependence of the martensitic transformation temperature M_s , as well as the difference in M_s between the first and the later cycles after aging at 713 K. The purpose of the present paper is to clarify this unique phenomenon with evidence, and to give explanation for the “irreversible features” mentioned above by using TEM and DSC measurements.

II. Experimental

Two kinds of Ni-rich Ti-Ni alloys were used for this experiment, which were prepared by plasma melting in water-cooled copper molds at Furukawa Electric Co. Ltd. The chemical composition of these two kinds of alloys were determined by chemical analysis to be Ti-51 at%Ni and Ti-52.6 at%Ni, respectively. All samples were annealed in evacuated quartz capsules at 1273 K for 3.6 ks and then quenched into ice water. The following heat treatments were performed as shown in **Table 1**. For group 1 of Ti-51 at%Ni alloy, the low- and high-temperature aging treatments were repeated for 9 times (cycles) with the same samples, in order to see if the transformation temperatures are solely dependent on aging temperature, and not on the number of alternating aging cycles. After each aging treatment the samples were quenched into ice-water. For group 2 of Ti-51 at%Ni alloy, the samples were treated in the similar way as that for group 1, except that the aging time for group 2 at 713 K was two times longer (172.8 ks) than that for group 1. The purpose for this operation was to see the influence of difference in the low temperature aging time. For Ti-52.6 at%Ni alloy (group 3), the samples were treated in the same way as that for group 2 of Ti-51 at%Ni alloy, except that the number of alternating aging cycles were made for only five times (cycles). Because it was only for checking whether this phenomenon (the reversible change in the transformation temperatures) is a common one or not in Ni-rich Ti-Ni alloys.

Following the above heat treatments, the martensitic (and R-phase) transformation temperatures were measured by differential scanning calorimetry (DSC) method with a cooling and heating rate of 10 K/min, using a MAC 3100 s calorimeter. Samples for transmission electron microscopy (TEM) were mechanically polished and finally electropolished using a twin-jet apparatus. The electrolyte consisted of 7.5 pct HClO_4 and 92.5 pct CH_3COOH (by volume). Microstructures of samples

Table 1 The types of alternating aging treatments.

Composition	Alternating aging treatments	The number of alternating aging cycles	
Ti-51at%Ni	713 K for 86.4 ks $\leftrightarrow$ 823 K for 0.6 ks	9	group 1
	713 K for 86.4 ks $\leftrightarrow$ 823 K for 3.6 ks	9	
	713 K for 86.4 ks $\leftrightarrow$ 823 K for 86.4 ks	9	
	713 K for 86.4 ks $\leftrightarrow$ 823 K for 172.8 ks	9	
	713 K for 172.8 ks $\leftrightarrow$ 823 K for 0.6 ks	9	group 2
	713 K for 172.8 ks $\leftrightarrow$ 823 K for 3.6 ks	9	
	713 K for 172.8 ks $\leftrightarrow$ 823 K for 86.4 ks	9	
	713 K for 172.8 ks $\leftrightarrow$ 823 K for 172.8 ks	9	
Ti-52.6at%Ni	713 K for 172.8 ks $\leftrightarrow$ 823 K for 0.6 ks	5	group 3
	713 K for 172.8 ks $\leftrightarrow$ 823 K for 3.6 ks	5	
	713 K for 172.8 ks $\leftrightarrow$ 823 K for 86.4 ks	5	
	713 K for 172.8 ks $\leftrightarrow$ 823 K for 172.8 ks	5	

were observed using a JEM 2010 electron microscope operated at 200 KV.

III. Experimental Results

1. Reversible change in the transformation temperatures with alternating aging

Figure 1 shows the transformation temperatures as a function of the number of alternating aging cycles between 713 K and 823 K. The transformation temperatures show an interesting reversible change, which corresponds to the two aging temperatures. Aging at 713 K (low temperature) leads to higher transformation temperatures, and aging at 823 K (high temperature) leads to lower transformation temperatures. This phenomenon is very similar to that reported by Horikawa *et al.*⁽²⁷⁾, despite the marked difference in aging time between theirs (120 s at 783 K) and ours (up to 172.8 ks at 823 K). The nearly reversible change in the transformation temperatures suggests that there are two equilibrium states corresponding to the two aging temperatures.

