Low Temperature Transformation of Fe-Pd and Fe-Pt Invar Alloys

著者	Matsui Masaaki, Adachi Kengo, Asano Hidefumi
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	29
number	特別号
page range	61-66
year	1981
URL	http://doi.org/10.50974/00043272

Sci. Rep. RITU A29, Suppl.1 (1981)

Low Temperature Transformation of Fe-Pd and Fe-Pt Invar Alloys

Masaaki Matsui, Kengo Adachi and Hidefumi Asano

Department of Iron and Steel Engineering, Faculty of Engineering

Nagoya University, Chikusa-ku, Nagoya

Synopsis

Low temperature structures of Fe-Pd and Fe-Pt alloys in the Invar region have been determined by means of low temperature X-ray diffraction experiment. The phase diagrams are obtained. A new fct phase is found in the ordered and disordered Fe-Pt and the disordered Fe-Pd systems. An effect of the degree of order for Fe_3Pt to the structural transformations are examined. The lattice instability of Fe-based fcc Invar alloys are discussed from the low temperature structures with the lattice softening effect and the lattice distortion anomaly.

I. Introduction

Fe-based fcc Invar alloys such as Fe-Ni, Fe-Pd and Fe-Pt systems, contain 60 to 76%Fe. The composition is situated closely to the martensitic transformations. As a basic Invar problem, it is desirable to elucidate relations between the martensitic transformation and the Invar anomaly.

Toward solving this problem, temperature dependences of the elastic stiffness constants C_{ij} of Fe-Ni and Fe-Pt Invar alloys and the Young's modulus of Fe-Pd Invar were reported by Hausch and Warlimont[1,2] and Nakayama et al.,[3] respectively and the low temperature Debye temperature Θ_M of Fe-Ni Invar[4] was reported by present authors.[4] Moreover a random static atom displacement of Fe-Ni Invar at low temperatures was evaluated from Θ_M.[5] For the Fe-Pd Invar, a new face centered tetragonal structure was confirmed by present authors.[6,7] It seems that the decrease of C_{ij} and Θ_M associated with a lattice softening effect and the atomic displacement are strongly related to the lattice instability of the Fe-based Invar alloys.

In the present paper, in order to make clear the lattice instability, low temperature structures of Fe-Pd and Fe-Pt Invar alloys are investigated in detail by means of low temperature X-ray diffraction experiment and a unified discussion on the lattice instability of the Fe-based Invar alloys is given.

II. Experimental procedures

Purities of elements prepared were 99.99%, 99.95% and 99.95% for Fe, Pt and Pd, respectively. After melted in a plasma-jet furnace, the alloys were annealed at 1373 K for more than 7 days in the silica tube for the homogenization. The loss of the weight of alloys during the above procedure was too small to shift the weighted composition. The well ordered Fe-Pt alloys were slowly cooled from 1173 K to 570 K during 1 month. The partially ordered alloy was cooled at the rate of 3 degree a minute. The degree of order of Fe_3Pt superlattice was evaluated by comparing the intensity of the (100) and (110) peaks with that of (200) and (220).

A low temperature cryostat (Oxford Instr.) was utilized for the powder X-ray diffraction experiment. The temperature range of X-ray experiment was 21.5 to 300 K, measured by a AuCo-Cu thermocouple buried in the powder sample.

III. Results

1. Fe-Pd Invar

The martensitic transformation of the Fe-Pd Invar alloys ($\leq$ 30% Pd) has been believed for a long time as a simple transformation between the fcc and bcc structures. Recently, however, we have found a new face centered tetragonal (fct) phase[6,7] in the composition range 29.5% to 33.5%Pd at low temperatures.

