Inter-element miscibility driven stabilization of ordered pseudo-binary alloy

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An infinite number of crystal structures in a multicomponent alloy with a specific atomic ratio can be devised, although only thermodynamically-stable phases can be formed. Here, we experimentally show the first example of a layer-structured pseudo-binary alloy, theoretically called Z3-FePd3. This Z3 structure is achieved by adding a small amount of In, which is immiscible with Fe but miscible with Pd and consists of an alternate L10 (CuAu-type)-PdFePd trilayer and Pd-In ordered alloy monolayer along the c axis. First-principles calculations strongly support that the specific inter-element miscibility of In atoms stabilizes the thermodynamically-unstable Z3-FePd3 phase without significantly changing the original density of states of the Z3-FePd3 phase. Our results demonstrate that the specific inter-element miscibility can switch stable structures and manipulate the material nature with a slight composition change.
he crystal structure is a crucial factor for determining the physical and chemical properties because the atomic arrangement dominates the atomic-orbital hybridization\(^1\)–\(^8\). In a multicomponent alloy system, even with a specific atomic ratio, a number of geometrically available crystal structures can be devised\(^9\)–\(^7\). Although this geometrical possibility means that there is a number of geometrically available crystal structures can be produced by mixing of Fe, Pd, and In at the nanoscale is crucial for the formation of Z$_3$-type structure. Experimental results and first-principles calculation show that the stabilization of Z$_3$-Pd(In$_3$)$_2$ is induced by not only a nanosize or a kinetic effect but a specific inter-element miscibility of In, which is miscible with Pd but immiscible with Fe. This idea that the inter-element miscibility of the third element works as a stabilizer of an ordered structure gives us an opportunity for the experimental discovery of a variety of novel ordered structures.

Results

Creation of layer-structured Fe–Pd–In alloy nanoparticles. Fe–Pd alloy nanoparticles (NPs) containing a small amount of In atoms were synthesized by a step-by-step chemical synthesis (Supplementary Table 1): (i) synthesis of 23-nm Pd NPs (Fig. 1a)\(^{17,18}\), (ii) alloying of In with Pd NPs to form A1-PdIn NPs (Fig. 1b), (iii) growth of FeO$_x$ shells on A1-PdIn NPs (Fig. 1c)\(^{17,18}\), and (iv) diffusion of Fe atoms into A1-PdIn NPs through the reductive annealing of FeO$_x$ shells at 600 °C or 800 °C for 3 h under a 4% H$_2$ gas flow (Ar balance) (Fig. 1d). First, we analysed the NPs with the Pd/In/Fe atomic ratio of 63/14/23 (Pd/In = 82/18 at.% and Pd/Fe = 73/27 at.%), which was confirmed by energy-dispersive X-ray spectrometry (EDX). Figure 1e–g show Rietveld refinement for the powder X-ray diffraction (XRD) patterns and the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the final NPs. These NPs could not be assigned to any structures in the Fe–Pd and Pd–In systems\(^3\), but it was found that they had the P4/mmm structure with the atomic coordinates of Fe\(^{1d}\) (0, 0, 0), Fe\(^{1c}\) (0.5, 0.5, 0), Pd\(^{1i}\) (0.5, 0.23), Fe\(^{1h}\) (0, 0.5), and Pd\(^{1d}\) (0.5, 0.5, 0.5) in the unit cell, where the superscripts refer to the multiplicities and Wyckoff letters. Therefore, the NPs had a