In that figure the aging time for the lower temperature (713 K) is fixed (*i.e.*, 86.4 ks), while those for higher temperature (823 K) are changed from (a) to (d). It can

also be seen that the martensitic transformation temperatures (M_s , A_f) for the same aging temperature slightly increase with the number of alternating aging cycles for short- and medium-time aging (Figs. 1(a) and (b)), while basically do not change for long-time aging (Figs. 1(c) and (d)) except for the first cycle. By contrast, R-phase transformation temperature (R_s) for the same aging temperature is not dependent on the number of alternating aging cycles for all the cases. Furthermore, comparing Figs. 1(a), (b), (c) and (d), the magnitude of changes in martensitic transformation temperatures ΔM_s ($=M_s(713\text{ K})-M_s(823\text{ K})$) and ΔA_f ($=A_f(713\text{ K})-A_f(823\text{ K})$) show the largest values for Fig. 1(a), while they show intermediate values for Fig. 1(b) and the smallest (same) ones for Figs. 1(c) and (d). However, for the magnitude of R-phase transformation temperature change ΔR_s ($=R_s(713\text{ K})-R_s(823\text{ K})$), it exhibits the same value for all the cases. One more feature is that the transformation temperature M_s after aging at 713 K in the first cycle are obviously lower than those in the later cycles.

The heat treatment for **Fig. 2** is essentially the same as that for Fig. 1, except that the low temperature (713 K) aging time is doubled (172.8 ks). As shown in Fig. 2, it exhibits nearly the same features as Fig. 1 *i.e.*, the reversible change in the transformation temperatures,

Fig. 1 The transformation temperatures as a function of the number of alternating aging cycles for Ti-51at%Ni alloy: (a) cycling between aging at 713 K for 86.4 ks and at 823 K for 0.6 ks; (b) cycling between aging at 713 K for 86.4 ks and at 823 K for 3.6 ks; (c) cycling between aging at 713 K for 86.4 ks and at 823 K for 86.4 ks; (d) cycling between aging at 713 K for 86.4 ks and at 823 K for 172.8 ks.

Fig. 2 The transformation temperatures as a function of the number of alternating aging cycles for Ti-51at%Ni alloy: (a) cycling between aging at 713 K for 172.8 ks and at 823 K for 0.6 ks; (b) cycling between aging at 713 K for 172.8 ks and at 823 K for 3.6 ks; (c) cycling between aging at 713 K for 172.8 ks and at 823 K for 86.4 ks; (d) cycling between aging at 713 K for 172.8 ks and at 823 K for 172.8 ks.

and some irreversible features mentioned above. Comparing Fig. 1 with Fig. 2, it can be seen that by increasing the low temperature (713 K) aging time to 172.8 ks, the transformation temperature M_s in the first cycle in Fig. 2 is higher than that in Fig. 1. However, prolonged aging does not bring about significant changes in the cyclic behavior.

Figure 3 shows the transformation temperatures as a function of the number of alternating aging cycles for a different Ni-rich alloy (Ti-52.6 at%Ni), which experienced the same heat treatment as that for Ti-51 at%Ni alloy in Fig. 2. We can see that the transformation temperatures also show the same behavior as shown in Figs. 1 and 2 for Ti-51 at%Ni alloy with alternating aging. When the high temperature (823 K) aging time is short, they are also slightly dependent on aging time and on the number of alternating aging cycles (Figs. 3(a), (b) and (c)). For long aging time, they are almost completely reversible, independent of aging time and the number of alternating aging cycles (Fig. 3(d)). Compared with Ti-51 at%Ni alloy of the same heat treatment (Fig. 2), Ti-52.6 at%Ni alloy (Fig. 3) seems to need longer time (about 823 K/172.8 ks) to build the completely reversible cycles (Ti-51 at%Ni alloy needs only 823 K/86.4 ks). Meanwhile, M_s after aging at 713 K in the first cycle for Ti-52.6

at%Ni alloy is lower than that for Ti-51 at%Ni alloy (Fig. 2). On the other hand, R-phase transformation temperatures R_s exhibit the same values as for Ti-51 at%Ni alloy (Figs. 1 and 2). R_s seems to be controlled only by the aging temperature, which is about 321 K for aging at 713 K and 279 K for aging at 823 K, respectively.

