Shape Memory Characteristics of TiNi-TiPt Pseudobinary Alloys

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Abstract: Although platinum (Pt) is known to raise the martensitic transformation temperature (M_s) of Ti-Ni alloys, the mechanical and shape-memory characteristics of the Ti-Ni alloys containing Pt have not yet been fully understood. In this study, therefore, the TiNi-TiPt pseudobinary alloys are systematically investigated. The Ti₅₀Ni_{50-x}Pt_x alloys with x ranging from 0 to 50 were made by Ar arc-melting followed by hot-forging at temperatures between 1273 and 1673 K for 10.8 ks. Then, the alloys were examined by XRD, DSC, micro-Vickers hardness tests and tensile tests. It was found that either or both of the B2 and the B19' phases appear at room temperature for TiNi containing less than 10 mol% Pt and the B19 phase appears for the other alloys. M_s of TiNi alloys containing more than 10 mol% Pt increases linearly with increasing Pt concentration. Tensile elongation decreases with increasing Pt content. The Ti-Ni alloy containing 20mol%Pt is hopeful for practical high temperature applications.

Keywords: Pt, TiNi, TiPt, martensitic transformation, high-temperature shape memory alloys, shape memory characteristics

1. INTRODUCTION

Shape memory alloys (SMAs) characterized by the shape memory effect and superelasticity are fascinating functional materials and are now being practically used for pipe couplings, antennas for cellular phones and various actuators, for example. Furthermore, SMAs have attracted attention as smart materials due to their sensing and actuating functions. Although various SMAs have been reported previously, binary Ti-Ni alloys are only one class of practical SMAs because of their favorable combination of excellent shape memory characteristics and good mechanical properties such as sufficient ductility (e.g, 60% in elongation). However, the practical applications of TiNibased alloys are limited up to about 373 K (100 °C) due to their low martensitic transformation temperature (M_s) . The need for high-temperature SMAs (HTSMAs) has recently increased for application to actuators in automobiles, aircrafts and engines [1].

TiNi-based alloys were studied to improve their M_s . Especially, platinum-group metals were added to substitute for the Ni-site and M_s was found to be raised up to 793 K (520 °C) by addition of palladium [1]. Platinum (Pt) is also known to raise M_s of TiNi-based alloys [2]. However, knowledge of the mechanical and shape-memory char-

acteristics of Ti-Ni alloys containing Pt is quite insufficient. In this study, therefore, the TiNi-TiPt pseudobinary alloys have been systematically investigated.

2. EXPERIMENTAL PROCEDURE

Pseudobinary TiNi-TiPt alloys with a fixed Ti concentration (50 mol%) were prepared. It is known that (1) Pt atoms substitute for the Ni-site of TiNi and (2) Pt and Ti form B2 TiPt as a parent phase. The concentrations of Pt (in mol%) selected were 0 (binary TiNi), 5, 10, 20, 30, 40 and 50 (binary TiPt). Hereafter, the alloys are called in terms of the concentration of Pt (*e.g.*, 10Pt for Ti-40 mol%) Ni-10 mol%Pt).

Button ingots of xPt (x : mol%) alloys were made by arcmelting in Ar-1 %H₂ with a non-consumable W electrode and then hot-forged into 1mm thick disks in a similar environment at temperatures between 1273 and 1673 K for 10.8 ks depending on melting point of the alloys. Specimens were obtained from the disks after polishing them mechanically. No chemical analysis was made for the alloys because the weight changes during these processes were small, usually less than 0.1 wt.%.

The crystal structure of constituent phases at room temperature (RT) was identified by X-ray diffraction (XRD) with CuK α using Philips X'pert PRO system with X'Celerator. The phase transformation temperatures were measured by DSC using Shimadzu DSC-60 and Netzsch STA449C Jupiter over the temperature range from 153 to 1823 K at the heating and cooling rate of 10 K/min. The hardness measurement was carried out by Akashi HM-103 micro-Vickers tester with the load of 500 g and the loading time of 15 s. At least 7 readings were made for each alloy and averaged without highest and lowest values. Tensile testing was done by Shimadzu Autograph Instron-type machine at the strain rate of 1 x 10⁻⁴/s. The specimens with gauge size of 2 mm x 0.2 mm x 15 mm were electro-discharge machined and then polished to remove damaged surfaces.

3. RESULTS AND DISCUSSION

3.1 Crystal structures

TiNi and TiPt binary alloys undergo martensitic transformations to monoclinic B19' and orthorhombic B19, respectively [3]. Thus in the present TiNi-TiPt pseudobinary system, it is of interest to determine the composition where the transition from B19' (or B2) to B19 occur.

Figure 1 shows XRD profiles for all the TiNi-TiPt alloys examined. The data for 5Pt and 10Pt exhibit B2 and B19' peaks whereas those for the alloys from 20Pt to 50Pt display B19 peaks. Thus the transition from B19' to B19 takes place between 10Pt and 20Pt. Although a small amount of B19' also seems to be contained in 20Pt, it is difficult to determine this conclusively from the profile.

