Effect of Heat Treatment after Cold Working on the Phase Transformation in TiNi Alloy*

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The effect of heat treatment in the range 633 K-933 K on the phase transformations among three types of phases, i.e. the CsCl (B2)-, rhombohedral (R)- and monoclinic (M)-phases in Ti-49.7, 50.2 and 50.6 at%Ni alloys have been investigated using the differential scanning calorimetry (DSC) method. It has been confirmed that the phase transformations that occur during heating and cooling can be classified into the following three types depending on the heat treatment temperature; (a) B2→R→M during cooling and M→R→B2 during heating for lower heat treatment temperatures, (b) B2→R→M during cooling and M→B2 during heating for intermediate heat treatment temperatures and (c) B2→M during cooling and M→B2 during heating for higher heat treatment temperatures. It is also shown that the temperature range in which R-phase is stable becomes wider with increasing Ni content. The transformation temperature of R-phase was found to decrease with increasing heat treatment temperature. The starting point of the R-phase transformation in these alloys heat-treated at 633 K was estimated approximately at 330 K, which was almost independent of Ni content.

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I. Introduction

Extensive studies have been made on the phase transformation in TiNi alloy(1)-(6) and TiNi (Fe) alloy(5)(7)-(9) which exhibit a shape memory effect(10). It has been confirmed that three kinds of phases appear with different ambient temperatures; i.e. high temperature CsCl (B2) phase(1), low temperature monoclinic (M) phase(4) and intermediate rhombohedral (R) phase(1). Therefore, three types of transformation such as B2→M, B2→R and R→M occur in these alloys. Hereinafter B2→R is referred to as R-transformation, while B2→M and R→M as M-transformation. The stability of each phase depends on the composition of the alloys and aging treatments(5)(11)(12), and furthermore on the heat treatment after hot- or cold-working(13) and thermal cycling(2)(14)(15). Moreover, M-transformation is larger in hysteresis and its transformation temperature is more stress dependent as compared with R-transformation(5)(16)-(18), so that the transformation behavior becomes more complicated in this alloy system.

Miyazaki and Otsuka(17) have recently outlined thermomechanical conditions under which R-phase appears in substantial quantities. It is known at present that R-transformation is not premartensitic but independent of M-transformation(19).

On the other hand, it has been reported that the optimum condition of the heat treatment to get better practical characteristics is to anneal at 773 K(13)(20) or below(21)-(23) after cold-working. Annealing between 673 K and 773 K is commonest in the industrial field. Both facts that mechanical and shape memory properties critically vary with heat treatment near 773 K, and that R-phase appears through annealing below 773 K after cold-working(18)(23) suggest that the transformation behavior strongly depends on the heat treatments. Therefore, it is important to investigate systematically the effect of heat treatment near 773 K on the transformation behaviors in detail.

The transformation behaviors can be ob-
served using the related properties such as thermal, electrical and magnetic ones, and the shape changes accompanying them. The most frequently used are the electrical resistance and the DSC (Differential Scanning Calorimetry) methods. Although the scanning rate, weight of specimen and the definition of the base line affect the transformation temperatures, the DSC method is the most suitable for TiNi alloys according to the present authors(26).

One of the authors has recently reported that the transformation behavior can be clarified by both complete and incomplete cycles. In the latter, R-phase transformation alone occurs even when both R- and M-transformations take place in the complete cycle(18). In the present study, we made a systematic investigation of the effects of composition and heat treatment near 773 K on the transformation behavior mainly using the DSC method. The electrical resistance and the shape change measurement were also carried out.

II. Experimental Procedures

1. Specimen preparation

Three kinds of TiNi alloys having compositions of 49.7, 50.2 and 50.6 at%Ni were used. After cold-drawn to wire 0.75 mm in diameter, an extension type coil spring with mean diameter of 5.6 mm was cold-formed by a coiling machine. Then it was heat-treated at various temperatures between 633 K and 933 K for 3.6 ks in air to memorize the original close-coiled shape and finally cooled in air. Oxidized films were removed by pickling using a solution of H2O:HNO3:HF=5:4:1.

2. DSC measurement

The DSC curves obtained can be classified into three types as shown in Fig. 1, in which the definition of each transformation temperature is also illustrated. In the notation of transformation temperatures, subscripts "s" and "f" denote start and finish temperatures, respectively, and "′" mark denotes R-transformation temperature. It was noted that the

![Fig. 1 Classification of DSC data and determination of transformation temperatures.](image-url)
finish temperatures of transformations were much more influenced by the scanning rate or weight of the specimen than the start temperatures\(^{(24)}\)(\(^{25}\)). In this measurements, the scanning rate was 0.33 K/s and the specimen was 20 mg in weight. The three types of DSC curves are characterized as follows.

