

Hydrogen Absorption of Oxide Composite Materials Prepared from Melt-Spun Zr–Pd–Ni Alloys*¹

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Melt-spun $\text{Zr}_{65}\text{Pd}_{35-x}\text{Ni}_x$ ($x = 0\text{--}35$) amorphous alloys were produced by the single-roller melt-spinning technique and then oxidized at 553 K ($x = 0$) or 673 K ($x = 5\text{--}35$) in air. Hydrogen absorption of those oxide specimens was measured at 323 K by the conventional volumetric technique (Sieverts method). There was a tendency that the plateau of Pd disappeared and the maximum hydrogen absorption content (at about 5 MPa) decreased with increasing Ni (decreasing Pd) content in the starting alloys in the composition range of precursors, $x = 0\text{--}25$ as shown in the P–C–T curves. However, hydrogen absorption content of the oxidized specimen prepared from precursors of $x = 27.5\text{--}35$ peculiarly increased and the oxidized specimen prepared from the precursors of $x = 32.5$ showed the largest hydrogen absorption of about 1.8 mass% H among the series of specimens used in this study. Moreover, comparing XRD patterns of these oxidized specimens obtained before and after hydrogen absorption, it can be known that the mixed microstructure of ZrO_2 and PdO appears before hydrogen absorption in the oxidized specimens prepared from $\text{Zr}_{65}\text{Pd}_{35-x}\text{Ni}_x$ ($x = 0\text{--}25$) precursors. On the contrary, in the oxidized specimen prepared from $\text{Zr}_{65}\text{Pd}_5\text{Ni}_{30}$ precursor, Zr_3NiO and NiO oxides appear before hydrogen absorption and their peaks move to lower angle after hydrogen absorption due to the lattice expansion by hydrogenation while ZrO_2 phase did not appear so much. The significant behavior of the oxidized specimen prepared from $\text{Zr}_{65}\text{Pd}_{35-x}\text{Ni}_x$ ($x = 27.5\text{--}35$) alloy precursors is related to the outstandingly different microstructure produced in this specimen. The authors expect these specimens to be used not only as hydrogen storage materials but also as catalysts in future.

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1. Introduction

Recently, nanostructured materials have attracted rapidly increasing interest since it is expected that various new functional properties in various engineering fields would be discovered because of their characteristic structures. Amorphous alloys containing large amount of solute elements have been regarded as one of the most useful precursor to produce nanostructured materials. In 1992, some of the present authors reported that nanostructured composite material with nanoscale Pd particles dispersed in the ZrO_2 matrix was obtained by oxidizing the melt-spun $\text{Zr}_{65}\text{Pd}_{35}$ amorphous alloy at 553 K in air.^{1,2)} The authors studied the hydrogen absorption of such composite materials and reported that the hydrogen absorbability of Pd metal could be improved by dispersion of nanoscale Pd particles due to extremely large surface region between Pd particles and the ZrO_2 matrix.³⁾

It was also reported by many researchers that activated precursors such as Zr–Pd and Zr–Ni amorphous alloys can be used as catalysts for hydrogenation of CO_2 ^{4,5)} and benzene⁶⁾ and for methanation of CO.^{7,8)} Yokoyama *et al.* reported that the catalytic activity of amorphous Zr–Pd alloys for methanation of CO remarkably increased with reaction time by *in situ* activation and concluded that the activation was attributed to the formation of an active complex oxide consisting of Zr–Pd–O from amorphous Zr–Pd alloy precursors.⁷⁾

As mentioned above, studying hydrogen absorption of composite materials produced by oxidizing Zr–Pd and Zr–Ni amorphous alloys must be useful for developing a new-type hydrogen storage material and catalyst because those composites also show high reactivity even with hydrogen.

So, the objective of this work is to study the hydrogen absorption of the oxide composite materials prepared from the Zr–Pd–Ni alloys with varying Pd and Ni contents systematically.

2. Experimental

Binary and ternary alloys with compositions of $\text{Zr}_{65}\text{Pd}_{35-x}\text{Ni}_x$ ($x = 0\text{--}35$) were examined in this study. Their alloy ingots were prepared from the mixture of pure Zr, Pd and Ni metals by arc melting in an Ar atmosphere. Amorphous alloy ribbons were produced by melt-spinning technique in an Ar atmosphere from the alloy ingot. These alloy ribbons were oxidized in air at 553 K ($x = 0$) or at 673 K ($x = 5\text{--}35$).