The lattice constants of B2, B19' and B19 in the TiNi-



Fig. 1 XRD profiles for TiNi-TiPt pseudobinary alloys at RT (Cu $K\alpha$ radiation). R, m and o refer to rhombohedral, monoclinic B19' and orthorhombic B19 phases, respectively.



Fig. 2 Lattice parameter of TiNi-TiPt pseudobinary alloys as a function of Pt concentration.

TiPt pseudobinary alloys were calculated and plotted in Fig. 2 as a function of Pt concentration. The reported value of 302 pm for the binary TiNi B2 phase is shown by a solid symbol [4]. A good linear relationship between lattice constant and Pt concentration can be seen for the B2 phase. The lattice constant of B19 phase increases lineally with the Pt concentration over 20 mol%. In both B19' and B19, the lattice parameter changes with Pt concentration naturally depend on the crystal axes.

3.2 Phase transformation temperatures

Figure 3 shows DSC cooling curves obtained for the alloys containing (a) 0 (binary TiNi), 5 and 10 mol%Pt alloys, and (b) 20, 30, 40 and 50 mol%. In Fig. 3 (a), single peaks are observed, indicating one-step martensitic transformation. M_s becomes lower with increasing Pt content. In Fig. 3 (b) for the alloys with more than 20 mol%Pt, however, M_s becomes higher with increasing Pt content. The increase in M_s by Pt addition is similar to that reported previously [3]. The profiles for the alloys containing more than 30 mol%Pt seem to indicate multistage martensitic transformation. The M_s of 50Pt (binary TiPt) obtained in



Fig. 3 DSC curves of TiNi-TiPt pseudobinary alloys: (a) for alloys containing less than 10 mol%Pt and (b) for alloys containing more than 20 mol%Pt.

this work is consistent with the results by Biggs and coworkers [3].

The Pt concentration dependence of M_s is shown in Fig. 4. M_s slightly decreases by Pt addition when Pt is less than 10 mol%; in other words, M_s of B19' decreases with increasing Pt content. When Pt is more than 10 mol%, on the other hand, M_s increases largely in proportion to the amount of Pt. That is, M_s of B19 increases with increasing Pt content. The rate of M_s increase for B19 is 27 K/mol%Pt. The effect of Pt on M_s is different, depending on the crystal structure of martensite phase.

3.3 Vickers Hardness

Figure 5 shows the Vickers hardness of the TiNi-TiPt pseudobinary alloys as a function of Pt concentration. The hardness value for 50Pt (binary TiPt) is HV 320 and this is similar to that reported [5]. It was found that hardness increases with increasing addition of Pt and becomes the maximum at around 20-30 mol%Pt. This hardening must be caused by solid-solution hardening by replacing Ni with Pt in the pseudobinary alloys.

3.4 Tensile tests

Figure 6 shows tensile stress-strain curves of the TiNi-



Fig. 4 Martensitic transformation-start temperature, M_s , as a function of Pt concentration. The rate of M_s increase is 27 K/mol% over 10 mol% Pt.



Fig. 5 Vickers hardness of TiNi-TiPt pseudobinary alloys as a function of Pt concentration.



Fig. 4 Tensile stress-strain curves of TiNi-TiPt pseudobinary alloys (5, 10, 20, 30 and 40Pt).

TiPt pseudobinary alloys (5, 10, 20, 30 and 40Pt) tested at RT. It should be noted that the result for 50Pt is not drawn in the figure since 50Pt was fractured under 110 MPa at the strain of 0.6 %. It can be seen that both yield stress and tensile strength increase and elongation decreases with increasing Pt content except for 50Pt. However, the 20Pt alloy has sufficient ductility together with high tensile strength.

From the above, the 20Pt alloy is of particular interest as a HTSMA in terms of its high M_s (563 K), UTS (600 MPa) and elongation (6 %).

4. SUMMARY

The phase constitution, martensitic transformation and mechanical properties in TiNi-TiPt pseudobinary alloys were systematically investigated with an aim at developing high temperature shape memory alloys (HTSMAs) based on TiNi. The results are summarized as follows.

- At room temperature, either or both of the B2 and B19' (monoclinic) phases constitute Ti-Ni-Pt alloys containing less than 10 mol%Pt whereas the B19 (orthorhombic) phase does the alloys containing more than 20 mol%Pt. Thus the transition from B19' to B19 for the marteisitic phase occurs at around 20 mol%Pt.
- (2) The martensitic transformation temperature (M_s) abruptly increases proportionally with increasing Pt concentration over 10 mol%. The rate of M_s increase is found to be 27 K/mol%Pt.

- (3) The alloys containing 20-30 mol% Pt exhibit high hardness values of around HV 450. This must be due to the solid solution hardening.
- (4) The alloy containing 20 mol% Pt exhibits a high martensitic transformation temperature of 563 K, ultimate tensile strength (UTS) of 600 MPa and elongation of 6 %. In view of these properties, this alloy is a strong candidate for the development of high temperature shape memory alloys.

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