Martensitic Transformation Behavior and Shape Memory Properties of Ti–Ni–Pt Melt-Spun Ribbons

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Martensitic transformation behavior and shape memory properties of a Ti_{50}Ni_{50}Pt_{10} (TiNiPt) melt-spinning ribbon fabricated by a single roll melt-spinning technique were characterized. The constituent phases of the as-spun ribbon were B2 (parent phase) and B19 (martensite phase) at room temperature. The B2–B19 martensitic transformation temperatures of the as-spun ribbon were 100 K higher than those of the bulk material with the same chemical composition. The martensitic transformation temperatures of the as-spun ribbon were decreased with increasing the temperature of the heat-treatment made after the melt-spinning. The as-spun ribbon and the heat-treated ribbons exhibited shape recovery by heating and/or pseudoelasticity. The martensitic transformation temperatures determined from the temperature dependence of the 0.2% flow stress of the pseudelastic deformation were in good agreement with those of B2–B19 martensitic transformation determined by DSC. It was confirmed that the observed shape recovery and pseudoelasticity are shape memory effect and superelasticity due to the B2–B19 martensitic transformation. Shape memory effect and superelasticity of melt-spin TiNiPt alloys were found to appear at higher temperatures compared to those of bulk material with the same composition.

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1. Introduction

TiNi alloys have a thermoelastic martensitic transformation from B2 phase (parent phase) to B19 phase (martensite phase) and exhibit superelasticity and shape memory effect.1) Actuation temperature of shape memory alloys (SMAs) is determined by the martensitic transformation temperature ($M_s$) of TiNi binary alloy is at most around 400 K.1) The shape memory effect of TiNi alloy cannot be, therefore, used at the high-temperatures above 400 K. Development of TiNi based SMAs with high $M_s$, compared to the TiNi binary alloy, has been strongly required to expand the applications related with SMAs.

Effects of ternary additions on $M_s$ of TiNi have been investigated. It is known that most of the ternary elements such as Co, Fe, Mn, Cr and V decrease $M_s$ of TiNi.2–5) On the other hand, Hf, Zr and platinum group metals (PGMs) such as Au, Pd and Pt are known to raise $M_s$ of TiNi.6–8) Especially, the Pt addition to TiNi is expected to very effective on raising $M_s$ because TiPt binary alloy has B2–B19 martensitic transformation around 1300 K and exhibits shape memory effect.9–11) We have, therefore, investigated phase stability, $M_s$, and mechanical properties of TiNi alloys which were ternary added with PGMs.2–5) It has been revealed that $M_s$ of TiNi is raised by Pt addition by 27 K/mol%Pt, and that TiNi–TiPt pseudo-binary alloys exhibit shape memory effect.15,16) The TiNi–TiPt pseudo-binary alloys exhibit ductile deformation behavior with Pt addition lower than about 20% and are hopeful material for high temperature SMAs.15,16)

It is generally known to be difficult to obtain thin-films of ternary added TiNi alloys by a conventional rolling due to poor workability of TiNi. Rapid solidification technique such as single roll melt-spinning technique is a convenient technique for fabrication of thin-films. Microstructure, $M_s$ and shape memory effect of rapidly solidified TiNi alloys with some ternary elements have been investigated by some researchers.17,18) A common conclusion of these studies is that microstructures, martensitic transformation behavior, mechanical properties and shape memory properties of rapidly solidified TiNi alloys are quite different from those of bulk material. For examples, rapidly solidified Ti_{50}Ni_{25}–Cu_{25} alloy is amorphous and becomes very brittle after a crystallization heat-treatment due to the formation of fine precipitates.17) Rapidly solidified Ti_{32}Ni_{50}Zr_{18} and Ti_{32}Ni_{50}–Hf_{18} have $M_s$ of 50–100 K higher than that of bulk materials and are brittle.18) Though effects of rapid solidification of TiNi alloys with some ternary elements have been investigated as above, there are few studies on rapidly solidified TiNi alloys which were ternary added with PGMs. The objective of this study is to investigate phase constitution, martensitic transformation behavior and shape memory properties of TiNi–TiPt melt-spinning ribbons.

