

Ti–Zr–Ni and Ti–Hf–Ni quasicrystals and approximants as hydrogen storage alloys

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Abstract

X-ray and neutron powder diffraction data previously collected from the Ti–Zr–Ni quasicrystal have been analyzed. The data were modeled by an 8/5 rational approximant (RA) that was constructed using the known structure of the 1/1 RA and then refined. Ab initio total energy calculations were made for small structures with between 81 and 123 atoms, in which atomic positions were allowed to vary while minimizing the energy. The final structure is in good agreement with that obtained from the scattering data. Interstitial sites in which H is stable in the 1/1 model, and the H binding energies, were identified. An excellent fit to existing pressure-composition isotherms was obtained, but those data cannot be inverted to obtain experimental site binding energies. At 250 °C the Ti–Hf–Ni alloy can be loaded with H without the formation of any detectable crystal hydride phase, which is always found in similarly loaded Ti–Zr–Ni alloys.

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1. Introduction

We have developed a model for the structure of the stable Ti–Zr–Ni quasicrystal based on decorations of the canonical cell tiling [1,2]. The initial atomic decoration was based on the structure of the 1/1 rational approximant (RA). The model structure for the icosahedral phase (i-phase) was an 8/5 RA, which has 52 392 atoms per 9.8 nm edge-length cubic cell. The chemical decoration of the ideal atomic positions was optimized in a refinement using X-ray and neutron powder diffraction data. The atomic positions used were checked by an ab-initio total energy calculation for small tilings containing between 81 and 123 atoms, in which atomic positions were allowed to vary while minimizing the energy.

Twenty-five interstitial sites in which H is stable in the 1/1 model were identified and their binding energies computed. An excellent fit to existing pressure-compo-

sition isotherms (PCT) was obtained by adjusting the concentration-dependent excess chemical potential that represents H–H interactions in the alloy in a mean-field description. An excellent fit was also obtained with just two H binding energies and the same concentration-dependent excess chemical potential.

Rapidly-quenched Ti–Hf–Ni alloys appear quasicrystalline in X-ray powder diffraction data, but single-grain electron diffraction has shown that they are RAs, close to the 3/2 [3]. At 250 °C a Ti–Hf–Ni alloy can be loaded with H without the formation of any detectable crystal hydride phase, which is always found in similarly loaded Ti–Zr–Ni alloys [3].

2. Experiments and calculations

Alloy ingots of the desired compositions were made by arc-melting mixtures of 99.9% purity elements on a water-cooled Cu hearth in a high-purity Ar atmosphere. Oxygen concentrations in the elements were less than 200 parts per million. (Ti_{41.5}Zr_{41.5}Ni₁₇)₉₈Pb₂ ingots were then annealed at 600 °C for 64 h in Ar with an O getter

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present. The added Pb accumulates in grain boundaries and enhances the formation of larger quasicrystal grains [4].

X-ray diffraction data were collected using a Rigaku Geigerflex powder diffractometer in the Bragg–Brentano geometry, Cu K_α radiation, and a graphite exit monochromator. The phases present were determined using these data, and microstructures and phase compositions were determined using a JEOL 2000FX transmission electron microscope with a Noran energy-dispersive X-ray spectrometer. Neutron powder diffraction data were collected at the University of Missouri research reactor in collaboration with Majzoub and Yelon, using a wavelength of 0.17675 nm. Twenty-three peaks in the neutron data and 15 in the X-ray data were indexed to the i-phase. Their structure factors were used in a least-squares refinement of the chemical decoration of the ideal atomic positions in the structural model. The chemical composition was constrained by using a penalty function.

The ab initio total energy calculations were done with the Vienna Ab Initio Simulation Package (VASP) [5–7], a density functional method using a plane-wave basis and ultrasoft pseudopotentials. The small, periodic tilings used were the A_6 , the B_2C_2 , and the D_2 [1]. The atomic positions and the shapes and volumes of the unit cells were relaxed until the total energy changes were smaller than 1 meV.

X-ray and neutron powder diffraction data from the 1/1 RA Ti–Zr–Ni were used to refine atomic positions and chemical decorations using the generalized structure analysis system (GSAS) [8]. Ab initio total energy calculations were done as described above. Twenty-five sites in which H is stable were identified and their binding energies were computed, using the VASP code and allowing the H positions to relax. The binding energies were in the range [–0.88, –0.19] eV. Equating expressions for the chemical potential of H dissolved in the alloy to one-half the chemical potential of a gas-phase molecule leads to an expression for the H concentration in the alloy in terms of the vapor pressure of H_2 around it. The concentration dependence of an excess chemical potential [9] that represents H–H interactions in the alloy in a mean-field description was approximated by a four-term polynomial.

