

## Hydrogen storage in Ti–Zr and Ti–Hf-based quasicrystals

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The depletion of the world's petroleum reserves and the increased environmental impact of conventional combustion-engine-powered automobiles are leading to renewed interest in hydrogen storage materials. In the mid 1990s, Ti/Zr/Hf-based quasicrystals were demonstrated to store more hydrogen than competing crystal intermetallic phases. Unfortunately, recovery of the hydrogen required temperatures in excess of 400°C, severely limiting the technological application of these materials. Here, the Ti/Zr-Hf-based quasicrystals and crystal approximants are reviewed and their hydrogenation properties are discussed. We also report the discovery of a relatively flat pressure plateau for hydrogenated TiZrNi quasicrystals at modest pressures (100–200 psi) that extends to hydrogen concentrations in excess of 4 wt.%. Approximately 2 wt.% of the hydrogen is easily recovered by heating at temperatures as low as 200°C.

### 1. Introduction

Estimates vary on the timing, but all agree that the world's petroleum reserves are within a few decades of severe depletion. This, the remarkably increasing demand from regions of the world outside the United States, particularly China, and the negative environmental impact of oil-based combustion engines, are forcing attention toward the use of hydrogen as an alternate transportation fuel. Hydrogen contains three times the energy of conventional hydrocarbon fuels, and since the byproduct of hydrogen combustion with oxygen is water, the environmental impact is greatly reduced.

Hydrogen storage is a key issue preventing the development of hydrogen-powered automobiles. The figure of merit for hydrogen-storage materials is the weight of the materials needed to store the hydrogen; recently, the US Department of Energy set a goal of 6.5 wt.% for transportation needs. Hydrogen atoms can be absorbed into either interstitial sites or on surfaces of materials.

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Much of the past research has focused on crystalline and amorphous metallic alloys, which can store hydrogen in amounts between 2 and 4 wt.%. The recovery of the hydrogen, however, typically requires heating the material to high temperatures. Lightweight carbon-based storage materials, such as carbon nano-tubes, and high porosity metal-organic framework materials, provide potential alternatives, but studies of these materials have only recently started and their properties are not yet optimised. The more mature technology of metal hydrides makes them attractive candidates for meeting the immediate need.

The numerous tetrahedral interstitial sites in icosahedral quasicrystals, structurally favourable sites for hydrogen absorption, give these novel phases potential technological importance. Since hydrogen atoms favour Ti, Zr or Hf alloys, Ti/Zr/Hf-based quasicrystals are most promising. As an added benefit, the constituent materials are low-cost. In the mid-1990s Ti–Zr–Ni quasicrystals were found to store large amounts of hydrogen (to a weight percent of 2.5%, exceeding that of  $\text{LaNi}_5$ ) with relatively rapid absorption [1–3]. At that time, however, the hydrogen equilibrium vapour pressures were too low at reasonable desorption temperatures to be of practical importance. Recent advances have improved their prospects, revealing a relatively flat plateau at high pressures (100–200 psi) for hydrogen concentrations to 3 hydrogen atoms per metal atom ( $\text{H}/\text{M} = 3$ ) in the  $\text{Ti}_{41.5}\text{Zr}_{41.5}\text{Ni}_{17}$  quasicrystal, exceeding 4 wt.%. Hydrogen desorption from  $\text{H}/\text{M} = 3$  to 1.5 was demonstrated at temperatures as low as 200°C. Absorption and cycling are improved in mechanically milled powders that contain nanometer quasicrystal grains [4]. Furthermore, the hydride formation is dramatically reduced in  $\text{Ti}_{40}\text{Hf}_{40}\text{Ni}_{20}$  compared to  $\text{Ti}_{41.5}\text{Zr}_{41.5}\text{Ni}_{17}$ , suggesting an improved cycling ability for this phase [5].

Here, past studies of hydrogen in these quasicrystals and related phases are discussed, and recent results of hydrogen storage capacities exceeding those of traditional intermetallics are presented. Hydrogenated quasicrystals may also afford the opportunity to gain additional fundamental insight, using hydrogen as a local probe of quasicrystal structure and dynamics. Results from existing studies are discussed.