Fig. 1 Synthesis and characterization of monodisperse Fe–Pd alloy NPs with a small amount of In. a–d, TEM images of 23-nm Pd NPs (a), A1-PdIn, NPs with Pd/In = 82/18 at.% (b), A1-PdIn$_{@}$FeO$_x$ core@shell NPs with Pd/Fe = 73/27 at.% (c) and the NPs obtained by the reductive annealing of c at 600 °C for 3 h (d) (the inset shows the HAADF-STEM image of d). e, Rietveld refinement for powder XRD patterns of the NPs obtained by the reductive annealing of c at 800 °C for 3 h, where the black markers are raw data, the red is the fitting curve, the gray line is a difference curve of raw data and the fitting curve, and the green bars stand for the whole diffraction-peak positions. $R_{wp}$ and GOF are a reliability factor and a goodness of fit, respectively. f, g, Magnified HAADF-STEM image (f) and the fast Fourier transform (FFT) image (g) of the inset in d.
superlattice structure with an alternate stacking of a single Fe-atomic layer and three Pd-atomic layers along the c axis (Fig. 1e–g), which is called the Z3-FePd$_3$.$^{6,7,19}$ However, it was quite difficult to detect the In atoms from the intensity ratio of the XRD peaks and the Z contrast of the HAADF-STEM image, because the electron density of In is very close to that of Pd. To identify the In sites in the Z3 framework, we performed elemental mapping by EDX at the atomic resolution. As a result, In atoms were found to be selectively excluded from both the Fe and In atoms and preferentially occupied the 1$d$ or 1$b$ site, which corresponded to the middle Pd layer among the three Pd layers (Fig. 2a–e). Consequently, the resulting Z3 structure with the In atoms at the 1$d$ site was precisely denoted to be Z3-Fe(Pd,In$_d^d$)$_3$.

**Dependence of Fe–Pd–In alloy phase on In quantity.** Next, to investigate the In composition inducing the formation of the Z3-type structure, the Pd–In@FeO$_5$ core/shell NPs (Pd/Fe $\approx 70/30$ at.%) were annealed at 800 °C for 3 h (Supplementary Table 1). Powder XRD patterns verified that the reductive annealing for Pd–In@FeO$_5$ core/shell NPs with the Pd/In of 89/11 at.%, 85/15 and 73/27 at.% gave the L1$_2$-type phase, the Z3-type phases and a mixture of all three phases (A1-Fe$_{10}$Pd$_{90}$, Pnma-PdIn$_2$, and I4/mmm phases), respectively (Supplementary Fig. 2). This indicated that the Z3-type structure can be formed in a narrow range of In compositions.

To further confirm the In sites in not only the Z3-type but also the L1$_2$-type structures, we performed the X-ray absorption fine structure (XAFS) measurement for these structures at the Fe-, Pd- and In-K edges. The In environment determined from the extended XAFS (EXAFS) regions at the In-K edge revealed that the In atoms in the L1$_2$-type and Z3-type structures were surrounded only by approximately 12 Pd atoms, that is, L1$_2$-(Fe$_{10}$In$_{90}$)Pd$_{12}$ and Z3-Fe(Pd,In$_d^d$)$_3$, were formed by partially replacing Fe and Pd (1$d$ site) far from the Fe with In, respectively (Supplementary Fig. 3 and Table 2). This tendency strongly implied that the inter-element miscibility of In with other elements, that is, immiscible with Fe and miscible with Pd, dominated the In sites.

**Investigation of driving force for stabilizing Z3-type structure.** Although we found that the formation of Z3-type structure depends on the In composition, the driving force for stabilizing Z3-type structure is yet to be clarified. Besides the thermodynamic effect, the kinetic and/or the nano-size effects$^9$ should be considered as the candidates of the driving force for forming Z3-type structure. First, to investigate whether Z3-type structure was a kinetically or a thermodynamically stable phase below 800 °C, we conducted in situ XRD measurement for A1-PdIn$_x$@FeO$_5$@SiO$_2$ nanoparticles under the reductive annealing at 800 °C (SiO$_2$ was coated on A1-PdIn$_x$@FeO$_5$ nanoparticles to avoid the interparticle fusion). As a result, only Z3-type phase was formed by the reductive annealing at 800 °C for 4 min and further annealing at 800 °C for 25 h did not change the crystal phase (Supplementary Fig. 4). Therefore, we concluded that the Z3-type structure was a thermodynamically stable phase below 800 °C.

