Electronic Supplementary Information

First synthesis of air-stable NiZn homogeneous alloy nanoparticles through chemical reduction

Shinya Okamoto,[a]* Kohei Kusada,[b] Hiroshi Hashiba,[a] Satoshi Yotsuhashi[a] and Hiroshi Kitagawa[b]

[a]Technology Division, Panasonic Corporation, 1006 Kadoma, Kadoma-City, Osaka 571-8508, Japan.

[b]Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan.

Correspond to: Shinya Okamoto (shinya.okamoto001@jp.panasonic.com)

Materials

$NiCl_2$-$CH_3O(CH_2)_2OCH_3$ (Sigma-Aldrich), $ZnCl_2$ (Sigma-Aldrich), naphthalene (Sigma-Aldrich), sodium (Sigma-Aldrich), tetrahydrofuran (Wako Pure Chemical Industries, Ltd.), absolute methanol (Wako Pure Chemical Industries, Ltd.), Ni powder (Wako Pure Chemical Industries, Ltd.), Zn powder (Wako Pure Chemical Industries, Ltd), nickel(II) acetylacetonate (Sigma-Aldrich), diethylzinc (Tokyo Chemical Industry Co., Ltd.), oleylamine (Wako Pure Chemical Industries, Ltd.), and 1-octadecene (Sigma-Aldrich) were used as received.

Synthesis of nanoparticles

The β_1-NiZn alloy nanoparticles were synthesized under an argon atmosphere using Schlenk techniques at room temperature as described at the manuscript. First, a flask containing naphthalene (1890 mg) was filled with argon at room temperature. Then, tetrahydrofuran (THF, 35 mL) was injected by syringe, and cut sodium (322 mg) was dropped into the solvent. The solution was stirred for 12 h. Second, a precursor was prepared with $NiCl_2$-$CH_3O(CH_2)_2OCH_3$ (0.07 mmol) and $ZnCl_2$ (0.14 mmol) dissolved in THF (17 mL). After injection of sodium-naphthalenide in THF (5 mL) into the precursor, the as-synthesized nanoparticles were removed to air and separated with the use of a centrifuge (Hitachi Koki, CS100FNX) at 210,000 g-force (50,000 rpm) for 2 h. The nanoparticles were filtered from absolute methanol and dried in vacuum. Finally, the powder was sintered at 300 °C for 1 h in hydrogen.

For comparison, phase-separated particles (Figures S5 and S6) were synthesized by a chemical reduction method in the liquid-phase at high temperature.[1] Nickel(II)acetylacetonate (1 mmol) was reduced in a solution of oleylamine (2 mL) and 1-octadecene (18 mL) at 220 °C for 2 h under an argon atmosphere. After that, diethylzinc (1 mmol) was added into the solution as the starting material

for Zn(0) at 250 °C. The solution was aged at 250 °C for 3 h. The synthesized nanoparticles were separated with the use of a centrifuge after the addition of acetone/hexane mixture, and dried in vacuum.

Characterizations

Transmission electron microscope (TEM), scanning transmission electron microscope (STEM), and STEM- energy-dispersive X-ray (EDX) analysis were performed on a JEOL ARM 200F STEM instrument operated at 200 kV. The crystal structure of the synthesized nanoparticles was characterized by synchrotron X-ray diffraction (XRD) analysis measured on the BL02B2 beamline at SPring-8. The radiation wavelength was 0.636038 Å. Ni powder with the particle size of 0.5 μm and Zn powder were used for the synchrotron XRD analysis as bulk standards. The size of the Ni particles is smaller than that of the Zn particles. In addition, powder XRD analysis was performed with a diffractometer operating with Cu-Kα radiation.

