

Regular article

Composition and structure dependence of specific heat of disordered iron-palladium alloys

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ABSTRACT

Depending on Pd content, disordered Fe-Pd alloys take various crystal structures: body-centered cubic (BCC), body-centered tetragonal (BCT), face-centered tetragonal (FCT) and face-centered cubic (FCC) structures. We have measured specific heat of Fe-Pd alloys to understand the lattice stability and electronic state of the alloys. At the phase boundary between FCT and FCC phases, electronic specific heat coefficient shows a local maximum and the Debye temperature shows a local minimum. A local maximum of electronic specific heat coefficient also appears in the BCC region with Pd content of near 10 at.%.

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The binary iron-palladium phase diagram is characterized by the disordered A1-type structure (face-centered cubic structure, FCC) for the whole composition range at elevated temperatures. At lower temperatures, a disordered A2-type (body-centered cubic, BCC) structure, an ordered L1₀-type structure (FePd) and an ordered L1₂-type structure (FePd₃) appear as equilibrium phases in addition to the A1-type structure. The formation of the A2-type, L1₀-type, and L1₂-type structures can be prevented by quenching a specimen to ice water for the whole composition range, and the A1-type structure can be retained without phase decomposition. When the Pd content of an alloy is 33 at.% or lower, the retained A1-type structure is not stable at low temperatures, and the alloy shows a martensitic transformation (MT).

The structure of the martensite phase formed in an Fe-xPd (at.%) alloy depends on Pd content x [1,2]. According to the phase diagram proposed by Sugiyama et al. [1], three types of martensite phases appear in Fe-xPd alloys. The crystal structure of the disordered Fe-Pd alloys at cryogenic temperatures is as follows: BCC for $x < 26$; body-centered tetragonal (BCT) for $26 < x < 30$; face-centered tetragonal (FCT) for $30 < x < 33$. Although the Bravais lattice of the FCT martensite is body-centered tetragonal, we call the martensite as the FCT martensite in this paper following its traditional termination [1,2]. Alloys with $x > 33$ show no martensitic transformation, and the FCC phase retains to absolute zero temperature.

Among the three MTs, the FCC-FCT transformation is weak first-order. This transformation is associated with significant softening in elastic constant $C' = ((C_{11} - C_{12}) / 2)$ [3,4]. Because of the softening

of the lattice, alloys exhibiting the FCC-FCT transformations show various interesting properties. One is rearrangement of martensite variants by the application of magnetic field [5,6,7]. This behavior is related to small detwinning stress of the martensite phase due to the softening of the lattice as well as a large magnetocrystalline anisotropy of the FCT phase [8]. Another is a large elastic-like deformation of >6% when stress is applied in the [001] direction [9]. This behavior is related to the small value of Young's modulus in the [001] direction due to the small value of C' . One more interesting phenomenon is significant elastocaloric effect which appears in a wide temperature range around the FCC-FCT transformation temperature [10,11]. This behavior is related to significant temperature dependence of elastic strain because of softening of C' .

The small value of C' results in small sound velocity in the alloy. Therefore, the Debye temperature is expected to decrease when C' decreases. Measurement of specific heat at cryogenic temperatures is a direct method to evaluate the Debye temperature. Kuang et al. [12] examined composition dependence of specific heat of a series of Fe-Pd alloys and reported that the Debye temperature shows the lowest value at the composition which corresponds to the phase boundary between FCC and FCT phases. They also reported that the electronic specific heat coefficient is the highest at the phase boundary. The high value of specific heat coefficient could be related to the Invar effect of the alloy for the similar behavior was observed in Fe-Ni Invar [13] and Fe-Pt Invar [14] alloys.

