Martensitic Transformation in the Fe-Pd Alloy System*

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In Fe-Pd alloys containing about 30 at% palladium, fcc-fct thermoelastic transformation exists, and the fct martensite phase is further transformed non-thermoelastically to the bct martensite phase. The morphology and structure of the martensitic transformation have been extensively studied by means of X-ray diffractometry, optical and electron microscopy. The change in surface relief associated with the fcc-fct martensitic transformation was investigated in detail by using single crystals which were made by the Bridgman method. The concentration dependence of their M_s temperatures was determined by using polycrystalline specimens, and it was shown that the fct phase is a stable low temperature one. In the cooling process, faint band regions appeared dispersedly along the $\{101\}$ traces and grew with jerky motion. In the heating process, the fcc austenite regions partially arised from the fct martensite regions. The temperature hysteresis of the fcc-fct transformation was about 10 K, and cyclic treatment between cooling and heating showed a good reversibility of the process. Under the *in situ* electron microscope observation, plate type structures having the $\{101\}$ trace appeared, though their size was two orders of magnitude smaller than that of fct bands observed by optical microscopy.

In addition, it was confirmed that the fcc austenite containing palladium less than 25 at% is transformed to bcc martensite, and that the bcc martensite was clearly distinguished from the bct one.

(Received February 29, 1984)

Keywords: martensitic transformation, iron-palladium alloy, shape memory effect, electron microscopy, optical microscopy, X-ray diffractometry, invar alloy, thermoelastic martensitic transformation, non-thermoelastic martensitic transformation

I. Introduction

Alloys exhibiting thermoelastic martensitic transformation can be divided mainly into bcc and fcc-based alloys according to their matrix structures. The former alloys are represented by the β -phase alloys, which have ordered structures in both the matrix and martensite phases. On the other hand, the latter alloys are, for instance, In-Tl⁽¹⁾, Mn-Cu⁽²⁾, Fe-Pt⁽³⁾ and Fe-Pd⁽⁴⁾ alloys. They are transformed to the fct martensite phase, except the ordered Fe-Pt alloys, which are transformed to the bct martensite phase. It must be noted that In-Tl, Mn-Cu and Fe-Pd are disordered alloys in both the

matrix and martensite phases. The shape memory effect had been supposed to be related with the ordered structures, as the Fe-Pt alloy actually showed⁽³⁾. However, the thermoelastic behavior associated with the shape memory effect is not always connected with the ordered structure in the case of fcc-fct martensitic transformation, as the above examples show and Otsuka and Shimizu⁽⁵⁾ have discussed. In addition, the martensitic transformation in many of these alloys seems to be closely connected with their magnetic properties. For instance, it has been known that in the Mn-Cu alloy⁽⁶⁾ the martensite structure has a magnetically ordered structure arising from the para-antiferro magnetic transformation. In both of the Fe-Pt and Fe-Pd alloy systems, there is the so-called invar region in the vicinity of the martensitic transformation regions⁽⁷⁾⁽⁸⁾.

The martensitic transformation in the Fe-Pd alloy system showed several interesting characteristics⁽⁹⁾: The tetragonality of fct martensite gradually increased below the M_s temperature, and at a critical c/a ratio, of 0.92, the fct mar-

* This paper was partly presented at the Annual Autumn Meeting of the Japan Institute of Metals, Kyoto, (1981), and Akita, (1983).

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tensite was further transformed to the bct martensite non-thermoelastically. This successive martensitic transformation is quite peculiar among other alloys and could be a key phenomenon to clarify the crystallographic mechanism of the fcc-bct martensitic transformation. It must be also noted that the Fe-Pd alloys exhibiting the fcc-fct martensitic transformation showed not only a perfect shape memory effect but also a reversible shape memory effect, though the latter was imperfect.

Previous studies performed by other investigators for this martensitic transformation are as follows: Matsui *et al.*⁽¹⁰⁾ also confirmed the fcc-fct martensitic transformation of Fe-29~33 at%Pd alloys using X-ray diffractometry, but they did not find the fct-bct martensitic transformation. Foos *et al.*⁽¹¹⁾ reported the same type of transformation, but they considered the fct phase as a transitional phase or a precursor of bct martensite rather than an independent martensite phase. Accordingly, the study of the martensitic transformation in the Fe-Pd alloy system is still controversial.

The purpose of the present study is to make clear the process of the martensitic transformation in the Fe-Pd alloy system and the correlation between fcc-fct and fcc-bct martensitic transformations by means of optical and electron microscopy.

