1. Introduction

Intermetallic compound of TiPd is a shape memory alloy exhibiting a thermoelastic martensitic transformation from the B2-type structure to the B19-type (2H) structure near 800 K.\(^1\) Because of the high transformation temperature, TiPd is expected as a shape memory alloy actuating at high temperatures.\(^2\) When 3d-transition elements are added to TiPd, \(M_t\) temperature changes remarkably.\(^3,5\) Enami et al. found that the martensitic transformation temperatures are controlled over a wide temperature range from 300 K to 800 K by substituting Fe for Pd.\(^6,7\) Through the study, they also reported that Ti-(50-x)Pd-xFe alloys have several martensite phases such as 9R and 4H martensites in addition to 2H martensite.

One characteristic feature of a Ti-(50-x)Pd-xFe alloy (7 \(\leq x \leq 16\)) is that its electrical resistivity exhibits a negative temperature coefficient (NTC) above its martensitic transformation start temperature. Another characteristic feature is that diffuse satellites appear at incommensurate positions in electron diffraction patterns observed in the temperature range of NTC in electrical resistivity. From these observations, Enami et al. interpreted that a Ti-(50-x)Pd-xFe alloy exhibits a premartensitic transformation at the temperature where the resistivity shows a local minimum. The diffuse satellites in the premartensite state were then confirmed to appear by Li et al.\(^9\) and Murakami et al.\(^10\) by using Ti-36Pd-14Fe and Ti-34Pd-16Fe alloys and this state is called incommensurate phase. They also observed tweed microstructure, rod-like streaks and microdomains in incommensurate phase. However, the origin of the so-called premartensitic transformation is not clear. The present study is motivated to understand the origin of the incommensurate phase by measuring physical properties which are closely related to electronic structure.

Incidentally, the NTC in resistivity and diffuse satellites prior to a martensitic transformation were also known to appear in Ti-(50-y)Ni-yFe alloys, and the appearance of the incommensurate phase in this system is interpreted to be caused by Fermi surface nesting.\(^10\) In the Ti-(50-y)Ni-yFe alloys, it was also reported that the magnetic susceptibility has a kink (a significant change in \(d\gamma/dT\)) near the \(T_{\text{min}}\) of electrical resistivity.\(^11\) In addition, the electronic specific heat of the incommensurate phase was reported to be larger compared to that of the martensite phase or the stable B2-phase.\(^11\)

Considering the resemblance in electronic structure of the B2-phase between TiNi and TiPd,\(^12\) we can expect that similar characteristic features in magnetic susceptibility and specific heat exist in the incommensurate phase of Ti-(50-x)Pd-xFe alloys. If this expectation is correct, the electronic origin of instability of the B2-phase in Ti-based alloys will be further confirmed to be related to Fermi surface nesting. However, the physical properties in a wide temperature range for Ti-Pd based alloys exhibiting NTC have not been investigated.

In the present study, therefore, we will investigate the temperature dependence of physical properties in Ti-(50-x)Pd-xFe alloys with an iron content of \(x = 14, 16, 18, 19, 20\) at\%. The composition of the first two alloys are the same as those reported by Enami et al., and we expect the martensitic transformation is suppressed in other alloys.

2. Experimental Procedure

Ingots of Ti-(50-x)Pd-xFe (\(x = 14, 16, 18, 19, 20, 22\)) alloys (in at\%) were prepared by arc melting, and were homogenized at 1273 K for 24 h in quartz tubes. Each alloy is referred to by its iron content. For example, 14Fe represents the Ti-36Pd-14Fe alloy. Specimens for all the measurements described below were cut from the ingots and were heat treated at 1273 K for 1 h and then quenched into iced water. The oxidized surface layer was removed by electropolishing.
Electrical resistivity ($\rho$) was measured by a standard four point probe method with a cooling and heating rate of about 1 K/min and a constant current density of about 0.1 MA/m². Magnetic susceptibility ($\chi$) was measured by a superconducting quantum inference device magnetometer (SQUID) with an external magnetic field of $\mu_0H = 0.1$ T and a constant heating and cooling rate of about 1 K/min. Differential scanning calorimetry (DSC) measurement was made with a heating and cooling rate of 5 K/min. Specific heat was measured by using a relaxation method in a PPMS (Quantum Design). In every measurement of specific heat, the specimen was heated by two percent of its absolute temperature, and the heat capacity was calculated from the relaxation time of cooling by thermal conduction.

