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# Structure and hydrogen absorption properties of $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}(\text{Pd},\text{V})$ quasicrystals

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## ABSTRACT

The structure and hydrogen absorption properties of Pd and V doped TiZrNi quasicrystals were investigated in terms of the equilibrium vapor pressure of hydrogen, and the results were compared with those of undoped samples. Rapidly quenched  $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$  alloys formed quasicrystals and absorbed hydrogen H/M (hydrogen to host metal atom ratio) value of 1.79 at room temperature. This was attributed to their structure, which contains mostly tetrahedral interstitial sites that are chemically formed by atoms having a high affinity with hydrogen. However, the relatively low equilibrium vapor pressure of hydrogen, 0.14 Torr at 300 °C, prevents TiZrNi quasicrystals for the practical application on energy storage materials. To overcome this limitation, we replaced Ti with Pd and V to increase the vapor pressure of hydrogen and investigated the properties of hydrogen absorption behaviors. Results of XRD measurements revealed that the quasicrystal structure was maintained by the replacement of Ti with a maximum of 8 at. % of Pd and V. Total amounts of the absorbed hydrogen decreased from 1.33 to 1.06 and to 1.12 of the H/M values when the Ti was replaced by 8 at. % of Pd and V, respectively, at 300 °C. The pressure-composition-temperature data measured using an automatic gas-handling system revealed that the equilibrium vapor pressure increased from 0.14 to 0.21 and to 0.56 Torr at H/M value of 0.5 when Ti atoms were replaced by 8 at. % Pd, and V, respectively, without the appearance of an impurity phase. Our results demonstrate that the replacement of Ti with Pd and V is an effective method to increase the equilibrium vapor pressure of hydrogen without a phase transformation in a TiZrNi quasicrystal system.

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## Introduction

Since the first report on hydrogen absorption in quasi-periodic TiZrNi alloys by Viano et al., numerous studies on structural stability and hydrogen loading properties were reported in this system [1–10]. Quasicrystals (QCs) are well-ordered aperiodic materials exhibiting a five-fold rotational

symmetry which is theoretically forbidden in a concept of solid state physics [11]. Sharp diffraction patterns in TEM and X-ray observed in QCs demonstrate that QCs intrinsically contain a long range of coherence length in an order of a few hundreds of micrometers. The discovery of QCs influenced the International Union of Crystallography in 1993 to modify the definition of a crystal from “a substance in which the constituent atoms, molecules, or ions are packed in a

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regularly ordered, repeating three-dimensional pattern” to “any solid having an essentially discrete diffraction diagram”. The Nobel Prize for Chemistry in 2011 was awarded to Shechtman for the discovery of QCs.

Ti-based QCs form the second largest group of alloys followed by those that are Al-based. Among them, the TiZrNi QCs, first reported by Molokanov et al. [12] are strong candidates for the practical applications due to their easy formation, relatively large grain size, superior mechanical properties of wear resistance, corrosion protection, thermal insulation [13,14], and particular suitability for hydrogen storage applications [15–19]. TiZrNi QCs are thermodynamically stable [20,21], and are now known as a new type of a promising energy storage material based on the following factors. First, QC grains are found in a wide range of atomic concentrations mainly because of the chemical and atomic similarities of Ti and Zr that are favorable to hydrogen [22–24]. Second, they contain a large number of tetrahedral interstitial sites that are suitable to hosting hydrogen [25]. Third, an optimum amount of Ni (17–20 at %) moderates the strong binding of hydrogen with host materials, and hinders the easy formation of undesired Ti/Zr-rich hydride phase. In fact, TiZrNi QCs are known to store hydrogen at a higher amount than that of liquid hydrogen (70.8 kg/m<sup>3</sup>) [26]. This amount is higher or competitive with La-based ones in metal hydride batteries.

In spite of these proven and favorable results, TiZrNi QCs still have critical technical drawbacks for the practical use of renewable energy storage materials because of the following limitations: 1) low equilibrium vapor pressure of hydrogen mainly due to the strong interaction of hydrogen with Ti and Zr [27], 2) limited cycling ability of hydrogen [5], and 3) structural instabilities after hydrogenation [28]. Among these drawbacks, one of the most critical issues is the rise in equilibrium vapor pressure of hydrogen with the wide area of pressure plateau in a Pressure-composition-Temperature (P-c-T) diagram [29]. One needs to examine this issue when evaluating TiZrNi QCs as potential hydrogen storage materials. Technically, measuring the P-c-T data from metal hydrides is an essential process to estimate the site energies for hydrogen in interstitial sites because the heights and the widths of the pressure-plateau in the P-c-T curve determine the capacity of hydrogen reversibly stored without a phase transformation [30,31].