2. Experimental Procedures

Figure 1 shows Pt concentration dependence of $M_s$ of TiNi–TiPt pseudobinary alloy.15) $M_s$ is decreased with increasing the Pt concentration and the crystal structure of martensite is B19 (monoclinic) when the Pt concentration is lower than about 10 mol%. On the other hand, $M_s$ is increased with increasing Pt concentration and the crystal structure of martensite is B19 (orthorhombic) when the Pt concentration is higher than about 10 mol%. TiNi–TiPt pseudobinary alloys with Pt concentration higher than 10 mol% are, therefore, applicable for high temperature SMAs. Pt concentration of 10 mol% is the lowest Pt concentration to obtain B19 martensite which is responsible for the shape memory effect.

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at high-temperatures in this alloy. Ti$_{50}$Ni$_{40}$Pt$_{10}$ alloy was, therefore, selected in this study.

Master ingots of Ti$_{50}$Ni$_{40}$Pt$_{10}$ alloy (termed TiNiPt hereafter) were fabricated by Ar-arc melting in an Ar–1%H$_2$ atmosphere. The ingots were remelted five times for homogeneity. The weight of each ingot was about 5 g. No chemical analysis of the ingots was conducted because the change in weight before and after the arc-melting was less than 0.1 mass% and was judged to be negligible.

Rapid solidification was made using a single roll melt-spinning apparatus. Ingots were cut into several pieces by a spark-cutting machine. Some pieces of the cut ingots were put in a quartz crucible and set in the melt-spinning apparatus. Rapid solidification was carried out by induction melting in an Ar atmosphere followed by ejecting the molten alloy onto a copper wheel rotating at a surface velocity of few tens of 42 m/s and roll-gap of 400 mm. As-spun ribbons were termed ‘As-spun’ hereafter. The ribbons were heat-treated at 473, 623 or 773 K for 3.6 ks in vacuum and then furnace-cooled. The heat-treated ribbons are termed by the heat treatment temperature like ‘HT473 K’, hereafter.

A reference material was prepared by hot-forging at 1173 K for 3.6 ks followed by furnace cooling, and then it was solution-treated at 1273 K for 1.8 ks followed by furnace cooling. The reference material is termed ‘Bulk-material’ hereafter. It should be mentioned that $M_s$ in Fig. 1 is the experimental result for the similar materials fabricated by the hot-forging method.\(^{15}\)

Martensitic transformation temperatures were measured by differential scanning calorimetry (DSC) using SHIMADZU DSC-60 with a heating/cooling rate of 10 K/min in a temperature range from 100 to 500 K. Phase constitution was examined by $\theta$–20 X-ray diffraction (XRD) analysis at room temperature (RT) with CuK$\alpha$ using Philips X’pert pro equipped with X’Celerator. Si was used as an external standard material.

Shape memory properties were evaluated by constant strain increment tensile test. Tensile specimens with 20 mm in gauge length were cut from ribbons. A piece of copper was put on each grip of the specimen to prevent slip during testing. The tensile direction corresponded to the rolling direction of the melt-spinning. Tensile test was made using an instron-type testing machine (SHIMADZU Autograph 1 kN) equipped with an isothermal furnace. The test temperatures were selected in a range of 293–393 K. Strain rate was $10^{-3}$ s$^{-1}$ and strain increment per a loading-unloading cycle was set to be 1%. Cyclic loading was continued until the applied strain reached 10%. Some specimens were heated to about 500 K by a heat-gun during tensile tests to observe shape recovery by heating.

3. Results and Discussion

3.1 Phase constitution at RT

Melt-spun ribbons of TiNiPt were successfully fabricated under the conditions described above. The ribbons obtained were 35–40 $\mu$m in thickness and 1.7–1.8 mm in width. Grain size of As-spun was inhomogeneous and was in the order of a few tens of $\mu$m.\(^{19}\) No significant growth of grain by the heat-treatments was observed.\(^{19}\)

Figure 2 shows XRD patterns taken from the surface of wheel-side of each specimen. Only reflections from B2 phase (indicated by filled circles) were observed in the Bulk-material.

