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MARTENSITE TRANSFORMATIONS IN Fe-Pd ALLOYS

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Abstract.- Martensite transformations in Fe-Pd alloys have been extensively studied by means of X-ray diffractometry, optical and electron microscopy and Mössbauer effect. Successive martensite transformations were found in the Fe-Pd alloys with about 30 at% Pd. The first was a thermoelastic type transition from the fcc austenite to an fct martensite, and the second was of non-thermoelastic type from the fct martensite to a bct martensite. The shape memory effect was found in the alloys which exhibited the thermoelastic nature of the fcc to fct martensite transformation. The stress induced bct martensite was obtained in the alloys with Pd content higher than 30 at%, which did not show thermally induced bct martensite. Only bcc martensite was observed in as-quenched specimens of the alloys with Pd less than 27 at%.

Introduction.- Fe-Ni alloy is a typical ferrous alloy which undergoes a martensite transformation, and a great number of works have been reported on the transformation (1-3). Fe-Pt alloy with nearly 25 at% Pt is another interesting ferrous alloy exhibiting a martensite transformation. The austenite of this alloy has an order-disorder transition (4), and the martensite transformation depends on the long range order parameter (5). A disorder Fe-Pt alloy exhibits a non-thermoelastic martensite transformation, while the ordered alloy with L12 structure transforms thermoelastically. Among many ferrous martensite alloys the ordered Fe-Pt alloy has been known as a material which has a shape memory effect (6). The martensite transformation of this alloy also has been extensively examined (7-9).

The martensite transformation of Fe-Pd system has been less studied, in spite of the Pd position between Ni and Pt in the same column of the periodic table. The fcc-bcc martensite transformation was reported for an Fe-Pd alloy containing less than 20 at% Pd (10). On the other hand, the present authors and coworkers investigated Fe-Pd alloys with about 30 at% Pd and found a thermoelastic martensite transformation from the fcc austenite to an fct martensite (11). Similar fcc-fct phase transition was also reported in partially ordered Fe-Pt alloy (12,13). Recently it was found that the fct martensite of Fe-Pd alloys further transformed to a bct martensite non-thermoelastically (14).

In the present study the martensite transformations of Fe-Pd alloys containing Pd from 23 to 32 at% were investigated by means of various experimental techniques, and they were summarized. The stress effect and alloying effect on the martensite transformations were also studied.

Experimental.- Fe-Pd buttons containing Pd from 23.6 to 31.6 at% Pd were prepared by melting electrolytic iron and 99.9% palladium in an arc melting furnace. They were rolled to sheets 40 μm thick after homogenizing. The specimen sheets were solution treated at 900°C for 10 ks and quenched into iced water.

The martensite transformation was examined by X-ray diffractionmetry, optical and electron microscope observation and the Mössbauer spectroscopy.

Results and discussion.- Fig.1 is a sequence showing optical micrographs of surface relief effect by transformation of an Fe-29.7 at% Pd alloy on cooling. Some faint striped surface reliefs are already seen in the picture (a) taken at 15°C. As the temperature was successively lowered to -65°C, they became more distinct and the num-
ber increased as shown in the picture (c). These reliefs disappeared on heating from \(-85^\circ\)C to \(40^\circ\)C. The appearance and disappearance of the surface reliefs were reversible in thermal cycles between \(40^\circ\)C and \(-85^\circ\)C. Upon further cooling from \(-85^\circ\)C a burst type transformation was observed to take place simultaneously in several grains at \(-90^\circ\)C as in the picture (d), which was taken at \(-96^\circ\)C. Although the new surface relief contrast looked quite different from the preceding ones, their morphology approximately followed that of the former reliefs. The new surface reliefs never reverted to the state of picture (a) on heating up to room temperature.

X-ray diffractometry of this specimen was carried out between \(40^\circ\)C and \(-196^\circ\)C. Fcc austenite peaks were observed at \(40^\circ\)C, and the lattice parameter was 0.3750 nm. Upon cooling the specimen, the broadening of \([200]\) and \([220]\) peaks was found to occur at \(23^\circ\)C, where the surface relief effect was first seen by the optical microscope observation. With decreasing temperature from \(23^\circ\)C to \(0^\circ\)C split of each \([200]\) and \([220]\) peak into a triplet was observed, and the outer two peaks gradually became intense and well separated at the sacrifice of the original peak in the center. Upon successive cooling from \(0^\circ\)C to \(-80^\circ\)C the original fcc peaks no longer existed, and the separation of the outer peaks became large. The intensity ratios of the lower to the higher angle peak of the doublet of the \([200]\) and \([220]\) peaks were about 2 and 0.5. On the other hand, no change in the \([111]\) peak was observed. The X-ray diffraction results indicate that the fcc austenite transforms to an fct phase, and the degree of tetragonality of the fct structure developed with decreasing temperature, suggesting that this transition has the second order like nature. The lattice parameters were \(a=0.3860\) nm and \(c=0.3636\) nm, and the axial ratio of \(c/a\) was 0.916 at \(-80^\circ\)C. When raising the temperature from \(-80^\circ\)C to \(40^\circ\)C, the lattice parameters turn to the value of the original fcc phase, and the temperature hysteresis of the lattice parameter change by cooling and heating cycle was very small. The above reversible surface relief effect and small temperature hysteresis of the lattice parameter change indicate that the alloy undergoes a thermoelastic martensite transformation from fcc to fct. Upon further cooling below \(-90^\circ\)C new additional peaks which were attributed to a bct phase suddenly appeared. Coexistence of the fct peaks with new bct peaks continued down to \(-196^\circ\)C, though the fct peaks became too small to determine the lattice parameter below \(-130^\circ\)C due to the transition from the fct to the bct phase. The bct peaks were left by the subsequent heating to room temperature. The lattice parameters of the bct were \(a=0.296\) nm and \(c=0.300\) nm. Accordingly, it is concluded that a non-thermoelastic type martensite transformation takes place further from the fct martensite to the bct in this alloy.