Fig. 1 shows X-ray diffraction patterns of 32%Pd at various temperatures. Below 140 K, the peaks (200) and (220) split into two peaks (200)+(020), (002) and (220), (202)+(022), respectively, though the (111) peak remained as a single peak. The fct structure is clearly seen at 32 K. Thus the temperature dependences of the lattice constants and the ratio c/a are shown in Fig. 2. The lattice constants change gradually in the transformation region and the volume change accompanied with the transformation is estimated to be 0.16% for the

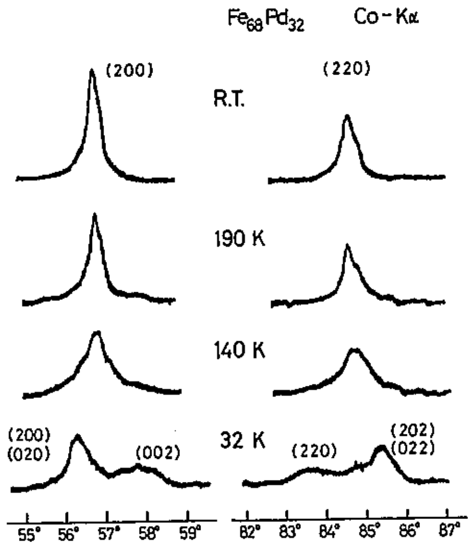

Fig.1. X-ray diffraction patterns at various temperatures for 32%Pd alloy.

32%Pd alloy. The low temperature phase diagram of the samples quenched from 1423 K is determined as shown in Fig. 3. The phases α, γ and γ' in the figure mean bcc, fcc and fct structures, respectively. The transformation γ to γ' is thermo-elastic and the thermal hysteresis is about 20 K. The upper figure in Fig. 3 indicates a composition dependence of the tetragonality (c/a) extrapolated to 0 K. Here we define $c/a=1$ and $c/a=1/\sqrt{2}$ for fcc and bcc lattices and fct and bct signify the lattice having the c/a value near fcc and bcc, respectively. The c/a value decreases from unity (34%Pd) to 0.92 (30%Pd) and the two phases of fct and bcc co-exist in the region 28% to 29.5%Pd. In this region, the volume ratio of bcc and fct phases at room temperature was changeable by the quenching speed from 1423 K. The volume of bcc phase increased after quenched to low temperature. Therefore it is concluded that the fct phase irreversibly transforms to bcc one. Between fct and bcc phases, any distinct bct structure could not be observed in this composition region, though the half width of Bragg reflection of bcc was larger than that of fct.

On the other hand, Θ_M of alloys in the fcc region has been measured by the same method to the case of Fe-Ni Invar alloys.[4] In the case of 34%Pd alloy, Θ_M decreases remarkably at low temperatures. So that the random static displacement are contained in this alloy as well as in the Fe-Ni Invar alloys.[5] The origin

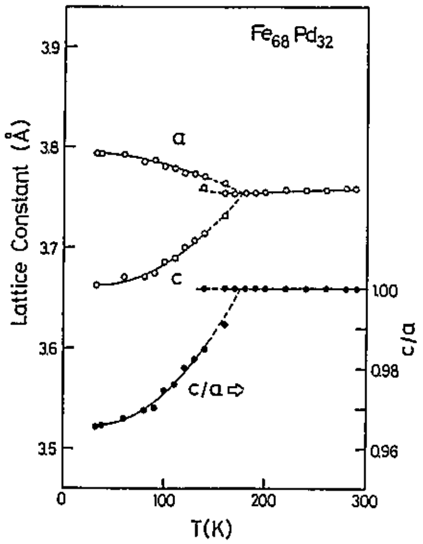

Fig.2. Temperature dependence of lattice constants of 32%Pd alloy.

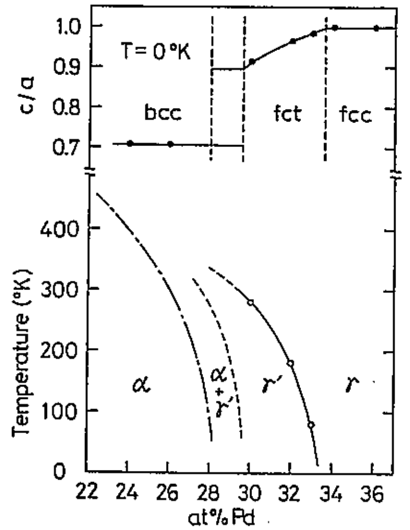

Fig.3. Low temperature phase diagram of Fe-Pd Invar alloys. Upper figure indicates the composition dependence of c/a (see text).

of the displacement can be interpreted to be due to the atomic volume of the low spin state of Fe atoms.