II. Experimental Procedure

Buttons of Fe-23.6~31.8 at%Pd alloys were prepared by melting 99.9% pure electrolytic iron and 99.95% pure palladium in an arc furnace. After homogenizing at 1373 K for 216 ks, they were sliced, and rolled into 40 μm thick foils. The foils were solution treated at 1173 K for 3.6 ks and quenched into iced water to obtain the disordered austenite phase. Otherwise, the alloy will be inevitably subjected to the two phase separation between the α -Fe(Pd) solid solution and the FePd ordered phase. The perfectly disordered single phase structure of the quenched specimens was checked by electron microscopy, electron and X-ray diffraction.

Some single crystals with the concentrations around 30 at%Pd were made by the Bridgman

method. The crystals obtained were sliced normal to their growth direction by a discharge cutting machine. The slices were chemically polished in a mixed solution of hydrogen fluoride, hydrogen peroxide and distilled water, and subjected to optical observations under a microscope equipped with a cooling and heating stage. A specimen 0.5 mm thick, on which a copper-constantan thermocouple was directly soldered, was fixed on the stage with a clamping copper plate having a round hole 5 mm in diameter for microscope observation. The obtained lowest temperature was 123 K, and no temperature heterogeneity was detected in the specimen. The transformation behavior of the sliced specimens was fairly different between the upper part and the lower part of the grown crystal, which was the most probable due to the composition difference. The fact that the specimens from the upper part contained more palladium suggests that this difference must have arisen not from the gravitational effect but from the zone refining effect. Nevertheless, the different transformation behavior was useful for achieving the general view and overall consideration of the martensitic transformation in a certain range of alloy compositions.

The M_s temperature was determined for all specimens by optical microscopy, while no change in the electrical resistivity was shown during the fcc-fct martensitic transformation. In addition, the foil specimens were electro-polished at 273 K in a mixed solution of 82% acetic acid, 5.5% perchloric acid, 11% ethanol and 1.5% glycerin, and were investigated by an electron microscope (JEM-200CX). A double tilting cooling gonio-stage was utilized for *in situ* observation, and the temperature was measured by a copper-constantan thermocouple which was drawn up to the specimen position on the gonio-stage.

III. Results and Discussion

1. General aspect of martensitic transformation of Fe-Pd alloy

The alloy concentration dependence of the M_s temperature in the Fe-Pd alloy system determined by the optical microscope observation

Fig. 1 Change in M_s temperatures of martensite in Fe-Pd alloys as a function of palladium concentration.

is shown in Fig. 1. The closed and open circles in the diagram indicate M_s temperatures of fct and bct martensites, respectively. It was found that the change in M_s temperatures is very sensitive to the palladium content. The M_s temperature of fct is lowered by about 10 K by increasing only 0.1 at%Pd, and that of bct changes more steeply with alloy concentration. A closed circle with the downward arrow, located at 31.8 at%Pd, indicates the fact that the fct martensite did not appear on cooling down to the liquid nitrogen temperature. It is expected by extrapolating the M_s temperature curve of fct martensite that the fct martensite can exist below the liquid nitrogen temperature in the palladium concentration region up to 32.0 at%. On the other hand, the fct and bct martensite phases coexisted at room temperature in an Fe-29.4 at%Pd alloy, and the bct martensite was not observed in an Fe-30.6 at%Pd alloy after being cooled to the liquid helium temperature, as indicated by an open circle with the downward arrow at the bottom of the diagram. The result clearly shows that the fct phase is not a metastable phase but a stable low temperature one in the region of palladium content from 30.6 at% to 32.0 at%.

It has been reported by Hultgren and Zapffe⁽¹²⁾ that the bcc martensite phase exists in the Fe-Pd alloys containing Pd less than 20 at%. Furthermore, we confirmed by the X-ray analysis that the fcc austenite phase containing at least Pd less than 24.9 at% was transformed to the bcc martensite phase and an Fe-27.7 at%Pd alloy was transformed to bct martensite. In order to see the difference in the internal structure between the bcc and bct martensites, an electron microscopical observation was carried out. Figure 2 is a bright field image showing the substructure of a bcc martensite leaf in an Fe-23.6 at%Pd alloy. Parallelogram-shaped fragments dispersed in the figure were identified as $\{211\}$ twin plates, and a lot of dislocations were observed in the regions where the twins did not exist. The morphology of these internal defects resembles that of the bcc martensite in an Fe-30%Ni alloy⁽¹³⁾. On the other hand, the bct martensite phase was clearly distinguished from the bcc martensite phase. Figure 3 shows the difference between the X-ray diffraction profiles of the 112 peaks of bcc and bct martensites at room temperature. The lattice parameters and the tetragonality of the bct martensite of an Fe-27.7 at%Pd alloy were determined as $a=0.2942$ nm, $c=0.2998$ nm and $c/a=1.019$ from the peak positions. The lattice parameter of the bcc martensite was $a=0.2953$ nm in an Fe-23.6 at%Pd alloy. In the bct martensite, no parallelogram-shaped fragments were observed. It was found that thin plate $\{112\}$ twins having