Comparing Figs. 1, 2 and 3, we can see that with increase in aging time, $\Delta M_s (=M_s(713\text{ K})-M_s(823\text{ K}))$ and $\Delta A_f (=A_f(713\text{ K})-A_f(823\text{ K}))$ decrease until reaching constants. These constant values, $\Delta M_s=37\text{ K}$, $\Delta A_f=35\text{ K}$, are independent of the alloy composition, being the same for Ti-51 at%Ni and for Ti-52.6 at%Ni alloys. However, $\Delta R_s (=R_s(713\text{ K})-R_s(823\text{ K}))$ is constant (42 K) for different aging time and for different alloys. Furthermore, we can also see that with increase in aging time and in the number of alternating aging cycles, M_s and A_f have a tendency to reach constants corresponding to each aging temperature, independent of the alloy composition; for aging at 713 K, $M_s=307\text{ K}$ and $A_f=341\text{ K}$, while for aging at 823 K, $M_s=270\text{ K}$ and $A_f=306\text{ K}$, respectively. On the other hand, R_s is irrespective of aging time and of the number of alternating aging cycles; it shows constants corresponding to each aging temperature for Ti-51 at%Ni and Ti-52.6 at%Ni alloys; $R_s=321\text{ K}$ (713 K) and $R_s=279\text{ K}$ (823 K).

2. Microstructures of samples observed by TEM after aging treatments

The microstructures of the samples after aging treatments were observed by TEM at room temperature (293 K), which are shown in **Fig. 4**. Figure 4(a) is a TEM image exhibiting the microstructure of Ti-51 at%Ni sample after aged at 713 K for 172.8 ks (the first cycle), while Fig. 4(b) is the diffraction pattern corresponding to it, the zone axis being parallel to the $[111]_{B2}$. It can be seen from Fig. 4(a) that three kinds of precipitates exist, which are marked 1, 2, 3. Their lengths are about 200 nm. From Fig. 4(b), it can be seen that there are $1/7$ superlattice diffraction spots observed along $\langle 123 \rangle_{B2}$ and $1/3$ superlattice diffraction spots observed along $\langle 110 \rangle_{B2}$ in the TiNi matrix. Figure 4(b) is a typical diffraction pattern, exhibiting the mixture of Ti_3Ni_4 precipitate ($1/7$) and R phase ($1/3$). The crystal structure of the Ti_3Ni_4 has been determined to be rhombohedral with $a_0=0.6704\text{ nm}$, $\alpha=113.85^\circ$, and the orientation relationship between the TiNi matrix and the Ti_3Ni_4 precipitate to be described as: $(001)_{Ti_3Ni_4} \parallel (111)_M$, $[010]_{Ti_3Ni_4} \parallel [\bar{2}\bar{1}3]_M^{(30)-(32)}$. All the spots from Ti_3Ni_4 precipitates (Fig. 4(b)) can be well explained by using the above parameters. There is no other spots observed except the ones which correspond to R phase and Ti_3Ni_4 precipitates. Figures 4(c) and (d) are the TEM image and the diffraction pattern, respectively, corresponding to the subsequent aging at 823 K for 0.6 ks, after aging at 713 K for 172.8 ks. It can be seen from Fig. 4(c) that there exist the Ti_3Ni_4 precipitates, and their lengths are almost the same as those in Fig. 4(a). Meanwhile, it can be seen that the corresponding diffraction pattern (Fig. 4(d)) is essentially

Fig. 3 The transformation temperatures as a function of the number of alternating aging cycles for Ti-52.6 at%Ni alloy: (a) cycling between aging at 713 K for 172.8 ks and at 823 K for 0.6 ks; (b) cycling between aging at 713 K for 172.8 ks and at 823 K for 3.6 ks; (c) cycling between aging at 713 K for 172.8 ks and at 823 K for 86.4 ks; (d) cycling between aging at 713 K for 172.8 ks and at 823 K for 172.8 ks.