## 2. Hydrogen absorption in quasicrystals

### 2.1. Overview of Ti/Zr/Hf-based quasicrystals

The two classes of Ti-based quasicrystals exhibit different hydrogen absorption properties. Only small quantities of hydrogen can be absorbed in the titanium–transition-metal–silicon–oxygen (Ti–TM–Si–O) quasicrystals [6], best represented by  $\text{i}(\text{TiCrSiO})$  [7], presumably due to blocking by the interstitial oxygen that is essential for the quasicrystal formation [8]. In contrast, the Ti–Zr/Hf–Ni type quasicrystals and approximant phases addressed in this review absorb large amounts of hydrogen, up to at least 4 wt.% (c.f. section 4).

The thermodynamically stable Ti–Zr–Ni quasicrystals are structurally related to  $\text{W}(\text{TiZrNi})$ , a bcc phase formed from a packing of Bergman clusters. The centre of the Bergman cluster is filled, unlike the case of the Al–Mg–Zn Bergman phase [9, 10]. *Ab-initio* calculations show that the formation of a cluster with a vacant centre in

W(TiZrNi) would require an energy of  $\sim 3$  eV [10]. The first shell in the cluster is occupied by Ti atoms and the third shell by Ni and Zr atoms. The local order in i(TiZrNi) appears to be dominated by stable, well-ordered clusters of this type. When packed together, however, the stability of the clusters forces a chemical and structural disorder in the cluster linkages. *Ab-initio* calculations show that the formation of anti-site defects is energetically more favourable in the region between the clusters than on the cluster, explaining the observed chemical disorder in the region between clusters, the so-called ‘glue’ region [10]. A canonical cell-tiling-based structural model for i(TiZrNi) has been constructed using 38 diffraction peaks (14 X-ray diffraction peaks and 24 neutron peaks), with 6 classes of atomic sites and 3 Debye-Waller factors [10]. Because the number of diffraction peaks was small (due to disorder in the quasicrystal), density functional theory relaxations ensured that the proposed structure is realistic. The local symmetry of the tiles is icosahedral, although individually they do not form complete icosahedra.

Although Chebotnikov *et al.* [11] reported quasicrystal formation in rapidly quenched Ti–Hf–Ni alloys, electron diffraction studies show systematic shifts of the diffraction spot locations from those of the quasicrystal [12]. They are in good agreement with those expected for a  $3/2$  rational approximant (RA) phase RA(TiHfNi).

## 2.2. Previous studies of hydrogen absorption in Ti/Zr/Ni quasicrystals

Previous work demonstrated that Ti–Zr–Ni quasicrystals could absorb large amounts of hydrogen, of order 1.7 hydrogen atoms for each metal atom ( $H/M \approx 1.7$ ) [2, 13]. This was a higher capacity than for  $\text{LaNi}_5$  ( $H/M \approx 1$ ), commonly used in hydride batteries, or Ti–Fe, one of the more promising materials for stationary hydrogen storage applications [13]. As will be discussed, an absorption in excess of 4 wt.% of H has recently been demonstrated in Ti–Zr–Ni quasicrystals (c.f. section 4). Hydrogen absorption from the gas phase in as-quenched i(TiZrNi) requires pressures of 5–40 atm. to overcome a surface barrier due to a thin surface oxide [1, 2]. The surface oxide is readily removed, however, by a short period of plasma etching followed by a thin ( $\approx 200$  Å) coating of Pd [14]. The Pd protects the sample and catalyses the dissociation of molecular hydrogen to the atomic hydrogen required for absorption, enabling the hydrogen to be easily absorbed at pressures less than 1 atm.

The quasilattice constant increases with hydrogenation [15], although the volume expansion is anisotropic, likely due to H–H-based elastic interactions [16]. EXAFS measurements indicate that the hydrogen atoms prefer to sit next to Zr and Ti atoms [17, 18], consistent with behaviour in crystal metal hydrides, causing the Ni–Zr and Ni–Ti distances to decrease with increasing H/M. The lattice expansion during hydrogenation makes the required atomic motion to accommodate this inversion of distances easier. However, the lattice contraction during desorption impedes the relaxation of the local atomic structure and may partially explain the difficulty in removing all hydrogen. The EXAFS studies also show that while W(TiZrNi) and i(TiZrNi) are similar in the as-prepared states, they are very different after hydrogenation, consistent with ultrasonic studies that