The shape memory effect was found in this alloy, associated with the thermoelastic fcc to fct martensite transformation. When the fct martensite was deformed and heated up through the reverse transition temperature, the specimen shape returned to the original shape. The shape memory effect, however, was lost once the bct martensite formed. X-ray diffractometry was performed for another Fe-Pd alloys too. In Fig.2 are shown some of the results. As seen in this figure, the fcc to fct transformation temperature shifted to lower temperature with increasing Pd content, and no fct-bct martensite transformation appeared when the Pd content exceeded 30at%.

The process of martensite transformation was also observed by electron microscopy.
Fig. 2: Change in lattice parameters and c/a for various Fe-Pd alloys on cooling.

Fig. 3 is an electron micrograph of the austenite of Fe-30.6 at% Pd taken at room temperature, showing a fine complicated image contrast. The selected area diffraction pattern of the austenite showed that the fcc reciprocal lattice spots were accompanied by satellite spots situated in the incident spot side on the <111> rows, suggesting that the fcc austenite becomes nonuniform. Streaks of both fundamental and satellite spots parallel to <011> were also found, possibly due to the disturbance of [011] stacking of the austenite. On cooling the specimen to a temperature just below the fcc to fct transformation, a tweed pattern appeared as seen in Fig. 4, and diffuse streaks were clearly observed along <011> directions of the diffraction pattern. With decreasing temperature, a banded structure began to nucleate at grain boundaries of the austenite as in Fig. 5. It was found that the banded structure consisted of microtwins with the twin planes parallel to [1[1]]. As the fcc to fct transition proceeded on cooling, the microtwin density increased with developing the degree of tetragonality. The subsequent non-thermoelastic martensite transformation from fct to bct was observed to take place suddenly on further cooling. In Fig. 6 is bct martensite of Fe-29.7at% Pd transformed in bulk by sub-zero treatment. It is notable that {112} internal
twins penetrate the whole martensite variant crystals, and no mid-rib is seen. Although the traces of (011) twin faults in the fct martensite sometimes remained in the bct martensite, it was not clear whether the (011) twin faults of the fct martensite are related with new (112) faults of bct martensites. With decreasing Pd concentration, only bct martensite became to be observed in an as-quenched specimen as shown in the photograph for Fe-27.7 at% Pd in Fig.7. The morphology of the bct martensite was quite similar to that of sub-zero cooled specimens of Fe-29.7 at% Pd, suggesting that the alloy also undergoes a martensite transformation from fcc to bct martensite through an fct structure. The X-ray diffraction patterns of Fe-Pd alloys containing less than 27 at% Pd indicate that the structure of martensite is not bct but bcc. The electron micrograph of Fig.8 shows the bcc martensite of an Fe-23.6 at% Pd alloy, of which microstructures are very similar to those reported for Fe-Ni alloys (1-2). As seen in Fig.2, no thermally induced martensite of bct structure was obtained in Fe-Pd alloys with Pd content higher than 30 at%, but this type of martensite appeared in the alloys with mechanical stressing. Fig.9 shows the stress induced martensite of Fe-30.6 at% Pd cold rolled at -180°C. Although the microstructure is more complicated than the thermally induced martensite in Fe-29.7 at% Pd, the morphology is almost same. Such a stress induced martensite of Fe-30.6 at% Pd co-existed with the fcc austenite, and their orientation relationship was examined. Since the Fe-Pd system is strongly ferromagnetic, the specimen edge was frequently deformed by the magnetic field of the objective lens of the electron microscope while using the gonio stage, resulting in difficulty in the determination of orientation relation. Careful examinations, however, indicate that the K-S relationship holds between the fcc austenite and the bct martensite. Figs.10 and 11 represent optical microscope observations of stress effect on the martensite transformation of Fe-Pd alloys. The interfaces of the fct martensite moved away and back with loading and unloading, respectively. Such an easy movement of the interface is possibly related
to the shape memory effect of this material. In Fig.11 the specimen was first cooled just below the Ms temperature of the fct to bct transition to obtain some amount of bct martensite as in (a), and it was stressed at this temperature. Additional bct martensites were observed to nucleate at grain boundaries of the fct martensite, suggesting that the internal stress accumulated at the grain boundaries of the fct martensite is relieved by the formation of the bct martensite.

