Effect of Co and Ni on Martensitic Transformation and Magnetic Properties in Fe-Pd Ferromagnetic Shape Memory Alloys

Koichi Tsuchiya¹, Takeru Nojiri¹,*, Hideyuki Ohtsuka² and Minoru Umemoto¹

¹Department of Production Systems Engineering, Toyohashi University of Technology, Toyohashi 441-8580, Japan
²Tsukuba Magnet Laboratory, National Research Institute for Materials Science, Tsukuba 305-0003, Japan

Effects of Co and Ni addition on fcc-fct transformation temperature and magnetic properties have been investigated for Fe-Pd ferromagnetic shape memory alloys. The addition of Co shifts the fcc-fct transformation temperature slightly higher while the Ni addition shifts it lower. The results suggest that the relative stability between fcc and fct phases is significantly affected by the electronic structure. Saturation magnetization values for Fe-Pd-Co and Fe-Pd-Ni were found to be slightly higher than those for binary Fe-Pd.

(Received August 4, 2003; Accepted October 2, 2003)

Keywords: ferromagnetic shape memory alloys, martensitic transformation, iron, palladium, nickel, cobalt

1. Introduction

Shape memory alloys (SMAs) are one type of actuator materials, which can convert the thermal energy into mechanical energy. It has about three orders of magnitude higher output energy density than that in other actuator materials, such as, magnetostrictive materials and piezo ceramics. One significant disadvantage of SMAs is, however, their slow response since it is limited by the heat conduction of the materials. Meanwhile, in ferromagnetic shape memory alloys (FSMAs), one can achieve a large displacement and rapid response by magnetic field-induced martensitic transformation or by field-induced rearrangements of martensitic twins (twinning magnetostriction). Therefore, several systems of FSMAs, such as, Ni-Mn-Ga,¹¹ Ni-Ga-Fe,² Co-Ni-Ga,³,¹⁰ Co-Ni-Al,⁵ Fe-Pt⁶ and Fe-Pd,⁷ have been attracting much attention. Ni-Mn-Ga alloy is the first SMA in which a large strain by field-induced twinning/detwinning was observed.¹¹ Up to 10% of magnetostriction has been observed for a single crystal Ni-Mn-Ga.³ Proto-type magnetic actuators using single crystal of Ni-Mn-Ga are already available commercially. However, this alloy has several disadvantages, such as, mechanical properties (intragranular fracture in polycrystalline samples) and low phase transformation temperatures. Regarding the phase transformation temperature, martensitic transformation temperature can be modified relatively easily by changing the chemical composition of the alloy, but the Curie temperature is around 360 K and insensitive to the composition. This can be a problem when the alloy is used for magnetic actuators since the temperature of the actuating element may rise due to the heat dissipation of the twin boundary motion at high frequency.

Fe-Pd alloy with Pd concentration of about 30 mol% undergoes thermoelastic martensitic transformation from fcc to fct, and exhibits shape memory effect.⁹ Relation between the alloy composition and martensitic transformation temperature has been determined by Sugiyama et al.¹⁰ The fcc-fct transformation temperature is about 295 K for Fe-29.7 mol%Pd; it decreases about 10 K by increasing only 0.1 mol%Pd. Stress-induced fcc-fct transformation in this alloy was studied by Kato et al.¹¹ By decreasing Pd content to 29.4 mol%Pd, another type of martensite, which is non-thermoelastic and is referred to as bct martensite,¹² appears at room temperature. Therefore, the stability range of fct martensite is rather limited in terms of both composition and temperature. Magnetostriction of fct martensite in Fe-Pd has been reported by James and Wuttig,¹³ and also by Furuya et al.¹⁴ Magnetostriction of 3.1% at 77 K has been reported for a single crystal of Fe-31.2 mol%Pd by Koeda et al.¹⁵ Compared with Ni-Mn-Ga, Fe-Pd alloys have an advantage of better mechanical properties, the higher Curie temperature (~763 K). The problem of this alloy is the limited stability of the fct phase. It may be possible to extend stability range of the fct martensite by an addition of Co or Ni, which are known as the austenite stabilizer. Oshima and Sugiyama¹⁶ reported that the addition of 2 mol% of Ni or Rh to Fe-28.3 mol%Pd suppressed the fct-bct transformation. However, no systematic investigation has been done on the effect of third elements on the fct phase stability. Therefore we investigated an effect of alloying elements on the martensitic transformation behavior of Fe-Pd system.