To increase the equilibrium vapor pressure of hydrogen in a reasonable temperature range, we replaced Ti with Pd and V in Ti<sub>53</sub>Zr<sub>27</sub>Ni<sub>20</sub> QCs and investigated the changes of structure and equilibrium vapor pressure with the maximum amount of hydrogen loading capacity.

## Experimental methods

Raw materials of Ti, Zr, Ni, and Pd, V were purchased from Alfa Aesar with purities higher than 99.9%. Totals of 2 g of Ti<sub>53-x</sub>Zr<sub>27</sub>Ni<sub>20</sub>Pd<sub>x</sub> (x = 0, 4, 8) and Ti<sub>53-y</sub>Zr<sub>27</sub>Ni<sub>20</sub>V<sub>y</sub> (y = 0, 4, 8) were prepared by using an electronic balance (AR2140, Adventurer) with an accuracy of 10<sup>-4</sup> g, and the mixed elements were arc-melted in an argon atmosphere on a Cu hearth cooled by water. To minimize oxygen contamination, the sample

chamber was evacuated to lower than 10<sup>-5</sup> Torr level and was backfilled at least three times using ultra-high purity argon. For the homogenous mixing of the elements, the ingot was flipped and re-melted three times. The molten ingot was subsequently quenched on a stainless steel wheel that rotated 3000 revolutions per minute. This method will produce thin metallic ribbons quenched by a cooling rate of ~10<sup>6</sup> °C/s, which was fast enough to solidify the liquids and form a non-equilibrium phase. The metallic ribbons obtained by this method measured 30–50 μm in thickness, 2–5 cm in length, and 2 mm in width.

Before hydrogen absorption, the samples were etched by Ar-plasma followed by a thin coating of Pd to remove the natural oxygen layer on the surface. This process also protected the samples from further oxidation when they were exposed to air prior to hydrogen loading. This step was essential because the oxygen layer blocks the hydrogen from the diffusion into the sample, which would render it impossible to measure the equilibrium vapor pressure of hydrogen between the solid and the gas phases of hydrogen. The oxygen layer was eliminated by etching the sample using Ar-plasma for 20 min with an RF power of 50 W at 3.5 mTorr of Ar atmosphere. Subsequently, a thin Pd layer was coated by employing an RF sputtering method for 10 min. A detailed etching procedure is further described elsewhere [5].

To measure the P-c-T data and the total amount of absorbed hydrogen, an automatic gas-handling system operated by a LabVIEW software was designed and built. The P-c-T curves of hydrogen from the samples were measured by using a baratron transducer (MKS Baratron Type 627B) which can measure the maximum pressure of 1000 Torr with a 0.001% resolution. Prior to collecting data, a series of P-c-T data were measured from a 0.5 g piece of Pd rod for the calibration of the system including the volume of the sample chamber. Variations of the system temperature were also recorded to calibrate the actual temperature of the cell containing the sample. An ‘equilibrium pressure’ during the P-c-T measurement was defined when a fluctuation of hydrogen pressure was maintained less than 0.5 Torr for 5 min.

The structures, morphologies, and selected area diffraction (SAD) patterns were determined by analyzing the data measured using X-ray diffractometer (Cu K-α radiation, D-8 Discover, Bruker) and transmission electron microscope (TEM, JEOL2011), respectively. The quasi-coherence length  $\tau$ , of the sample was estimated following the Scherrer equation, which is given by

$$\tau = \frac{K\lambda}{B \cos\theta}$$

where  $\kappa$ ,  $\lambda$ ,  $B$ ,  $\theta$ , represent the shape factor (normally 0.9), the wavelength of the X-ray, the full width at half maximum (FWHM) value of the diffraction peak, and the diffraction angle, respectively.

## Results and discussions

Prior to hydrogen loading, the dynamics of hydrogen absorption properties including the effects of the surface treatment in rapidly quenched TiZrNi alloys were investigated. For as-

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