It is considered that the successive martensite transformations of Fe-Pd alloys in the neighborhood of 30at%Pd take place in the following processes. The Mössbauer spectra showed that both fcc and fct phases are typical ferromagnetic, and they exhibit no distinct magnetic structure differences (15). The results suggest that the origin of the present fcc-fct transition is different from another similar type of transition observed in, for instance, Mn-Cu which is associated with an antiferromagnetic ordering of Mn atoms (16). As far as the electron energies of crystals are concerned, structures with higher symmetry become unstable and tend to transform to a lower symmetry lattice with decreasing temperature. This effect has been called a Jahn-Teller effect. Such Jahn-Teller induced phase transitions have been reported in many crystal systems, and, at the same time, lattice softening is found to occur near the transition temperature. Examples were shown in the martensite transition from cubic to tetragonal lattice of Fe-W type compounds Nb3Sn and V3Si (17-19). Recent neutron experiments of the temperature dependence of the elastic constants of Fe-Pd alloys indicated that the C"=1/2·(C11-C12) of Fe-28at%Pd became extraordinarily small near the fcc-fct transition temperature (20). The indication of lattice softening of Fe-31.2at%Pd was also obtained by the measurement of recoil-free fraction of the Mössbauer effect.

Fig.12 represents the temperature dependence of the total area of a Mössbauer spectrum which is normalized by the value of room temperature. With decreasing temperature, the area begins to decrease at a temperature several ten degrees above the fcc-fct transition temperature (Ms), and exhibits another temperature dependence in the fct phase. This means that the fcc austenite becomes soft before the transition. Concerning the atomic process of the present fcc-fct transition, a double shear mechanism of [111]<111> will be the most probable, which was already discussed in In-Cd (21) and Fe-Pt (13), because the mechanism is achieved by coupling the shear waves of soft phonon modes of [111]<111>. When temperature is lowered to the fcc-fct transition temperature, microdomains with tetragonal distortion are randomly nucleated by the austenite instability. Below the transition temperature, the preferential growth of such a domain with a particular c-axis occurs by means of the above-mentioned double shear mechanism.

Fig.11: Formation of stress induced bct martensite from partly thermal induced bct martensite of Fe-29.6at%Pd.

Fig.12: Temperature dependence of the Mössbauer absorbed area of Fe-31.2at%Pd.

Fig.13: Lattice parameter change of Fe-Pd-X alloys with cooling.
and at the same time [011] micro twins are introduced to relieve the strain induced by the formation of tetragonal martensite in the cubic lattice. Their density increases until the tetragonality develops to the axial ratio of 0.916. At lower temperatures the twin density becomes too high to nucleate more twins, and further cooling stores internal stress enough to trigger a burst martensite transformation to bct. The energy to induce a bct martensite is also supplied by mechanical stress. Such a stress induced martensite was observed in an Fe-30.6at%Pd alloy, which did not show thermally induced bct martensite transformation. As seen in Fig.2 the martensite transformation temperatures depended on the Pd concentration, suggesting that this transition was associated with the electronic structure of the alloy as aforesaid. In order to change the electronic band structure of the alloy, 2% of Pd was substituted by Ni, Pt, Rh or Ir which situated near Pd in the periodic table. Examples of the alloying effect on the lattice parameter change are shown in Fig.13 for Fe-Pd-Ni and Fe-Pd-Rh alloys, both of which exhibited a thermoelastic martensite transition from fcc to fct, but not fct to bct martensite transition. The shape memory effect was found in all of the alloys studied between -196°C and room temperature. The internal field distribution of the transmission spectrum from austenite was different from alloy to alloy, but no remarkable effect on the fcc-fct transition was found yet. For further detailed discussions electronic band structure calculations of the Fe-Pd alloy system will be needed.

Conclusions.- (1) The martensite transformations and their transformation temperatures of Fe-Pd alloys remarkably depend upon the Pd concentration. The martensite transformation of this alloy system is summarized in the following.

(i) Pd < 27at%, fcc non thermoelastic bcc,
(ii) 27at% < Pd < 30at%, fcc thermoelastic fct non thermoelastic bct,
(iii) 30at% < Pd < 31.5at%, fcc thermoelastic fct,
(iv) 31.5at% < Pd, no thermally induced martensite transformation.

(2) The thermoelastic phase change from fcc to fct, which is associated with lattice softening, is close to the second order transition, and it will be achieved by the same double shear mechanism as reported in In-Cd and Fe-Pt.

(3) The shape memory effect, which is associated with the thermoelastic type transition from fcc to fct, is found in Fe-Pd alloys. Stress induced martensite transformation takes place from fct to bct in the Fe-Pd alloys with more than 30at%Pd which exhibit no thermally induced bct martensite transformation.

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