Crystal Distortion and Magnetic Structure of $\gamma$-MnPd Alloys

Tomiei Hori$^1$, Yoshinori Tsuchiya$^1$, Yoshinobu Ishii$^2$ and Kiichi Hojou$^3$

$^1$Shibaura Institute of Technology, Saitama-City, Saitama 330-8570, Japan
$^2$Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan
$^3$Department of Materials Science, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan

We have made X-ray and neutron diffraction experiments and magnetic susceptibility measurements for $\gamma$-MnPd alloys. The alloy containing 10.5 at%Pd shows a face centered orthorhombic structure with $a = 0.3839$, $b = 0.3780$ and $c = 0.3717$ nm and a non-collinear antiferromagnetic structure with $\mu_a = 0$, $\mu_b = 1.26$ and $\mu_c = 2.14$ $\mu_B$/Mn atom at 10 K. The crystal distortion occurs from the orthorhombic structure to a tetragonal structure with $c/a < 1$ at 320 K, and finally to a cubic structure at 430 K. Another alloy with 13 at%Pd shows a face centered tetragonal with $a = 0.3800$ and $b = 0.3846$ nm ($c/a = 1.012$) at 293 K, and transforms to a cubic structure at 530 K. More Pd rich alloy with 15 at% shows [c] structure down to 27 K. A phase diagram for $\gamma$-MnPd alloy system with 8–17 at%Pd is proposed.

(Received October 19, 2001; Accepted December 21, 2001)

Keywords: antiferromagnetism, crystal distortion, magnetic structure, manganese palladium

1. Introduction

Pure $\gamma$-Mn having a face centered cubic is stable only at high temperatures (1352–1416 K), and can not be retained by quenching. If a small amount of some elements (e.g. Fe, Ni, Cu, Zn) are added, the $\gamma$-Mn phase can be retained at room temperature by quenching as a metastable phase. The most quenching $\gamma$-Mn alloys undergo a distortion from a face centered cubic [c] to tetragonal with $c/a < 1$ [t1] below the Néel temperature. In some cases, a distortion to a face centered tetragonal with $c/a > 1$ [t2] is observed. Furthermore, $\gamma$-MnNi alloys are distorted to a face centered orthorhombic [o] in addition to [t1] and [t2]; phase diagram was reported by Honda et al. Cowlam et al. have also reported existence of [o] in $\gamma$-MnAu alloys and [t2] in $\gamma$-MnPd alloys.

Jo et al. have proposed a theoretical phase diagram and magnetic structures for $\gamma$-Mn alloys on the basis of Landau expansion of free energy; the $a$, $b$ and $c$-axis components of the magnetic moments in [o] with $a > b > c$ are as follows: $\mu_c^0 > \mu_b^0 > \mu_a^0$. Recently, we have found that [t2] and [o] exist in $\gamma$-MnGa alloy, and determined the magnetic structure of [o]. Etherige et al. have also investigated the magnetic structure of $\gamma$-MnNi alloys. We have reported more detailed phase diagram and magnetic structures of $\gamma$-MnAu alloys. More recently, we also found [t1] and [o] in $\gamma$-MnRh alloys, and $\gamma$-MnRu alloys with a small amount Cu and $\gamma$-MnPt alloys, and determined the magnetic structures. The results in [o] with $a > b > c$ are as follows: $\mu_c^0 > \mu_b^0 > \mu_a^0 = 0$. In the present work, we have extended studies for $\gamma$-MnPd alloys, and found that there is [o] in the alloys. The results of magnetic susceptibility measurements, and X-ray and neutron diffraction experiments are reported here.

2. Sample Preparation and Experimental Procedure

Alloys were prepared by melting Pd (3N Purity) and electrolytic Mn (3N) using an argon arc furnace. The ingot was sealed in an evacuated quartz tube with argon gas of $2 \times 10^4$ Pa, annealed at 1273 or 1323 K for more than 2 days, and quenched in water. The powder sample for X-ray and neutron diffraction experiments was prepared by filing the ingot. In order to remove the stress by filing, the powder sample was re-annealed for 2 h at 1273 K. Weight loss during the thermal treatment is less than 0.6%. An Fe target was used for the X-ray diffraction. Temperature dependence of the lattice constants between 15 K and 530 K was determined using a cryogenic camera for X-ray diffraction. Neutron diffraction experiments were made by using the HRPD ($\lambda = 0.1823$ nm) and TAS 2 ($\lambda = 0.2453$ nm) diffractometers installed in the JRR-3M reactor at the Japan Atomic Energy Research Institute (JAERI). Susceptibility measurements were made by the Faraday method using a magnetic balance in an electromagnet.