Next, to investigate whether a particle size contributes to stabilizing the Z3-type structure, we synthesized micrometer-scale Fe–Pd–In ternary alloy particles via the interparticle sintering of PdIn@FeO$_5$ nanoparticles by the reductive annealing at 800 °C for 3 h, which gave the Z3-type structure (Supplementary Fig. 5). On the other hand, when the reductive annealing was conducted for a mixture of Pd@FeO$_5$ NPs (Pd/Fe = 74/26 at.%) and In powder (Pd/In = 82/18 at.%), in which In was inhomogeneously distributed, at 800 °C for 3 h, the Z3-type structure did not form (Supplementary Fig. 6). These results strongly support that the nanoparticulate precursor powders composed of homogeneously mixed Fe, Pd, and In at the nanoscale are crucial for the formation of Z3-type structure even if the Z3-type structure is not stable specifically at the nanoscale$^9$.

To determine why the Z3-Fe(Pd,In$_d^d$)$_3$ structure was preferentially formed, we undertook a theoretical approach using first-principles calculations. First, we calculated the formation energies ($E_{\text{form}}$) of various FePd$_3$ phases in L1$_2$ and Z3 structures before and after adding In by using the equation below:

$$E_{\text{form}} = E[\text{FePd}_x\text{In}_y] - (x \times \mu[\text{Fe}] + y \times \mu[\text{Pd}] + z \times \mu[\text{In}])$$

where $E[\text{FePd}_x\text{In}_y]$ represents the total energies of Z3- or L1$_2$-Fe$_x$Pd$_y$In$_z$ ((x, y, z) = (2, 6, 0), (2, 5, 1), or (1, 6, 1)) and $\mu[\text{Fe}]$, $\mu[\text{Pd}]$ and $\mu[\text{In}]$ are the chemical potentials of Fe, Pd and In, respectively, which are equivalent to their total energies of the ground states. As shown in Fig. 3a, the calculation results showed that the L1$_2$-(Fe$_{10}$In$_{90}$)Pd$_{12}$ and Z3-Fe$_x$Pd$_y$In$_z^d$ structures were most stable in each structural type, which was in good agreement with the In sites in L1$_2$-type and Z3-type structures estimated from XAFS analysis. Furthermore, the differences in $E_{\text{form}}$ values between L1$_2$-(Fe$_{10}$In$_{90}$)Pd$_{12}$ and Z3-Fe$_x$Pd$_y$In$_z^d$ ($0 < x < 1$) (see Methods) showed that the Z3-type structure became more stable than the L1$_2$-type structure from $x > 0.48$, or In/(In+Pd) > 8 at.% (Fig. 3b). The calculation results also agreed with the experimental tendency in terms of the phase transition and the critical In/Pd at. % from the L1$_2$-type to Z3-type phases when increasing the In composition. Therefore, although the L1$_2$-FePd$_3$ structure is thermodynamically stable for FePd$_3$ systems$^{2,7,8}$, introducing a
A small amount of In atoms into FePd₃ systems makes the Z₃-type structure more stable than the L₁₂-type structure. The In sites shown in the experimental and theoretical data were likely to reflect the inter-element miscibility of In with Fe and Pd. To investigate whether the inter-element miscibility of In contributed to the stabilization of Z₃-type phase, we conducted the same first-principles calculations for the nine 12–14 groups elements (M = Zn, Cd, Hg, Ga, In, Tl, Ge, Sn, and Pb) in the periodic table as that used for In. Very interestingly, the Z₃-type structure was more stable than the L₁₂-type structure when introducing Cd, Hg, In, Tl and Pb which possessed the same miscibility as In with Fe and Pd⁸,²⁰. On the other hand, the Z₃-type structure remained unstable when adding Zn, Ga, Ge, and Sn which are miscible with Fe and Pd⁸ (Fig. 3C). Since these calculations do not consider other candidates except for isotropic L₁₂-type and anisotropic Z₃-type phases, one should note the differences in these formation energies at this composition, however, in the Fe–Pd–Pb system, the formation of Z₃-Fe(Pd₀.₅Pb₀.₅)₃ structure was confirmed by the similar step-by-step chemical synthesis as the synthetic process inducing Z₃-Fe(PdₓIn₁₋ₓ)₃ structure (see Methods and Supplementary Fig. 7). These results strongly support our claim that a third element selected by specific inter-element miscibility possess the potential to stabilize a binary alloy like the Z₃ structure.

