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A new type of FCT martensite phase in single-crystalline Fe_3Pt Invar alloy

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HIGHLIGHTS

- TEM observations at room temperature reveal that the specimen is a single phase of $L1_2$-type structure.
- The spontaneous magnetization and magnetic susceptibility curves of Fe_3Pt with $S = 0.88$ have bend points at 60 K.
- XRD measurements reveal that this alloy exhibits a martensitic transformation to FCT and the transformation temperature is 60 K.
- The tetragonality c/a is larger than unity in the FCT martensite.
- This tetragonality is in contrast to the tetragonality $c/a < 1$generally observed in the FCT martensite with $S < 0.8$.

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ABSTRACT

Martensitic transformation in a highly ordered Fe_3Pt has been investigated by magnetization and X-ray diffraction measurements. We confirmed that a new type of face-centered tetragonal (FCT) martensite phase appears below 60 K in Fe_3Pt with a degree of order $S = 0.88$. The tetragonality c/a gradually increases with decreasing temperature, and is approximately 1.005 at 10 K. This is in contrast to the tetragonality $c/a < 1$ generally observed in the FCT martensite with a degree of order less than 0.8. The spontaneous magnetization increases in association with the transformation.

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1. Introduction

Iron–platinum alloys containing approximately 25 at.% platinum are known as Invar alloys and exhibit a negative thermal expansion. These alloys exhibit a disorder–order transformation from an A1-type structure to a $L1_2$-type structure at a temperature of around 1000 K [1]. Martensitic transformations are also observed, and the transformation behavior depends strongly on the degree of order S of the parent phase [2–5]. Up until now, three types of martensite phases have been reported: BCC, BCT, and FCT phases. The BCC martensite forms via a burst-type transformation when the degree of order of the parent phase is very low ($S \approx 0$). If the degree of order is in the intermediate range ($S \approx 0.50$), a thermoelastic transformation from the parent phase occurs and the BCT martensite is formed. For a degree of order $S \approx 0.80$, the FCT martensite forms through a second-like transformation. At the degree of order $S = 0.75$, the tetragonality c/a of the FCT martensite is approximately 0.94. Recently, we made a preliminary experiment of martensitic transformation in a highly ordered Fe_3Pt, and reported the possibility of a new type of FCT martensite phase [6]. In the present study, we have examined in detail the martensitic transformation in a highly ordered Fe_3Pt, and have confirmed the existence of FCT martensite phase in Fe_3Pt with $S = 0.88$, where the tetragonality is totally different from the tetragonality $c/a < 1$ in the FCT martensite generally observed until now.

2. Experimental procedure

An ingot of Fe–25Pt (at.%) was prepared by arc melting using an iron bar (99.99 mass%) and a platinum plate (99.95 mass%). A single-crystalline rod was grown from this ingot by the floating zone method. A disk specimen (3 mm in diameter) with its normal parallel to [0 0 1] was cut from the rod, and a plate-shaped specimen 3.0 mm × 3.0 mm × 0.5 mm in size was cut from the rod so that

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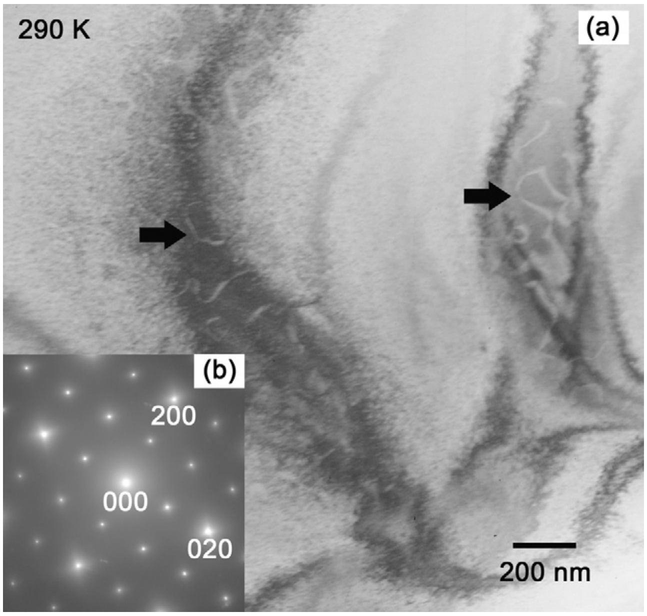

