

Stable Ti-based quasicrystal offers prospect for improved hydrogen storage

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The desorption of hydrogen from a novel material, a $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ -H quasicrystal, was observed using high-temperature powder x-ray diffraction, demonstrating the potential utility of Ti-based quasicrystals in place of crystalline or amorphous hydrides for hydrogen storage applications. The maximum observed change in hydrogen concentration was from 61 at. %, corresponding to a hydrogen-to-metal ratio (H/M) of 1.54, at 91 °C to less than 2.5 at. % (H/M=0.025) at 620 °C. The onset temperature of desorption is below 350 °C. Surface oxidation was found to promote the formation of crystalline hydride phases. Highly oxidized samples transformed to a mixture of the C14 Laves and C15 Laves crystalline hydrides, and the Ti_2Ni phase. When the oxidation was less severe, a reversible transformation between the quasicrystal and crystalline hydride phases was clearly observed, demonstrating the stability of the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ quasicrystal at very low hydrogen concentrations, and temperatures as high as 661 °C. This is the first evidence for a stable Ti-based quasicrystal and for reversible hydrogen storage in a quasicrystalline phase. © 1996 American Institute of Physics. [S0003-6951(96)01646-4]

Metal hydrides are increasingly important in the consumer market: the current generation of metal-hydride batteries powers most laptop computers; the next generation may power the electric cars of the future.¹ Our recent research has demonstrated that some Ti-based quasicrystals can store hydrogen at levels exceeding those found in most amorphous and crystalline materials currently being evaluated for hydrogen storage applications.² A key feature, not previously demonstrated for these novel materials however, is the ability to release the hydrogen when required. The reversible hydrogenation and the stability of the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ quasicrystal reported herein firmly establishes the potential of Ti-based quasicrystals for hydrogen storage.

Quasicrystals are a recently discovered³ solid phase, possessing properties similar to both crystals and glasses. Icosahedral phase (*i*-phase) quasicrystals are ordered structures with long-range quasiperiodic order and perfect icosahedral point group symmetry. The short-range icosahedral order of the *i* phase likely resembles that found in metallic glasses.⁴ Over one hundred different alloy systems are known to form *i*-phase quasicrystals, with Al-transition metal and Ti-transition metal alloys forming the two largest classes. Many Al-based alloys are generally well ordered, and in some cases stable. The Ti-based *i* phases are typically less well ordered and metastable. The Ti-Zr-Ni *i* phases are exceptional, having coherence lengths often over 350 Å, and appearing to be stable at the compositions $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ and $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$.

Both alloy structure and chemistry are critical for hydrogen storage. Though presumably all *i*-phase alloys have a high density of tetrahedral interstitial sites, structurally favorable for hydrogen storage, only the Ti-based alloys have favorable chemistry. Previous studies demonstrated the ability of the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ *i* phase to absorb up to 62 at. % hydrogen, corresponding to a hydrogen to metal (H/M) ratio of

1.6.⁵ Even greater hydrogen concentrations in the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ *i* phase, up to H/M 1.9, can be achieved by electrolytic loading.⁶

The hydrogenation of the *i* phase also raises the possibility for several new avenues of investigation into quasicrystalline structures. Used to modulate electron concentration, hydrogen in quasicrystals may provide insight into electronic structure and transport in quasiperiodic structures. Because hydrogen occupies interstitial sites in the *i* phase, neutron scattering and nuclear magnetic resonance studies can now be used to determine the structure, distribution, and chemistry of these previously inaccessible sites. One overriding question of both basic and technological interest to be addressed in future studies is whether quasicrystals have different hydrogen absorption and desorption properties than comparable crystalline and amorphous phases. This report takes a crucial first step toward answering that question by demonstrating hydrogen desorption from the *i* phase and the effect of hydrogen on the stability of the *i* phase.

Rapidly quenched $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ *i*-phase alloys were produced from arc melted ingots by melt-spinning onto a rotating copper wheel. Details of the quenching process can be found elsewhere.⁷ The resulting ribbons were ground by a gentle ball-mill technique in 5 atm of hydrogen to achieve a uniformly loaded *i*-phase powder.

High-temperature x-ray diffraction (HTXRD) measurements were made using a Scintag goniometer, Buehler HDK-2 diffraction furnace and a mBraun position-sensitive detector. The sample and a thermocouple were mounted on a fused silica substrate and the offset between the thermocouple temperature and the sample temperature was determined by measuring the phase transformation temperatures of NIST Standard Reference Materials (SRM) In, KClO_4 , AgSO_4 , KSO_4 , K_2CrO_4 , and 44f Al.⁸ Diffraction peak locations were corrected using the external calibration method