### 3. Results and Discussion

Figure 1 shows electrical resistivities of the 14Fe, 16Fe and 18Fe alloys measured in the cooling and heating processes. In the cooling process, the resistivity exhibits a local minimum at $T_{min}$ = 426 K, 372 K and 338 K for the 14Fe, 16Fe and 18Fe alloys, respectively, as indicated with an arrow. It then exhibits a sharp increase at $M_s$ due to the martensitic transformation as indicated by a double arrow. The martensite phase of the 14Fe alloy has an incommensurate structure and that of the 16Fe alloy has a 4H structure according to previous studies. After the increase, the resistivity decreases monotonically down to 10 K. In the heating process, the resistivity shows a sharp decrease due to the reverse transformation with an obvious hysteresis between the cooling and heating processes.

The $M_s$ of the 14Fe and 16Fe alloys are in good agreement with those reported by Enami et al. It should be noted that in addition to the sharp increase in the cooling process at $M_s$, a slight bend appears above $M_s$, which is known from the magnification of the electrical resistivity curve of the 14Fe alloy near the martensitic transformation start temperature (Fig. 2). As indicated by an arrow in Fig. 2, the gradient of resistivity against temperature ($d\rho/dT$) changes at 328 K. We define this temperature as $M_s'$. In order to investigate this change in more detail, we have measured the electrical resistivity only in the vicinity of $M_s'$. There is an obvious hysteresis in the electrical resistivity between the cooling and heating processes as shown in Fig. 3. In addition, the DSC cooling curve of the 14Fe alloy exhibits a small exothermic peak or a shift in base line above $M_t$ as shown in Fig. 4. These results suggest that a new phase exists between $M_s'$ and $M_t$. We refer this phase as X-phase. The crystal structure of the X-phase is not clear yet, and it is a subject in the future.

Figure 5 shows the electrical resistivity of the 19Fe, 20Fe and 22Fe alloys measured in the cooling and heating processes. These alloys exhibit neither a sharp increase nor a hysteresis between cooling and heating processes, meaning that martensitic transformation is suppressed. These alloys, however, exhibit a local minimum of resistivity at $T_{min}$ of 310 K, 265 K and 216 K, respectively. Below $T_{min}$, they exhibit a NTC in electrical resistivity, as in Ti-(50-y)Ni-yFe alloys with $y \geq 6$.

Figure 6 shows temperature dependence of magnetic susceptibility ($\chi$-$T$ curve) of the present alloys. The $\chi$-$T$ curve of the 14Fe and 16Fe alloys exhibit a sharp decrease in $\chi$ at 316 K and 240 K respectively, corresponding to the $M_s$ temperatures, which are in good agreement with those obtained by the $\rho$-$T$ curves shown in Fig. 1. These decreases in $\chi$ associated with the martensitic transformations may be
due to the decrease in electronic density of state at Fermi energy as in Ti-Ni based alloys. On the other hand, $M_s$ is not detected by magnetic susceptibility measurements within the present precision. This will be attributed to a small change in electronic structure associated with the B2-X transformation. Unlike the 14Fe and 16Fe alloys described above, the 18Fe alloy does not exhibit a sharp decrease. But, this alloy exhibits a small hysteresis between cooling and heating processes, which is characteristic to the first order nature of martensitic transformation. The $\chi$-$T$ curve of the 18Fe alloy also exhibits a kink at 320 K ($T_{kink}$) as indicated by an arrow, which is close to $T_{min}$ determined by electrical resistivity. It is noted in Fig. 6 that the 19Fe, 20Fe and 22Fe alloys exhibit neither a sharp change nor a hysteresis between cooling and heating processes. The $\chi$-$T$ curve of the 19Fe have a kink near 305 K and this temperature is close to $T_{min}$. The correspondence between $T_{min}$ in $\rho$-$T$ curve and $T_{kink}$ in $\chi$-$T$ curve in the 18Fe and 19Fe alloys described above is in good agreement with that reported in Ti-(50-$y$)Ni-$y$Fe alloys with $y \geq 6$. Thus, these results suggest that the anomalies of electrical resistivity and magnetic susceptibility in Ti-based shape memory alloys come from the same origin.

