

Hydrogen Absorption Study of Ti-based Alloys Performed by Melt-spinning

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The hydrogen absorption and desorption of $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ icosahedral quasicrystal (ICQ) and $\text{Ti}_{50}\text{Ni}_{50}$ shape memory alloy (SMA) melt-spun ribbons was studied. Samples were exposed to hydrogen gas at 623 K and 4 MPa for 1000 minutes. The total capacity of hydrogen obtained for $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ and $\text{Ti}_{50}\text{Ni}_{50}$ was 3.2 and 2.4 wt. % respectively. The Thermal Desorption Spectrometry (TDS) of the hydrogenated alloys shows that both alloys start to desorb hydrogen around 750 K. X-ray diffraction (XRD) patterns, performed after hydrogenation, indicate a complete amorphization of the $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ i-phase alloy, while the $\text{Ti}_{50}\text{Ni}_{50}$ alloy remained crystalline after hydride formation.

Keywords: hydrogen absorption, Ti-Ni alloy, Ti-Zr-Ni alloy

1. Introduction

Hydrogen storage is clearly one of the key challenges in developing hydrogen economy. A feasible way of storing hydrogen under moderate temperature and pressure is through intermetallic compounds which react with hydrogen to form metal hydrides.

Metal hydrides are the promising candidates for on-board applications due to their safety advantage with high volume efficient storage capacity. Intensive research has been conducted in the last years on the metal hydrides for improving adsorption/desorption properties based on hydrogen storage capacity, kinetics, thermal properties, toxicity, cycling behavior and cost¹⁻³.

Nowadays, the icosahedral quasicrystal alloys are in evidence because of the Nobel Prize concerning this class of materials recently awarded. The quasicrystals have a new type of translational long-range order, display non-crystallographic rotational symmetry and contain high amounts of interstitial sites¹. Ti-Zr-Ni icosahedral quasicrystal has been found to store large amount of hydrogen³⁻⁵ and thus, can be a promising candidate for hydrogen loader. Kim et al.⁶ reported that the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ ICQ alloy absorbs 2.5 wt. % of hydrogen. Meanwhile, Kocjan et al.⁷ have investigated the hydrogen properties of the $\text{Ti}_{40}\text{Zr}_{40}\text{Ni}_{20}$ that has a hydrogen capacity of 1.3 wt. %.

The literature reported that Ti-Ni shape memory alloys can also absorb hydrogen because Ti has high affinity for hydrogen and the addition of Ni accelerates hydrogen absorption⁸. Ti-Ni alloys have shape memory effect due to thermoelastic transformation. Hydrogen can affect the martensitic transformation temperature⁹ and form TiNi hydride phase depending on different levels of hydrogen concentrations¹⁰.

To evaluate the applicability of any of these structures as hydrogen storage devices, the absorption kinetics must be determined. The present study aims at determining the hydrogen absorption and desorption behavior of $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ ICQ and $\text{Ti}_{50}\text{Ni}_{50}$ SMA alloys and the structural transformation after hydrogenation.

1.1. Experimental procedure

The $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ and $\text{Ti}_{50}\text{Ni}_{50}$ metallic alloys were prepared in high frequency furnace under controlled atmosphere. After that, each alloy was submitted to melt-spinning technique in the form of ribbons with 8 mm and 1 mm respectively and the thickness is equal to 25 μm for both.

Hydrogen absorption tests were conducted using a Sievert's type apparatus, PCT Pro 2000 Hy Energy. To activate the sample to load hydrogen, the sample chamber was annealed for 2 hours at 623 K in vacuum. The studies were carried out at 623 K and 4 MPa for 1000 minutes. TDS technique with quadrupole mass spectrometer and a temperature range of 300 to 973 K and 3 K/min of heating rate, were used to evaluate the hydrogen desorption characteristics.

The XRD patterns were obtained in a Shimadzu XRD-6000 diffractometer using $\text{Cu-K}\alpha$ radiation, before and after hydrogenation to measure the phase structure of the as-cast sample and after absorption test.