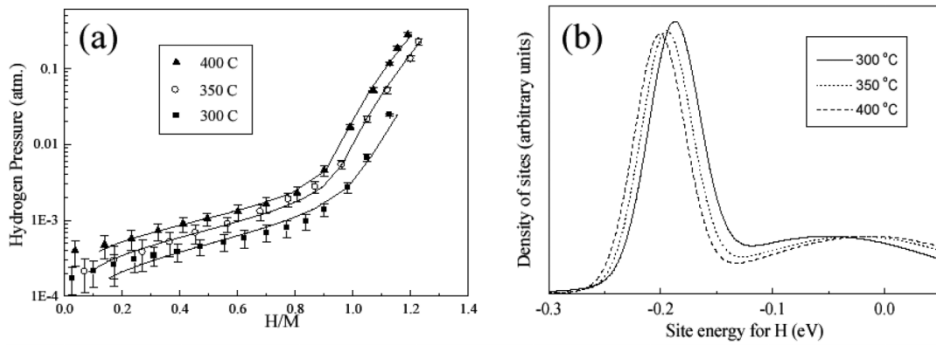


Figure 1. (a) The measured equilibrium vapour pressure of hydrogen as a function of hydrogen concentration for  $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$  quasicrystals. The solid lines are fits to the data assuming a Gaussian distribution of binding sites. (b) The site energies obtained from the PCT data in (a).

show an order of magnitude faster hydrogen motion in the quasicrystal than in the crystal approximant phase [19].

Measurements of NMR second moment data,  $M_2$ , as a function of H/M, suggest that the hydrogen atoms fill a set of evenly distributed sites [20], rather than clustering together. The  $M_2$  data are well fit using the distribution of interstitial sites predicted by the canonical cell tiling model for the quasicrystal, shown in figure 1. However, further studies showed that they could also be fit by a random distribution of sites, indicating that they are not sufficiently sensitive to discriminate between proposed structural models.

High resolution X-ray studies of  $i(\text{TiZrNi})$  show that the random phason disorder increases significantly with hydrogenation [21]. Mechanical spectroscopy studies of hydrogenated quasicrystals are sensitive to the short-range order and have been used to investigate the phason character of structural disorder and point defect relaxations. While the H-induced damping peaks are similar in  $i(\text{TiZrNi})$  and a Zr-based glass, there are differences in peak shape, which might reflect different local icosahedral structures in the two phases [22]. The directly measured activation energies for H diffusion in  $i(\text{TiZrNi})$ , 0.24–0.25 eV, are comparable with those measured in crystal Ti-alloys [23], suggesting that differences deduced from ultrasonic measurements between the diffusion rates in  $i(\text{TiZrNi})$  and  $\text{W}(\text{TiZrNi})$  [19] may simply reflect different hydrogen concentrations.

### 3. Hydrogen PCT measurements in quasicrystals

Isothermal measurements of the equilibrium vapour pressure of hydrogen as a function of hydrogen concentration in the metal (pressure-composition-temperature measurements, or PCT) are key for an evaluation of the technological usefulness of the material for hydrogen storage applications. The existence of a pressure plateau is important for technological applications, since it enables loading and unloading to be carried out at approximately constant pressure. PCT measurements also

provide information regarding the distribution of binding energies for hydrogen sites in the metal. The etching/Pd-coating technique discussed in the previous section enabled the native oxide to be circumvented, allowing studies of the Ti–Zr–Ni quasicrystals. Despite their high capacity for hydrogen storage, these studies indicated that the site binding energies are high for moderate levels of hydrogen absorption ( $H/M < 1.1$ ), leading to plateau pressures that are too low for technological applications (figure 1a). We have recently discovered a higher-pressure plateau that is promising for hydrogen storage applications (c.f. section 4).

The fractional hydrogen concentration,  $c = (H/M)/(H/M)_{\max}$ , can be expressed in terms of the interstitial site energy distribution in the metal host,  $\rho(\varepsilon)$ , and the site occupation probability,  $x(\varepsilon)$ ,

$$c = \frac{\int_{-\infty}^{\infty} \rho(\varepsilon)x(\varepsilon)d\varepsilon}{\int_{-\infty}^{\infty} \rho(\varepsilon)d\varepsilon} \quad (1)$$