Hydrogen absorption of these oxidized specimens was evaluated by measuring the hydrogen pressure-composition (hereafter denoted as P–C) isotherms with the gas-volumetric (Sieverts) apparatus at 323 K. We used the P–C isotherm automatic measuring system (Suzuki-shokan Co. Ltd., maximum hydrogen pressure up to 5 MPa). The structures of as-oxidized specimens and hydrogen absorbed ones after P–C isotherm measurement were examined by X-ray diffraction (XRD) using copper radiation ($\text{CuK}\alpha$) obtained at 40 kV and 30 mA.

As for calculating the specimen density that is needed for the P–C isotherm measurement, we adopted one assumption that the specimen produced by oxidizing Zr–Pd–Ni amorphous alloy contained only two phases such as ZrO_2 matrix and Pd+Ni metallic particles.

3. Results and Discussion

Figure 1 shows some results of P–C isotherm measurement for specimens produced in this study. Figure 2 shows the maximum hydrogen absorption content of the oxidized

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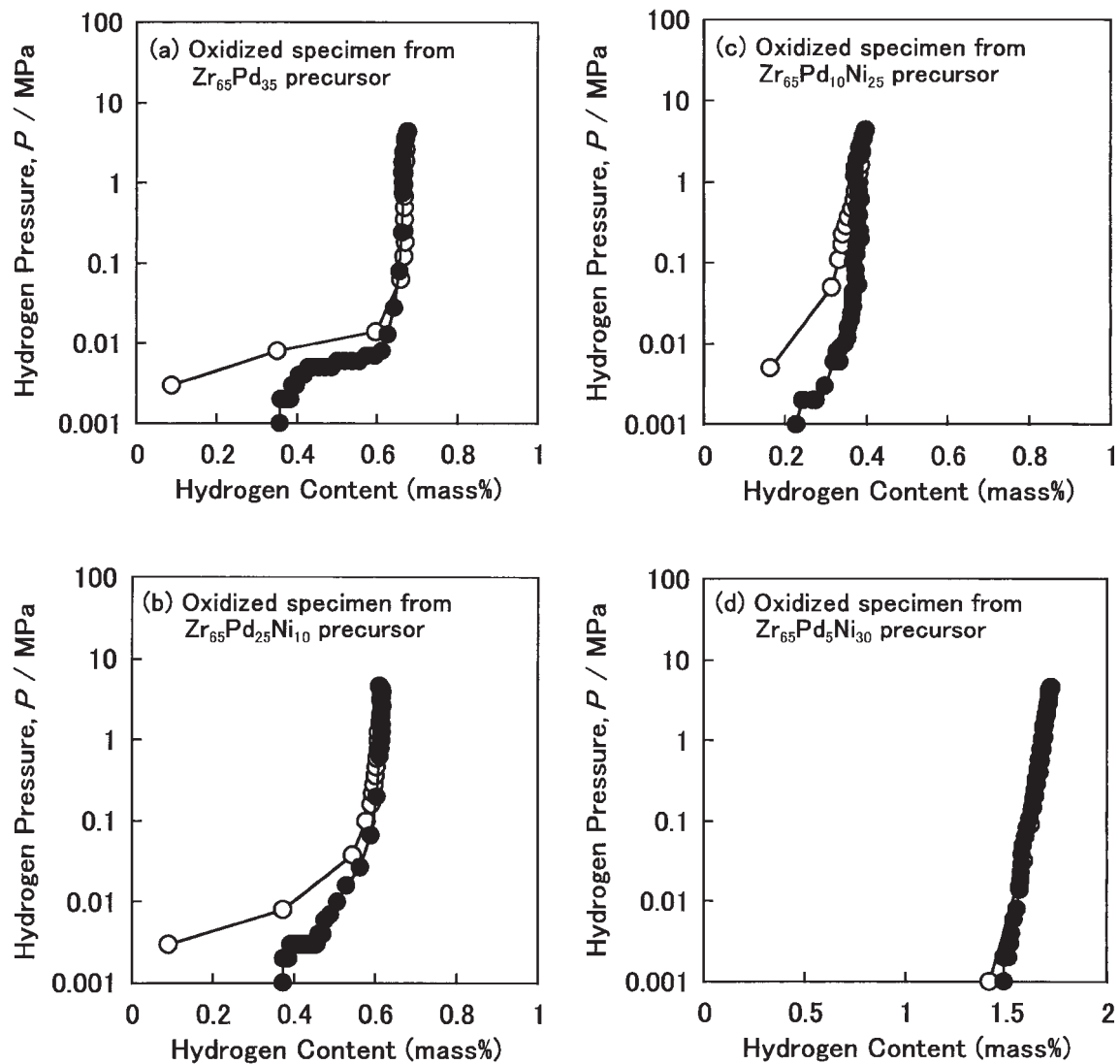


