Martensitic Transformation in Ti-Rich Ti–Pd Shape Memory Alloys

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A systematic study on martensitic transformation in Ti-rich Ti–Pd alloys has been carried out using differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). The alloys quenched from the single region of B2 parent phase show a successive transformation during DSC measurement. On the other hand, the furnace-cooled alloys show a single transformation. The successive transformation behavior is closely related to the formation of fine Ti2Pd precipitates with C11b-type structure during transformation cycle. The first peak on DSC heating curve is attributable to the reverse martensitic transformation of the TiPd matrix, while the second one is due to the reverse martensitic transformation in local regions around the Ti2Pd precipitates where Pd concentration is higher than that in matrix. Morphological characteristics of the precipitate are also discussed.

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1. Introduction

Ti–Pd shape memory alloys are well-known as potential materials for high temperature applications, since the intermetallic phase of TiPd undergoes a thermoelastic martensitic transformation around 800 K. Donkersloot and Van Vucht 1) firstly found the B2 to B19 type martensitic transformation in these alloys using high-temperature X-ray diffraction. They have determined the transformation temperatures, \( A_s \), \( A_f \), \( M_s \), and \( M_f \) from the intensity change of (101) \( B_{19} \), (010) \( B_{19} \) and (100) \( B_{19} \) reflections upon heating and cooling. They have reported that \( M_s \) is higher than \( A_s \) in Ti–45 and 55 at%Pd alloys which are close to the phase boundary of TiPd single phase at Ti-rich and Pd-rich sides, respectively. The inversion of \( M_s \) and \( A_s \) is unusual in martensitic transformation. It is likely that this phenomenon is peculiar case around the phase boundary, since the inversion does not occur at the equiatomic composition. However, the equilibrium phase boundary of TiPd, i.e., the homogeneity range, has not been clarified yet. Ti–Pd phase diagram assessed by Murray 2) shows that the homogeneity range is from 47 to 53 at%Pd and displays no significant variation with temperature on the both sides. On the other hand, a profile of the phase boundary TiPd compound reported by Shugo 3) is completely different. That is, the phase boundary at Pd-rich side is around 50 at%Pd and is almost independent of temperature, whereas the boundary at Ti-rich side is about 47.5 at%Pd at 1073 K and abruptly varies to 49 at%Pd at 973 K. A similar result has been obtained at both Ti and Pd-rich sides by Nishida et al. 4).

We made preliminary investigation on the phase diagram of Ti–Pd alloy, especially for the homogeneity range of TiPd phase. During this research we have found out the appearance of successive two-step transformation in Ti-rich alloys quenched from 1173 K or above. The purpose of present study is to investigate systematically martensitic transformation behavior in Ti-rich Ti–Pd alloys using DSC measurements and TEM observations. In order to clarify the microstructure change during the transformation, the specimens for TEM observations were subjected to the same thermal history of the DSC measurements. On the basis of these observations, the mechanism of successive martensitic transformation in quenched Ti-rich Ti–Pd alloys is discussed in connection with the morphological aspects of the microstructure.

2. Experimental Procedure

Ti-45 to 50 at%Pd alloys were prepared by arc melting in an argon atmosphere. The starting materials were pure Ti (99.7 mass%) and pure Pd (99.8 mass%). Ingots of 20 g in weight were melted repeatedly six times for homogenization. The obtained buttons were annealed in vacuum at 1273 K for 36 ks, and then furnace cooled to room temperature. The mass loss of each button after these treatments was less than 0.2%, and thus the chemical analysis has not been performed. Sheets of about 0.5 mm and 0.1 mm in thickness were cut from the buttons. The former was cut into appropriate size for DSC measurements. The latter was punched out into the disk of 3 mm in diameter for TEM observations. The half of DSC and TEM specimens was solution-treated at 1273 K for 3.6 ks and then quenched into ice water. The rest were furnace cooled to room temperature after the solution treatment at 1273 K for 3.6 ks. The cooling rate of 40 K/h was controlled from 1273 K to about 700 K, then the specimens were left in the furnace after turning off the electricity. Transformation temperatures were measured by using a Shimadzu DSC-50 calorimeter with heating and cooling rate of 10 K/min. Some of the quenched and the furnace cooled TEM specimens were subjected to the same thermal history of DSC measurement. In other words, they were heated up to prescribed temperatures with the rate of 10 K/min and then quenched into ice water. The TEM specimens were lightly mechanically polished to remove the surface scale. They were finally electropolished in an electrolyte consisting of 20% \( \text{H}_2\text{SO}_4 \) and 80% \( \text{CH}_3\text{OH} \) (by volume) using twin-jet method. The electrolyte temperature was around 253 K. TEM observations were carried out in a JEM-2000FX electron microscope operated at 200 kV.
The crystal structure of the B19 martensite is of MgCd type with an orthorhombic unit cell. The following lattice parameters were used for the present analysis: $a = 0.489$ nm, $b = 0.281$ nm and $c = 0.456$ nm.\(^{3}\)