Fig. 4 The microstructures and the corresponding electron diffraction patterns of the specimens after alternating aging treatments. (a) the microstructures after aging at 713 K for 172.8 ks for Ti-51at%Ni; (b) the corresponding electron diffraction pattern and incident beam is parallel to $[111]_{B2}$; (c) the microstructures after subsequently aging at 823 K for 0.6 ks after the previous aging in (a); (d) the corresponding electron diffraction pattern and incident beam is parallel to $[111]_{B2}$; (e) the microstructures after subsequently aging at 823 K for 172.8 ks after the previous aging in (a); (f) the corresponding electron diffraction pattern and incident beam is parallel to $[111]_{B2}$; (g) the microstructures after aging at 713 K for 172.8 ks for Ti-52.6at%Ni.

the same as that in Fig. 4(b), except that the sharp $1/3$ spots from R phase are replaced by $1/3$ diffuse spots at the same location. The $1/3$ diffuse spots indicate that the matrix is still in the parent state, because it is a precursor phenomenon in TiNi (B2) prior to R-phase transformation⁽³³⁾. This is consistent with the depression of R_s by aging at 823 K, as shown in Fig. 2. Figure 4(e) shows the results obtained after aging at 823 K for a long time of 172.8 ks, which was subjected to prior aging at 713 K for 172.8 ks in the first cycle. It can be seen that the Ti_3Ni_4 precipitate grows to larger size (about 900 nm) compared with Fig. 4(c) and some dislocations exist around the Ti_3Ni_4 precipitate as indicated by the arrow. Furthermore, the corresponding diffraction pattern (Fig. 4(f)) is the same as that in Fig. 4(d). Figure 4(g) is a micrograph, which corresponds to aging at 713 K for 172.8 ks of Ti-52.6 at%Ni alloy. It can be seen that the density of Ti_3Ni_4 precipitates is larger than that of Ti-51 at%Ni alloy (Fig. 4(a)), though their lengths are essentially the same as those of Ti-51 at%Ni alloy. From Fig. 4, we can conclude that the precipitates formed during aging at either 713 K or 823 K are always Ti_3Ni_4 , even for the longest aging time (172.8 ks) performed, and no Ti_2Ni_3 or TiNi₃ were found. Therefore, we need to consider only the Ti_3Ni_4 precipitation reaction to explain the interesting phenomenon described in Section 1.

IV. Discussion

1. A simple explanation of reversible change in the transformation temperatures by considering the metastable equilibrium between the TiNi matrix and the Ti_3Ni_4 precipitates

The reversible change in the transformation temperatures was first reported for short-time alternating aging⁽²⁷⁾, and it was considered to be connected to the reversion. But as shown in Figs. 1, 2 and 3, the transformation temperatures still show a reversible change in

an up-and-down manner even for alternating long-time aging (823 K for 172.8 ks). Therefore, it is evident that the nature of reversible change in the transformation temperatures for the Ni-rich Ti-Ni alloy is not due to reversion. Here we show that all the features of reversible change in the transformation temperatures can simply be explained by considering the metastable equilibrium between the TiNi matrix and the Ni-rich Ti_3Ni_4 precipitates at different aging temperatures, because Ti_3Ni_4 is the only precipitate appeared during aging (Fig. 4). As shown in Fig. 5, we can postulate that the solid solubility of Ni in the TiNi matrix, which is in equilibrium with the Ti_3Ni_4 precipitates, should decrease with decreasing temperature. Therefore, aging at different temperatures gives rise to different Ni-content in the TiNi matrix. Since Ni-content of the TiNi matrix strongly affect martensitic (and R-phase) transformation temperatures, 0.1 at% increase in Ni-content lowers the transformation temperature M_s by about 18.5 K⁽³⁴⁾. Aging at different temperatures results in significantly different transformation temperatures, as schematically shown in Fig. 5.

With this basic idea, we can simply explain the reversible change in the transformation temperatures with alternating aging for Ni-rich Ti-Ni alloy as follows. After aging at 713 K for some time, the supersaturated Ti-Ni (51 at%Ni or 52.6 at%Ni) alloys decompose into B2-TiNi and Ti_3Ni_4 precipitates, as shown in Fig. 5. The Ni-content in the TiNi matrix is now equal to the equilibrium Ni-content (approximately 50.13 at%Ni⁽³⁴⁾) for 713 K. But when the alloy is subsequently aged at higher temperature 823 K, the Ti_3Ni_4 precipitate has to partially dissolve into the TiNi matrix, because the solubility limit at 823 K is larger than that at 713 K. In this case, the Ni-content in the TiNi matrix increases and as a result the transformation temperatures become lower than those for 713 K. When the alloy is aged at 713 K again, the Ni-content is lowered to the equilibrium value for 713 K again by forming more Ti_3Ni_4 precipitates; thus the transformation temperatures increase. With the

Fig. 5 A simple explanation on the nature of reversible change in the transformation temperatures by considering the metastable equilibrium between the TiNi matrix and Ti_3Ni_4 precipitates.

