

Hydrogen Absorption in $\text{Ti}_{45}\text{Zr}_{38-x}\text{Ni}_{17+x}$ Quasicrystals and Measurements of the Equilibrium Vapor Pressure

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To evaluate their technological usefulness and to probe the local structure of the quasicrystal, p-c-T curves were measured for as-quenched $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ and $\text{Ti}_{45}\text{Zr}_{30}\text{Ni}_{25}$ quasicrystal ribbons at 350°C with a computer-controlled apparatus. For both quasicrystals, the p-c-T curves do not exhibit a clear pressure plateau. Instead, the equilibrium vapor pressure remains low (< 5 torr) below H/M \approx 1; it increases sharply for increasing H/M. Such p-c-T curves may reflect structural features of the quasicrystal. Due to the formation of the crystal hydride phase during the p-c-T measurements, however, the site energy distribution in the quasicrystals could not be obtained. Instead, qualitative conclusions are presented. For $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ quasicrystals, estimates of the site energy distribution for hydrogen suggest a prominent site located between -0.2 eV and -0.15 eV with a possible broad, weakly binding second peak at higher energy. The site energy locations for hydrogen for $\text{Ti}_{45}\text{Zr}_{30}\text{Ni}_{25}$ quasicrystals are similar. The $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ quasicrystals desorb most of the absorbed hydrogen at 650°C in one hour by continuous pumping without phase transformation, and do not become powder after three cycles.

Key words: quasicrystal, hydrogen, p-c-T measurement, site energy, x-ray diffraction

1. INTRODUCTION

Ti/Zr-based quasicrystals are candidate materials for hydrogen storage applications because they absorb a large amount of hydrogen, to a density exceeding that of liquid hydrogen [1]. Particular attention has focused on Ti-Zr-Ni alloys, where the quasicrystal is thermodynamically stable [2]. These quasicrystals reversibly store hydrogen, to a maximum hydrogen to host metal atom ratio (H/M) of nearly 1.7, at low temperatures and pressures, making them competitive with or superior to current commercial metal hydride materials [3]. Further, the light weight and low cost of Ti-3d transition metal alloys offer significant advantages for such applications. A realistic evaluation of their technological usefulness, however, requires knowledge of the equilibrium vapor pressure for hydrogen in the quasicrystal. This information also allows a deeper probe into the quasicrystal structure, reflecting the site energies for hydrogen. Here, we compare previously published measurements of the vapor pressures of hydrogen in $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ with new measurements in $\text{Ti}_{45}\text{Zr}_{30}\text{Ni}_{25}$ quasicrystals, obtaining the absorption pressure-composition isotherms (p-c-T). These data are used to estimate the site energies for hydrogen in quasicrystals, relative to the reference state of hydrogen gas at standard pressure. Also a limited cycling for hydrogen in the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ quasicrystal, a key require-

ment for any application, is demonstrated in this paper.

2. EXPERIMENTAL PROCEDURE

A computer-controlled apparatus was constructed to determine the p-c-T curves. Measurements for pure Pd using this apparatus are in good agreement with previous measurements by others [4], demonstrating the reliability of the system. Known quantities of high purity (99.9999%) hydrogen gas were introduced into an evacuated chamber (< 5×10^{-6} torr) of known volume (78.73 cc), which also contains the sample. The p-c-T curves for the as-quenched quasicrystal ribbons were determined at 350°C. The change in pressure during absorption was measured using two Barocel manometer gauges (Capacitance manometer 600 series, Edwards) with a scale from 0 to 10 torr for pressures lower than 10 torr, and with a scale from 0 to 1000 torr for pressures higher than 10 torr. Vapor pressures lower than 10 torr were assumed to be in equilibrium when they changed by less than 0.05 torr over one hour, while the vapor pressures higher than 10 torr were assumed to be in equilibrium when they changed by less than 0.5 torr over one hour. The H/M value was calculated from both the pressure change and from the weight gain after the p-c-T measurements using a Cahn micro-balance, having an accuracy of $\pm 5 \mu\text{g}$. Both measurements gave the