2. Experimental

Alloy ingots were prepared by melting the pure metals of Fe (99.95%), Pd (99.95%), Co (99.9%) and Ni (99.97%) in an Ar arc melting furnace. The ingots were subjected to a homogenization treatment at 1373 K for 518.4 ks (6 days). The ingots were then cold rolled to a sheet of 0.4 mm thick and then heat-treated at 1373 K for 18 ks followed by quenching into water. Samples for various measurements were cut out from the sheet. The final heat treatment was given at 1373 K for 18 ks followed by quenching into ice water. Alloy composition was determined by EDX analysis in scanning electron microscope (SEM) using JEOL JSM-6300. X-ray diffraction (XRD) measurements were carried out on Rigaku RINT-2500 equipped with a sample cooling stage using a Cu-Kα radiation. Magnetic properties were determined by a commercial vibrating sample magnetometer. X-ray diffraction was performed on Rigaku RINT-2500 with Cu-Kα radiation. The problem of this alloy is the limited stability of the fct phase. It may be possible to extend stability range of the fct martensite by an addition of Co or Ni, which are known as the austenite stabilizer. Oshima and Sugiyama¹⁶ reported that the addition of 2 mol% of Ni or Rh to Fe-28.3 mol%Pd suppressed the fct-bct transformation. However, no systematic investigation has been done on the effect of third elements on the fct phase stability. Therefore we investigated an effect of alloying elements on the martensitic transformation behavior of Fe-Pd system.

*Graduate Student, Toyohashi University of Technology. Present address: NTN corporation, Osaka 550-0003, Japan
measured on vibrating sample magnetometer (VSM). For the measurements at room temperature Riken BHV-55 was used with a maximum field of $1.19 \text{ MA/m}$. For low temperature measurements from room temperature to 5 K, Oxford Instruments VSM-12 was used.

3. Results and Discussion

X-ray diffraction pattern obtained for Fe-31.0 mol% Pd-3.1 mol% Co alloys obtained at room temperature is shown in Fig. 1, showing that the sample is in a single fcc phase ($a = 0.376$ nm).

A sequence of changes in the profile of the 220 peak on cooling is shown in Fig. 2. It can be seen that on cooling from 273 K the peak become broader, and below 223 K the peak splits into two, one at the lower $2\theta$ corresponds to $(220)_{hct}$ and the other at the higher to $(202)_{hct}$ and $(022)_{hct}$. The tetragonality, $c/a$, was deduced from the peak positions and plotted in Fig. 3 as a function of temperature. A decrease in $c/a$ is apparent in temperatures below 200 K.

Temperature dependence of magnetization under a constant magnetic field ($7.96 \text{ kA/m}$) was measured for various alloys. A representative result is shown in Fig. 4 for Fe-31.0 mol% Pd-3.1 mol% Co. A decrease in magnetization becomes significant at temperatures below 200 K. Similar temperature dependence of magnetization was observed for a single crystal of a binary Fe-31.2 mol% Pd alloy. This corresponds well to the fcc-fct transformation temperature deduced from the temperature variation of $c/a$ as shown in Fig. 3. Thus we take the temperature at which the magnetization start to decrease as the fcc-fct transformation temperature, $T_M$. Similar measurements were done for other alloys and the results were summarized in Fig. 5. In the figure, $T_M$ obtained for Fe-Pd (solid diamonds), Fe-Pd-Co (solid circles) and Fe-Pd-Ni (solid squares) are plotted as a function of Pd concentration. $T_{M8}$ deduced from the tetragonality are indicated by open symbols. The data for binary Fe-Pd alloys obtained by Sugiyama et al. is also indicated by the broken line. The dotted line shows the fct-bct transformation temperature determined also by Sugiyama et al. It should be noted that in Fe-Pd-Co alloys, $T_M$ is similar to or slightly higher than that in binary Fe-Pd alloys while in Fe-Pd-Ni alloys, it is lower than that in the Fe-Pd. It can be seen that $T_M$ is also sensitive to Ni content; about a 1 mol% increase of Ni leads to a $\sim 100$ K decrease in $T_M$. This is understandable since the Ni and Pd are in the same column in the periodic table and thus has the same number of valence electrons.