2. Results and Discussion

The phase structure of $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ and $\text{Ti}_{50}\text{Ni}_{50}$ alloys was determined by XRD. Figure 1a shows the XRD patterns of the $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ alloy at the conditions as cast, melt-spun and hydrogenated after melt-spun. The $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ as cast ingot presents C14 Laves, which has a hexagonal structure,

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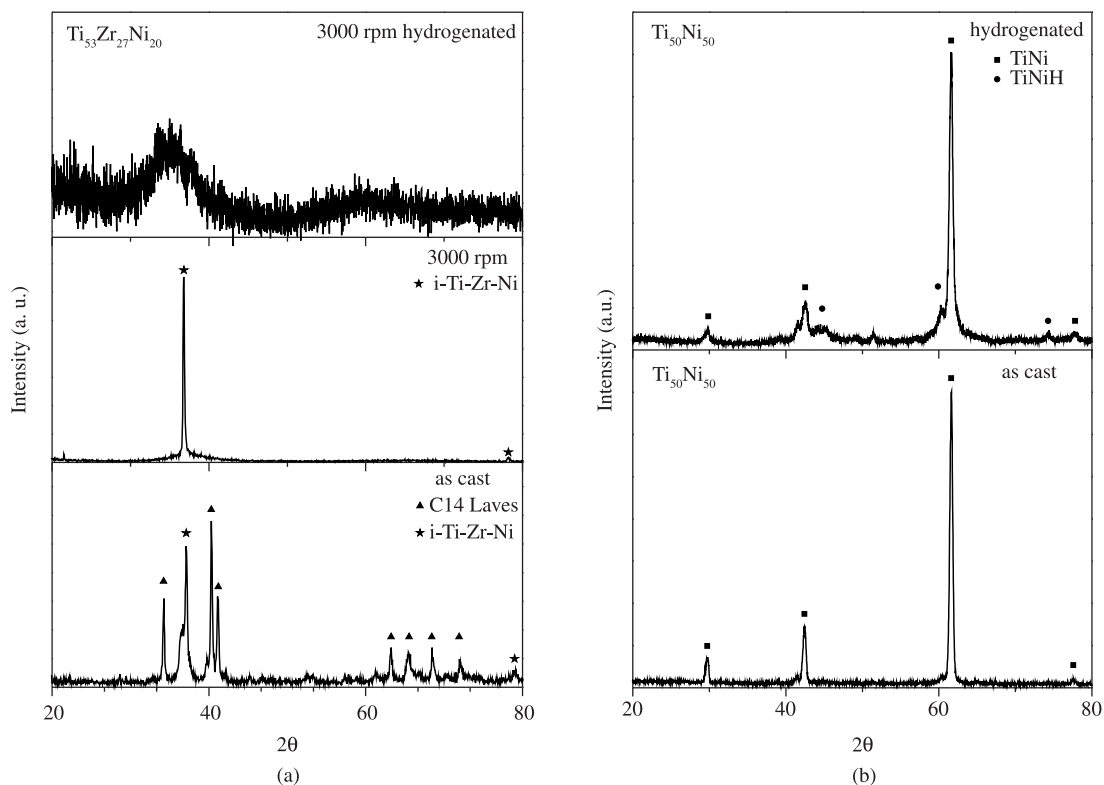


Figure 1. XRD patterns for (a) $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ alloy and (b) $\text{Ti}_{50}\text{Ni}_{50}$.

and i-phase. The ingots, after the rapid cooling step, led to a complete i-phase formation, as reported before^{6,7,11}. After hydrogenation, the X-ray spectrum shows only a broad peak characteristic of amorphous materials. This behavior can be associated to the phenomenon known as hydrogen-induced amorphization (HIA) and/or disproportionation that lead to the amorphization of some intermetallic compounds¹².

The XRD patterns of $\text{Ti}_{50}\text{Ni}_{50}$ as cast and hydrogenated samples presented in Figure 1b show the presence of cubic TiNi and the formation of TiNi hydride after hydrogenation.