same result. Prior to loading, all samples were plasma-etched for two hours in an argon atmosphere to remove the oxygen layer. Etched samples were then immediately coated by a thin layer of Pd (≈ 200 Å) [5]. These treatments effectively removed the surface barrier, allowing the equilibrium vapor pressure to be attained. Powder x-ray diffraction data were taken on all samples before and after p-c-T measurements using Cu-K α radiation, to identify the phases present and to correlate peak shifts with the amount of hydrogenation. The microstructures of the as-prepared and hydrogenated samples were examined using a JEOL 2000FX transmission electron microscope (TEM) equipped with a Noran energy dispersive x-ray spectrometer (EDS).

3. RESULTS

3.1. P-c-T measurements in Ti-Zr-Ni quasicrystals

When plasma etched and Pd coated quasicrystal ribbons are exposed to hydrogen gas, the hydrogenation proceeds readily at elevated temperatures, while no hydrogen absorption by the quasicrystal ribbons is observed at room temperature with 100 torr of hydrogen pressure. Fig. 1 shows the measured equilibrium vapor pressure for the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ and $\text{Ti}_{45}\text{Zr}_{30}\text{Ni}_{25}$ quasicrystal phase ribbons as functions of H/M at 350°C. The vapor pressure remains low (< 5 torr) until $\text{H/M} \approx 1$, after which it increases sharply with increasing H/M. No clear evidence for a pressure plateau was observed. Such p-c-T curves are uncharacteristic of either crystal or amorphous metal hydrides. They presumably reflect the different structural characteristics of the quasicrystal.

The distribution of site energies for hydrogen in the quasicrystals was estimated from a fit to the data. Because

each interstitial site can only be filled by one hydrogen atom, the occupation statistics are described by a Fermi-Dirac distribution. Also, the distribution of possible energy sites for hydrogen atoms are assumed to follow a Gaussian distribution. These assumptions lead to a relation between x , the normalized concentration of hydrogen relative to the maximum H/M value (taken to be $\text{H/M} = 1.7$), and $\Delta\mu_i$, the i -th site energy relative to the reference state of hydrogen gas at standard pressure [6].

$$x = \frac{\frac{H}{M}}{\left(\frac{H}{M}\right)_{\text{Max}}} = \frac{\sum_{i=1}^k A_i \left(1 + \text{erf}\left(\frac{\Delta\mu_i + RT \ln \sqrt{p}}{\sigma_i}\right)\right)}{2N} \quad (1)$$

Here A_i and σ_i represent the areas and widths of the peaks for the i -th site, and R , T , P , N are the gas constant, temperature, measured pressure, and number of possible interstitial sites for hydrogen in the sample, respectively. Non-linear least square fits of Eq. 1 agree well with the experimental p-c-T curves for the quasicrystals. For the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ quasicrystal, the fits suggest one prominent site energy for hydrogen centered between -0.2 eV and -0.5 eV with a suggested tail of broad weakly binding sites at higher energy (Fig. 2). Site energy distribution calculations, however, are strongly dependent on the local slope of the p-c-T curves. The integrated area of the prominent peak, reflecting the number of interstitial sites occupied by hydrogen, is about half of the total area, suggesting that half of the absorbed hydrogen atoms are strongly bound by Ti or Zr atoms, and the other