Fig. 2 Transmission electron micrograph showing the substructure of bcc martensite of an Fe-23.6 at%Pd alloy, in which parallelogram-shaped $\{112\}$ transformation twins and dislocations were observed.

Fig. 3 112 X-ray diffraction peaks obtained at room temperature showing the difference between the bcc martensite of an Fe-23.6 at.%Pd alloy and the bct martensite of an Fe-27.7 at.%Pd alloy.

Fig. 4 Transmission electron micrograph showing the substructure of bct martensite of an Fe-27.7 at.%Pd alloy, in which $\{112\}$ twins were formed from boundary to boundary.

the thickness of about 10 nm were formed between opposite boundaries in each martensite plate, as shown in Fig. 4. It is not clear whether or not a phase boundary between the bcc and the bct phases exists, and so a dotted boundary line is tentatively drawn at around 26 at.%Pd.

2. Optical microscope observations of fcc-fct martensitic transformation

It was shown in a previous paper⁽⁴⁾ that under an optical microscope surface relief with the contrast of black and white bands appeared during the martensitic transformation from fcc

Fig. 5 A series of optical micrographs showing the formation of fct martensite plates during the cooling process of an Fe-29.6 at.%Pd single crystal.

to fct in the Fe-Pd alloys, but their morphology was not investigated in detail because of polycrystalline specimens, in which grain boundaries may disturb the initiation, growth and extinction processes of martensite. Accordingly, single crystals were mainly used for the observation of morphology in the present experiment.

Figure 5 shows a series of optical micrographs showing the growth process of fct martensite in a single crystal specimen on cooling. The palladium concentration of this specimen is 29.6 at% and M_s temperature is 293 K. The crystallographic orientation of the observed surface is determined by the back Laue reflection method and shown in Fig. 6. Since a small fct martensite region was found in the specimen even before cooling, as indicated by the arrow in Fig. 5(a), the specimen was heated up to 323 K, but the martensite was not transformed to the fcc austenite. This stabilization of martensite is presumably due to the effect of either local residual strain or local concentration fluctuation.

At a cooling speed of 1 K/min, faint bands $3\text{ }\mu\text{m}$ wide appeared dispersedly at about 293 K, and as the temperature was lowered, further banded surface relief became gradually pronounced and extended. This gradual change can be explained in terms of the tetragonality of fct martensite studied by X-ray diffractometry⁽⁴⁾. The average size of the fct regions was about $50\text{ }\mu\text{m}$ in diameter, and the bands in this area were found by the stereographic analysis to be the traces of the (101) and (0 $\bar{1}$ 1) planes. It was

always observed that the bands grew not only in a direction perpendicular to their length, producing new bands side by side, but in a direction parallel to them, increasing their lengths, and that boundary movements in the two directions were always jerky with intermediate pauses of a few seconds, as the temperature was lowered. As the bands grew, their width also increased and the banded structure was coarsened, as the figures (c), (d) and (e) show. Moreover, the preexisted fct bands sometimes shrank, when crossed by another set of fct bands, leaving partially interpenetrated regions, as shown in Figs. 5(d) and (e). These results show that the interfaces between fct variants are mobile and an martensite variant can easily be converted into another variant as a result of the impingement from others.

Another area of the same specimen showed two sets of bands of the (10 $\bar{1}$) and (011) traces, and their slight interpenetration. Such interpenetrated or interwoven sets of bands were frequently observed in the Fe-Pd alloy system. The feature of the transformation was similar to that of In-Tl alloy system⁽¹⁴⁾, but in any case, no substructure was observed in each band under the optical microscope, despite of careful chemical etching.