Fig. 1. (a) Bright field image of the parent phase at 290 K. (b) Selected area electron diffraction pattern of the [0 0 1] zone axis.

each edge was parallel to ⟨1 0 0⟩. The samples were homogenized at 1373 K for 24 h, and then slowly cooled from 1073 K to 773 K over 30 days. The degree of order *S* was determined by X-ray diffraction (XRD) to be 0.88. A thin foil for TEM observations was prepared by ion milling. TEM observations were performed by using a HITACHI H-800. The magnetic properties of the alloy were examined by a magnetic property measurement system (MPMS). XRD measurements were made by using a diffractometer with Cu Kα radiation.

3. Results and discussion

First, we checked the microstructure of the present specimen after the ordering heat-treatment by a transmission electron microscope. Fig. 1 shows the bright field image of the parent phase at 290 K (a) and the selected area electron diffraction pattern of [0 0 1] zone axis (b). We can see from the bright field image that the specimen is a single phase state although there are some anti-phase boundaries of the $L1_2$-type phase as indicated by arrows. The electron diffraction pattern is also indexed by single phase of $L1_2$-type structure.

Fig. 2(a) shows the temperature dependence of the spontaneous magnetization of this alloy measured in the cooling process. The same measurements were also made in the heating process, but no hysteresis was detected between the cooling and heating processes. There is a bend point in the spontaneous magnetization curve as indicated by the arrow, suggesting a change in magnetic property at this temperature. Fig. 2(b) shows the temperature dependence of the magnetic susceptibility for a magnetic field of 40 kA/m applied along $[0\,0\,1]_P$ ('P' stands for the 'parent' phase). During the cooling process, the susceptibility starts to increase at 60 K as indicated by the arrow. The characteristic temperature (60 K) common to Fig. 2(a) and (b) is the martensitic transformation temperature T_M ('M' stands for the 'martensite' phase) of the Fe_3Pt alloy, which is confirmed by changes in the XRD pattern. Incidentally, the deviation in the susceptibility obtained by the heating and cooling process is likely due to changes in the configuration of magnetic domains.

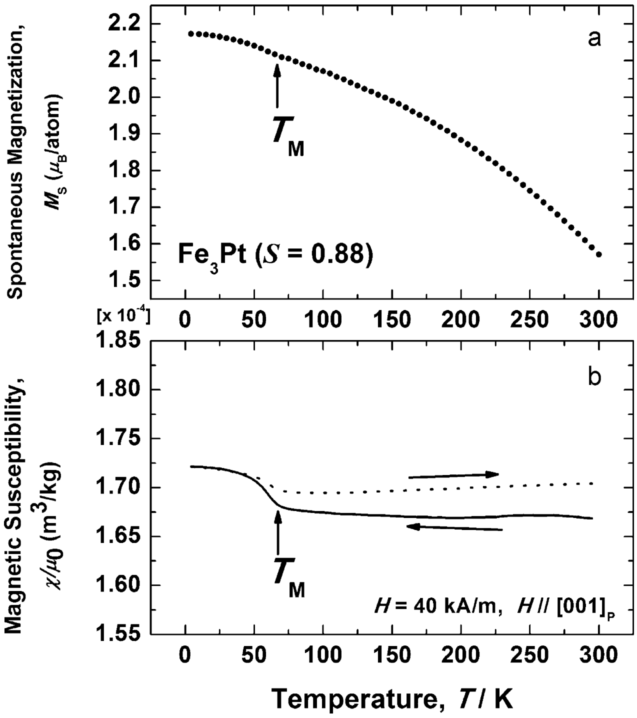

Fig. 2. (a) Temperature dependence of the spontaneous magnetization. (b) Temperature dependence of the magnetic susceptibility. The martensitic temperature T_M is indicated by an arrow.