The hydrogen absorption kinetic of samples was investigated at 623 K under an initial pressure of 4 MPa. $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ presented the highest hydrogen absorption capacity, 3.2 wt. % in 828 minutes (Figure 2). The hydrogen absorption of $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ alloy occurred rapidly at 623 K. However, the absorption capacity increased slowly to about 0.5 wt. % in 300 minutes. From that time on an absorption reaction occurred very fast and the absorption capacity of hydrogen increased to 2.5 wt. % in about 1 minute. Then the absorption rate became slow again until it reached the full capacity.

The incubation time observed can be attributed to hydrogen reacting with the surface, the diffusion in solid solution through the volume of the alloy and also interaction with grain boundaries and defects. When the surface is oxide free, the kinetics of hydrogen absorption is very fast which allows the hydride transformation through the material. The same behavior was also reported by Martinez et al.¹³ for TiCrV alloys.

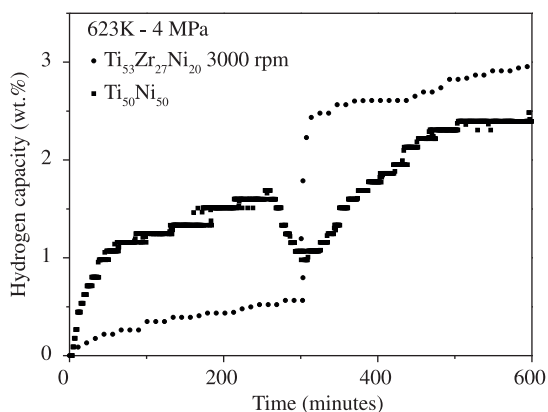


Figure 2. Absorption kinetics for $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ alloy presents 3.2 wt. % and $\text{Ti}_{50}\text{Ni}_{50}$ presents 2.4 wt. % of hydrogen capacity.

The activation of the surface at high temperature under vacuum is a procedure intended to disrupt the oxide layer thereby facilitating its removal by hydrogen. In tests conducted by Kocjan⁷ with $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ under 300 °C (573 K), 4.5 MPa for 1000 minutes without sample activation, the hydrogen absorption was only 1.7 wt. %. The deleterious effect of the oxide layer was also discussed by Viano et al.¹⁴ who identified that the oxidized surface layer slows down the absorption and desorption may be inhibited. Kim et al.⁶ verified that removing the oxide and coating with Pd, the hydrogen absorption for $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ alloy increases to 2.5 wt. %.

Table 1. Hydrogen absorption parameters obtained in this work, compared with the one obtained from the literature.

Alloy	Hydrogenation condition	Phase	wt. % H	Reference
Ti ₄₀ Zr ₄₀ Ni ₂₀	523 K, 1 MPa	ICQ	0.7	11
Ti ₄₅ Zr ₃₈ Ni ₁₇	303 K, 1 MPa	C14 Laves phase + ICQ+β(Ti,Zr)	1.5	3
Ti ₄₅ Zr ₃₈ Ni ₁₇	333 K, 1 MPa	C14 Laves phase + ICQ+β(Ti,Zr)	2.9	3
Ti ₅₃ Zr ₂₇ Ni ₂₀	573 K, 4.5 MPa	ICQ	1.7	7
Ti ₅₈ Zr ₂₄ Ni ₁₈	573 K, 4.5 MPa	C14 Laves phase + ICQ	1.8	7
Ti ₅₃ Zr ₂₇ Ni ₂₀	623 K, 4 MPa	ICQ	3.2	this work
Ti ₅₀ Ni ₅₀	623 K, 4 MPa	Crystalline	2.4	this work