Fig. 1 The P-C isotherms of oxide composite specimens prepared from the (a) $Zr_{65}Pd_{35}$, (b) $Zr_{65}Pd_{25}Ni_{10}$, (c) $Zr_{65}Pd_{10}Ni_{25}$ and (d) $Zr_{65}Pd_5Ni_{30}$ precursors.

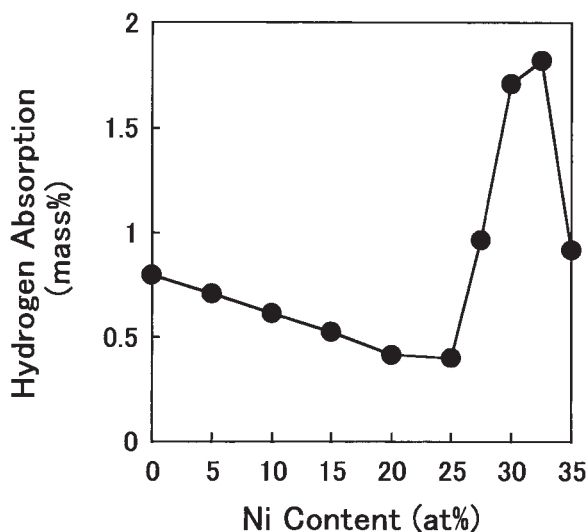


Fig. 2 The maximum hydrogen absorption content of the specimens as a function of Ni content, x in $Zr_{65}Pd_{35-x}Ni_x$ amorphous precursors.

specimens at 5 MPa as a function of Ni content in Zr-Pd-Ni amorphous precursors. There are tendencies that Pd plateau disappeared with increasing Ni (decreasing Pd) content and that the maximum hydrogen absorption content decreased with increasing Ni (decreasing Pd) content in the composition range of precursors from $x = 0$ to 25. Considering Pd content involved in these oxidized specimens, the hydrogen absorption amount of these specimens was considerably large. For instance, the oxidized specimen prepared from $Zr_{65}Pd_{35}$ precursor has the multiphase-structure of nanoscale Pd particles embedded in ZrO_2 matrix. It can absorb hydrogen up to about 0.7 mass%H in the experiment while the estimated hydrogen absorption may be about 0.18 mass%H assuming that Pd metal changes into $PdH_{0.6}$ after hydrogenation. There is a large difference between the experimentally measured hydrogen absorption (0.7 mass%H) and the estimated absorption (0.18 mass%H). This may be because the estimated hydrogen absorption was calculated with the assumption that the properties of nanoscale Pd particles were regarded to be same with those of bulk Pd metal. It has previously been reported that nanoscale metal

particles/clusters exhibit significantly different behavior from the bulk metal.^{9,10)} Thus observed absorption of about 0.7 mass% H in the oxide specimen prepared from $\text{Zr}_{65}\text{Pd}_{35}$ precursor in this work is reasonable. On the other hand, the maximum hydrogen absorption content of each specimen increased drastically in the composition range of precursors

from $x = 27.5$ to 35. And the composite specimen prepared from the melt-spun $\text{Zr}_{65}\text{Pd}_{2.5}\text{Ni}_{32.5}$ amorphous alloy showed about 1.8 mass% of hydrogen absorption at maximum in the series of specimens.