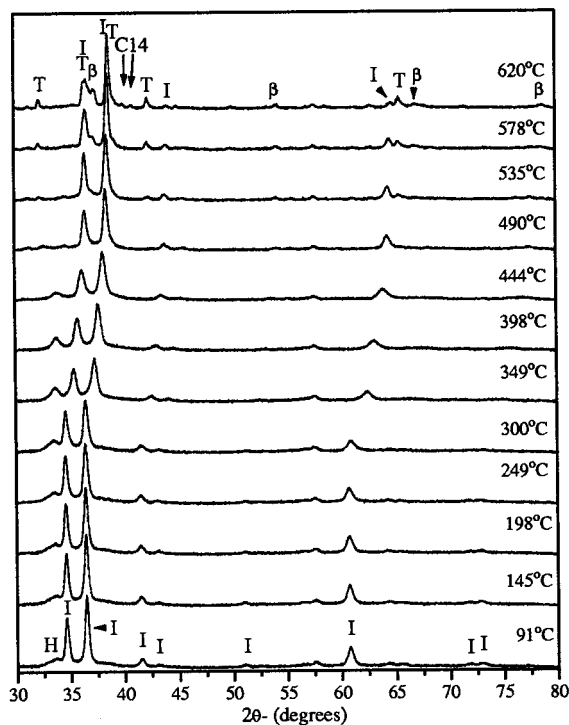


FIG. 1. High-temperature x-ray diffraction of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}\text{-H}$. The peaks from left to right are: I, hydrogenated *i*-phase quasicrystal (see Ref. 10), (100 000), (110 000), (111 101), (210 001), (111 000), (101 000), (110 010), (200 000); H, (Ti-Zr) H_2 fcc, (111); β , β -(Ti,Zr), (110), (200), (211), (220); T, fcc Ti_2Ni , (331), (422), (511), (440), (660); C14, C14 hexagonal Laves, (112), (201).

employing NIST SRM 640b silicon⁸ and the thermal expansion polynomial for Si.⁹ The furnace was evacuated to less than 1 mTorr and filled to 2 psi above atmospheric pressure with high-purity oxygen-gettered He.

Transmission electron microscopy (TEM) studies of the as-quenched *i*-phase ribbons, the as-hydrogenated *i*-phase powder and the desorbed *i*-phase powder were made using a JEOL 2000FX TEM equipped with a Noran energy dispersive x-ray spectrometer (EDS).

Desorption of hydrogen from the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ *i*-phase alloys is evidenced in the HTXRD patterns (Fig. 1) by the shift of the *i*-phase peaks to higher angle, starting at 349 °C. The peak positions and hydrogen concentration have been correlated previously⁵ using both pressure changes during hydrogenation and sample mass gain. The as-hydrogenated alloy in Fig. 1 indexed to a mixture of the hydrogenated *i*-phase (61 at. % H) plus a small fraction of a face-centered cubic (fcc) (Ti-Zr) H_2 hydride phase. As this powder was heated from 91 to 578 °C in a flowing He atmosphere, the primary (100 000)¹⁰ *i*-phase peak shifted from 34.600° to 36.583°. This corresponds to desorption of 91% of the absorbed hydrogen, and a final concentration of 5.3 at. % H. The *i* phase continued desorbing hydrogen until it began to transform, near 620 °C, to the stable high-temperature hexagonal C14 Laves ($a=5.3$ Å, $c=8.6$ Å)+ β -(Ti,Zr) ($a=3.41$ Å) phase mixture, as was previously observed in nonhydrogenated $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ *i*-phase alloys.¹¹ The *i* phase which was not transformed at 620 °C had a quasilattice constant, $a_q = 5.187$ Å, matching that of the as-quenched *i* phase exactly.

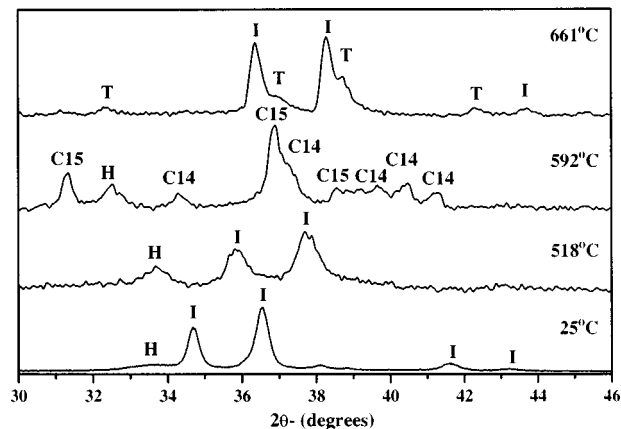


FIG. 2. High-temperature x-ray diffraction of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}\text{-H}$. The as-hydrogenated $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ alloy is primarily *i*-phase quasicrystal, with a small fraction of (Ti-Zr) H_2 precipitates. As the alloy is heated, hydrogen is desorbed from the *i* phase, and the precipitates grow. By 592 °C the alloy has transformed to a mixture of the C14 and C15 Laves hydrides. Further heating and hydrogen desorption results in the reappearance of the *i* phase by 661 °C, accompanied by a small fraction of the Ti_2Ni phase that results from surface oxidation. The peak labels from left to right are: I, hydrogenated *i*-phase quasicrystal, (100 000), (110 000), (111 101), (210 001); H, fcc (Ti-Zr) H_2 , (111); C15, C15 fcc Laves, (220), (311), (222); C14, C14 hexagonal Laves, (110), (103), (200), (112), (201); T, fcc Ti_2Ni (331), (422), (511), (440).