1. **Two peaks in both heating and cooling processes (Fig. 1-(a))**
   
   Peak C1 on the high temperature side during cooling corresponds to the B2\(\rightarrow\)R and peak C2 to the R\(\rightarrow\)M transformation. Separation of the peaks H1 and H2 was scarcely observed during heating. Peak H3 which corresponds to the R\(\rightarrow\)B2 transformation, appears in the incomplete cycle when the specimen heating starts at a temperature between C1 and C2. Since the peaks H2 and H3 appears at the same temperature, H2 corresponds to R\(\rightarrow\)B2 transformation and hence H1 corresponds to M\(\rightarrow\)R transformation. This type of curves can be observed in the specimen heat-treated at relatively low temperatures.

2. **Two peaks in the cooling process and one peak in the heating process (Fig. 1-(b))**
   
   The Peaks C1 and C2 during cooling correspond to B2\(\rightarrow\)R and R\(\rightarrow\)M transformations, respectively, the same as in the previous case. The peak H3, which appears when heated from between C1 and C2, corresponds to the R\(\rightarrow\)B2 transformation. As the start temperature during heating in the incomplete cycle approaches C2, another peak H5 appears and becomes larger as the start temperature becomes lower, and finally grows into peak H4 in the complete cycle. That is, H4 is M\(\rightarrow\)B2 transformation without R-phase. This type of curves can be observed in the specimen heat-treated at an intermediate temperature.

3. **One peak in both heating and cooling processes (Fig. 1-(c))**
   
   The peaks C3 and H4 are B2\(\rightarrow\)M and M\(\rightarrow\)B2 transformations, respectively, judging from the size of hysteresis. This type occurs in the specimen heat-treated relatively high temperature.

### III. Results and Discussion

#### 1. Ti-49.7 and 50.2 at%Ni alloys

Since quite similar tendencies in the transformation behavior were observed in the 49.7 and 50.2 at%Ni alloys, only the results of the former are discussed in detail. Figure 2 shows the effect of heat treatment on the DSC curves in the Ti-49.7 at%Ni alloy. The results in the incomplete cycle, where only R-transformation occurs, are also shown.

1. **Cooling process (Fig. 2-(a))**
   
   Peak C2 due to R\(\rightarrow\)M transformation is too broad when heat-treated at 633 K to determine the transformation temperatures precisely. Peak C1 due to B2\(\rightarrow\)R transformation is not sharp as compared with other C1 peaks. Both C1 and C2 peaks become steeper and closer to each other with increasing heat treatment temperature indicates that the transformation temperature range becomes narrower and the temperature range for the R-phase to exist becomes also narrower. Both peaks are nearly coalesced when heat-treated at 873 K, and become peak C3 due to B2\(\rightarrow\)M transformation at 933 K.

2. **Heating process (Fig. 2-(b))**
   
   Complete cycle: The peak trails on the low temperature side when heat-treated at 633 K. It becomes separate H1 and H2 peaks with increasing heat treatment temperature. While, single peak H4 due to M\(\rightarrow\)B2 transformation appears when heat-treated at 743 K or above. Careful examination makes it clear that the H4 peaks for 823 K or above are a little lower and broader than those for 743 K and 773 K. The reasons for this will be discussed later.
Incomplete cycle: Peak H3 corresponds to the R→B2 transformation, as mentioned above. Since peak H3 appears at the same temperature as H2 when heat-treated between 633 K and 713 K, peaks H2 and H1 in the complete cycle correspond to R→B2 and M→R transformations, respectively. Heat treatment between 743 K and 773 K causes peak H3 to shift to the lower temperature side of peak H4 in the complete cycle. In the case of 823 K, two peaks appear, of which the one on the lower temperature side is on the extention of H3 peaks. While peak H5 on the higher temperature side appears at the same position of H4 in the complete cycle. That is, heating in the incomplete cycle starts from the (R+M) phases in the case of 823 K, so that both R→B2 and M→B2 transformations occur. Peaks H4 and H5 are due to M→B2 transformation.