In order to examine the reverse transformation, the cooled specimen was reheated. On heating, the fcc austenite regions partially arose from the fct martensite regions at 280 K, as indicated by the arrows in the Figs. 7(a), (b) and (c). They expanded like an exhaling faint mist, when the temperature was raised further. At 305 K, most of the fct martensite regions were reversed into the fcc austenite, except the small regions which were already stabilized before cooling, as mentioned before. The characteristic temperatures of this specimen were $M_s=293\text{ K}$, $M_f=270\text{ K}$, $A_s=280\text{ K}$ and $A_f=305\text{ K}$, the temperature hysteresis being about 10 K. The cyclic treatment between cooling and heating showed that the same surface relief appeared and disappeared alternately, even after the specimen was heated up to 30 K above the M_s temperature. This suggests that some residual strains exist after the transformation and they can be a trigger

Fig. 6 Orientation of the specimen used.

Fig. 7 A series of optical micrographs showing the diminution of fct martensite plates during the heating process of an Fe-29.6 at%Pd single crystal.

for the successive transformation. However, the comparison between Fig. 5 and Fig. 7 shows that the reverse transformation does not always follow the process of exact backward motion of the fct bands already grown but also starts with the nucleation of austenite amidst the fct bands. A similar observation was done by Nittono and Koyama⁽¹⁵⁾ on the reverse transformation of fcc-fct of an In-21.0 at%Ti

alloy.

3. Fct-bct martensitic transformation

As described in the previous section, the average domain size of the fct regions which appeared in the beginning of the fcc-fct transformation was about $50\text{ }\mu\text{m}$, which was comparable to the average grain size of the present polycrystalline Fe-Pd specimens. This suggests that in the polycrystalline specimens, the fcc-fct martensitic transformation easily takes place over the whole volume of each crystallite. In the present case, accordingly, it is difficult to confirm if the bct martensite is formed from the fcc austenite directly, or from the fct martensite. Actually, the bct martensite seemed to appear always from the fct phase, as reported in the previous paper⁽⁹⁾.

Figure 8 shows two bct martensite masses appearing at room temperature in the midst of the fct martensite regions in an Fe-29.5 at%Pd single crystal. It was found that the bct martensite emerges from only the fct martensite regions, satisfying a certain specific orientation relationship for the fct martensite. With this composition, the M_s temperature of bct martensite is very close to that of fct martensite, as indicated in the martensite phase diagram of Fig. 1. The fct martensite regions extended on cooling, and consequently some of them turned into bct martensite regions. However, no bct martensite appeared from the fcc austenite regions during the cooling process. The results show that there are fcc-fct and fct-bct martensitic transformations in the Fe-Pd

Fig. 8 Optical micrographs of an Fe-29.5 at%Pd single crystal taken at room temperature showing the appearance of bct martensite masses in the fct martensite regions.

alloy system. The orientation relationship between the fct and bct martensites is not yet fully determined.

On heating, the fct bands were observed to disappear without interfering with the existence of the bct martensite. This indicates that the shape memory is not affected by the existence of the bct martensite if the alloy is used above the M_s temperature of bct martensite. The reverse transformation from bct to fct martensite could not be observed, because the A_s temperature of bct martensite was so high that the phase separation started before the reverse transformation from the bct martensite to the austenite.

4. Transmission electron microscope observations of fcc-fct martensitic transformation

In situ electron microscope observations of the fcc-fct martensitic transformation were performed using Fe-29.8~31.2 at%Pd polycrystalline specimens. Figure 9 reproduces a typical electron micrograph and a diffraction pattern showing the appearance of plate type structures, taken at 263 K for an Fe-29.8 at% Pd alloy whose M_s temperature was determined from optical microscopy to be 268 K. The thickness of these plates is about 10 nm, and the streaking in the $[101]$ direction is observed on the diffraction pattern. The foil orientation was close to the $[110]$ direction, and $1\bar{1}1$ series of

Fig. 9 Transmission electron micrograph and the diffraction pattern of an Fe-29.8 at%Pd alloy taken at 263 K showing the appearance of thin plate type structures having the trace of (101) plane.