Figure 3 shows the XRD patterns of the composite specimens before and after P-C isotherm measurement. As

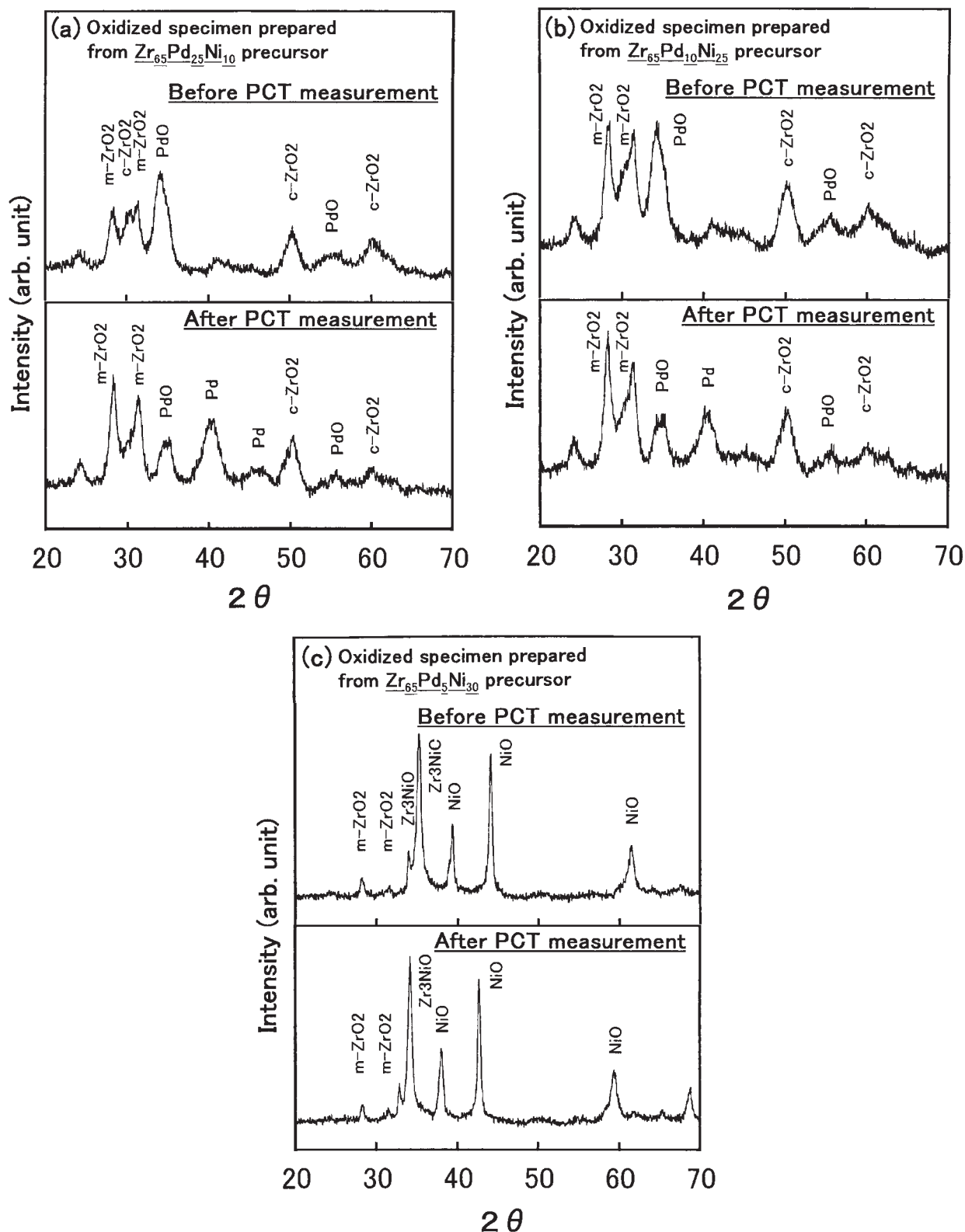


Fig. 3 The XRD patterns of the oxide composite specimens before and after P-C isotherm measurement prepared from the (a) $\text{Zr}_{65}\text{Pd}_{35}\text{Ni}_{10}$, (b) $\text{Zr}_{65}\text{Pd}_{10}\text{Ni}_{25}$ and (c) $\text{Zr}_{65}\text{Pd}_5\text{Ni}_{30}$ precursors.

shown in the figure, an oxide composite structure was formed including ZrO_2 phase and PdO phase before the P-C isotherm measurement in the oxidized specimens prepared from the melt-spun $\text{Zr}_{65}\text{Pd}_{35-x}\text{Ni}_x$ ($x = 0\text{--}25$) amorphous precursors. And then Pd particles were precipitated by deoxidation of PdO while the ZrO_2 phase was not changed after the P-C isotherm measurement in those specimens.

