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REGULAR PAPER

Hydrogen absorption of Pd/ZrO_2 composites prepared from $Zr_{65}Pd_{35}$ and $Zr_{60}Pd_{35}Pt_5$ amorphous alloys

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Metal-dispersed composites were derived from amorphous $Zr_{65}Pd_{35}$ and $Zr_{65}Pd_{30}Pt_5$ alloys and their hydrogen absorption behavior was studied. X-ray diffractograms and scanning electron micrographs indicated that mixtures containing ZrO_2, the metallic phase of Pd, and PdO were formed for both amorphous alloys heat-treated in air. In the composites, micron-sized Pd-based metal precipitates were embedded in a ZrO_2 matrix after heat treatment at 800 °C in air. The hydrogen temperature-programmed reduction was applied to study the reactivity of hydrogen gas with the oxidized $Zr_{65}Pd_{35}$ and $Zr_{65}Pd_{30}Pt_5$ materials. Rapid hydrogen absorption and release were observed on the composite derived from the amorphous alloy below 100 °C. The hydrogen pressure–concentration isotherm showed that the absorbed amount of hydrogen in materials depended on the formation of the Pd or Pt-doped Pd phase and its large interface area to the matrix in the nanocomposites. The results indicate the importance of the composite structure for the fabrication of a new type of hydrogen storage material prepared from amorphous alloys.

1. Introduction

Amorphous alloys and their composites have unique physical and chemical properties including catalytic ones.[1–4] Since large extended compositions enable the preparation of amorphous alloys using advanced processing techniques, they are possible raw materials for preparing new metals including porous metals and composite intermediates between metals and ceramics.[5–10] One example of previous studies on Pd-based alloys is nanocrystalline metal/ceramic composites consisting of Pd particles embedded in a ZrO_2 matrix directly formed from an amorphous phase upon heat treatment in air. Since nanocrystalline materials in metal and ceramic systems have attracted increasing interest, the fabrication route using an amorphous alloy may lead to unique characteristics. Regarding applications as catalysts, Christian et al. prepared metal catalysts from amorphous metal alloys by in situ activation with a reaction gas mixture.[6] A few papers have reported the catalytic oxidation and other reactions such as hydrogenation over ZrPd alloys after treatment in air and reaction gas mixtures.[7–10] Since derivatives from amorphous ZrPd become Pd-based composites, the resulting materials should be useful as Pd catalysts in various applications such as synthetic reactions and environmental catalysis.[11–13] Yamaura and coworkers proposed a strange hydrogen absorption behavior of specimens produced by oxidizing Zr–Pd and Zr–Pd–Ni amorphous alloys at temperatures lower than 300 °C.[14,15] However, in general applications in gas reactions, the thermal stability of materials is important even when they are subjected to treatments in the moderate-temperature region over 500 °C.

The aim of this study is to examine hydrogen absorption and the release properties of thermally stable composites that are derived from amorphous $Zr_{65}Pd_{35}$ and $Zr_{65}Pd_{35}Pt_5$ alloys at a high temperature of 800 °C. It has been confirmed that the amorphous phase is formed by liquid quenching on the Zr-rich side around Zr_2Pd, as shown by the phase diagram of the Zr–Pd system.[16–18] $Zr_{65}Pd_{35}$ belongs to the family of the expected Zr-related amorphous alloy materials with possible electric properties.[19–21] Because the Pt doping effects of a Zr_2Pd amorphous alloy and its derivatives are unknown, the impact of Pt addition was examined in this study in terms of microstructural development during the transformation of the amorphous alloy to a composite. In this work, both hydrogen temperature-programmed reduction (H_2-TPR) and hydrogen isotherm measurement are carried out to study the interaction and reactivity of hydrogen gas over the microstructured $Zr_{65}Pd_{35}$ and $Zr_{60}Pd_{35}Pt_5$ materials after oxidizing treatment at 800 °C in air. We compared the hydrogen absorption and release behavior on the resultant composites; the results indicate the promising thermal stability of the present material.

2. Experimental methods

2.1 Sample preparation

A mixture of 99.6 wt% pure zirconium, 99.99 wt% pure palladium, and 99.99 wt% pure platinum metal was melted in a purified argon atmosphere on a water-cooled copper mold in an arc furnace. Amorphous $Zr_{65}Pd_{35}$ and $Zr_{65}Pd_{30}Pt_5$ (whose composition represents the atomic ratio) ribbon specimens with a thickness of about 0.02 mm and a width of about 1 mm were prepared from the mixed alloy in argon atmosphere by the single-roller melt-spinning method. The resultant amorphous alloys were heated at 800 °C for 3 h in air, inducing thermally stable composite materials of Pd (or Pd/Pt) and ZrO_2.

2.2 Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku MiniFlex diffractometer with Cu Kα radiation at 15 kV and 30 mA. The X-ray diffractogram was recorded at a scanning rate of 1°/min with a 0.02° step size in the 2θ range between 10 and 90°. Scanning electron microscopy (SEM) and reflection electron microscopy (REM) images, and the corresponding element map were obtained by field-emission scanning electron microscopy (FE-SEM; Hitachi S-4800) at 15 keV and analyzed using an energy dispersion spectrometer (EDS; Gatan).