An initial analysis of the i(TiZrNi) PCT data was based on an approach that is widely used for analysing absorption data in metallic glasses [24], assuming a multi-mode Gaussian function for the site energy distribution

$$\rho(\varepsilon) = \sum_{i=1}^k \frac{A_i}{\sigma_i \sqrt{\pi}} e^{-\left(\frac{\varepsilon - \varepsilon_i}{\sigma_i}\right)^2}, \quad (2)$$

where  $A_i$ ,  $\sigma_i$  and  $\varepsilon_i$  are the heights, widths and energies of the  $i^{\text{th}}$  Gaussian. Since a site is either occupied or not,  $x(\varepsilon)$  is described by Fermi-Dirac statistics allowing only one hydrogen atom per interstitial site,

$$x(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu_{HM})/k_B T} + 1} \quad (3)$$

where  $\mu_{HM}$  is the chemical potential of the hydrogen dissolved in the metal. Assuming equilibrium between the hydrogen in the vapour phase and in the metal,

$$\mu_{HM} = \frac{1}{2}\mu_{H_2} = \frac{1}{2}k_B T \ln \frac{p}{p_0} = -\frac{1}{2}\mu_{H_2}^0 + k_B T \ln \sqrt{p} \quad (4)$$

Assuming that  $\mu_{HM} \gg k_B T$ , then  $x(\varepsilon) = 1$  for  $\varepsilon < \mu_{HM}$ , and  $x(\varepsilon) = 0$  for  $\varepsilon > \mu_{HM}$ , and defining the energy of the  $i$ th site relative to the reference state of hydrogen gas at standard pressure,  $\Delta\mu_i = -\frac{1}{2}\mu_{gas}^0 - \varepsilon_i$ , gives

$$c = \frac{\sum_{i=1}^k A_i (1 + \operatorname{erf}(\Delta\mu_i + k_B T \ln \sqrt{p}/\sigma_i))}{2(H/M)_{\max}}. \quad (5)$$

Based on this analysis, two sets of energy sites were deduced (figure 1b). The deep site, located near  $-0.2$  eV explains the low equilibrium vapour pressures. The less tightly bound sites, however, near zero binding energy, could give reasonable vapour pressures and cycling ability of the hydrogen.

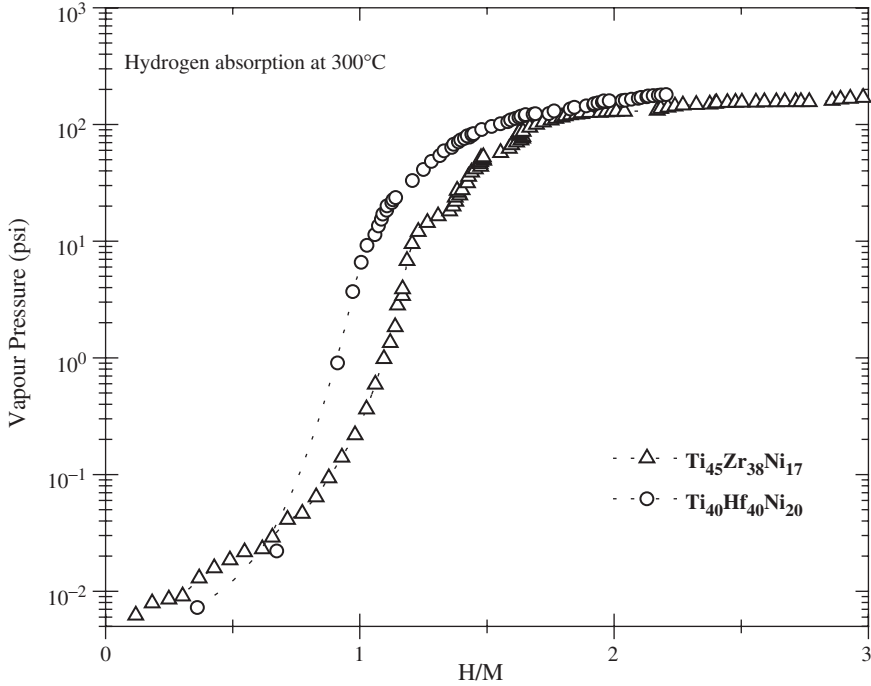


Figure 2. Equilibrium hydrogen vapour pressure for icosahedral phase ( $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ ) and 3/2 rational approximant phase ( $\text{Ti}_{40}\text{Hf}_{40}\text{Ni}_{20}$ ) samples produced by rapid quenching, measured as a function of hydrogen concentration during absorption at  $300^\circ\text{C}$ .