*After Tang⁽³⁴⁾

Fig. 6 The microstructure of Ti-51at%Ni alloy after aging at 823 K for 172.8 ks followed by aging at 713 K for 3.6 ks.

alternating aging, Ni-content undergoes reversible change, and consequently reversible change in the transformation temperatures occurs.

Now we give a proof to this idea. When aged at 823 K for long time (172.8 ks), the Ti_3Ni_4 precipitates grow to large size (about 900 nm) and no fine Ti_3Ni_4 precipitates exist between the bigger ones, as shown in Fig. 4(e). If the specimen is subsequently aged at lower temperature (713 K) for a short time, it can be expected from Fig. 5 that new Ti_3Ni_4 precipitates will form to lower the Ni-content in the TiNi matrix. It is possible that some fine

Ti_3Ni_4 precipitates will form among the bigger ones by aging at 713 K for a short time. As shown in Fig. 6, after aging at high temperature (823 K) for long time (172.8 ks) followed by aging at low temperature (713 K) for short time (3.6 ks), it can be seen that there indeed appear many very small Ti_3Ni_4 (about 100 nm) between the bigger ones (about 1000 nm), as indicated by arrows. This result directly proves that there exists a TiNi- Ti_3Ni_4 metastable equilibrium as shown in Fig. 5. This TiNi- Ti_3Ni_4 metastable equilibrium is of significance for practical applications of Ti-Ni alloys, because the desired transformation temperatures can be controlled by choosing suitable aging temperature.

2. The effect of the precipitate size on the martensitic transformation temperatures

Although the essential feature of alternating aging, *i.e.*, the reversible change in the transformation temperatures, found a simple explanation by considering the metastable equilibrium between the TiNi matrix and the Ti_3Ni_4 precipitates as described above, the slight cycle dependence (Figs. 1(a) and (b), Figs. 2(a) and (b), Figs. 3(a), (b) and (c)) and aging-time dependence of the martensitic transformation temperatures, suggest that other factors also play some role in this phenomenon. Because the slight irreversible changes disappear after long time aging (Figs. 1(c) and (d), Figs. 2(c) and (d), Fig. 3(d)), it is reasonable to consider them as due to the changes in Ti_3Ni_4 size.

When the Ti_3Ni_4 precipitates from the matrix, an important consequence arises, that is, coherency stresses develop, because the new phase (Ti_3Ni_4) has a different lattice parameter and crystal structure (rhombohedral) from the TiNi matrix (B2). If precipitates are small, complete coherency is possible; then a large coherency stress arises. On the other hand, if precipitates are large, complete coherency cannot be maintained, and dislocations are introduced to accommodate the lattice misfit. The misfit dislocations can be clearly seen at the interface of the large precipitate (arrowed) in Fig. 4(e). The loss of coherency with increasing Ti_3Ni_4 size leads to the release of the coherency stress. Since the coherency stress acts as a resistance to the martensitic transformation (which produces a lattice distortion), it can be expected that the coherency stresses suppress martensitic transformation temperatures. Therefore, it follows that the smaller the Ti_3Ni_4 the lower the transformation temperatures. This reasoning well explains why short-time aging (corresponding to small Ti_3Ni_4 precipitates) leads to low M_s , A_f , while long-time aging (corresponding to large Ti_3Ni_4 precipitates) leads to high M_s , A_f . Because aging time is accumulated with increase of the number of alternating aging cycles, it is natural that the effect of increasing the number of alternating aging cycles equals to the increase in aging time, leading to higher M_s , A_f , as shown in Figs. 1, 2 and 3. Another common irreversible feature shown in Figs. 1, 2 and 3, is that the M_s in the first cycle after aging at 713 K are obviously lower than those in the later cycles. This phenomenon can also be explained by con-

sidering the effect of Ti_3Ni_4 precipitate size. It should be noted that except for the 1st cycle aging at 713 K, aging at 713 K for the later cycles are in fact performed after aging at high temperature (823 K). Therefore, it is expected that for the later 713 K aging cycles, Ti_3Ni_4 precipitates are significantly larger than that for the 1st 713 K aging cycle, leading to a marked increase in transformation temperature M_s .