Although Kuang et al. [12] reported an interesting composition dependence of specific heat for Fe-Pd alloys as mentioned above, no confirmation has been made by other researchers. In addition, their report is limited to alloys with Pd content of between 30 and 80 at.%; therefore,

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there is no information on the BCC region. Moreover, the temperature range is limited to below 20 K in their report, and no information is available about specific heat at elevated temperatures. We will be able to obtain difference in entropy between the FCC, FCT, BCT and BCC structures as a function of temperature by the specific heat measurements at elevated temperatures. In the present study, therefore, we will reexamine the specific heat in Fe-Pd system by extending the composition range and the temperature range. We also evaluate the electronic specific heat coefficient of disordered Fe-Pd alloys using a first-principles calculation and compare the result with experimentally obtained value.

Button ingots of Fe- x Pd alloys ($x = 5.0, 10.0, 15.0, 20.0, 24.0, 28.0, 31.2, 33.2, 35.0, 40.0, 45.0, 55.0, 60.0, 70.0, 80.0, 90.0$ in at.%) were prepared by arc melting a high purity Fe rod (99.998%) and a Pd sheet (99.9%). After homogenization at 1373 K for 24 h, these specimens were quenched into ice water to retain the disordered parent phase. The alloys as well as pure Fe and Pd were cut into a rectangle sheet with a dimension of about $2.5 \times 2.5 \times 0.5$ mm³ and heat-treated at 1373 K for 2 h in evacuated quartz tubes followed by quenching into ice water. The long range ordering to the L1₀-type structure in the Fe-55.0Pd alloy can be prevented by quenching into ice water from 1373 K [15]. The martensitic transformation temperature of the Fe-31.2Pd alloy is 230 K [9]; that for alloys containing less Pd is above room temperature [1]. The martensitic transformation is missing in alloys containing Pd of 33.2 at.% Pd and more [16]. The magnetic state of the examined alloys is ferromagnetic below room temperature except for pure Pd.

Specific heat was measured by a relaxation method using a physical properties measurement system (Quantum Design PPMS) in the temperature range between 2 K and 250 K considering the temperature limit of the instrument and martensitic transformation temperatures of the examined alloys. In every measurement of the specific heat, the specimen was heated by 2% of its absolute temperature, and the heat capacity was calculated from the relaxation time of temperature decrease. The measurement was repeated three times, and the average was evaluated. In addition, the electronic specific heat coefficient of Fe-Pd alloys was calculated from the electronic density of states. The density of states was evaluated by a Green's function method [17,18] (Machikaneyma2000) with a coherent potential approximation (KKR-CPA method).

Fig. 1(a) shows the specific heat C_p vs temperature T curves of pure Fe, pure Pd and Fe-33.2Pd alloys in the temperature range between 2 K and 250 K. The specific heat of the Fe-33.2 Pd alloy is between Fe and Pd, but the value exceeds that of Pd in the temperature range of

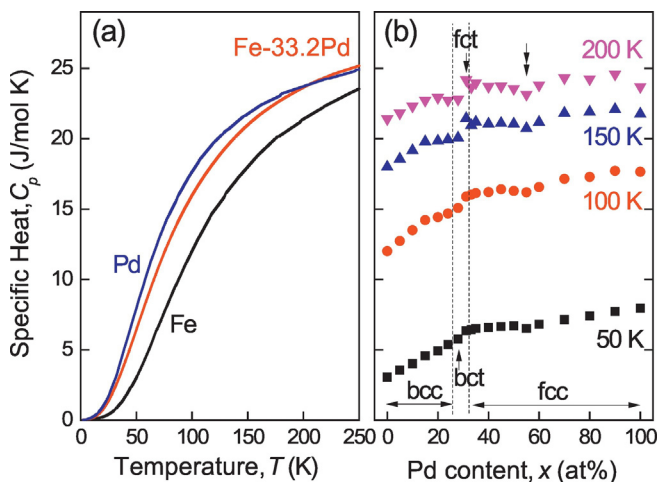


Fig. 1. Specific heat C_p as a function of temperature T of pure Fe, pure Pd and Fe-33.2Pd (at.%) alloy in the temperature range between 2 K and 250 K (a), and composition dependence of specific heat C_p at selected temperatures of 50 K, 100 K, 150 K and 200 K of Fe- x Pd alloys (b).