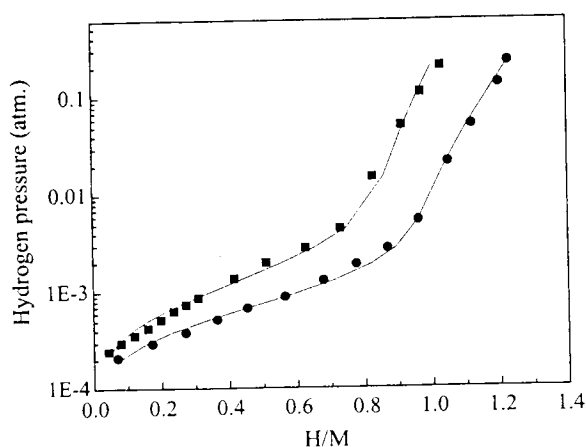


Fig. 1. The equilibrium vapor pressure of hydrogen versus hydrogen concentration measured for $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ (solid circle) and $\text{Ti}_{45}\text{Zr}_{30}\text{Ni}_{25}$ (solid square) quasicrystals. Fits to equation 1 are shown by solid lines. The measurement uncertainties are not shown, but are reflected in the fit error given in Fig. 2.

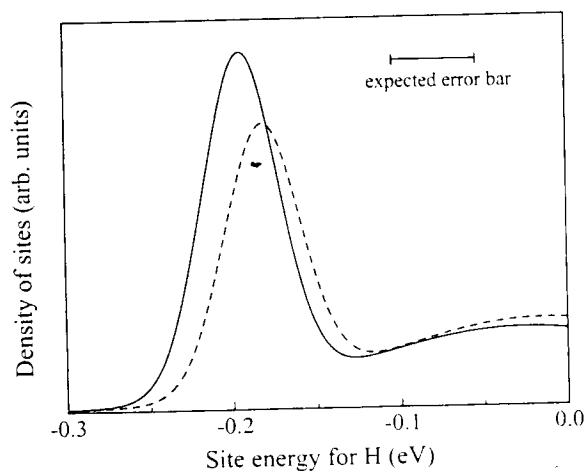


Fig. 2. The site energies for hydrogen obtained by a non-linear least squares fit to the p-c-T data for $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ (solid line) and $\text{Ti}_{45}\text{Zr}_{30}\text{Ni}_{25}$ (dashed line) quasicrystals. Note that these data are schematic only because the formation of a crystal hydride phase makes a quantitative interpretation impossible. The uncertainty in the peak positions (shown by the error bar) is ≈ 0.05 eV.

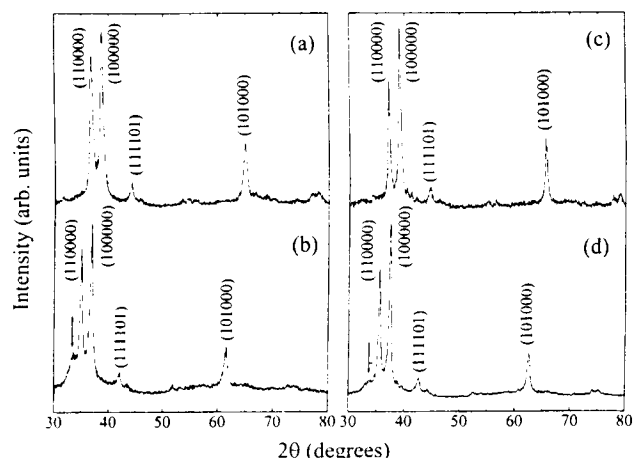


Fig. 3. X-ray diffraction patterns taken from $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ and $\text{Ti}_{45}\text{Zr}_{30}\text{Ni}_{25}$ quasicrystal ribbons before ((a) and (c) respectively) and after hydrogenation ((b) and (d) respectively). The (Ti,Zr)-H₂ hydride phase peak (an fcc (Ti,Zr)-H₂ phase with a lattice constant of 4.6 Å) is indicated by an arrow in (b) and (d). The quasicrystal phase peaks are indexed by the scheme proposed by Bancel *et. al* [7].

half of the hydrogen atoms are weakly bound by Ni atoms. As shown in Fig. 1, the p-c-T curve shows an abrupt change in slope around an H/M value of 0.9; this likely signals the filling of the less tightly bound sites. As shown in Fig. 3(b) the formation of a crystal hydride phase, which has an extremely low vapor pressure, can significantly influence this, making these results of a qualitative nature only.