3. Results

3.1 Transformation behavior

The transformation behavior of the Ti-rich Ti–Pd alloys used in the present investigation was essentially the same except for the transformation temperatures which are specific to each composition as discussed later. Therefore, we will exemplify mainly the results of Ti–47 at%Pd alloy hereinafter.

The DSC curves of quenched Ti–47 and 50 at%Pd alloys are shown in Fig. 1. In the Ti–50 at%Pd alloy only a single sharp peak is observed upon heating and cooling and there is no inversion between reverse and forward transformations. On the other hand, two endothermic and two exothermic reactions are clearly observed in the Ti–47 at%Pd alloy upon heating and subsequent cooling. We define the first and second peaks on heating as $A_2^*$ and $A_1^*$, respectively. In the same way, the first and second peaks on cooling are denoted as $M_1^*$ and $M_2^*$, respectively. The inversion of $A_2^*$ and $M_2^*$ is clearly seen. However, it must be also noted that $A_1^*$ lies very close to the reverse transformation peak temperature of the Ti–50 at%Pd alloy, which will be discussed later.

In order to establish the correspondence between the reactions observed on heating and cooling in the quenched Ti–47 at%Pd alloy, the incomplete thermal cycling experiments have been performed as shown in Fig. 2. In Fig. 2(a) the specimen is heated from room temperature to just beyond the $A_2^*$ peak and then cooled. A one-to-one correspondence between the $A_2^*$ and the $M_2^*$ transformations can be confirmed by the appearance of the exothermic peak on cooling. In the same way, a one-to-one correspondence between the $A_1^*$ and the $M_1^*$ transformations can be confirmed in Fig. 2(c), where the specimen is heated just beyond the $A_1^*$ peak. In this case $M_1^*$ lies at almost identical temperature with that of the single peak observed on cooling in the equiatomic alloy. There is no inversion between $A_2^*$ and $M_2^*$ in Figs. 2(a) to (c). The $A_2^*$ and $M_2^*$ peak temperatures increase and $M_1^*$ decreases with increasing the maximum heating temperature, which will be discussed later, then the inversion between $A_2^*$ and $M_2^*$ occurs, as shown in Fig. 2(e). However, $A_1^*$ is independent of the maximum heating temperature as clearly seen in Figs. 2(c) to (e).

Based on these measurements it is apparent that successive transformation takes place in Ti-rich Ti–Pd alloys. Comparing the individual peak area of the $A_2^*$ and $A_1^*$ or $M_2^*$ and $M_1^*$ reactions, it is likely that the lower temperature reaction is attribute to the transformation in almost entire volume of the specimen. On the other hand, the reaction at higher temperature may be due to the transformation in a small volume of the specimen.

Figure 3 shows DSC curves of the furnace cooled Ti–47 and 50 at%Pd alloys. In the Ti–50 at%Pd alloy the transformation behavior is identical to that of the quenched alloy in...
Fig. 1. On the other hand, in Ti–47 at%Pd alloy a rather broad single peak denoted as A* is only observed on heating instead of two peaks in the quenched alloy. A* lies nearly at the same temperature as the A1* of the quenched Ti–47 at%Pd alloy.

Compositional dependence of transformation peak temperatures during heating process in the quenched and the furnace cooled alloys is plotted in Fig. 4 and the obtained DSC results so far are summarized as follows. There is no difference of transformation behavior and temperature in the quenched and the furnace cooled Ti–50 at%Pd alloy as pointed out above. In the furnace cooled Ti-rich alloys, only one peak was observed on heating curve. The temperature of this peak for all the compositions lies very close to the endothermic peak temperature of Ti–50 at%Pd alloy. On the other hand, two peaks appear on the heating curves of quenched Ti-rich alloys. The temperature of A2* rises gradually with increasing Pd content and reaches the maximum at 50 at%Pd. The temperature of A1* is almost constant with Pd content and is identical to the transformation peak temperatures A* of the furnace cooled specimens. The change of transformation behavior with Pd content and thermal history suggests that the phase boundary of TiPd compound in Ti-rich side has significant variation with temperature and concentration. In order to establish the phase boundary, aging experiments are now in progress.