Fig. 10 Transmission electron micrograph of an Fe-29.8 at%Pd alloy taken at 260 K showing the grown-up thin plate type structures under the *in situ* observation.

reflections were excited. Under the electron microscope, several thin plates which had the traces of (101) planes appeared suddenly at 268 K with a few hundred nm in length, as seen for instance in the center of the photograph, and each plate instantly increased its length. This fact shows that their emergence takes place with the macroscopic shear movements of lattice planes. On further cooling, they extended up to the specimen edge, or the grain boundary, and also new plates emerged among the preexisted plates, and their density increased, as shown in Fig. 10 which was taken at 260 K. It was characteristic that the increase in thickness of each plate was not observed. During the cooling process, some different sets of those plates appeared with traces of other $\{110\}$ planes and grew together with the first set of parallel plates.

In the reverse process, each plate began to shrink from the specimen edge, or the grain boundary. The reverse process traced back the original growth of the plate structure produced on cooling.

With the above observations, it must be noted that the size of the thin plate structure is two orders of magnitude smaller than that of fct bands observed by optical microscopy. It seems that the difference is too large to be interpreted only by the thin foil effect. More plausible interpretation is that the thin plates appearing in the electron micrograph correspond to internal twins of fct martensite.

However, it is difficult to decide whether they are fct martensite themselves or the internal twins, because both of them could satisfy the same $\{110\}$ twin orientation relationship. If they are internal twins, the matrix must be already transformed to the fct phase. Therefore, it will be difficult to determine the so-called Ms temperature only by the *in situ* electron microscope observation, suggesting that the fcc-fct martensitic transformation is of the second order.

IV. Conclusion

The martensitic transformation in the Fe-Pd alloy system has been studied by means of X-ray diffraction analysis, optical and electron microscopy, by using single crystals containing about 30 at%Pd and polycrystalline specimens containing 23.6~31.8 at%Pd. The results are summarized as follows:

(1) The fcc-bcc martensitic transformation took place in Fe-Pd alloys containing palladium less than 25 at%, and the bct martensite, which appeared in the palladium concentration region higher than 27 at%, was identified as a different martensite from the bcc martensite. Both the bcc and bct martensites were nonthermoelastic, but their internal structures were different.

(2) At higher concentrations than 27 at%Pd, the fcc-fct and fct-bct martensitic transformations were observed. The concentration of the stable fct martensite was determined to be from 29.5 to 32 at%Pd below room temperature, and it was shown that the fct martensite was not a precursor of the bct martensite but a stable low temperature phase.

(3) The process of fcc-fct martensitic transformation on cooling and heating was studied in detail by means of *in situ* optical and electron

microscopy. The boundaries between the fct variants and those between the fct and fcc regions were mobile forward and backward on cooling and heating, showing that the process was reversible.

(4) The trace of fct bands observed under an optical microscope was confirmed to be along the $\{101\}$ planes.

Acknowledgment

This work was partly supported by a Grant-in-Aid for Scientific Research from Ministry of Education, Science and Culture, Japan.

REFERENCES

- (1) J. S. Bowles, C. S. Barrett and L. Guttaman: Trans. AIME, **188** (1950), 1478.
- (2) Z. S. Basinski and J. W. Christian: J. Inst. Metals, **80** (1951-52), 659.
- (3) D. P. Dunne and C. M. Wayman: Met. Trans., **4** (1973), 137.
- (4) T. Sohmura, R. Oshima and F. E. Fujita: Scripta Met., **14** (1980), 855.
- (5) K. Otsuka and K. Shimizu: Scripta Met., **11** (1977), 757.
- (6) N. Cowlam, G. E. Bacon and L. Gillot: J. Phys. F; Metal Phys., **2** (1977), 2315.
- (7) A. Kussmann and K. Jessen: J. Phys. Soc. Japan **17** Suppl. **B1** (1962), 136.
- (8) A. Kussmann: Phys. Z., **38** (1937), 41.
- (9) R. Oshima: Scripta Met., **15** (1981), 829.
- (10) M. Matsui, T. Shimizu, H. Yamada and K. Adachi: J. Magn. Magn. Mat., **15-18** (1980), 1201.
- (11) M. Foos, C. Frantz and M. Gantois: Proc. of Int. Conf. on Martensitic Transformations, ICOMAT 82, Leuven (Belgium), (1982), 389.
- (12) R. Hultgren and C. A. Zapffe: Nature, **142** (1938), 395.
- (13) K. Shimizu: J. Phys. Soc. Japan, **17** (1962), 508.
- (14) Z. S. Basinski and J. W. Christian: Acta Met., **2** (1954), 148.
- (15) O. Nittono and Y. Koyama: J. Japan Inst. Metals, **42** (1978), 56 (in Japanese); Trans. JIM, **23** (1982), 285.