3. Experimental Results and Discussion

The $\gamma$-MnPd alloy with 8.0 at%Pd shows the f.c.t. structure with $a = 0.3821$ and $c = 0.3684$ nm ($c/a = 0.964$) at 293 K. Temperature dependence of the lattice constants $a$ and $c$ of [t1] was determined by X-ray diffraction experiments using 200 and 002 lines. Figure 1 shows the results for this alloy. As seen in Fig. 1, the crystal distortion occurs from [t1] to [c] above $T_1$ (= 470 K). We also observed an anomaly around 470 K in the magnetic susceptibility versus temperature curve for this alloy as shown in Fig. 2. The susceptibility reversibly depends with increasing and decreasing around anomalous temperature at 470 K. So, we assumed that $T_1$ is nearly equal to the Néel temperature $T_N$. We have confirmed that the alloy with 10.5 at%Pt shows [o] with $a = 0.3839$, $b = 0.3780$ and $c = 0.3717$ nm at 293 K. The temperature dependence of the lattice constants $a$, $b$ and $c$ of [o] was also determined by X-ray diffraction using 200, 020 and 002 lines. Figure 3 shows...
the temperature dependence of lattice constants for this alloy. The crystal distortion occurs from [o] to [t1] at \( T_o \) (= 320 K), and form [t1] to [c] at \( T_t \) (= 430 K). We have also determined \( T_N \) from the temperature dependence of the susceptibility; \( T_N \) is nearly equal to \( T_t \). In the X-ray diffraction pattern of the alloy with 10.5 at%Pd at low temperature, diffraction lines 200, 020 and 002 for [o] are well separated from each other. However, we could not accurately determine the lattice constants of the alloy with 11 at%Pd since both 020 and 002 lines are close to each other. Furthermore, it is difficult to distinguish [o] with \( a > b \sim c \) and [t2] for the alloy with 12 at%Pd. In addition, the \( \gamma\)-MnPd alloy with 13 at%Pd shows clearly [t2] with \( a = 0.3800 \) and \( c = 0.3846 \) \( \text{nm} \) \( (c/a = 1.012) \) at 293 K. We determined that the composition of the phase boundary between [o] and [t2] is around 12 at%Pd. Figure 4 shows temperature dependence of lattice constants for the alloy with 13 at%Pd. The crystal distortion also occurs from [t2] to [c] at 350 K. Our results for the 13 at%Pd alloy are not contradictory to the results of Hicks et al. [2]; they have reported that the 13 at%Pd alloy shows a tetragonal structure with \( c/a < 1 \) at low temperature. The alloys containing more than 15 at%Pd show [c] structure down to 27 K.

Figure 5 shows the neutron diffraction pattern for the \( \gamma\)-MnPd alloy with 10.5 at%Pd at 10 K obtained by HRPD. The pattern is explained by assuming the f.c.o. structure with \( a = 0.3839 \), \( b = 0.3780 \) and 0.3717 \( \text{nm} \) and a non-collinear antiferromagnetic structure similar to that of the \( \gamma\)-MnGa alloy. The magnetic reflection intensities 011, 101 and 110 are proportional to \( \mu_b^2 \), \( \mu_c^2 \) and \( \mu_a^2 \), respectively. It is remarkable that the 011 line is absent in the observed diffraction pattern. We can easily obtain \( \mu_a = 0 \). Other magnetic components \( \mu_b \) and \( \mu_c \) were determine using the intensities 101 and 110 and some nuclear reflections 111 and 200 etc.: \( \mu_b = 1.26 \) and \( \mu_c = 2.14 \mu_B \)/Mn atom. We also measured the temperature dependence of the magnetic diffraction lines 110 and 101 by TAS 2 diffractometer. Although the 110 and 101 reflections were not resolved, we obtained the intensities, \( I_{110} \) and \( I_{101} \), by curve-fitting analysis using double Gaussian
functions. The results are shown in Fig. 6. The total intensity, $I_{110} + I_{101}$, monotonically decreases with increasing temperature, and vanishes around 430 K ($= T_N$), which is nearly equal to $T_t$. In summary, we propose a phase diagram for the $\gamma$-MnPd alloy system as shown in Fig. 7. The present results are very similar to our recent results for other $\gamma$-Mn alloy systems and consistence with Jo’s theory.

### 4. Conclusions

We have found that there is a face centered orthorhombic region for the $\gamma$-MnPd alloy with 10.5 at% Pd. The lattice constants and magnetic moments at 10 K are as follow: 

- $a = 0.3839$, $b = 0.3780$ and $c = 0.3717$ nm and $\mu_a = 0$
- $\mu_b = 1.26$ and $\mu_c = 2.14 \mu_B$/Mn atom. Another alloy with 13 at% Pd shows a face centered tetragonal with $c/a > 1$ at 293 K. We have also determined a phase diagram for $\gamma$-MnPd alloy system. The present results are consistent with Jo’s theory.

### REFERENCES