**Physical properties of Z₃-Fe(PdₓIn₁₋ₓ)₃ structure.** Finally, we investigated the novel physical properties characteristic of the Z₃-type structure. First, the Z₃-type structure was expected to show high coercivity because of having a L₁₂-type PdFePd trilayer¹⁷,²¹,²². Magnetization–magnetic field (M–H) curves were measured for the L₁₂-(FeₓIn₁₋ₓ)Pd₃ and Z₃-Fe(PdₓIn₁₋ₓ)₃ NPs (Pd/Fe ≈ 70/30 at.%) synthesized by annealing at 600 °C for 3 h with the Pd/In at.% of 89/11 and 83/17, respectively, at room temperature by means of a vibrating sample magnetometer (VSM). Both the L₁₂-type and Z₃-type NPs showed a ferromagnetic feature with almost the same saturation magnetization, while the Z₃-type NPs possessed a coercivity that was 15 times higher than the L₁₂-type NPs and behaved as a magnetically hard phase similar to the L₁₀ NPs²¹,²² (Fig. 4). This coercivity enhancement could be explained by the drastic increase in the magnetic anisotropy energy²³ induced by the crystal structure change from L₁₂ to Z₃ frameworks (−1.38 μeV atom⁻¹ for L₁₂-type structure and −0.213 meV atom⁻¹ for Z₃-type structure (see Methods)).
As another structure-specific physical property, the Z3-type structure is also likely to possess a hydrogen-storage ability, owing to one Pd–In ordered alloy layer sandwiched by two Pd layers similar to the Pd-rich alloy structure. However, it was found from the pressure-composition isotherms at 30 °C and 60 °C that this Z3-type structure had no hydrogen-storage ability (Supplementary Fig. 8). This hydrogen-storage ability can be understood by the small amount of 4d hole of Pd in the Z3-type structure shown by the density of states (DOS), which are obtained from first-principles calculations (Supplementary Fig. 9). The DOS feature also showed no significant difference in DOS between the Z3-Fe4(Pd6,In4)6 and Z3-Fe3Pd6 structures. No significant change in DOS of Z3-Fe4(Pd6,In4)6 and Z3-Fe3Pd6 structures indicates that the physical properties characteristic of the Z3-FePd3 structure are still observed even if a small amount of In atoms are introduced into the Z3-FePd3 framework.

Discussion

We proposed the concept that the inter-element miscibility stabilizes a binary alloy with an ordered structure. As an example, we demonstrated that introducing a small amount of In atoms enabled the formation of Z3-Fe(Pd,In)3 NPs with an almost identical DOS as the Z3-FePd3 structure, where the synthetic procedure using the nanoparticulate precursor powders such as A1-PdIn@FeOx NPs were crucial for creating the Z3-type structure. These results indicate that ordered alloy structures can be experimentally discovered according to the binary-phase diagrams rather than searching for synthesizable structures using first-principles calculations. We expect that a variety of ordered alloy nanostructures will be discovered that exhibit identical DOS as the Z3-FePd3 framework.