2. Fe-Pt Invar

Though the bct structure of the ordered Fe_3Pt less than 24%Pt has been reported by some authors[8,9] with respect to the martensitic transformation, the detailed structure of the disordered alloy at low temperatures has not been observed so far, which is important from the standpoint of the low temperature anomaly of Invar.

On the other hand, a fct structure was found for the well ordered alloys near 25%Pt by ref. (10) and the present authors,[11] though the structure was not observed by refs. (8) and (9). The discrepancy between the results is expected to be due to the degree of order (S) of Fe_3Pt superlattice. Therefore further investigations on the samples with different S value were carried out. The precise results will be published elsewhere.

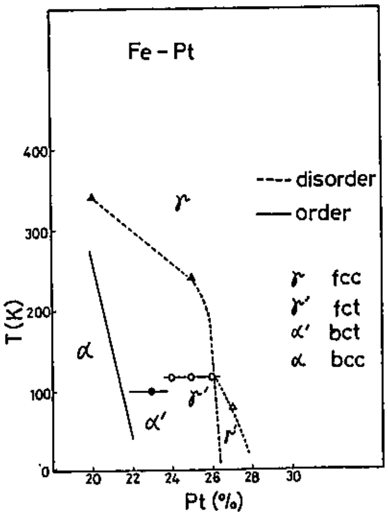

Fig.4. Low temperature phase diagram of Fe-Pt Invar alloys. Solid and dashed curves indicate the well ordered and disordered alloys, respectively.

As the results, Fig. 4 shows a low temperature phase diagram of Fe-Pt Invar alloys. The structures of the well ordered 23, 25 and 27% Pt alloys at the lowest temperature is bct(α'), fct(γ') and fcc(γ), respectively, while that of disordered 25, 27 and 28%Pt alloys quenched from 1423 K is bcc(α), fct and fcc, respectively. The transformation temperatures are indicated by solid and dashed curves in Fig. 4. From the present investigation, the following conclusions on the low temperature transformations of Fe-Pt Invar are given: For well ordered alloys, fcc→bct for less than 23%Pt, fcc→fct for 24 to 26 %Pt and no transformation for more than 27%Pt; while for the disordered alloys, fcc→bcc for less than 26%Pt, fcc→fct for 26 to 28%Pt and no transformation for more than 28%Pt. Thus a new fct phase was found in the ordered and disordered Fe-Pt Invar alloys similar to the case of Fe-Pd Invar mentioned above.

In the next place, an effect of the degree of order to the transformations was examined for the 25%Pt alloy having a partially ordered state. The degree of order $S \fallingdotseq 0.45$ was determined by X-ray diffraction. The single partially ordered state was confirmed by the measurement of the magnetic Curie temperature. The X-ray diffraction patterns at various temperatures are shown in Fig. 5. The fcc structure transforms to fct at 120 K and immediately the fct transforms to bct below 90 K. Where the transformation point of fcc→fct was defined as a broadening temperature of the (200) and (400) peaks, though the half width of the reflections (111) and (222) did not change at this point. Below 90 K two phases fct and bct coexist each other. It should be noted that the peak broadening between 120 K and 90 K signify a local tetragonal distortion along the three cubic axes in the crystal, that is, a short range distortion and when the temperature is decreased below 90 K, a long range tetragonal distortion takes place.

In Fig. 6, temperature dependences of the lattice constants for these phases are shown. In the fct phase, the c/a value changes co-operatively, while in the bct, it nearly keeps a constant below 90 K. The extrapolated c/a values to 0 K are given to be 0.96 and 1.06 for fct and bct respectively. The volume change owing to both the transformations fcc→fct and fct→bct is less than 0.4% and fct phase has a largest atomic volume.

Thus we have found the transformations of the partially ordered 25%Pt as fcc→fct→bct and the transformation points depend on the degree of order. The variation of these transformations is important to clarify the microscopic mechanisms of martensitic transformation of the iron based Invar alloys.