In Fig. 6, the fcc-fct transformation temperatures, $T_M$, are plotted as a function of valence electron concentration per atom, $e/a$. In order to calculate the value of $e/a$, the
The following numbers of valence electrons are assumed: 8 for Fe, 9 for Co, 10 for Ni and 10 for Pd. It is clear in Fig. 6 that the $T_M$ data for Fe-Pd-Co and Fe-Pd-Ni alloys forms a single curve when plotted against $e/a$, shown by the solid line, while they are three separated lines when plotted against Pd concentration (solid lines in Fig. 5). It should be also noted that this curve does not coincide with the $T_M/e/a$ curve for the binary Fe-Pd alloys, shown by the broken line. The results seem to indicate that the addition of about $0.3$ mol% of Co or Ni to the Fe-Pd leads to a significant modification in electronic structure of the alloys. Further discussion for this point requires calculation of electronic band structure.

The compositions of the samples in which major phase at room temperature was the bct phase are indicated as the gray symbols in Figs. 5 and 6. It is difficult to find a systematic relation between the alloy composition and the stability of the bct phase although addition of Co or Ni seems to stabilize the bct phase. Also the stability of the bct phase cannot be explained by $e/a$. Oshima et al. reported the stress-induced bct in Fe-30.6Pd, in which thermally induced bct was not observed, and suggested that the internal stress could induce the bct phase. Our preliminary experiments indicated the fraction of the bct phase decreases with decreasing quenching rate, which seems to support the importance of internal stress for the formation of the bct phase.

Magnetization curves of Fe-Pd-Co alloys measured at
room temperature (fcc) and 5 K (fct) are shown in Fig. 7. Unlike the case of Ni-Mn-Ga alloys, the slope for the initial part of the magnetization curves are similar for both fcc and fct phases. Saturation magnetization (taken as the magnetization value at 1.19 MA/m) was plotted as a function of Pd concentration in Fig. 8. Magnetization was plotted in a unit of the Bohr magneton ($\mu_B$). The data for the binary alloys\textsuperscript{16} is also plotted. The broken line and open symbols represent the calculated value assuming simple mixing ($2.2 \mu_B$ for Fe, $1.7 \mu_B$ for Co and $0.6 \mu_B$ for Ni). The present results and the previous data indicate that the magnetization is higher than those expected from simple mixing and that the addition of Co and Ni seems to shift the magnetization value slightly higher than that of the binary Fe-Pd in spite of a large scatter in the data.

4. Conclusion

Effects of addition of Co and Ni on fcc-fct transformation temperature and magnetic properties have been investigated for Fe-Pd ferromagnetic shape memory alloys. The addition of Co shifts the fcc-fct transformation shifts slightly higher while the Ni addition shifts it lower. The obtained transformation temperature data for the Fe-Pd-Co and Fe-Pd-Ni form a single curve when they are plotted against the valence electron density, $\epsilon/a$. But the curve does not coincide with that for the binary Fe-Pd alloys. Saturation magnetization values for Fe-Pd-Co and Fe-Pd-Ni were found to be slightly higher than those for binary Fe-Pd.

REFERENCES