TEM observation of NiZn nanoparticles

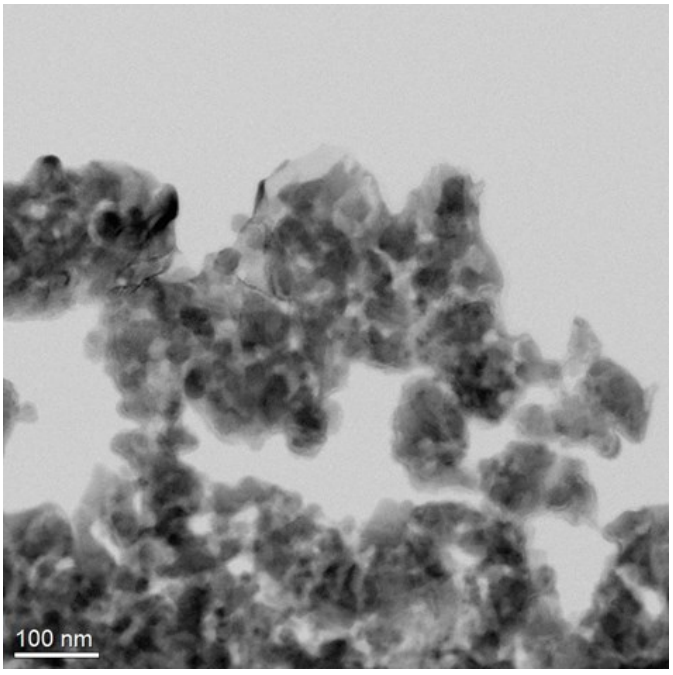


Fig. S1 TEM image of NiZn nanoparticles synthesized by sodium-naphthalenide reduction.

Rietveld refinement for the NiZn nanoparticles

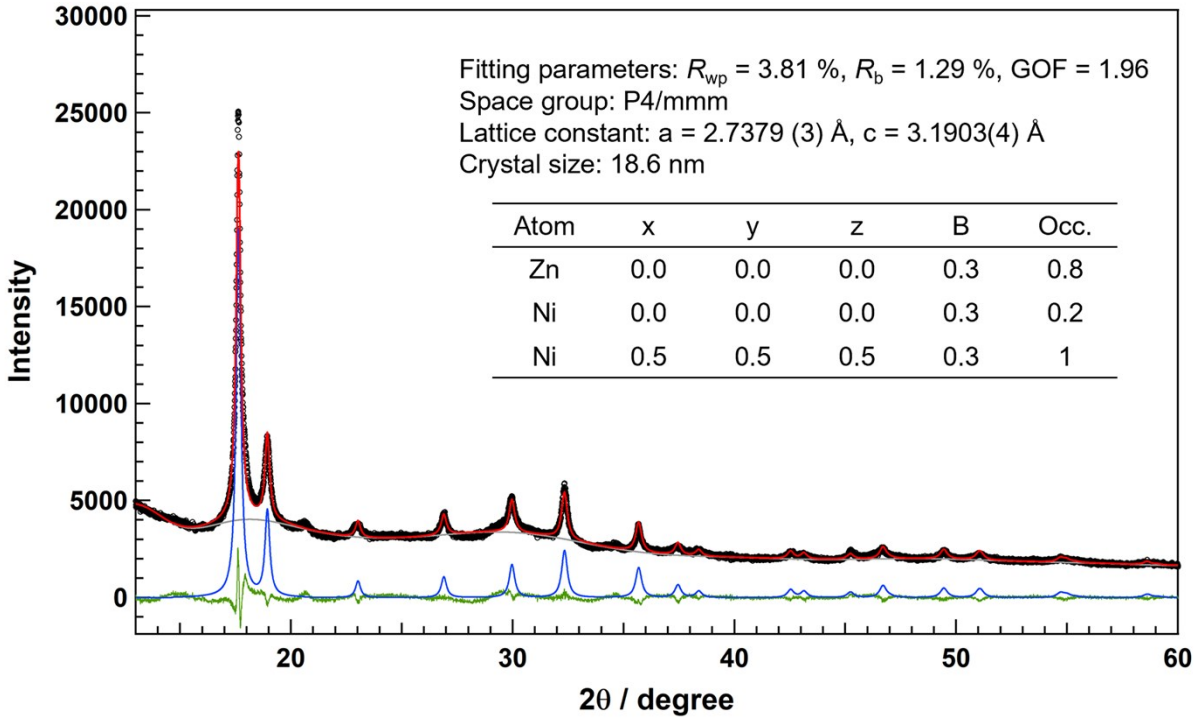


Fig. S2 Rietveld refinement for the NiZn nanoparticles. Diffraction pattern is shown as black circles. Calculated pattern is shown as red line. Difference profile, background profile, and fitting curve of the tetragonal component are shown as green, grey, and blue lines, respectively.