Figure 3 suggests that Ti-52.6 at%Ni alloy need more time to complete reversible change in the transformation temperatures compared with Ti-51 at%Ni alloy. This is due to the large percentage of the Ti_3Ni_4 compared with Ti-51 at%Ni alloy. It can be expected that Ti-52.6 at%Ni alloy produces higher density of Ti_3Ni_4 precipitates than Ti-51 at%Ni alloy, thus has lower M_s in the first cycle compared with Ti-51 at%Ni alloy (Fig. 2).

3. The main factor which controls the R-phase transformation temperature

Figures 1, 2 and 3 show that R_s is not affected by aging time and by the number of alternating aging cycles. This can be considered to be related to the very small transformation strain which is about 1/10 of martensitic transformation. The small transformation strain makes R-phase transformation less susceptible to stress according to the Clausius-Clapeyron relation. Therefore, the coherency stress has much smaller effect on R-phase transformation than on martensitic transformation. This is why aging time and aging cycles (which change Ti_3Ni_4 sizes and coherency stresses) have little effect on R_s temperature. As shown in Figs. 1, 2 and 3, the R-phase transformation temperature R_s seems to be solely controlled by the aging temperatures (about 321 K for aging at 713 K and 279 K for aging at 823 K), and is almost independent of alloy composition. This can be easily understood from Fig. 5, by considering the metastable equilibrium between the TiNi matrix and the Ti_3Ni_4 precipitates. No matter what the composition of the Ti-Ni alloys is, the Ni-content of the TiNi matrix after aging is the same for the same aging temperature. Thus, R-phase transformation temperature exhibits the same value corresponding to each aging temperature and does not change with increasing the aging time and the number of alternating aging cycles.

V. Conclusion

Ti-51 at%Ni and Ti-52.6 at%Ni alloys were aged alternately between 713 K and 823 K. The transformation temperatures were measured by using DSC method. Furthermore, the microstructures of samples after aging treatments were observed by using the TEM. The results can be concluded as follows.

(1) The transformation temperatures (R_s , M_s , A_f) showed nearly reversible changes, even for long-time aging. Aging at 713 K (low temperature) leads to higher transformation temperatures, and aging at 823 K (high temperature) leads to lower transformation temperatures. The nature of this interesting behavior for Ni-rich

Ti-Ni alloys found a simple explanation by considering the temperature dependence of the solubility of Ni in the TiNi matrix, which is in equilibrium with the metastable Ti_3Ni_4 precipitates. The low temperature aging yields a lower Ni-content in the TiNi matrix, leading to higher transformation temperatures; the high temperature aging results in a higher Ni-content, leading to lower transformation temperatures.

(2) Besides the essential feature (the reversible change in the transformation temperatures), there also exist some irreversible features, such as the aging time and the cycle dependence of the martensitic transformation temperatures. The irreversible features are due to the effect of the Ti_3Ni_4 precipitate size, which changes with aging time and aging cycles.

(3) R-phase transformation temperatures R_s is affected only by the equilibrium Ni-content in the TiNi matrix corresponding to each aging temperature.

(4) The technical implication of the present study is that aging is a simple but effective way to control or change the martensitic (and R-phase) transformation temperatures of Ni-rich Ti-Ni alloys.

Acknowledgments

This work was supported by a Grant-in-Aid for Research on Priority Area of Phase Transformation and a Grant-in-Aid for International Scientific Research (1997–1999) from the Ministry of Education, Science and Culture of Japan, and partly supported by Project Research A from University of Tsukuba.