3.2 Microstructure modification

Figure 5(a) presents the microstructure of the quenched Ti–47 at%Pd alloy. The micrograph shows typical B19 martensite morphology consisting of alternating platelets with [111] Type I twin relation.6,7) Since no secondary phase is observed in the alloy, it is apparent that the alloy is quenched from a single region of B2 parent phase and no decomposition occurs during quenching. A similar twinned martensite was observed in the quenched and the furnace cooled Ti–50 at%Pd alloys, therefore we do not reproduce those here. It can be concluded that there is no microstructure change in the Ti–
50 at%Pd alloy irrespective of heat treatment. In other words, no phase decomposition occurs in the stoichiometric composition. Bright field image of the furnace cooled Ti–47 at%Pd alloy is shown in Fig. 5(b). There are three precipitate variants marked with I, II and III in the B19 martensite matrix. The electron diffraction patterns taken from the variants I, II and III are shown in Figs. 5(c) to (e), respectively. The pattern in (e) is a micro area pattern obtained only from the variant III. All the diffraction spots from precipitate can be indexed by assuming Ti$_2$Pd phase of C11$_b$-type structure with $a = 0.3090$ and $c = 1.0054$ nm. The orientation relationship between the precipitates and the martensite matrix are as follows,

Variant I: (001)$_{C11b}$ $\parallel$ (101)$_{B19}$, [010]$_{C11b}$ $\parallel$ [010]$_{B19}$

Variant II: (001)$_{C11b}$ $\parallel$ (101)$_{B19}$, [100]$_{C11b}$ $\parallel$ [010]$_{B19}$

Variant III: (001)$_{C11b}$ $\parallel$ (010)$_{B19}$, [011]$_{C11b}$ $\parallel$ [010]$_{B19}$

We can notice that apparent habit planes of the variants I, II and III are (101)$_{B19}$, (101)$_{B19}$ and (010)$_{B19}$, respectively.

Fig. 6 Bright field images of: (a), (c) water quenched and (e) furnace cooled Ti–47 at%Pd alloy after heated up in DSC at 973 K and then quenched into ice water. (b), (d) Selected area electron diffraction patterns taken from (a) and (c) showing [010]$_{B19}$ and [101]$_{B19}$ zone axes, respectively. Subscripts M and T are used to denote matrix and twin, respectively.
These notations of the variants are used invariantly hereinafter with respect to the apparent habit planes in the martensite matrix. According to the orientation relationship between the B2 parent and the B19 martensitic phases, these planes are derived from $[001]_{B2}$. The shape of precipitate is estimated to be disk-like and/or elliptic plate. Similar crystallographic and morphological characteristics of precipitates of the C11$_b$ phase in B2 and/or B19 matrices have been reported in Ti–Ni–Cu shape memory alloys.\textsuperscript{9,10}

In order to clarify the microstructure change during DSC measurement, the same thermal history was given to the quenched and the furnace cooled Ti–47 and 50 at\%Pd alloys. There was no microstructure change in both Ti–50 at\%Pd alloys, as expected from the above results. Figure 6 shows bright field images and corresponding electron diffraction patterns in the quenched and the furnace cooled Ti–47 at\%Pd alloys after DSC. There are fine precipitates in the martensite matrix in the quenched alloy as seen in Figs. 6(a) and (c). The electron diffraction pattern in Fig. 6(b) is taken from area B in (a). The pattern can be indexed the same as those in Figs. 5(c) and/or (d). Therefore, the precipitates are Ti$_2$Pd phase. It seems that there is only one variant in Fig. 6(a), which is more obvious in Fig. 6(c). A bright field image in Fig. 6(c) is taken along $[10\bar{1}]_{B19}$ as recognized from the corresponding diffraction pattern in (d). The pattern consists of three sets of reflections in which two of them are in mirror symmetry with respect to the $(111)_{B19}$ plane, thus alternate platelets are $(111)_{B19}$ twins. The rest pattern, as indicated by arrows, represents $[001]_{C11b}$ zone axis, the same as that in Fig. 5(e). From these observations the morphology of the precipitates formed in the quenched Ti–47 at\%Pd alloy after DSC measurement is disk-like with an average size about 40 nm in diameter and 15 nm in thickness. In addition, the habit plane of precipitates in Figs. 6(a) and (c) is $[101]_{B19}$, which corresponds to the variants I or II. We could not observe the variant III with habit plane of $(010)_{B19}$ in the quenched Ti–47 at\%Pd alloy after DSC measurement throughout the present experiment, which will be discussed later. Figure 6(e) shows a bright field image of the furnace cooled Ti–47 at\%Pd after DSC. There is no significant difference in comparison with the microstructure before DSC seen in Fig. 5. Therefore, it can be assumed that the successive transformation is closely related to the formation of fine Ti$_2$Pd precipitate during DSC measurement.