Methods

Materials. All reagents and solvents were commercially available. Sodium tetra-chloropalladate(II) (Na2PdCl4, 98%), polyvinylpyrrolidone (PVP, Mw = 55,000), ascorbic acid (AA, 99 + %), potassium bromide (KBr, ≥ 99%), oleylamine (OAm, 80–90%), 1-octadecene (ODE, 90%), indium(III) chloride (InCl3, 98%), indium powder (In, > 99.99%), eicosane (99%), ammonium hydrogen solution (NH4NCO, 28–30%), tetraethyl orthosilicate (TROS, 98%), and polyoxyethylene (20) nonylphenylether (Igepal@CO-520, Mw = 441) were purchased from Sigma-Aldrich. Iron pentacarbonyl (Fe(CO)5, 95%) was purchased from Kanto Chemical Corporation. Oleic acid (OA, ≥ 85%) was purchased from Tokyo Chemical Industry. Lead (II) acetate trihydrate (Pb(OAc)2·3H2O), ethanol, acetone, n-hexane, chloroform, and cyclohexane were purchased from Wako Pure Chemical Industries. Boron nitride (BN, > 99.5%) powder was purchased from Nacalai Tesque. Chemical reagents were used as received without further purification except for the synthetic process of Pd-Pb@FeOx NPs.

Synthesis of Pd NPs. Pd NPs were synthesized by the previously reported procedure. After the rapid injection of an aqueous solution (30 mL) of Na2PdCl4 (1.5 g) and KBr (8.0 g) into an aqueous solution (270 mL) of PVP (2.8 g) and AA (0.66 g), the reaction solution was kept at 80 °C for 3 h and then cooled to room temperature. The above black solution of Pd seeds (15 mL) was injected into an aqueous solution (250 mL) of Na2PdCl4 (1.5 g) and KBr (3.0 g) at 40 °C and then an aqueous solution (25 mL) of PVP (2.8 g) and an aqueous solution (25 mL) of AA (1.8 g) were injected every 30 min at 40 °C. This solution was kept at 40 °C for 48 h, heated from 40 °C to 60 °C and kept at 60 °C for 48 h. Finally, the reaction solution was cooled to room temperature and the Pd NPs with an average edge length of 23 nm were collected by centrifugation with acetone and then purified with an ethanol/acetone (1/4 vol%) mixed solvent.

Synthesis of Pd-In alloy NPs. To react the Pd NPs with the In precursor in an organic solution, the surface ligand passivating the PD NPs was exchanged from PVP to OAm by heating a mixture of OAm (10 mL), chloroform (20 mL) and Pd NPs (0.5 mmol) at 50 °C for 30 min. The solution was cooled to room temperature and the OAm-protected Pd NPs were collected by centrifugation with ethanol and purified twice with a chloroform/ethanol (2/3 vol%) mixed solvent.

Synthesis of Pd-In@FeOx NPs. The FeOx shells were grown on the Pd-In alloy NPs by the almost same procedure as the previous report, namely, injecting Fe(CO)5 (nFe, mmol) into the ODE solution (63 mL) containing the Pd-In alloy NPs (0.50 mmolPd), OAm (2.0 mL) and OA (3.2 mL) with stirring at 80 °C for 1 h under an N2 atmosphere, and the reaction temperature was increased from 80 °C to 180 °C at the heating rate of 3 °C/min (Table S1), where the amount of OAm was sensitive for the decomposition of Fe(CO)5 decomposition. Finally, after the solution was kept at 180 °C for 1 h and cooled to room temperature, the Pd-In@FeOx NPs were collected by centrifugation with ethanol, purified twice with a n-hexane/ethanol (3/1 vol%) mixed solvent containing OAm (0.50 mL) and OA (0.50 mL), washed 3 times with ethanol and dried in a desiccator overnight.

Synthesis of Pd-Pb@FeOx NPs. The Pd-In@FeOx NPs were covered on the Pd-Pb alloy NPs by injecting Fe(CO)5 (7.4 mmol) at 80 °C for 1 h under an N2 atmosphere into the mixture solution of ODE (32 mL), distilled-OAm (1.0 mL) and the Pd-Pb alloy NPs (0.25 mmolPd) after degassing by freeze-pump-thaw cycle (3 times) and increasing from 80 °C to 140 °C at the heating rate of 3 °C/min. After the solution reached at 140 °C and was cooled to room temperature, Pd-Pb@FeOx NPs were collected by centrifugation with ethanol, purified twice with a n-hexane/ethanol (5/3 vol%) mixed solvent containing OAm (0.50 mL) and OA (0.50 mL), washed one time with ethanol and dried in a desiccator overnight.