BF-STEM and HAADF-STEM images of the surface of a NiZn nanoparticle

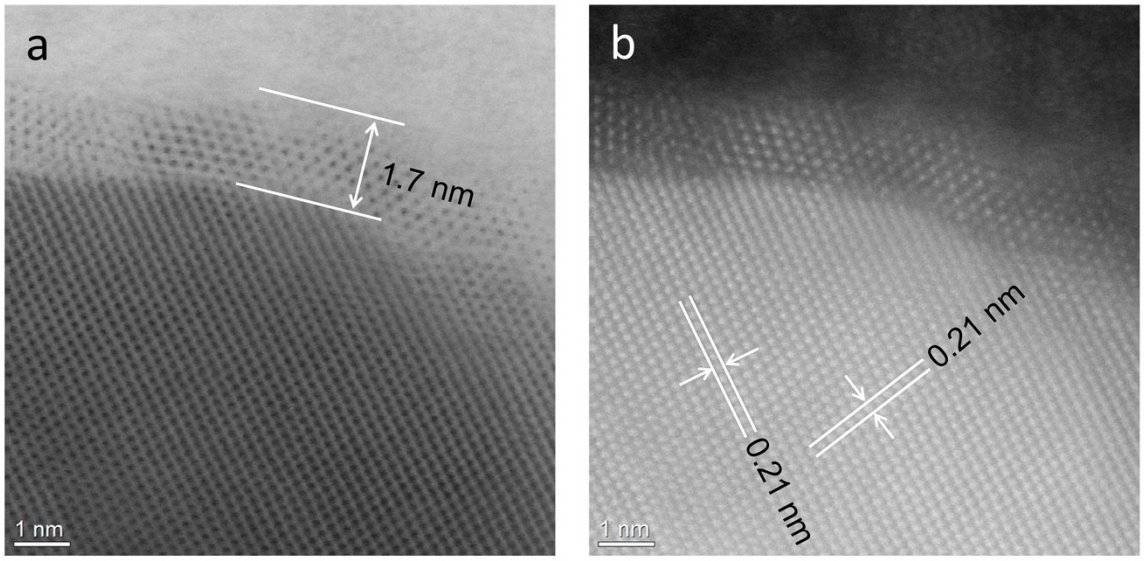
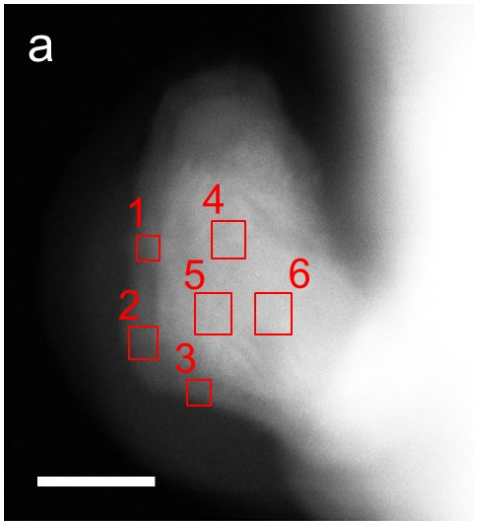


Fig. S3 BF-STEM (a) and HAADF-STEM (b) images of the surface of a NiZn nanoparticle. The thickness of the layer near the surface was measured and estimated to be approximately 2 nm regarding it as the oxidation layer because the arrangement of atoms is different from that of inner area. The interplanar spacing of the lattice fringes in inner area was measured and found to be approximately 0.21 nm; this value corresponds to that of the {101} planes of the β_1 phase of a NiZn intermetallic compound. The lattice image in inner area corresponds to the atomic arrangement of the β_1 phase of a NiZn intermetallic compound from the [010] zone axis.

Elemental analysis of a NiZn nanoparticle



b

atom%	O	Ni	Zn
1	19.02	45.81	35.16
2	25.00	48.41	26.59
3	17.36	42.05	40.60
4	8.55	52.30	39.14
5	6.69	56.53	36.78
6	5.66	58.19	36.16

Fig. S4 (a) HAADF-STEM image of a NiZn nanoparticle. (b) Average stoichiometries determined from the EDX data in the area shown in (a). Scale bar corresponds to 10 nm.