(3) Dependence of transformation temperature on the heat treatment

Figure 3 shows the effect of heat treatment on the transformation temperatures. Those for R-transformation were determined from the DSC peaks in the incomplete cycle, and the other from the peaks in the complete cycle. If the latter cycle is employed, it is impossible to define the A_s and A_f points for 773 K and 823 K. When two peaks overlap during heating in the complete cycle, the A_f temperature in the M→R transformation is nearly equal to the A_f on the assumption that peaks are symmetrical with respect to their tops.

The present results for the transformation temperatures in the cooling process agree with those reported before. R-transformation temperatures decrease and M-transformation temperatures increase with increase in heat treatment temperature. Both transformations overlap when the specimen is heat-treated at 823 K or above. M_s temperature becomes minimum for the specimen heat-treated at 713 K.

Until now, correspondence between DSC peaks and phase transformations in the heating process has not been cleared when two peaks overlap. In this study, however, measurements of the incomplete and complete cycles clarified the relation between the DSC curves and transformations. It was revealed that the reverse transformation temperature of R-transformation decreased whereas that of M-transformation increased with increase in heat treatment temperature which intersected at approximately at 740 K, as shown in Fig. 3.

The same tendencies were observed in Ti-50.2 at%Ni alloy as shown in Fig. 4.

Both B2→R→M and B2→M transformations occur in the same temperature range during cooling when Ti-49.7 at%Ni alloy is heat-treated at around 850 K, and both M→R→B2 and M→B2 transformations occur in the same
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Fig. 3 Effect of heat treatment after cold work on the transformation temperatures of Ti-49.7 at%Ni alloy.

Fig. 4 Effect of heat treatment after cold work on the transformation temperatures of Ti-50.2 at%Ni alloy.

Fig. 5 Change in the DSC curves with heat treatment after cold work for Ti-50.6 at%Ni alloy.

temperature range during heating when heat-treated at around 740 K. Corresponding heat treatment temperatures in the Ti-50.2 at%Ni alloy were 870 K and 770 K, respectively, as seen from Fig. 4.

It should be again pointed out that peaks during heating for the specimen heat-treated at 743 K and 773 K are steeper than those for 823 K, 874 K and 933 K. This difference may result from the difference in the transformation process during cooling which may change the internal structure of produced M-phase. Dislocation introduction is less in B2→R→M transformation than in B2→M transformation, judging from the fact that strong residual
texture makes the DSC peak broad as seen in the specimen heat-treated at low temperature. It has also been found that dislocations can be easily introduced in B2→M transformation\(^{(29)}\). Furthermore, according to Monasevich and Paskal\(^{(30)}\), a small difference exists in the lattice parameter between the M-phases produced by B2→M and B2→R→M processes. This difference may affect the shape of DSC peaks during heating.

2. Ti-50.6 at\%Ni alloy

Figure 5 shows the effect of heat treatment on the DSC curves in Ti-50.6 at\%Ni alloy. Change in peaks in the case of heat treatment at 773 K or below is similar to that in the other two compositions. The separation of peaks H1 and H2 becomes more definite in heat treatment below 713 K. However, the peaks exhibit a peculiar shift in the specimen's heat-treated at
773 K or above. The transformation temperature rises and then falls with increase in heat treatment temperature. In order to clarify the transformation behavior in the alloy heat treated between 793 K and 873 K, the shear strain- and the electrical resistance-temperature curves were measured simultaneously.

The results are shown in Fig. 6 along with the DSC curves.

(1) Cooling process
The whole tendency is summarized as follows: i.e. B2→R and R→M transformations, separated in heat treatment at 793 K or
below, take place in succession with increase in heat treatment temperature. Then $B_2 \rightarrow R$ transformation is inferior to $B_2 \rightarrow M$ transformation, resulting in prevailing of the latter.

The DSC peaks for 813 K are not steep but separated, showing slight increase in shear strain and increase in electrical resistance corresponding to the peak on the higher temperature side, and gradual increase in shear strain and decrease in electrical resistance corresponding to the peak on the lower temperature side. Therefore, these peaks correspond to $B_2 \rightarrow R$ and $R \rightarrow M$ transformations, respectively. These two peaks overlap in the specimen heat-treated at 823 K, causing a broad one with obscure three peaks in which shear strain increases gradually. The electrical resistance increases according to the DSC peak on the higher temperature side, and decreases according to the one in the middle. Therefore, the former peak corresponds to $B_2 \rightarrow R$ transformation, and $M'_s$ temperature was obtained from this peak. It is not clear at present whether appearance of three peaks is due to the overlap of $R \rightarrow M$ and $B_2 \rightarrow M$ transformations or to the existence of multiple kinds of the M-phases, which have been argued by various authors\(^{(2)(11)(30)-(32)}\). Two different transformations, however, may occur besides the $B_2 \rightarrow R$ under limited conditions, since the existence of three peaks during cooling has been observed after a number of thermal cycles\(^{(33)}\). In any case, since decrease in electrical resistance takes place at middle and low temperature peaks, $M$-transformation has a part in them. The peak of the electrical resistance coincides with the saddle point of the DSC curve, and this point was taken as $M_s$ temperature.