A small amount of H_2O can be generated during deoxidation of PdO . The mole of generated H_2O is same as that of consumed H_2 . Since the total moles of gases inside the vessel is kept constant even before/after deoxidation assuming that the generated H_2O is gaseous, H_2O may not affect the P-C isotherm measurements. Moreover, in the case that generated H_2O is fluid, there is no effect of H_2O on the P-C isotherm measurements because the amount of H_2O is very small. However, the surface damage of powder specimens by H_2O , that causes the degradation of hydrogen absorption, may not be negligible. Since it is difficult to investigate such a damage in more detail, we do not refer to that problem in this work.

The complex oxide composite structure was formed including Zr_3NiO phase and NiO phase before the P-C isotherm measurement in the oxidized specimen prepared from the melt-spun $\text{Zr}_{65}\text{Pd}_{35-x}\text{Ni}_x$ ($x = 30\text{--}35$). And then the XRD peaks of Zr_3NiO and NiO shifted to the lower angle because of the volume expansion caused by hydrogen absorption. Therefore, the drastic increase of hydrogen absorption in the oxidized specimen prepared from the melt-spun $\text{Zr}_{65}\text{Pd}_{35-x}\text{Ni}_x$ ($x = 27.5\text{--}35$) precursors corresponds to the structural change of composite specimens. It is well-known that complex oxides such as $\text{Zr}\text{--}\text{Ni}\text{--}\text{O}$ and $\text{Zr}\text{--}\text{Pd}\text{--}\text{O}$ can absorb large amount of hydrogen.^{11,12} For instance, hydrogenated oxides such as $\text{Zr}_4\text{Pd}_2\text{OH}_{4.7}$ ¹¹ and $\text{Zr}_4\text{Ni}_2\text{O}_{0.6}\text{H}_{8.2}$ ¹² were previously reported. Particularly, it was reported that the $\text{Zr}_4\text{Ni}_2\text{O}_{0.6}$ oxide could absorb hydrogen up to 1.64 mass% H . To our knowledge, there may be no reports studying on hydrogen absorption of Zr_3NiO and NiO . However, many reported similar oxide phases can absorb large amount of hydrogen. Moreover we observed that the XRD peaks of the Zr_3NiO and NiO phases moved to the lower angle after hydrogenation indicating even indirectly a large amount of hydrogen absorption. The complex oxides were formed only in the specimens prepared from the precursors with Ni content of $x = 27.5\text{--}35$ among the series of specimens studied in this work. The reason of irregularity of oxides formation in this series of specimens is not clear yet. The authors expect these specimens to be used particularly as catalysts in future.

4. Conclusions

The hydrogen absorption of the oxide composite specimens decreased gradually with increasing Ni content (decreasing Pd content) in the composition range of precursors, $x = 0\text{--}25$. However, the hydrogen absorption increased drastically in the composition range of precursors, $x = 27.5\text{--}35$. The oxide composite specimen produced from the precursor of $x = 32.5$ exhibited the largest hydrogen absorption of about 1.8 mass% H among the series of specimens used in this study. The mixed microstructure of ZrO_2 and PdO appears before hydrogen absorption in the oxidized specimens prepared from $\text{Zr}_{65}\text{Pd}_{35-x}\text{Ni}_x$ ($x = 0\text{--}25$) precursors and that Pd phase appears by deoxidation of PdO during hydrogen absorption. On the contrary, in the oxidized specimen prepared from $\text{Zr}_{65}\text{Pd}_5\text{Ni}_{30}$ alloy precursor, Zr_3NiO and NiO oxides appear before hydrogen absorption and their peaks move to lower angle after hydrogen absorption due to the lattice expansion while ZrO_2 phase did not appear so much. The systematic change of hydrogen absorption of the oxide composite specimens corresponds to the microstructural change, especially to the appearance of the Zr_3NiO and the NiO phases in the oxide composite specimens.

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