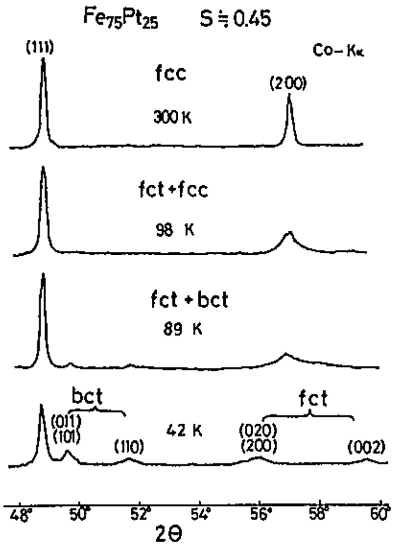

Fig.5. X-ray diffraction patterns at various temperatures for partially ordered (S≒0.45) 25%Pt alloy.

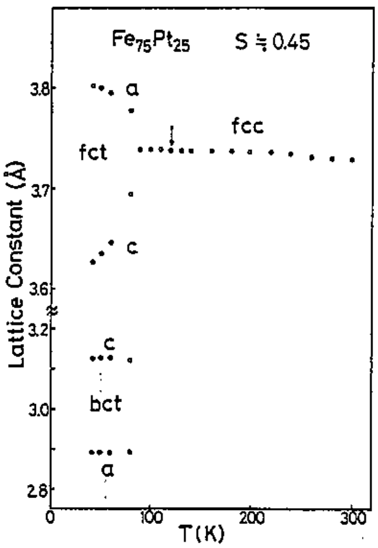

Fig.6 Temperature dependence of lattice parameters of partially ordered (S≒0.45) 25%Pt alloy. The arrow indicates the broadening temperature of (200) and (400) reflections (see text).

IV. Discussion

As mentioned above, the low temperature structures of Fe-Pd and Fe-Pt Invar alloys were made clear, that is, the martensitic transformation does not take place as a simple fcc to bcc transition, but it occurs through a few steps of the structural change.

On the other hand, even in the fcc phase above the martensitic transformation point in Fe-Ni, Fe-Pd and Fe-Pt Invar alloys, the lattice softening effects were observed for the Debye temperature,[4] the elastic constants[1-3] and the phonon dispersion.[12,13] Besides, these alloys showed the lattice deviation anomaly in the fcc phase: For the Fe-Ni and Fe-Pd alloys it appeared as a random static displacement from the regular fcc lattice point, while for Fe-Pt alloys (ordered and disordered), the local distortion was observed. The lattice softening effect and the deviation anomaly can be interpreted as a pre-martensitic phonomenon. The lattice instability of the Fe-based Invar alloy is induced by them under the same microscopic origin. The origin of the lattice deviation anomaly can be explained by the volume difference between high and low spin states of Fe atoms.[5]

The present investigation was partly supported by the Grant-in-Aid for Cooperative Research from Ministry of Education.

References

1) G. Hausch and Warlimont: Acta Metall. 23 (1978) 201.
2) G. Hausch: J. Phys. Soc. Jpn. 37 (1974) 819, 824.
3) T. Nakayama, M. Kikuchi and K. Fukamichi: J. Phys. F 10 (1980) 715.
$) M. Matsui and K. Adachi: J. Magn. Magn. Mat. 10 (1979) 152.
4) M. Matsui, K. Adachi and S. Chikazumi: J. Appl. Phys. 51 (1980) No. 11.
6) M. Matsui, T. Shimizu, H. Yamada and K. Adachi: J. Magn. Magn. Mat. 15-18 (1980) 1201.
7) M. Matsui, H. Yamada and K. Adachi: J. Phys. Soc. Jpn. 48 (1980) 2161.
8) T. Tadaki and K. Shimizu: Scripta Met. 9 (1975) 771.
9) M. Umemoto and C. M. Wayman: Met. Trans. A 9A (1978) 891.
10) M. Foos, C. Frantz and M. Gantois: "Martensitic Transformations", ICOMAT, Boston (1979).
11) M. Matsui, K. Sumiyama, H. Asano, K. Adachi and Y. Nakamura: to be published.
12) K. Tajima, Y. Endoh, Y. Ishikawa and W. G. Stirling: Phys. Rev. Lett. 37 (1976) 519.
13) Y. Endoh, Y. Noda and Y. Ishikawa: Solid State Commun. 23 (1977) 951.