Rapidly-quenched samples were quenched from a graphite crucible in an Ar atmosphere onto a Cu wheel with a surface speed of approximately 30 m s^{-1} , to produce ribbons 10–15 cm long, 1 mm wide, and 30 μm thick. As-quenched $\text{Ti}_{40}\text{Hf}_{40}\text{Ni}_{20}$ contains nearly single-phase 3/2 RA [3]. Prior to hydrogenation, the surface oxide was removed from the samples by plasma etching, which was followed immediately by vapor deposition of a thin layer of Pd. Samples were loaded with H in a computer-controlled, modified Sievert's apparatus that produced PCT data [10]. Temperatures of 350 and

250 °C were used for comparison with existing data from Ti–Zr–Ni.

3. Results and discussion

The 1/1 RA in Ti–Zr–Ni was found to have a structure [11] similar to those of the Frank–Kasper phases AlLiCu [12] and AlMgZn [13]. Atomic displacements in the total energy calculations, with relaxation of the atomic positions allowed, were less than 0.013 nm. The positions were within 0.019 nm of the corner, mid-edge, and body-diagonal positions of the Penrose tiling of a 1/1 RA. This made the structure a good starting point for the modeling of the i-phase by a larger, 8/5 RA constructed by the canonical cell tiling method of Henley [1]. Each of the four tiles was decorated with rhombohedra, which were in turn decorated with atoms. The rhombohedra were a prolate rhombohedron, an oblate rhombohedron, and a rhombic dodecahedron, shown in Fig. 1. The b bond was in a twofold direction, for example the cubic cell edge in a 1/1 RA. The c bond was in a threefold direction, for example the corner-to-body-center vector in a 1/1 RA. The atomic sites used are shown in Fig. 2. The decorations of the interiors of the larger B, C, and D cells were completed using the 1/1 RA structure as a guide.

After the refinement and total energy calculations were completed, the results were in good agreement with the diffraction data ($X^2 = 1.4$, $R_W = 5.1\%$), as shown in Fig. 3. The results can be found in a recent paper [2] and in the PhD thesis of Hennig [14].

The distribution of H site energies found in the 1/1 RA is given in Fig. 4, along with the concentration-dependent excess chemical potential. An excellent fit to existing pressure-composition isotherms (PCT) was obtained (Fig. 5) by adjusting the coefficients in the polynomial representation of that potential to give the result shown in Fig. 4. The potential is negative, indicating an attractive H–H interaction that is likely elastic [9]. A

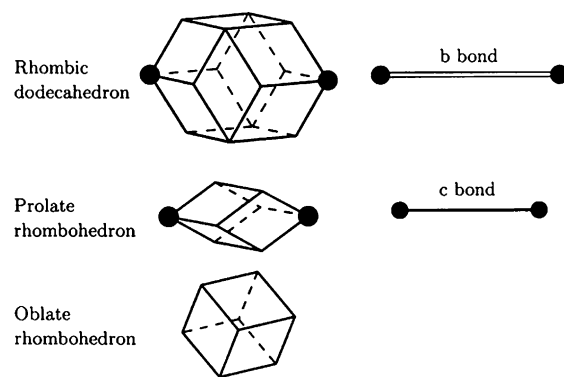


Fig. 1. Three of the rhombohedra into which the canonical cell tiling can be decomposed.

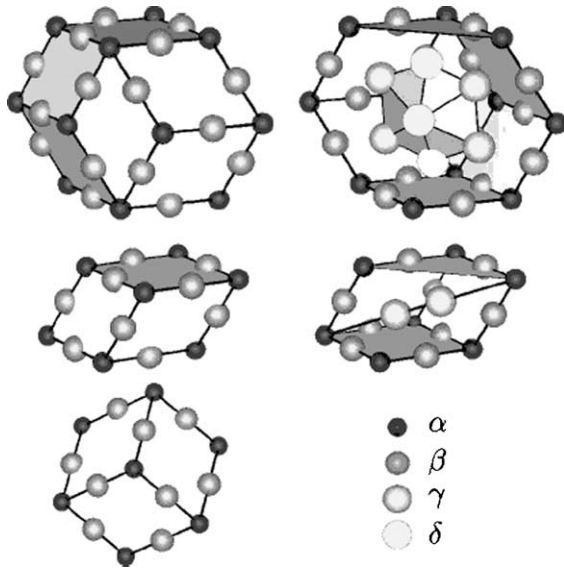


Fig. 2. Atomic sites used in the rhombic dodecahedron (top), the prolate rhombohedron (middle), and the oblate rhombohedron (bottom). On the right are the same rhombohedra with interiors visible.