above 210 K. We obtained similar curves for other alloys (refer to Supplementary Fig. S1), and the composition dependencies of specific heat at selected temperatures of 50 K, 100 K, 150 K and 200 K are plotted in Fig. 1(b). In the figure, we notice that C_p of the BCC and BCT phases is distinctively lower than that of the FCT and FCC phases. We also notice a dip at the Pd content of approximately 55 at.% in the FCC region. The dip becomes significant with increasing temperature. The reason of the appearance of the dip is not clear but could be related to short range ordering of Fe-Pd alloys with Pd content of near 55 at.%. The decrease of specific heat by ordering heat-treatment in an Fe-50.0Pd alloy was reported by Kuang et al. [12]. Presumably, the short range ordering cannot be prevented by conventional ice water quenching in Fe-Pd system in the composition range where the L1₀-type ordered phase is the equilibrium phase.

Specific heat at cryogenic temperatures is frequently plotted as C_p/T vs T^2 . Fig. 2 shows the relation in the temperature range between 2 K and 10 K. We notice that there is a linear relation for all the alloys. However, in the case of the Fe-33.2Pd and Fe-35.0Pd alloys, the temperature range for the linear relation is much narrower than that in other alloys; the value of C_p/T shows a down turn as T^2 increases. The down turn means increase in Debye temperature. Probably, the down turn is related to the hardening of lattice with increasing temperature in these alloys. Although there is no report of elastic constants of these alloys,

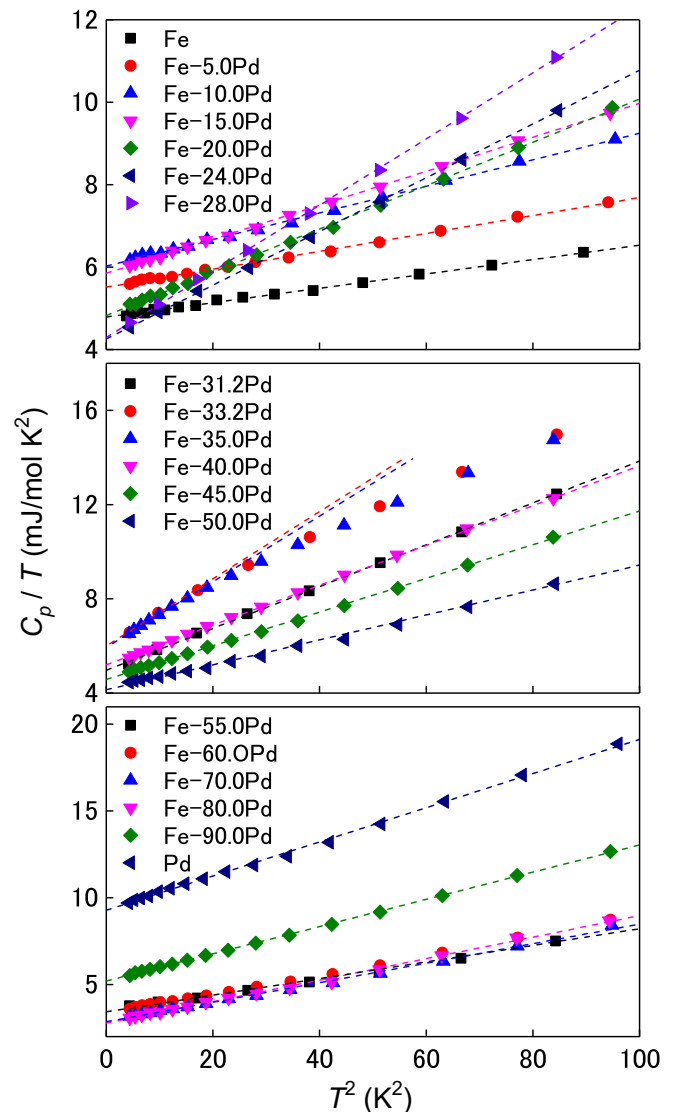


Fig. 2. The C_p/T vs T^2 relation at cryogenic temperatures of Fe- x Pd alloys.

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