For the $\text{Ti}_{45}\text{Zr}_{30}\text{Ni}_{25}$ quasicrystals, the best fit to Eq. 1 suggests that the main peak is shifted slightly to higher energy. The integrated area of the prominent peak is slightly reduced from that of the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ quasicrystal. These observations are consistent with the higher concentration of the less tightly binding element, Ni. X-ray diffraction patterns taken from these samples after the p-c-T measurements (Fig. 3(d)), however, show less crystal hydride phase, increasing the uncertainty of the comparison between these two quasicrystals.

3.2. Hydrogen cycling ability in Ti-Zr-Ni quasicrystals

The desorption p-c-T curves for hydrogen in the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ quasicrystal were not determined due to the low vapor pressure from the sample. Instead, the hydrogen cycling ability of the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ quasicrystal was measured as follows: after the p-c-T measurement, the absorbed hydrogen was desorbed by continuous pumping from the sample at 650°C for one hour using a turbo-molecular pump. After the hydrogen was desorbed, a second p-c-T measurement was made at 300°C for the same sample. The second p-c-T curve is almost the same as the first one, only offset by H/

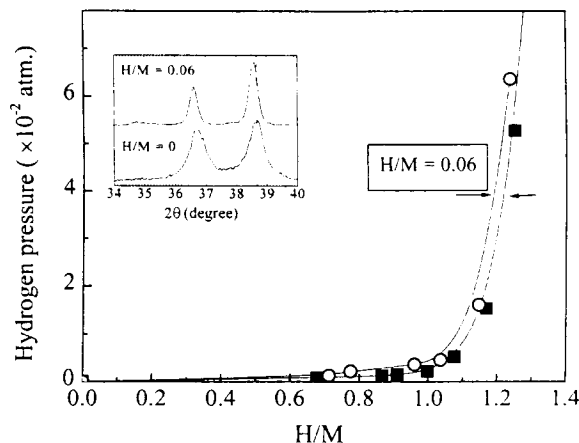


Fig. 4. The p-c-T curves for the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ quasicrystal phase sample measured at 300°C for the first run (solid square) and the second run (open circle). The second run was measured after the hydrogen was desorbed at 650°C by continuous pumping for one hour.

M = 0.06 (Fig. 4), demonstrating that almost all of the hydrogen was removed and showing the cycling ability of the quasicrystal. The 2θ position of the (100000) peak in the x-ray diffraction pattern taken from the quasicrystal phase after the hydrogen was desorbed differed by only 0.078° from its position in the as-quenched sample before hydrogenation (H/M = 0), confirming that 96% of the absorbed hydrogen was desorbed (insertion in Fig. 4). Throughout three absorption-desorption-absorption cycles, the quasicrystal phase and the sample integrity were maintained (*i.e.* no reduction to powder), giving a limited demonstration of the reversibility of hydrogen storage.

4. CONCLUSION

The hydrogen absorption pressure-composition isotherms in as-quenched $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ and $\text{Ti}_{45}\text{Zr}_{30}\text{Ni}_{25}$ quasicrystal ribbons were presented. Results have demonstrated: 1) a highly sloping pressure plateau, presumably reflecting the different structural characteristics of the quasicrystal from the crystal and amorphous phases; 2) a lower binding energy for hydrogen in quasicrystals containing more Ni, although this result is partially influenced by the reduction of a crystal hydride phase that forms during hydrogenation in the higher Ni samples; and 3) the maintenance of the sample integrity of the quasicrystal during a limited number of hydrogenation/desorption cycles. These results provide valuable new structural information on this novel phase, and hint a possibility for the use of Ti-Zr-Ni quasicrystals in hydrogen storage applications, if their hydrogen vapor pressure can be increased.

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