In order to confirm this hypothesis, the microstructure change during DSC measurement is observed in detail along the DSC curves upon heating as shown in Fig. 7(a). The quenched Ti–47 at\%Pd alloys are heated from ambient temperature to 743, 848 and 873 K with a heating rate of 10 K/min as in DSC and finally quenched into ice water. (b)–(d) Bright field images of the specimens quenched from designated temperatures in (a), observed from $[010]_{B19}$ direction.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig7.png}
\caption{(a) Schematic illustration of the following heat treatment applied to quenched Ti–47 at\%Pd alloy TEM specimens: heated up to 743 K, 848 K and 873 K with the same heating rate of 10 K/min as in DSC and finally quenched into ice water. (b)–(d) Bright field images of the specimens quenched from designated temperatures in (a), observed from $[010]_{B19}$ direction.}
\end{figure}
4. Discussion

4.1 Transformation mechanism

On the basis of TEM observations and DSC measurements the successive transformation mechanism in the quenched Ti-rich Ti–Pd alloys can be summarized with schematic illustration in Fig. 8. Below A2* peak fine Ti2Pd precipitates nucleate in the martensite matrix during heating. By increasing the heating temperature the Ti2Pd precipitates grow as shown in Fig. 7. The first endothermic peak represents the reverse martensitic transformation of the matrix. As clearly seen in Fig. 4 this peak shows a remarkable compositional dependence. The A2* peak temperature increases with increasing Pd content and reaches the maximum at 50 at%Pd.

Since the Pd concentration inevitably increases in the local regions around the Ti2Pd precipitates, in these areas martensitic phase must be preserved after the occurrence of the first peak. Therefore, the A1* peak can be attributed to the reverse martensitic transformation of the local regions around the precipitates. The A2* peak position of all quenched Ti-rich alloys used in the present study is nearly the same as the single endothermic peak of the Ti–50 at%Pd alloy as seen in Figs. 1, 2 and 4. This fact indicates that the equilibrium between the Ti2Pd precipitates and the local regions around the precipitates with nearly equiatomic composition is completed. Although we do not represent the scheme of the forward transformation during cooling, the direct transformation may proceed as follows. At the M1* the martensitic transformation takes place in the local regions around the Ti2Pd precipitates. On further cooling the matrix transforms to the martensitic phase at the M2*. However, to confirm the above transformation sequences both in-situ TEM observations and investigation of the local composition around precipitates by precise EDX analysis must be completed in future.

The shift of transformation peaks with increasing the heating temperature in the incomplete thermal cycle experiments in Fig. 2 is explained as follows. The increase of A2* and M2* is due to the increase of Pd concentration in the matrix with the precipitation of Ti2Pd phase. Since the precipitate reaction occurs not only during heating but also during cooling, the Pd concentration of the matrix is different between the heating and cooling processes. It is also likely that the reaction during cooling becomes more active with increasing the heating temperature. Therefore, the Pd concentration in the matrix during cooling may be higher than that during the previous heating. Consequently, the inversion between A2* and M2* takes place in Fig. 2(e). The decrease of M1* in Figs. 2(c) to (e) may be related to the strain field around the coherent precipitates which usually stabilizes the parent phase in the martensitic transformation. We notice the strain contrast around the Ti2Pd precipitate in Figs. 6(a), (c) and 7(b) to (d).