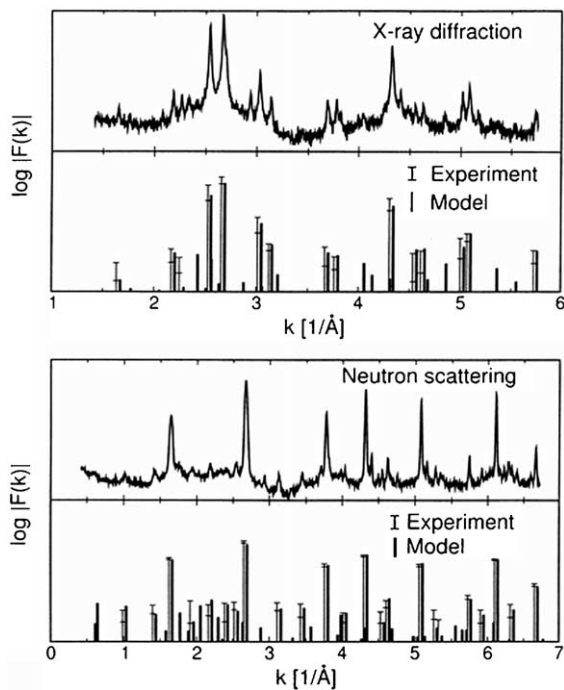


Fig. 3. Comparison of the measured X-ray and neutron diffraction from icosahedral Ti-Zr-Ni with simulated diffraction from the structural model.

model with just two H sites and the same excess chemical potential produced an identical computed PCT curve (Fig. 5). This demonstrates that PCT data alone cannot be used to determine the distribution of H binding energies in these materials.

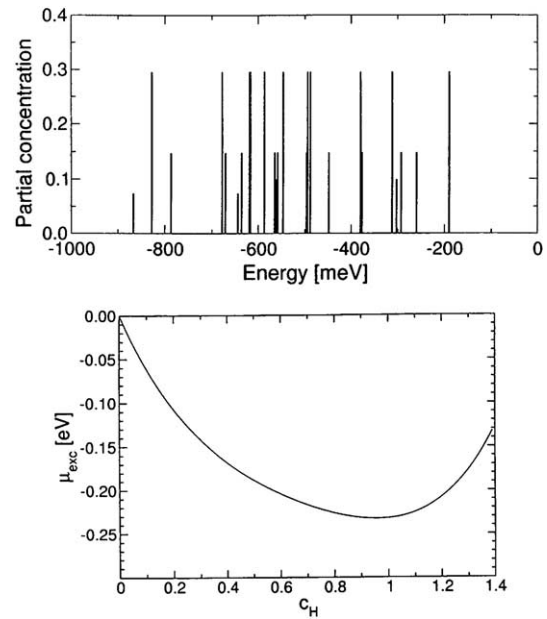


Fig. 4. The distribution of hydrogen site energies calculated in 1/1 RA Ti-Zr-Ni (top), and the excess chemical potential of H in the 1/1 RA vs. hydrogen concentration in units of the hydrogen-to-metal-atom ratio H/M (bottom).

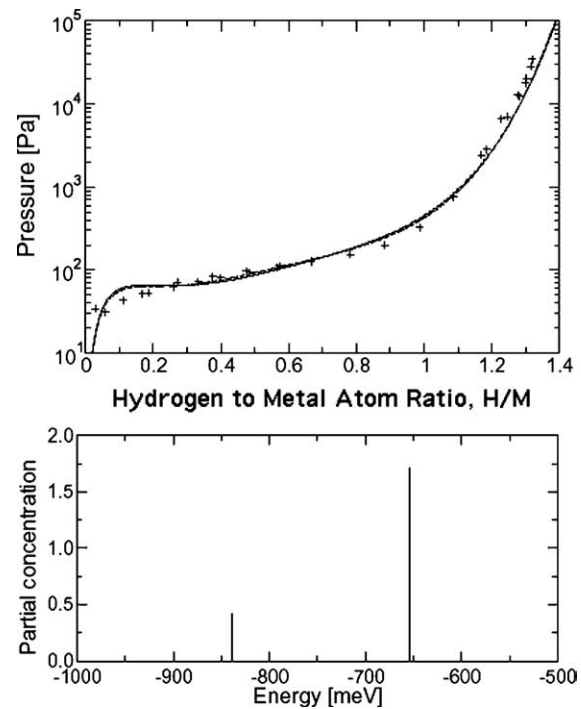


Fig. 5. The equilibrium H_2 vapor pressure vs. H concentration in Ti-Zr-Ni in units of the hydrogen-to-metal-atom ratio H/M (top). Crosses are measured values; the solid line is a calculation using the energy distribution and excess chemical potential shown in Fig. 4; and the dashed line is a calculation using the energy distribution shown (bottom).