XRD measurements were undertaken to investigate any structural change of the alloy. Fig. 3 shows XRD diffractograms in the angle range $108° \leq 2\theta \leq 113°$ and temperature range 10–295 K. The single peak for a temperature of 295 K splits into two peaks when the temperature is 10 K. This indicates that the alloy changes from the $L1_2$-type cubic structure to a tetragonal structure. In order to determine the temperature at which splitting starts, we plotted full width at half maximum (FWHM) of the 400_P peak in Fig. 4. The FWHM increases abruptly at 60 K, the temperature at which the spontaneous magnetization and also the magnetic susceptibility exhibits a bend point. Thus, this temperature (60 K) is considered to be a martensitic transformation temperature T_M. An analysis of the XRD results reveals the temperature dependence of the lattice parameters *a* and *c*, unit cell volume, and tetragonality *c*/*a*. The results are shown in Fig. 5. We note that *a* decreases and *c* increases gradually as the temperature decreases in the martensite phase. However, the unit cell volume is relatively constant over the temperature range. It is likely that the martensitic transformation in this alloy is close to second order because the lattice parameters change gradually in association with the transformation. The tetragonality *c*/*a* at 10 K for this alloy ($S = 0.88$) is 1.005. This is significantly different from that of the FCT martensite phase in Fe_3Pt with $S = 0.75$ where the tetragonality *c*/*a* was less than 1 [7].

Then a question arises. That is, what is the structure of low-temperature phase in Fe_3Pt with a certain degree of order $0.75 < S < 0.88$. By considering the mechanism proposed by Bowles et al. [8] to explain the FCC–FCT transformation in In–Tl alloys, the structure could be predicted to be orthorhombic, tetragonal ($c/a < 1$), tetragonal ($c/a > 1$) or cubic ($c/a = 1$). It would be possible for an orthorhombic phase to appear in between the two tetragonal phases. It is known that low-temperature phase in Mn–Ni alloys changes from the tetragonal ($c/a < 1$) phase to the tetragonal ($c/a > 1$) phase via an orthorhombic phase as the composition of Ni increases [9].

Incidentally, highly ordered Fe_3Pt alloys have been investigated by several research groups to ascertain the origin of Invar properties. Sasaki and Chikazumi [10] investigated the magnetic properties such as magnetostriction and magnetic torque in a highly ordered Fe_3Pt with $S \approx 1$ and found that there were anoma-

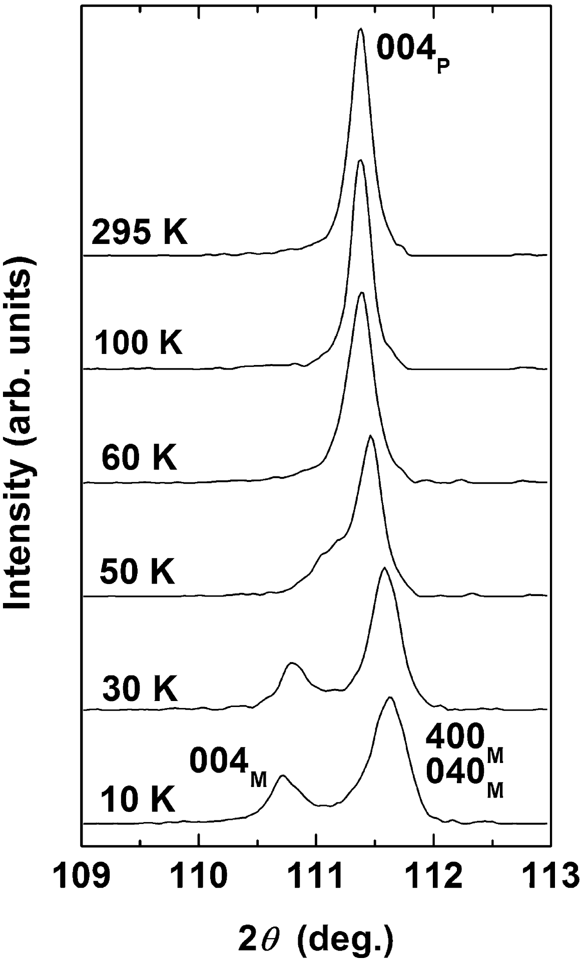

Fig. 3. XRD diffractogram of Fe_3Pt for a degree of order $S = 0.88$ in the temperature range 10–295 K. The $K\alpha_2$ radiations are eliminated.