4.2 Morphological aspect of precipitates

There are three variants of Ti3Pd precipitate in the furnace cooled Ti–47 at%Pd alloy as shown in Fig. 5, since the nucleation of precipitates must occur uniformly on three [001]B2 planes in the parent phase. The three variants are clearly observed in the Ti–47 at%Pd alloy aged at 873 K for 1.8 ks as shown in Fig. 9. The aging temperature is about 20 K higher than A1*. The nucleation of the precipitates takes place certainly in the parent phase and then the parent phase transforms to martensitic phase upon quenching. Two types of precipitates denoted as B and C with their apparent habit plane parallel to the incident beam direction are observed in Fig. 9(a). The third precipitate denoted as D in Fig. 9(a) is clearly seen in the enlarged micrograph in Fig. 9(b) which is slightly tilted from [101]B19 zone axis in Fig. 9(c) to reveal the contrast. The pattern in Fig. 9(c) consists of five sets of reflections. The three of them are the same as those in Fig. 6(d), i.e., (111)B19 twin pattern and [001]C11b, zone axis. The rest two patterns are [100]C11b zone axes derived from the precipitates B and C. Since the apparent habit plane is parallel to the image plane of (101)B19 we can recognized without doubt that the precipitate D is the variant II. We cannot determine exactly the apparent habit plane of the other two precipitates from this incident beam direction because of the twinned martensite matrix. Therefore, the precipitates B and C are the variants I and III or vice versa. However, there is no doubt that the nucleation of precipitates occurs uniformly on three [001]B2 planes in the parent phase.

Only one or two precipitate variants are seen in Figs. 6(a), (c) and 7, and the observed variants correspond to the Variant I or/and II as already mentioned above. In those case, the nucleation of precipitates occurs in the martensitic phase. From the lattice parameters of both precipitate phase and B2 parent phase (\( \alpha = 0.3180 \text{nm}^{11} \)) and the orientation relationship between them, the difference between the corresponding interplanar spacing is roughly estimated to be 5.4% \( (= |d(003)_{\text{C11b}} - d[100]_{\text{B2}}|/d[100]_{\text{B2}}) \). Similarly, in the case of precipitates nucleated in the B19 martensitic phase the corresponding interplanar spacing difference for Variants I and II is about 0.9% \( (= |d(003)_{\text{C11b}} - d[101]_{\text{B19}}|/d[101]_{\text{B19}}) \). On the other hand, that of the Variant III is about 20% \( (= |d(003)_{\text{C11b}} - d[010]_{\text{B19}}|/d[010]_{\text{B19}}) \). Therefore, within martensitic phase the formation of the Variants I and II is more preferable than that of the Variant III. This preferential precipitation may be apparently cancelled by the presence of twin. Nevertheless, a single or two precipitate variants are observed throughout the present experiment as shown in Figs. 6(a), (c) and 7. One of the difficulties of the analysis is that the original twinned martensite disappears during heating and the observed martensite in Figs. 6 and 7 transforms from the
parent phase containing densely dispersed fine precipitates. Details of interaction between the original twin structure and the preferential precipitation are now under study by using the specimen aged at martensitic state for prolonged time and will be reported in the due course.

5. Conclusions

The martensitic transformation behavior of the Ti-rich Ti–Pd shape memory alloys has been studied by DSC measurements and TEM observations. The obtained results are summarized as follows.

(1) There is no difference of transformation behavior and temperatures in quenched and furnace cooled Ti–50 at%Pd alloy. The quenched Ti-rich alloys from single region of B2 parent phase show a successive transformation during DSC measurement. On the other hand, the furnace cooled alloys show a single step transformation, in which the peak temperature for all compositions lies very close to that for Ti–50 at%Pd alloy.

(2) The successive transformation behavior in quenched Ti-rich alloys is closely related to the formation of fine Ti$_2$Pd precipitates. It is considered that the first peak on DSC heating curve represents the reverse martensitic transformation of the TiPd matrix. The peak temperature increases with increasing Pd content and reaches the maximum at 50 at%Pd. In other words, the first peak overlaps the second peak at 50 at%Pd. The second peak is due to the reverse martensitic transformation in the local neighboring areas around the precipitates in which Pd concentration is considered to be equiatomic, since the peak temperature is almost constant with Pd content and is identical to that of Ti–50 at%Pd alloy.

(3) The precipitate is Ti$_2$Pd with C11$_b$-type structure. There are three variants of precipitates, i.e., I, II and III with the apparent habit planes of (101)$_{B19}$, (101)$_{B19}$ and (010)$_{B19}$, respectively, in the furnace cooled Ti–47 at%Pd alloy in which the precipitate nucleates in the B2 parent phase. On the other hand, the variants I and II are only observed in case of the nucleation in the B19 martensitic phase.

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