The estimated uncertainty of the quasilattice constant is 0.005 Å, which places an upper limit on the hydrogen content in the *i* phase at 620 °C at 2.5 at. %. Growth of the fcc Ti_2Ni phase ($a=12.08$ Å) was also observed; this is due to the eventual oxidation of the powder.¹¹

Surface oxidation acts as a barrier to hydrogen desorption, altering the desorption rate and the phases that form. If the powder is held at intermediate temperatures, high enough for oxidation to occur, but low enough that desorption is slow, hydrogen can be trapped in the powder in the form of crystalline hydrides. In such cases, hydrogen is partially desorbed from the quasicrystal, followed by the formation of the fcc C15 Laves (Ti_2ZrH_4) and C14 Laves (Ti-Zr-Ni-H) phases, and finally the Ti_2Ni phase. This desorption/phase transformation sequence was also found in earlier differential scanning calorimetry studies² during which significant surface oxidation was unavoidable.

In measurements made using a static overpressure of gettered He, the *i* phase transformed to the crystalline hydride phase mixture, and then back to the quasicrystal after further heating and desorption, as shown in Fig. 2. At 592 °C, the alloy transformed to a phase mixture of the C14 Laves phase ($a=5.23$ Å, $c=8.50$ Å), the C15 Laves phase ($a=8.08$ Å) and the (Ti-Zr) H_2 phase ($a=4.77$ Å). After further heating to 638 °C, the *i* phase ($a_q=5.24$ Å) reappeared, and on reaching 661 °C the *i* phase ($a_q=5.23$ Å) was the majority phase, accompanied by a small fraction of the fcc Ti_2Ni phase ($a=12.06$ Å). The *i* phase was retained as the dominant phase upon cooling to room temperature.

The phase equilibrium as a function of hydrogen concentration and temperature is a complicated issue, frequently obscured by surface oxidation effects. The observed transformation sequences varied with the type of furnace atmosphere, static or flowing gas, and the heating rates. If the

hydrogen desorbed quickly enough, little oxidation occurred and few or no crystalline hydrides were observed. When desorption was slow, due to a slow heating rate and surface oxidation, the transformation to the crystalline hydrides occurred at temperatures between 500 and 600 °C. The exact transformation temperature depended on the remaining hydrogen concentration. That the hydrogenated *i* phase sometimes transformed to the crystalline hydride mixture and back to an almost fully desorbed *i* phase, indicates that with little or no hydrogen, the *i* phase is the stable phase in Ti₄₅Zr₃₈Ni₁₇ alloys for temperatures as high as 662 °C. This is remarkable because no other Ti-based quasicrystal is known to be stable, and although previous high temperature studies of Ti-Zr-Ni suggested the stability of the *i* phase in Ti₅₃Zr₂₇Ni₂₀ and Ti₄₅Zr₃₈Ni₁₇, no reversible transformation of the *i* phase was observed.

Definitive proof of the reversibility of the *i*-phase transformation is provided by TEM measurements. Microbeam electron diffraction patterns (MBED) from the dehydrogenated *i*-phase powder were obtained along the five-fold and three-fold axes of one quasicrystalline grain. The grain size observed in TEM studies was 10–20 nm, in agreement with the grain size calculated from the x-ray peak widths using the Scherrer formula.¹² The MBED and EDS measurements of the thinnest powder particles confirm the additional presence of the Ti₂Ni phase resulting from oxidation of the powder.

Isothermal hydrogen desorption in a static He atmosphere was measured at 383 and 412 °C. Most of the desorption, from 61 at. % (H/M=1.56) to 49 at. % (H/M=0.96), occurred before the completion of the first x-ray scan at 383 °C; after eight hours at 383 °C the hydrogen concentration decreased to 43 at. % (H/M=0.76). Further desorption, to 41 at. % (H/M=0.71), occurred on heating to 412 °C and continued over the next 4 h, reaching 38 at. % (H/M=0.61) when the experiment was stopped. The minimum temperature at which isothermal desorption was observed was 355 °C, where H/M decreased by 9% to 1.42 (59 at. %) in 14 h.

Several questions about the hydrogen-quasicrystal phase dynamics remain unanswered, including whether full desorption can be achieved at lower temperature without crystalline hydride growth. Oxygen is a complicating factor and may limit the temperature of desorption onset. The hydrogenated powder used in these experiments had been exposed to air for several weeks and therefore likely exhibited a higher de-

sorption onset temperature than less oxidized samples would.

The hydrogen desorption from the Ti₄₅Zr₃₈Ni₁₇-H *i*-phase alloy demonstrated in this paper establishes the potential use of Ti-based quasicrystals for hydrogen storage applications. Near full desorption, to 2.5 at. % or less, is possible provided oxidation is minimized. The reversibility of the *i*-phase-hydride phase transformations is affected by surface oxidation, however, this work confirms that the *i* phase is the stable phase in the Ti₄₅Zr₃₈Ni₁₇ alloy below 662 °C. Continued work is underway to optimize the Ti-based quasicrystals for hydrogen storage applications, and to determine the dynamics and structure of the hydrogenated quasiperiodic structure.

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