As-spun ribbons seemed to be fully crystallized and to contain a large amount of martensitic phase (indicated by the open triangles). The apparent phases of As-spun were B19 (orthorhombic) and B2 (cubic). The lattice parameters of B19 martensite in As-spun was determined to be $a_{B19} = 0.2799 \pm 0.0002$ nm, $b_{B19} = 0.4340 \pm 0.0001$ nm and $c_{B19} = 0.4612 \pm 0.0001$ nm. Where, subscript ‘B19’ indicates B19 martensite. It was also confirmed by transmission electron microscopy (TEM) observation that the martensite in As-spun has an orthorhombic lattice.\(^{19}\) B19'-phase and R-phase (rhombohedral phase)\(^{19}\) was not detected in the TEM observation and no second phase and precipitate such as Ti$_3$Ni$_4$ were observed even after the heat treatments.\(^{19}\)

Space group of B19 is Pmnb for the notation used in this study.\(^{20}\) The extinction rule for Pmnb is that h0l reflections are not observed for odd l.\(^{21}\) Based on the atom positions reported in Ref. 20), we can deduce that disordered B19 takes, for the notation in this study, space group of Bmnb. Structure factors of 011 and 100 reflections are zero in Bmnb.\(^{21}\) It should be noted that the as-spun ribbon was ordered enough to generate superlattice reflections of 100$_{B2}$.
011_{B19} and 100_{B19} reflections with significant intensity in XRD profiles in Fig. 2.

As the heat-treatment temperature was raised, relative intensity of reflections from B2-phase increased compared to those from martensite in Fig. 2. The apparent phase at RT in HT773 K was B2 as was observed in Bulk-material. The lattice parameter of B2 phase was calculated for HT773 K as \( a_{B2} = 0.30428 \pm 0.00003 \) nm, where subscript ‘B2’ indicate B2-phase. Relative intensity of 100_{B2} superlattice line is seen to be decreased with increasing the heat-treatment temperature in Fig. 2. It should be noted, however, that the relative intensity of 200_{B2} fundamental line is also decreased with increasing the heat-treatment temperature. The decrease in relative intensity of 100_{B2} reflection is, therefore, not due to the decrease in the degree of atomic order but mainly due to change in microstructure such as texture in this study.

The lattice correspondence for B2–B19 martensitic transformation has been proposed in AuCd alloy. Maximum normal strains generated by the lattice deformation of the B2–B19 transformation were evaluated to be +7.2% almost along (110)_{B2} and –8.0% almost along (001)_{B2}.

### 3.2 Martensitic transformation temperature

Figure 3 shows DSC curves obtained during cooling. All the specimens seemed to have one-step transformation in the measured temperature range. The transformation was deduced to be B2–B19 martensitic transformation according to the phase constitution analyzed in the above section. \( M_s \) and \( M_f \) (martensite transformation finish temperature) are indicated in the DSC curves. \( M_s \) of Bulk-material was 233 K and that of As-spun was 335 K. \( M_s \) of As-spun was 102 K higher than that of Bulk-material. \( M_s, M_f, A_s \) (reverse transformation start temperature) and \( A_f \) (reverse transformation finish temperature) are summarized in Table 1. As the heat-treatment temperature becomes lower. \( M_s \) of HT773 K was 293 K and was 42 K lower than that of As-spun. \( M_s \) was, however, still 60 K higher than that of Bulk-material. These results were in good agreement with the phase constitution at RT determined by the XRD analysis.