Reduction-diffusion process for Pd-In@FeOx and Pd-Pb@FeOx NPs. The Pd-In@FeOx NPs powders were heated at the rate of 10 °C/min, annealed at 600 °C or 800 °C for 3 h and cooled at the rate of 10 °C/min under an Ar–H2 gas flowing at 0.5 L/min. The Pd-Pb@FeOx NPs powders were also annealed at 600 °C for 3 h via the same heating and cooling process under the same atmosphere.

Growth of SiO2 shell on Pd-In@FeOx NPs. In a typical method, the SiO2 shell was coated on A1-PdIn@FeOx NPs by adding TEOS (200 μL) in the cyclohexane solution (68 mL) containing A1-PdIn@FeOx NPs (0.25 mmolPd), IGE@PAlCo50 (9.6 mL) and NH2aq (1.6 mL) with stirring at room temperature for 16 h. After the reaction, the A1-PdIn@FeOx@SiO2 NPs were collected by centrifugation with ethanol, purified twice with EtOH and dried in a desiccator overnight.

XAFS measurement. Fe K-edge, Pd K-edge, and In K-edge EXAFS measurements were carried out by using the BL19B1 beamline of SPring-8 in Japan, where the incident X-ray beam was monochromated by a Si(311) double crystal monochromator. The sample powder was mixed with BN powder and pressed into a pellet. XAFS spectra of the L11-(Fe,In)Pd3 pellet were measured at 300 K, while XAFS spectra of the Z3-(Fe,Pd)In3 pellet were measured at 10 K in a Cu folder attached on a cryostat. The EXAFS analysis was carried out by using the REX2000 Ver. 2.5 program (Bigaku Co). In the curve-fitting analysis of the EXAFS oscillation and Fourier transform (FT) of EXAFS, the phase shift and the back-scattering amplitude function of the Fe–Fe, Fe–Pd, Pd–Pd, In–Fe and In–Fe were estimated from a Fe (PDF#00-006-0069), L11-FePd3 (PDF#03-065-9971), B2-PdIn3 (PDF#03-065-8004) and the crystal information file obtained from Rietveld refinement for Z3-(Fe,Pd)In3, respectively, by using the FEFF program.

TEM, HAADF-STEM and elemental-maps observations. The Pd NPs, the Pd-In alloy NPs, and the Pd-In@FeOx NPs before and after the reduction-diffusion process were dispersed in chloroform and dropped on amorphous carbon-coated copper grids (iEOL). The TEM samples of the Pd–Fe–In ternary alloy NPs were prepared by dispersing the Pd-In@FeOx NPs on TEM grids. TEM images were recorded on a JEM1011 (JEOL) at an acceleration voltage of 100 kV. HAADF-STEM images and EDX maps were obtained by a JEM-ARM200CF at an acceleration voltage of 120 kV for the samples prepared by dropping Fe–Pd–In(Pb) ternary alloy NPs on TEM grids.

Powder XRD measurement. The XRD patterns were recorded on a PANalytical X’Pert Pro MPD diffractometer with Cu Ka radiation (λ = 1.542 Å) at 45 kV and 40 mA. Rietveld refinements were performed by using the computer program RIETAN-2000 (Ref. 31).
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Author contributions
K.M., R.S., and T.Te. conceived the study. K.M. and R.S. designed the synthesis scheme. K.M. performed the synthesis, the characterizations and the magnetic measurements. Y.T. performed the first-principles calculations. K.M., R.T., and S.Y. measured and analysed the XAFS spectra. M.Y. and Y.I. measured the pressure-composition isotherms for hydrogen gas. Y.H., M.K., T.To., M.A., M.H., and H.K. observed the EDX elemental maps and HAADF-STEM. K.M., R.S., Y.T., and T.Te. co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
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