The $M$-transformation peak on the higher temperature side for 823 K becomes steeper in the specimen heat-treated at 833 K. The electrical resistance increased and then decreased corresponding to the broad and steep peaks, respectively. The shear strain also rapidly increased at the latter peak. These facts imply that the broad and steep peaks are more or less due to $B_2 \rightarrow R$ and $R \rightarrow M$ transformations, respectively. $M'_s$ temperature is determined from the initial peak, and $M_s$ is taken to be at the saddle point of the DSC curve where the electrical resistance starts to decrease. For higher heat treatment temperature, the $B_2 \rightarrow R$ transformation is inferior to $B_2 \rightarrow M$ transformation and only the $B_2 \rightarrow M$ peak appears for 908 K. Both $B_2 \rightarrow R$ and $B_2 \rightarrow M$ transformations are thought to occur where two peaks overlap, because two peaks appear during heating in the incomplete cycle as shown in Fig. 6(c) and (d).

(2) Heating process

Both $M \rightarrow R$ and $R \rightarrow B_2$ transformations occur in the same temperature range in the specimen heat-treated at 793 K. This is proved by the fact that the peak appears in the same temperature range in both complete and incomplete cycles. An asymmetrical peak, which is composed of two peaks separated by the incomplete cycle, appears in the complete cycle at heat treatment between 813 K and 873 K. The peak on the lower temperature side is inferior to the peak on the higher temperature side with increase in heat treatment temperature, resulting in prevailing of the latter for 908 K.

Slight increase in electrical resistance corresponding to the DSC peak at 275 K, as is seen in Fig. 7(b), suggests that $M \rightarrow R$ transformation occurs at the early stage. On the other hand, appearance of the steeper peak in the complete cycle at the same temperature as the one in the incomplete cycle suggests that $R \rightarrow B_2$ transformation is also predominant in the complete cycle. Therefore, in the specimen heat-treated at 813 K, $M \rightarrow R$ and $R \rightarrow B_2$ transformations may take place almost simultaneously in the complete cycle. Electrical resistance increase at the early stage becomes less and swelling of the latter half of the DSC peak becomes more for 823 K. The prevailing $M \rightarrow B_2$ transformation may cause these phenomena. Heat treatment at higher temperature promotes this tendency. The transformation temperatures $A'_s$, $A'_i$ and $A_f$ for 813 K and 823 K are measured as the start point of the lower temperature peak, the transition point of the two peaks and the finish point of the higher temperature peak, respectively. The $A_s$ and $A_f$ temperatures are determined from the main peak, and the $A'_s$ from the foot
of the lower temperature side for 833 K and 853 K.

(3) Dependence of the transformation temperatures on the heat treatment

Figure 7 shows the effects of heat treatment on the transformation temperatures. All the transformation temperatures increase in the range of heat treatment temperature from 793 K to 873 K. Such the tendency closely relates with stress field around precipitates and depletion of nickel in the matrix accompanying precipitation, as has been observed in aging after solution treatment of nickel-rich alloys\(^{(34)}\), and actually precipitates were observed in the present investigation.

### 3. Effect of nickel content and heat treatment temperature on the transformation behavior

The classification of three transformations with nickel content and heat treatment temperature is shown in Table 1, and also the effects of nickel content on the transformation behavior are summarized in Table 2. Composition and heat treatment affect the transformation behavior in the following way.

The temperature range of R-phase becomes wider and the dependence of R-phase transformation temperature on the heat treatment temperature becomes more pronounced with increase in Ni content. The separation of the peaks in the reverse transformation is also definite in the specimens heat-treated at lower temperature. The transformation temperature

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**Table 1** Phase transformations determined by DSC measurement for each alloy and heat treatment temperature.