![Fig. 3 DSC curves during cooling.](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>( M_s )</th>
<th>( M_f )</th>
<th>( A_s )</th>
<th>( A_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>233 K</td>
<td>190 K</td>
<td>211 K</td>
<td>266 K</td>
</tr>
<tr>
<td>HT773 K</td>
<td>293 K</td>
<td>260 K</td>
<td>250 K</td>
<td>313 K</td>
</tr>
<tr>
<td>HT623 K</td>
<td>326 K</td>
<td>293 K</td>
<td>315 K</td>
<td>338 K</td>
</tr>
<tr>
<td>HT473 K</td>
<td>324 K</td>
<td>293 K</td>
<td>315 K</td>
<td>335 K</td>
</tr>
<tr>
<td>As-spun</td>
<td>335 K</td>
<td>305 K</td>
<td>328 K</td>
<td>352 K</td>
</tr>
</tbody>
</table>

The \( M_s \) of As-spun was 100 K higher than that of Bulk-material. \( M_s \) depends not only on chemical compositions but also on microstructures, amount and arrangement of lattice defects in general. This is understood by the idea that internal stress generated by the lattice defects interacts with the transformations. Fine precipitates are formed in rapidly solidified Ti–Ni–Zr, Ti–Ni–Hf and Ti–Ni–Cu by a heat-treatment. Neither second phase nor precipitates such as Ti,NiNi were, however, observed in the present material even after the heat treatment at 773 K. The decrease in \( M_s \) in this study was, therefore, not due to precipitation. Contamination of Si or O from quartz crucible is inevitable in melt spinning in general and should affect the transformation temperatures. The \( M_s \) of TiNi is, however, decreased with the increase in the concentration of Si or O in general. According to this, it is plausible to consider that Si and O should lower \( M_s \) of Pt added TiNi, similar to the case of TiNi. The contamination of Si and O was, therefore, considered not to be the reason for the higher \( M_s \) of rapidly solidified material in this study. \( M_s \) of As-spun was lowered and approached to the \( M_s \) of Bulk-material by increasing the heat-treatment temperature after the melt-spinning. According to this result, it is suggested that (1) internal stress was generated by lattice defects introduced during the melt-spinning, (2) the internal stress raised \( M_s \) of As-spun, (3) relaxation of the internal stress and the annihilation of defects occurred by the heat-treatments and then (4) \( M_s \) of heat-treated ribbons approached to that of Bulk-material. Possible defects introduced during the melt-spinning are supposed to be frozen-in vacancies and dislocations introduced by a thermal stress.

### 3.3 Shape memory properties

Bulk-material exhibited neither shape memory effect nor superelasticity and fractured at about 10% in tensile strain at RT. Martensitic transformation was not induced in Bulk-material and only plastic deformation by slip occurred in the tensile test at RT. This was because that stress for inducing martensite was higher than critical stress for slip, due to relatively lower \( M_s \) in Bulk-material. On the other hand, the melt-spin ribbons had \( M_s \) higher than that of Bulk-material as seen in the above section. It was expected, therefore, that shape memory effect and superelasticity appears in the melt-spin ribbons above RT.

Figure 4 shows stress–strain curves of As-spun, HT473 K, HT623 K and HT773 K, extracted from the 2nd cycle of the cyclic tensile test at 313, 333, 353 and 373 K. The test temperatures were selected to be around \( A_s \) of each material. As-spun, HT473 K and HT623 K exhibited shape recovery of 90% in recovery rate by heating after the tensile deformation at 313 K. \( A_s \) of these three materials were above 313 K and
then martensites induced during loading did not transform into parent phase during unloading. Shape recovery was due to the reverse transformation of these martensites by heating after the deformation. On the other hand, pseudoelasticity was observed in HT773 K tested at 313 K. Applied strain was almost perfectly recovered only by unloading. \( A_f \) of HT773 K was 313 K. It is plausible to consider that martensite induced during loading was fully reverse transformed into parent phase during unloading. The pseudoelastic shape recovery observed in HT773 K at 313 K was, therefore, judged to be superelasticity.

At testing temperature of 333 K, As-spun exhibited shape memory effect by heating after deformation. Superelasticity was observed in HT473 K and HT623 K. The recovery strain during unloading after the tensile deformation of 2% was 1.7% and 1.5% in HT623 K and HT473 K, respectively. No significant difference between the recovery strain of HT623 K and that of HT473 K was observed. This result was in good agreement with that \( A_f \) of both materials were higher than 333 K and \( M_s \) of both materials were close to each other. On the other hand, HT773 K yielded at about 150 MPa and fractured with elongation of 2% at testing temperature of 333 K. Though HT773 K fractured before unloading, the yielding at about 150 MPa was deduced to be due to stress-induced martensitic transformation, according to the fact that HT773 K exhibited superelasticity at 313 and 353 K. At the testing temperatures of 353 and 373 K, all the ribbons exhibited superelasticity. Applied strain was almost perfectly recovered only by unloading, except for HT773 K. The residual strain observed in HT773 K was plastic deformation by slip.