In the case of the 20Fe and 22Fe alloys, the kink is not detected clearly.

The present results of characteristic temperatures obtained in the resistivity measurements and magnetic susceptibility measurements are summarized in Fig. 7, where those temperatures reported by Enami et al. are also shown by open marks. In addition, the crystal structures of Ti-(50-$x$)Pd-$x$Fe ($0 \leq x \leq 16$) alloys identified by Enami et al., Li et al. and Murakami et al. are also shown in this figure. The crystal structure of 18Fe alloy is confirmed by transmission electron microscope observation to be 4H. We recognize in
Fig. 7 that $T_{\text{min}}$ decreases linearly with increasing iron content and that $M_f$ and $M'_f$ decreases linearly with increasing iron content up to $x = 18$, and then suddenly disappears between $x = 18$ and $x = 19$.

In order to understand the nature of transformation suppressed state further, we have measured specific heat $C_p$ at cryogenic temperatures and the result is plotted as $C_p/T$ vs $T^2$ in Fig. 8. In this figure, the results obtained for Ti-20Pd-30Fe and Ti-10Pd-40Fe and TiFe alloy are also shown. Each alloy exhibits a linear relation below $T \leq 10$ K. From the linear relation, we obtain the Debye temperature $\Theta_D$ and electron specific heat coefficient $\gamma$ as follows. The value of $\Theta_D$ is obtained from the gradient $\beta$ using the relation $\beta = (12/5)\pi^2 N_A k_B / \Theta_D$, where $N_A$ is Avogadro’s number and $k_B$ is the Boltzmann constant. The value of $\gamma$ is obtained as the $C_p/T$-intercept of Fig. 8. The results obtained for $\Theta_D$ and $\gamma$ are shown in Figs. 9 and 10, respectively.

We can see from Fig. 9 that the $\Theta_D$ of the martensitic transformation suppressed state in the 19Fe, 20Fe and 22Fe alloys is lower than that of the martensite phase and the stable B2-phase in TiFe. The low value of $\Theta_D$ is related to the low value of elastic constant, and it suggests that the lattice is not stable enough. In addition, the martensitic transformation suppressed state has a high value of electronic specific heat coefficient $\gamma$. The high value of $\gamma$ suggests that electron-phonon interaction is strong in the incommensurate phase, and that the lattice is strongly influenced by electronic instability. Similar results of low $\Theta_D$ and high $\gamma$ have been reported in Ti-(50-y)Ni-yFe alloys.\textsuperscript{11} Thus we speculate that the origin of NTC and diffuse satellites in Ti-(50-x)Pd-xFe alloys will be nesting effect of Fermi surface and a large electron-phonon interaction will exist, as in Ti-(50-y)Ni-yFe alloys.\textsuperscript{12,13} The electronic structure calculation of Ti-(50-x)Pd-xFe alloys is required for further discussion.

4. Conclusions

We have examined the transformation behavior of Ti-(50-x)Pd-xFe alloys ($14 \leq x \leq 22$) by electrical resistivity and magnetic susceptibility and specific heat measurements. The 14Fe, 16Fe and 18Fe alloys exhibit a first order martensitic transformation preceded by a weak first order transformation. On the other hand, first order transformation is suppressed in the 19Fe, 20Fe and 22Fe alloys. They, however, exhibit a negative temperature coefficient in electrical resistivity, and a kink in magnetic susceptibility. The Debye temperature of the transformation suppressed state is lower than that in the martensite state and the electronic specific heat coefficient of the transformation suppressed state is higher than that in the martensite state. These behaviors resemble those observed in an incommensurate phase of Ti-(50-y)Ni-yFe alloys. This suggests that the so-called precursor phenomena observed in Ti-Pd based shape memory alloys is caused by the instability of electronic structure of the B2-phase, as in the Ti-Ni based alloys.
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REFERENCES