HAADF-STEM image and EDX map of phase-separated particles

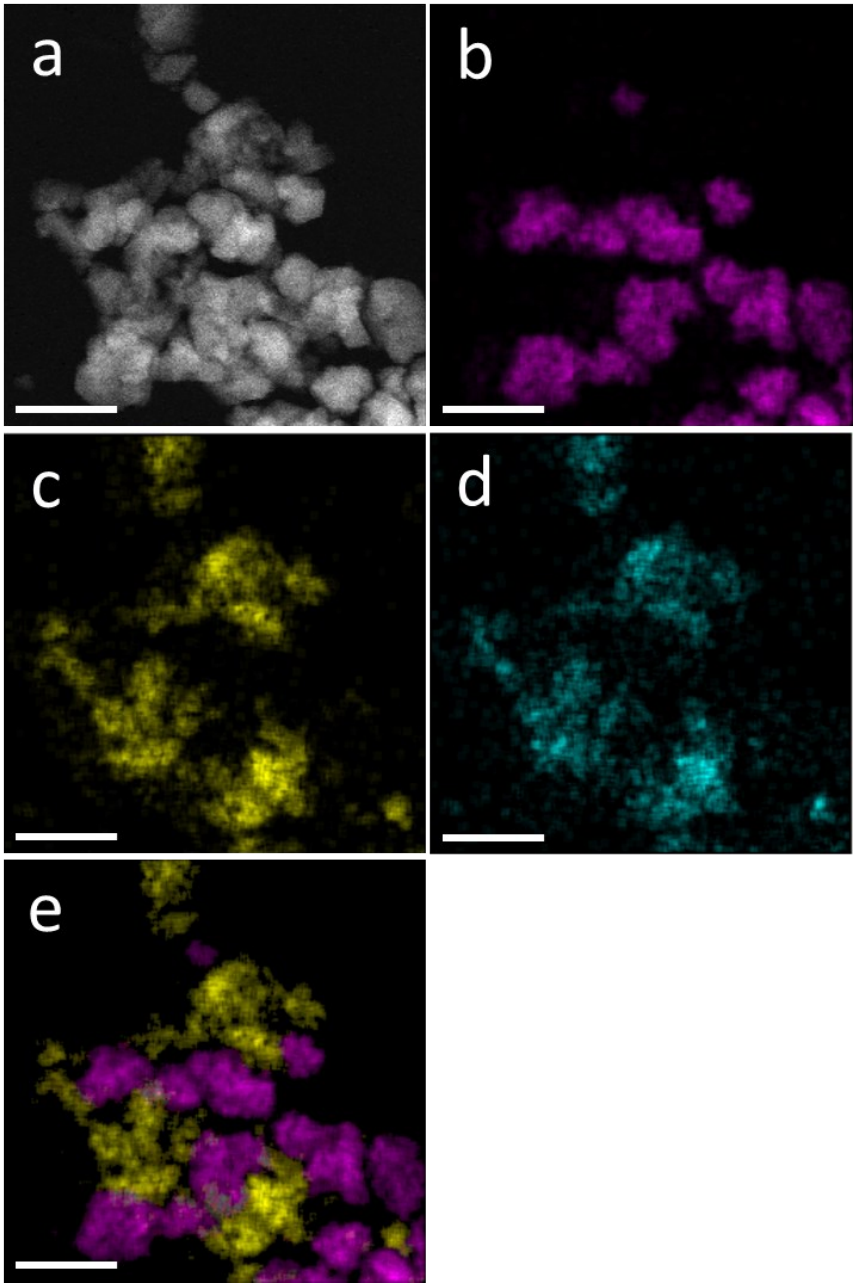


Fig. S5 (a) HAADF-STEM image, (b) Ni-K STEM-EDX map, (c) Zn-K STEM-EDX map and (d) O-K STEM-EDX map of synthesized particles. (e) Overlay image of (b) and (c). Scale bars correspond to 100 nm.

Powder XRD of the phase-separated particles

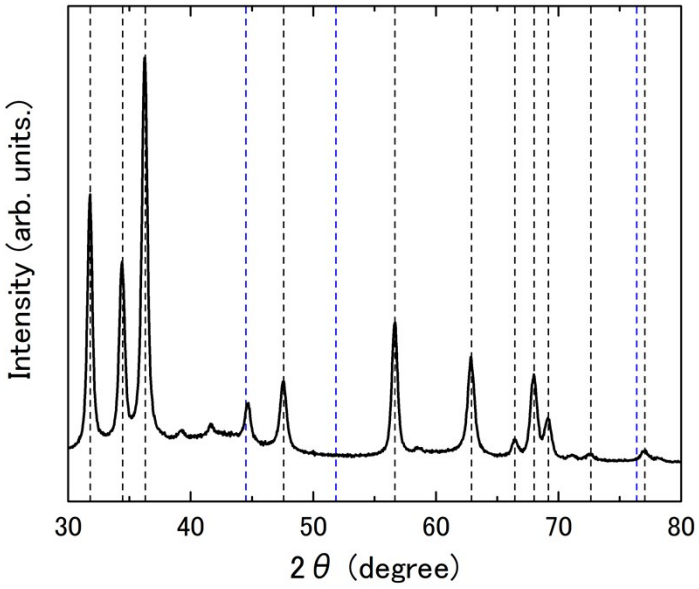


Fig. S6 XRD pattern of phase-separated particles shown in Figure S5 after sintering at 300 °C for 1 h in hydrogen. Black and blue dash lines correspond to peak positions of ZnO and Ni, respectively.

References

(1) S. Jana, J. W. Chang, R. M. Rioux, *Nano Lett.* 2013, **13,** 3618–3625.