Hydrogen absorption in Ti–Zr–Ni quasicrystals and 1/1 approximants

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Abstract

Ti/Zr-based quasicrystals and their approximants draw attention as new candidate materials for hydrogen storage applications based on recent discoveries that they absorb a large amount of hydrogen, reversibly, at low temperatures and pressures. In fact, $Ti_{45}Zr_{38}Ni_{17}$ quasicrystals take hydrogen to a maximum value of hydrogen to host metal atom ratio (H/M) of nearly 2. To evaluate their technical usefulness and to probe the local structure of the quasicrystals, pressure–composition isotherms (p–c–T) were measured above 250 °C using a computer-controlled apparatus. In the Ti–Zr–Ni quasicrystal, 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 and increases sharply for increasing H/M. In the Ti–Zr–Ni 1/1 approximant phase, which is a large unit cell bcc structure ($a = 13.13$ Å), the p–c–T measurements show similar curves with a hint of pressure plateau consistent with a structural similarity between the phases. The quasicrystals desorb most of the absorbed hydrogen above 600 °C for 2 h in dynamical vacuum without phase transformation, and they do not become powder, even after a few absorption–desorption cycles. Interestingly, a small amount of Pd inhibits the growth of the $(Ti,Zr)H_x$ hydride phase during hydrogenation.
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1. Introduction

Recently, Ti-based quasicrystals have been suggested as potential hydrogen storage materials, especially for battery applications. Particular attention has focused on Ti–Zr–Ni alloys, where the quasicrystal is thermodynamically stable [1]. These quasicrystals are known to reversibly store large quantities of hydrogen (to a density exceeding that of liquid hydrogen) at low temperatures and pressures, making them competitive with or superior to current commercial metal hydride materials [2]. Further, the light weight and low cost of Ti-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. In this paper, we present the measurements of the vapor pressure of hydrogen in quasicrystals and related phases, obtaining the absorption pressure–composition isotherms (p–c–T). These data are further used to estimate the site energies for hydrogen in these phases relative to the reference state of hydrogen gas at standard pressure. Also, a limited cycling for hydrogen in the Ti–Zr–Ni quasicrystal, a key requirement for any application, is demonstrated.

2. Experiments

A computer-controlled apparatus was constructed to determine the p–c–T curves. 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 samples were determined for temperatures between 200 and

400 °C. The change in pressure during absorption was measured using a Barocel manometer gauge with a scale from 0 to 10 Torr (gauge resolution of 0.005 Torr). The vapor pressure above the sample was assumed to be equilibrium when it changed by less than 0.05 Torr over 1 h. The validity of this definition of the equilibrium pressure was tested in the as-quenched $Ti_{45}Zr_{38}Ni_{17}$ samples at 350 °C by calculating the asymptotic values that were obtained from the last 200 data points, where equilibrium was assumed. The amount of hydrogen absorbed by the sample, denoted by the hydrogen to host metal ratio (H/M), was calculated from both the pressure change and the weight gain after the *p–c–T* measurement, using a Cahn micro-balance, with an accuracy of ± 5 μg. Both measurements gave the same result within 5%. Prior to loading, all samples were plasma-etched (400 V DC, 80 mA) for 2 h in an argon atmosphere to remove the oxygen layer. Etched samples were then immediately coated by a thin layer of Pd (≈ 200 Å). These treatments effectively removed the surface barrier, allowing the equilibrium vapor pressure to be attained [3]. A JEOL 2000FX TEM was used to obtain the morphology, high resolution image, and diffraction patterns from individual grains in the sample. A Noran Voyager/Pioneer energy dispersive X-ray spectrometer (EDXS), equipped with an ultra-thin NORVAR window, was used to measure the chemical compositions of the phases present.

3. Results and discussions

3.1. Isotherms

When etched, nonoxidized, as-quenched quasicrystal ribbons are exposed to hydrogen, the hydrogenation proceeds readily at elevated temperatures. Notable hydrogen diffusion into the ribbons was obtained when the ribbons were heated above 250 °C. Hydrogen absorption was fast for H/M < 0.6 and equilibrium was reached within 5 h.

Fig. 1(a) shows the measured equilibrium vapor pressure for the $Ti_{45}Zr_{38}Ni_{17}$ quasicrystal phase as a function of H/M. The vapor pressure remains low (<5 Torr) until H/M $\approx$ 1, after which it increases sharply with increasing H/M. No clear

evidence for a pressure plateau was observed. They presumably reflect the different structural characteristics of the quasicrystal.