Although widely used,  $\mu_{HM} \gg k_B T$  is not satisfied at the absorption temperatures for either the amorphous or quasicrystal phases. Also, no account is taken of H–H interactions, which give rise to a concentration dependence for  $\mu_{HM}$ . These approximations provide a reasonable picture of the centroid energies of the site energy distribution, but are insensitive to the precise nature of the distribution. They are particularly inaccurate for the very high H/M data taken recently (c.f. figure 2). A more realistic approach, suggested by Griessen *et al.* [25–28], is to solve equation (1) iteratively without assuming the low temperature form for  $x(\varepsilon)$ , which is modified to take into account elastic,  $\Delta\mu_{\text{elast}}$ , and electronic,  $\Delta\mu_{\text{elec}}$ , contributions from H–H interactions

$$x(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_b + \Delta\mu_{\text{elast}}(c) + \Delta\mu_{\text{elec}}(c) + \mu)/k_B T} + 1}, \quad (6)$$

where  $\varepsilon_b$  is one-half the binding energy of molecular hydrogen. Estimates of  $\Delta\mu_{\text{elast}}$  and  $\Delta\mu_{\text{elec}}$  can be made following Feenstra *et al.* [26], which requires values for  $\overline{v_{HM}}(c)$ , the molar volume of hydrogen in the metal as a function of hydrogen concentration, the bulk modulus, and the density of states at the Fermi Energy,  $N(\varepsilon_F)$ .

#### 4. Technologically relevant recent results

In Ti–Zr–Ni quasicrystals, hydrogenation is frequently accompanied by the formation of small amounts of a crystal hydride phase, which could impair cycling ability. This structural phase transition is likely induced by a degradation of the local icosahedral order by hydrogen incorporation and by local heating. The amount of hydride formation is smaller during electrolytic loading, favouring the latter possibility [29]. Hydride phase formation increases during high temperature desorption treatments; studies indicate that this is largely due to a surface barrier that prevents the easy release of the hydrogen from the sample. Interestingly, although  $\text{Ti}_{40}\text{Hf}_{40}\text{Ni}_{20}$ , RA(TiHfNi), has nearly identical hydrogenation properties to those of the icosahedral  $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$  phase, no evidence of a hydride phase is observed after loading from the gas phase at  $250^\circ\text{C}$ , suggesting that RA(TiHfNi) could have superior cycling properties [5].

The absorption and desorption characteristics are improved for nanocrystalline hydrides. Limited studies have shown similar results for i(TiZrNi) and RA(TiHfNi) [4, 30, 31]. In both cases, long induction times for loading are observed for the first absorption, requiring over 200 hours for complete loading. Subsequent absorption times after desorption are more rapid, requiring approximately 50 hours. Based on measured diffusion coefficients for H in i(TiZrNi), diffusion distances are long at the loading temperatures (9–14 mm in 10 minutes, for example). These are much larger than the powder sizes, indicating that the time lag is due to surface processes.

The most dramatic recent result is the discovery of a higher-pressure plateau at higher hydrogen concentrations for both i(TiZrNi) and RA(TiHfNi). Figure 2 shows the PCT curves measured at  $300^\circ\text{C}$  for both samples. Significantly, both indicate the existence of a pressure plateau beginning at an H/M of about 1.2–1.5 and extending to an H/M of 3, for the case of TiZrNi shown here. Since there is no noticeable upturn, the plateau must extend above H/M of 3. Since the vapour pressure exceeded that measurable in our current apparatus, however, this could not be explored. Desorption between 3 and 1.5 is rapid at temperatures as low as  $200^\circ\text{C}$  (based on X-ray diffraction measurements of the samples after removal from the chamber). The hydrogen can be completely desorbed at higher temperatures ( $\geq 400^\circ\text{C}$ ), but with significant hydride phase formation. The ability to cycle hydrogen in the material is crucial; those studies are currently underway.

#### 5. Conclusions and future directions

While early studies of Ti–Zr–Ni quasicrystals showed that hydrogen could be used as a novel probe of the structure and dynamics of the quasilattice, the vapour pressures were too low to be of practical importance. Recent results, however, changed that picture, showing a pressure plateau at 80–200 psi corresponding to a storage capacity in excess of 4 wt.% and an ability to cycle significant quantities of hydrogen in the quasicrystal. The loading/unloading characteristics can be improved by tailoring the quasicrystal microstructure. These results suggest that

Ti/Zr/Hf-based quasicrystals are promising materials for meeting immediate hydrogen storage needs.

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