Figures 5(a), (b), (c) and (d) shows temperature \( (T) \) dependence of stress for inducing martensite \( [\sigma_{SIMT}, 0.2\% \text{ flow stress}] \) of As-spun, HT473 K, HT623 K and HT773 K, respectively. \( M_s \) of each material determined by DSC and \( M_s \) of Bulk-material is additionally plotted in Fig. 5 for comparison. The transformation detected in DSC analysis was B2–B19 martensitic transformation. The temperature dependence of \( \sigma_{SIMT} \) of TiNi alloys is generally explained by the Clausius–Clapeyron relationship. \( \sigma_{SIMT}(T) \) is regarded as a linear function of \( T \) and the intersection of \( \sigma_{SIMT}(T) \) and \( T \)-axis (horizontal axis of Fig. 5) gives \( M_s \) under zero stress, as indicated by arrows in Fig. 5. \( d\sigma_{SIMT}/dT \) was 4.4 MPa/K for As-spun and decreased with increasing the heat-treatment temperature. \( d\sigma_{SIMT}/dT \) of HT773 K was 2.1 MPa/K. Change in \( d\sigma_{SIMT}/dT \) is suggested to be partially due to rearrangement of lattice defects during heat-treatment as mentioned above. The \( M_s \) determined from the Clausius–Clapeyron relationship and that determined from DSC are in good agreement with each other, as demonstrated in Fig. 5. From this result it was certainly confirmed that the superelasticity observed in the tensile tests were originated to the B2–B19 martensitic transformation.

All the materials except for HT773 K exhibited fracture
strain of 6–10%. For an example, fracture strain and superelastic strain of As-spun reached 8 and 5.7% even at 373 K, respectively. Though the fracture strain of melt-spun ribbons was decreased with increasing testing temperature, it was found that ductility was not seriously degraded by the melt-spinning. Rapidly solidified Ti$_{32}$Ni$_{50}$Zr$_{18}$ and Ti$_{32}$Ni$_{50}$Hf$_{18}$ alloys become brittle after aging heat-treatment due to the formation of fine precipitates. 17,18) In this study, no precipitates were formed even after the aging treatment at 773 K.19) This is the reason for that TiNiPt melt-spun ribbons were not degraded in ductility by the heat-treatment. It was clearly demonstrated that shape memory effect and superelasticity of melt-spun Ti$_{50}$Ni$_{40}$Pt$_{10}$ appear at higher temperatures compared to those of Bulk-material with the same composition.

4. Conclusions

Following conclusions were obtained for martensitic transformation behavior and shape memory properties of Ti$_{50}$Ni$_{40}$Pt$_{10}$ melt-spun ribbons.

(1) As-spun Ti$_{50}$Ni$_{40}$Pt$_{10}$ is fully crystallized and composed of B2 (parent phase) and B19 (martensite phase).

(2) $M_s$ of As-spun was 100 K higher than that of Bulk-material. $M_s$ of the melt-spun ribbon is lowered by increasing the heat-treatment temperature and approaches to that of Bulk.

(3) The transformation of the ribbons detected by DSC was one-step transformation and was B2–B19 martensitic transformation.

(4) Serious degradation in mechanical properties was observed in the heat-treated ribbons. Shape memory effects and superelasticity due to B2–B19 martensitic transformation appeared in melt-spun Ti$_{50}$Ni$_{40}$Pt$_{10}$ alloy. It was found that shape memory effect and superelasticity of melt-spun Ti$_{50}$Ni$_{40}$Pt$_{10}$ appear at higher temperatures compared to those of Bulk-material with the same composition.

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