One of the simple ways to determine the distribution of sites for hydrogen is described as a relation between *x*, the normalized concentration of hydrogen relative to the maximum H/M value, and $\Delta \mu_i$ [4–6]

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

where $\Delta \mu_i$ is the energy of the *i*th site relative to the reference state of hydrogen gas at standard pressure obtained by non-linear least square fits to the experimental *p–c–T* curves. When the maximum H/M value is equal to 2, the fits indicate one prominent site energy for hydrogen, $\Delta \mu_1$, of -0.187 eV with an FWHM of 0.05 eV. A broad background, a second peak, is centered near $\Delta \mu_2 = -0.025$ eV (Fig. 1(b)).

While the isotherm measurements made between 300 and 400 °C were reproducible, the measurements made at lower temperatures were not. At 250 °C, for example, the equilibrium pressures showed 0.2 Torr variations from sample to sample. This may be due to a slow hydrogen diffusion rate at low temperature, or an incomplete removal of the oxygen layer by etching reducing the hydrogen absorption rate. When samples were heated above 400 °C under hydrogen pressure below 100 Torr, a significant volume fraction of the ribbons (>40%) transformed into the $(Ti,Zr)H_x$ hydride phase, which made it difficult to accurately measure the vapor pressure for the quasicrystal. The combined X-ray diffraction and TEM studies including EDXS measurements indicate that the hydride phase is a fcc structure ($a = 4.63$ Å) with a chemical composition of 40–49 and 60–51 at.% for Ti and Zr, respectively. Since hydrogen is a light atom, the accurate concentration of hydrogen in the hydride phase could not be determined from EDXS measurements.

For a $Ti_{45}Zr_{38}Ni_{17}$ 1/1 approximant phase which was prepared by annealing in vacuum at 570 °C for 64 h [7], the site energy for hydrogen, $\Delta \mu_1$, is -0.187 eV with a FWHM of
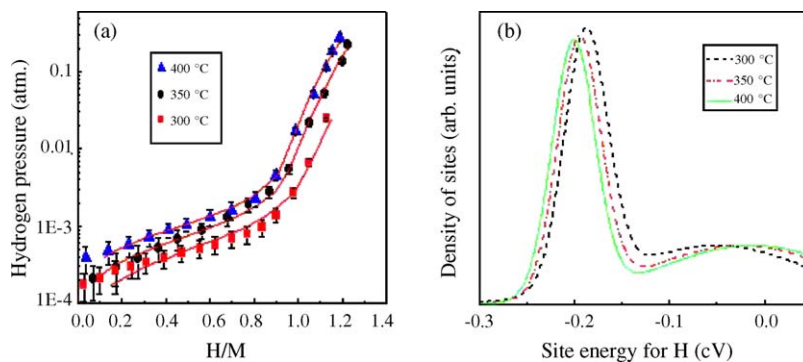

Fig. 1. The equilibrium vapor pressure of hydrogen vs. hydrogen concentration (a) and the site energies for hydrogen obtained by the non-linear least squares fit to the *p–c–T* data (b) measured for $Ti_{45}Zr_{38}Ni_{17}$ quasicrystals. In (a), fits to the equation in the text are shown by solid lines.

0.03 eV. This energy distribution is narrower than that of the quasicrystal phase, suggesting more homogeneous site chemistry than in the quasicrystal. Again, a broad second peak ($\Delta\mu_2 = -0.08$ eV, FWHM = 0.3 eV) is obtained. The similar values of the site energy distributions reflect structural similarities between the quasicrystal and 1/1 phases [8]. The narrower distribution of site energies in the 1/1 crystalline approximant phase is similar to that for AB_2 Laves-phase intermetallic hydrides (A = Zr, B = V, Cr, Mn) [9,10].

3.2. Effects of Pd

Pd was added to the $Ti_{45}Zr_{38}Ni_{17}$ quasicrystals forming $Ti_{45}Zr_{36}Ni_{17}Pd_2$ and $Ti_{45}Zr_{34}Ni_{17}Pd_4$ to increase the vapor pressure, and to be a suitable hydrogen storage application material. Once hydrogenation begins, it proceeds at a faster rate (nearly four times faster than for the $Ti_{45}Zr_{38}Ni_{17}$ quasicrystals) in the samples prepared with 2 at.% Pd. This suggests a higher diffusion rate in the samples prepared with Pd. The X-ray diffraction pattern from these samples show a reduction of the hydride phase after hydrogenation (see Fig. 2 (a)).