lies in these physical properties below 60 K. They speculated the existence of a martensitic transformation. Sakashita et al. [11] observed the martensitic transformation below 60 K in Fe_3Pt with $S > 0.75$ by XRD measurements, but concluded that it was caused by the surface strain due to the polishing procedure. Our results suggest that these anomalies are due to the martensitic transformation to the FCT with $c/a > 1$.

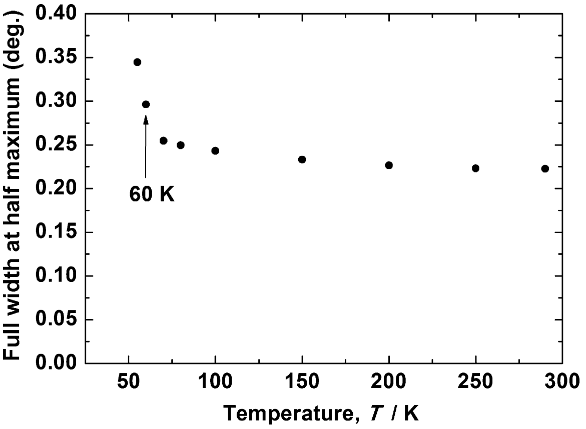

Fig. 4. Temperature dependence of full width at half maximum of 004_P peak.

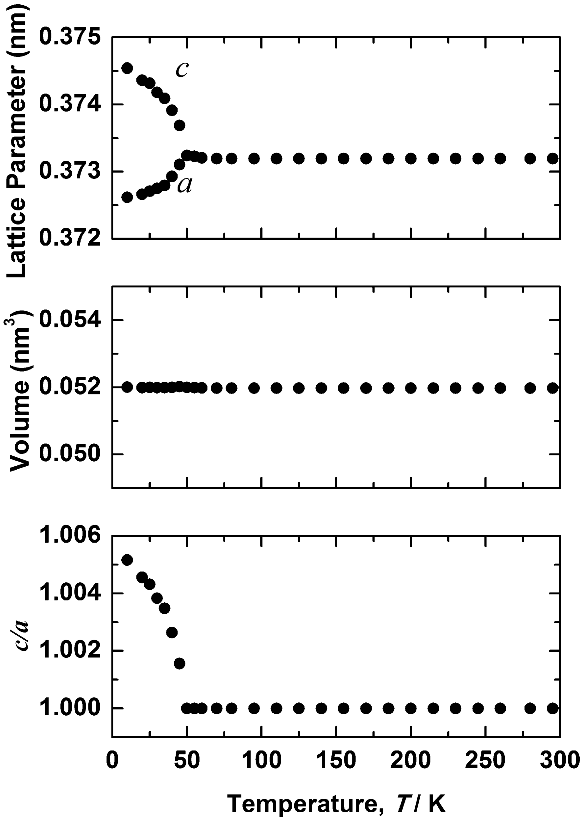

Fig. 5. Temperature dependence of lattice parameters, unit cell volume, and the tetragonality c/a.

4. Conclusions

XRD measurements of a highly ordered Fe_3Pt single crystal with a degree of order of $S = 0.88$ have confirmed a new type of FCT martensitic transformation with a tetragonality $c/a = 1.005$. The magnetization of the FCT martensite phase is larger than that of the parent phase. Fe_3Pt exhibits at least four different martensite phases depending on the degree of order: BCC, BCT, FCT ($c/a < 1$), and FCT ($c/a > 1$). We intend to examine the possibility of an orthorhombic martensite phase in Fe_3Pt in the future.

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