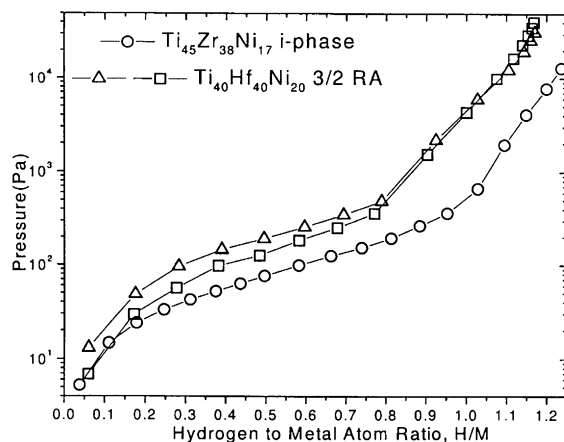


Fig. 6. The equilibrium H_2 vapor pressure at 350 °C vs. H concentration in Ti–Hf–Ni and Ti–Zr–Ni in units of the hydrogen-to-metal-atom ratio H/M. The curves measured using two different Ti–Hf–Ni samples are presented to provide an estimate of errors.

The PCT isotherms (350 °C) from rapidly-quenched 3/2 RA Ti–Hf–Ni are compared with one from icosahedral-phase Ti–Zr–Ni in Fig. 6. The vapor pressures are similar, suggesting similar site-energy distributions. Yet at 250 °C the 3/2 RA Ti–Hf–Ni can be loaded with H without the formation of any detectable Ti–Hf crystal hydride phase; the Ti–Zr crystal hydride phase is always found in similarly loaded Ti–Zr–Ni alloys [3] (Fig. 7). The crystal hydride formation is irreversible and limits the repeated cycling of H in and out of these materials. That no hydride forms in Ti–Hf–Ni may make it a better candidate for hydrogen-storage applications.

4. Conclusions

A large, realistic structural model for the Ti–Zr–Ni quasicrystal was constructed in real, 3D space by the

canonical cell tiling method. It has the correct density and composition with no voids, and no atomic separations that are too small. The structure is consistent with the alloy composition, neutron and X-ray powder diffraction data, and is a stable, minimum-energy state according to total energy calculations on small models of the quasicrystal. That the i-phase grows at lower temperatures than the 1/1 RA, which in turn grows at lower temperatures than other crystalline phases [15,16], suggests that the i-phase may be the low-temperature equilibrium phase. In the 1/1 RA the distribution of hydrogen binding energies has been computed. Using an excess chemical potential to model unknown H–H interactions, the concentration-dependent potential was determined and an excellent fit to existing PCT data was obtained. Another, two-site distribution, used with the same excess chemical potential, also gave an excellent fit, demonstrating that the distribution of H binding energies cannot be determined from PCT data alone. Two-site distributions can be used to compare different alloys. That the 3/2 RA in Ti–Hf–Ni can be loaded with hydrogen at 250 °C with no detectable formation of the crystalline Ti–Hf hydride phase may make it a better material than Ti–Zr–Ni for repeated loading and unloading of H, and therefore a better candidate for hydrogen-storage applications.

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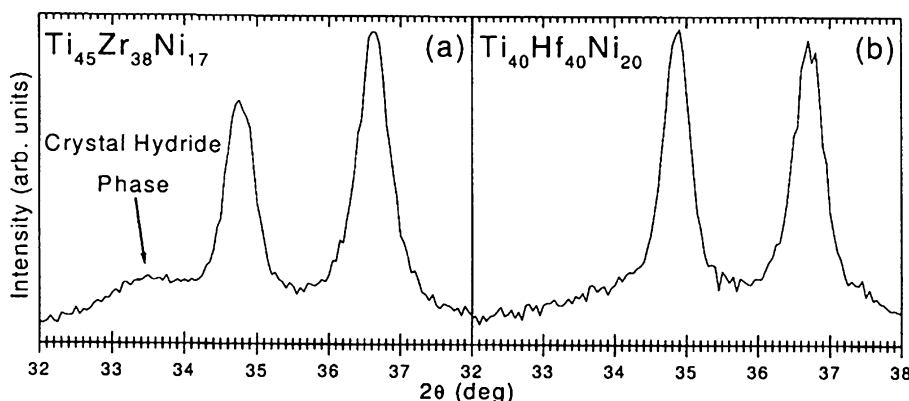


Fig. 7. X-ray diffraction from samples hydrogenated at 250 °C. A peak from a Ti–Zr crystal hydride phase is indicated by an arrow in the left panel.

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