3.3. Hydrogen cycling

The desorption *p–c–T* curves for hydrogen in the $Ti_{45}Zr_{38}Ni_{17}$ quasicrystal were determined by measuring the pressure rise in the evacuated sample chamber from a sample of known H/M. The stabilized pressure should be the equilibrium vapor pressure. The H/M in the sample was computed from the number of moles of hydrogen lost to the gas phase. The *p–c–T* curves were the same for desorption and absorption down to H/M ≈ 0.8, the lower limit for the desorption measurements. For smaller values, the change in H/M during
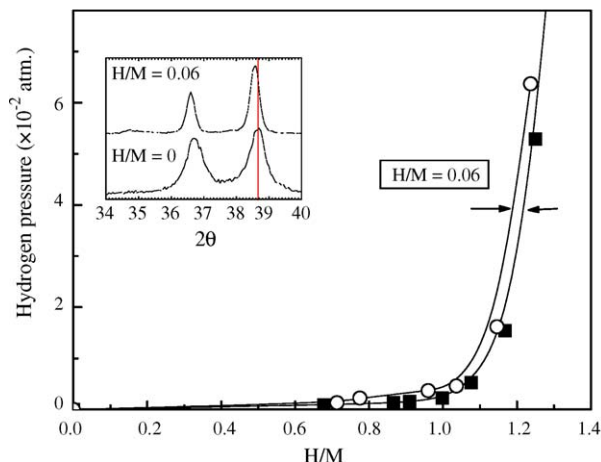
Fig. 3. The *p–c–T* curves for the $Ti_{45}Zr_{38}Ni_{17}$ quasicrystal phase sample measured at 300 °C for the first run (solid square) and the second run (open circle). The second run was measured after the hydrogen was desorbed at 650 °C by continuous pumping for 1 h.

each evacuation became so small due to the low vapor pressure that continued measurements were not practical with the current apparatus.

When the hydrogenated quasicrystal ribbons were annealed in vacuum at temperatures above 400 °C, they transformed to the hydride phase and a C14 Laves phase ($a = 5.23$ Å, $c = 8.75$ Å). High-temperature X-ray and TEM data, however, have demonstrated that the quasicrystal phase reappears above 638 °C [11], making it possible to perform hydrogen cycling experiments. The hydrogen in the quasicrystal was desorbed by pumping on the sample at 650 °C for 1 h. The 2θ position of the (100,000) peak in the X-ray diffraction pattern taken from the quasicrystal phase after the hydrogen was desorbed differed by only 0.078 °C from its position in the as-quenched sample before hydrogenation (H/M = 0), suggesting that 96% of the absorbed hydrogen was desorbed. 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/M = 0.04 (Fig. 3), demonstrating the cycling ability of the quasicrystal. Throughout the absorption–desorption–absorption cycle, the quasicrystal phase and the sample integrity (i.e. no reduction to powder) were maintained, giving a limited demonstration of the reversibility of the hydrogen storage.

4. Conclusions

The measurements of the hydrogen absorption pressure–composition isotherms in quasicrystals were presented. Results have demonstrated that: (1) the distribution of site energies for hydrogen is intermediate to results from other crystal metal hydrides, such as the C14 phases, and amorphous metals, (2) the local atomic structures in the quasicrystal and the corresponding 1/1 crystal approximant are similar based
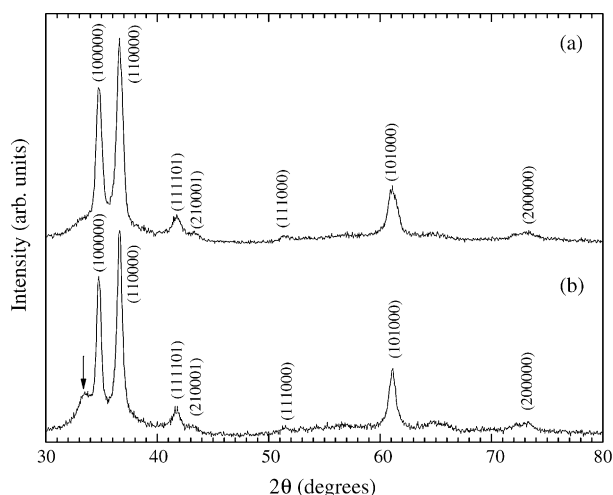

Fig. 2. X-ray diffraction ($\lambda = 1.542$ Å) pattern taken from $Ti_{45}Zr_{36}Ni_{17}Pd_2$ quasicrystal ribbons (a) and $Ti_{45}Zr_{36}Ni_{17}$ quasicrystal ribbons (b). Both samples were hydrogenated at 350 °C and cooled down to room temperature (H/M = 1.8). The (Ti,Zr)-H_2 hydride phase peak formed in the samples without Pd is indicated by an arrow in (b).

on the computed site energy distributions and (3) the sample integrity of the quasicrystal is maintained during a limited hydrogen cycling. These results provide valuable new structural information on this novel phase and support continued study for the potential use of Ti–Zr–Ni quasicrystals in energy storage applications.

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