<table>
<thead>
<tr>
<th>Ni content, at.%</th>
<th>B2→M</th>
<th>B2→R→M</th>
<th>B2→R↔M</th>
</tr>
</thead>
<tbody>
<tr>
<td>49.7 at.%Ni</td>
<td>933 K, 873 K</td>
<td>823 K, 773 K, 743 K</td>
<td>673 K, 633 K</td>
</tr>
<tr>
<td>50.2 at.%Ni</td>
<td>933 K, 873 K</td>
<td>823 K, 773 K</td>
<td>743 K, 673 K, 633 K</td>
</tr>
<tr>
<td>50.6 at.%Ni</td>
<td>933 K</td>
<td>(∗)</td>
<td>773 K, 743 K, 673 K, 633 K</td>
</tr>
</tbody>
</table>

(∗) Heat treatment between 823 K and 873 K yields complicated phase transformation.
drastically decreases with increase in Ni content in the specimen heat-treated at 933 K, for which the matrix is considered to be almost free from the strain field due to cold-working or precipitates. On the other hand, $M_s$ temperature for the 633 K heat treatment, at which heat treatment leaves a strong internal strain or stress field, depends less on Ni content and is approximately 330 K. Nishida and Honma\(^{(34)}\) have reported that $M$-transformation temperature was significantly changed but $R$-transformation temperature was hardly changed by aging of nickel-rich alloys. It is also pointed out that the lower the heat treatment temperature, the higher the $M_s$ temperature. It is noted from a practical view point that $M_s$ temperature cannot be greatly controlled, while $M_t$ temperature can be easily controlled by changing the Ni content.

4. Successive transformations in TiNi alloy

It can be now pointed out that, in addition to the composition of the alloys, heat treatment after cold-working is also an important factor which affects the transformation behavior. External stress would also become important in practical application. The effects of these factors on the cooling process are shown in Fig. 8. Figure 8(c) is quoted from Khachin et al. for heat treatment at 1073 K for 3.6 ks\(^{(16)}\). These figures show the analogy in their effects on the phase stabilities.

Khachin et al.\(^{(5)}\) classified the transformation behaviors from the view point of nickel content. The low nickel, equiatomic and high nickel alloys correspond to ST1, ST3 and ST2, respectively, in Fig. 8(c) (nomenclature "ST" is after Monasevich and Paskal\(^{(30)}\)). According to them, ST1, ST2 and ST3 correspond to the $B2 \rightarrow (B2+M) \rightarrow M$, $B2 \rightarrow R \rightarrow (R+M) \rightarrow M$ and $B2 \rightarrow (B2+M) \rightarrow (R+M) \rightarrow M$ transformations, respectively. Monasevich and Paskal\(^{(30)}\) have subsequently reported that there are monoclinic (M’) and triclinic (M”) M-phases, and that a small difference in the lattice parameter exists between M’-phases generated from B2- and R-phases which are referred to as $M_t$ and $M_s$, respectively, so that ST1, ST2 and ST3 correspond to the $B2 \rightarrow (B2+M_t) \rightarrow M’_t$.
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The effects of heat treatment between 633 K and 933 K after cold-working on the transformation behavior of Ti-49.7, 50.2 and 50.6 at.%Ni alloys were investigated systematically using mainly the DSC method and shear strain- and electrical resistance-temperature measurements supplementally. Combined use of the complete and incomplete cycles made it possible to investigate the relative phase stabilities of R-phase and M-phase. The results are summarized as follows.

1. Three kinds of transformations take place depending on the heat treatment temperatures.
   (a) At low heat treatment temperatures; B2→R→M during cooling and M→R→B2 during heating.
   (b) At intermediate heat treatment temperatures; B2→R→M during cooling and M→B2 during heating.
   (c) At high heat treatment temperatures; B2→M during cooling and M→B2 during heating.

2. The temperature range for the R-phase to exist becomes larger and more definite during heating with increase in nickel content. Dependence of the R-phase transformation temperatures on the heat treatment temperature is also promoted.

3. Only the M-transformation takes place when heat-treated at 933 K, leaves almost no strain accompanying cold-working or precipitation, and the M_s temperature drastically drops with increase in nickel content. However, M_f temperature of the specimen heat-treated at
633 K which has a strong residual strain due to cold-working is almost independent of nickel content, and is approximately 330 K.

(4) Precipitation occurs in Ti-50.6 at% Ni alloy heat-treated between 823 K and 873 K. This causes all the transformation temperatures to rise, and a complicated transformation behavior appears.

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REFERENCES

(17) S. Miyazaki and K. Otsuka: Phil. Mag., 50 (1984), 393.