REFERENCES

- (1) K. Otsuka and C. M. Wayman (eds): *Shape Memory Materials*, Cambridge University Press, Cambridge, (1998), pp. 1–284.
- (2) K. H. Eckelmeyer: *Scripta Metall.*, **10** (1976), 667–672.
- (3) J. E. Hanlon, S. R. Butler and R. J. Wasilewski: *Trans. TMS-AIME*, **239** (1967), 1323–1329.
- (4) M. Nishida and T. Honma: *Scripta Metall.*, **18** (1984), 1293–1298.
- (5) S. Miyazaki, Y. Ohmi, K. Otsuka and Y. Suzuki: *J. de Phys.*, **43** (1982), C4-255–260.
- (6) W. B. Cross, A. H. Kariotis and F. J. Stimler: "Nitinol Characterization Study," NASA., September (1969), CR-1433.
- (7) T. Saburi, T. Tatsumi and S. Nenno: *J. de Phys.*, **43** (1982), C4-261–266.
- (8) F. E. Wang, B. F. DeSavage, W. J. Buehler and W. R. Hosler: *J. Appl. Phys.*, **39** (1968), 2166–2175.
- (9) G. P. Sandrock, A. J. Perkins and R. F. Hehemann: *Metall. Trans.*, **2** (1971), 2769–2781.
- (10) C. M. Wayman, I. Cornelis and K. Shimizu: *Scripta Metall.*, **6** (1972), 115–122.
- (11) S. Miyazaki, Y. Igo and K. Otsuka: *Acta Metall.*, **34** (1986), 2045–2051.
- (12) M. Matsumoto and T. Honma: *New Aspects of Martensitic Transformation*. JIM. Kobe, (1976), 199–204.
- (13) T. H. Nam, T. Saburi and K. Shimizu: *Mater. Trans.*, JIM, **31** (1990), 959–967.
- (14) T. Honma, Y. Shugo and M. Matsumoto: *Bulletin of Research Inst., Mineral Dressing and Metallurgy (Tohoku Univ.)*, **28** (1972), 209–219.
- (15) O. Mercier and K. N. Melton: *Metall. Trans.*, **10A** (1979), 387–389.
- (16) P. G. Lindquist and C. M. Wayman: *Int. Conf. on Engineering Aspects of Shape Memory Alloys* ed. by T. W. Duering, K. N. Melton, D. Stockel and C. M. Wayman, Butterworth-Heinemann,

- London, (1990), pp. 58–68.
- (17) P. Duwez and J. L. Taylor: *Trans. AIME*, **188** (1950), 1173–1176.
- (18) D. M. Poole and W. Hume-Rothery: *J. Inst. Met.*, **83** (1954–55), 473–480.
- (19) G. R. Purdy and J. G. Parr: *Trans. Metall. Soc. AIME*, **221** (1961), 636–639.
- (20) D. Koskimaki, M. J. Marcinkowski and A. S. Sastri: *Trans. Metall. Soc. AIME*, **245** (1969), 1883–1890.
- (21) R. J. Wasilewski, S. R. Butler, J. E. Hanlon and D. Worden: *Metall. Trans.*, **2** (1971), 229–238.
- (22) S. P. Gupta, K. Mukherjee and A. A. Johnson: *Mater. Sci. Eng.*, **11** (1973), 283–293.
- (23) G. F. Bastin and G. D. Rieck: *Metall. Trans.*, **5** (1974), 1817–1826.
- (24) M. Nishida, C. M. Wayman and T. Honma: *Metall. Trans.*, **17A** (1986), 1505–1515.
- (25) T. B. Massalski, H. Okamoto, P. R. Subramanian and L. Kacprzak (eds): *Binary alloy phase diagrams*, 2nd., ASM International, **3** (1990), pp. 2874–2876.
- (26) T. Honma, T. Matsumoto, Y. Shugo and M. Nishida: *Res. Rep. Nucl. Sci. Lab. Tohoku Univ.*, **12**(2) (1979), 183–190.
- (27) H. Horikawa, H. Tamura, Y. Okamoto, H. Hamanaka and F. Miura: *MRS Int'l. Mtg. on Adv. Mats.*, **9** (1989), 195–200.
- (28) R. Beton, E. C. Rollason: *J. Inst. Metals.*, **86** (1957–58), 77–85.
- (29) J. Zhang, X. Ren and K. Otsuka: *Scripta Metall.*, **4** (1999), 1109–1113.
- (30) T. Saburi, S. Nenno and T. Fukuda: *J. Less-Common Met.*, **125** (1986), 157–166.
- (31) M. Nishida, C. M. Wayman, R. Kainuma and T. Honma: *Scripta Metall.*, **20** (1986), 899–904.
- (32) T. Tadaki, Y. Nakata, K. Shimizu and K. Otsuka: *Trans. Japan Inst. Metals*, **27** (1986), 731–740.
- (33) T. Tamiya, D. Shindo, Y. Murukami, Y. Bando and K. Otsuka: *Mater. Trans., JIM*, **39** (1998), 714–723.
- (34) W. Tang: *Metall. Trans.*, **28A** (1997), 537–544.