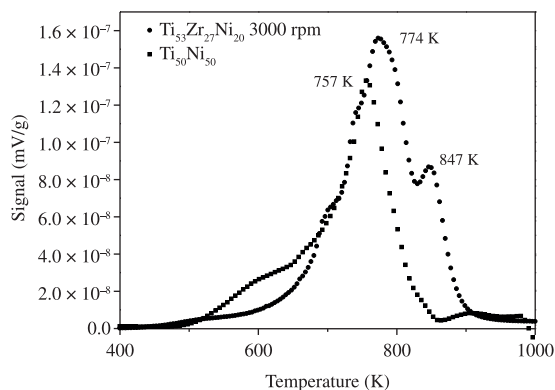
The absorption curve of Ti₅₀Ni₅₀ sample shows a very different behavior. It presented the fastest absorption kinetics, 500 minutes, to absorb 2.4 wt. % of hydrogen (Figure 2). For this alloy, the absorption capacity of 1.5 wt. % was reached in 200 minutes then a decrease of hydrogen absorption occurred. This drop can be attributed to an abrupt phase transformation during absorption of hydrogen, corresponding to hydride formation, which causes a variation of temperature and affects the absorption itself.

The differences between the absorption curves in Figure 2 are exclusively due to induced hydrogen phase transformations. The reduction of hydrogen absorption in Ti₅₀Ni₅₀ alloy is associated with a variation of temperature and in Ti₅₃Zr₂₇Ni₂₀ alloy, during hydrogen absorption a reaction of amorphization, which is endothermic, competes with hydride formation that is an exothermic reaction. The different absorption time can be attributed to different compositions and structures of the alloys.

The hydrogen absorption results obtained for the two alloys are in agreement with the performance of other alloys or other methods of sample preparation and hydrogenation. Table 1 compares the hydrogen absorption capacity of the alloys determined in the present study with other results shown in the literature. Some parameters, such as the hydrogenation condition and the phases present in the alloys were considered since they are important in evaluating the hydrogen absorption capacity. Similar hydrogen absorption capacity value was obtained by Huang et al.³ for the Ti₄₅Zr₃₈Ni₁₇ alloy, containing a mixture of ICQ, β(Ti-Zr) and C14 Laves phases.

The TDS spectrum of the hydrogenated Ti₅₃Zr₂₇Ni₂₀ sample presented two peaks at about 774 K and 847 K as indicated in Figure 3. This suggests two distinct reactions during hydrogen desorption. Since the formation of the hydride in the Ti₅₃Zr₂₇Ni₂₀ alloy promoted the phase transformation from ICQ to amorphous, the resulting structure of an amorphous hydride could not be defined. Therefore, the two reactions observed can be attributed to different energy sites that have distinct potential energy levels for hydrogen trapping.¹⁵

Similar result was reported by Kim et al.¹⁶ using hydrogen as a local probe in pressure-composition-temperature measurements on the Ti₄₅Zr₃₈Ni₁₇ quasicrystalline i-phase, where a double-peaked distribution was attributed to different hydrogen site energies. They suggested that there are two essentially different kinds of interstitial sites: a tetrahedral site with no Ni and another one with a Ni

**Figure 3.** TDS spectra of the hydrogenated Ti₅₃Zr₂₇Ni₂₀ and Ti₅₀Ni₅₀ alloys. The data are not normalized.

atom sitting on a vertex. Similar results were reported by Gibbons et al.¹⁷

Kocjan et al.⁷ investigated the desorption characteristics of different Ti-Zr-Ni alloys, including Ti₅₃Zr₂₇Ni₂₀, and concluded that the Ti-rich samples possess additional desorption peaks (one at 833 K and other at 983 K to the Ti₅₃Zr₂₇Ni₂₀ alloy), presumably because of the difference in the composition and, as a consequence, the electronic structure, which opens two additional sites for protons, and so results in a larger wt. % of hydrogen being absorbed in addition to the effect of density decrease. Further studies should be conducted to elucidate these phase transformations.

Otherwise the TDS spectrum of the hydrogenated Ti₅₀Ni₅₀, Figure 3, displayed only one peak very well defined at 757 K. However, two reactions might have been involved during hydrogen desorption. At low temperature, part of the hydrogen was desorbed from interstitial solid solution of TiNi structure and the other was associated to desorption from the hydride phase. Saito et al.¹⁸ studied the hydrogen desorption from the Ti₅₀Ni₅₀ alloy. Hydrogen desorption spectra, measured by TDS, shown one or two peaks at temperatures around 500 and 770 K depending on the hydrogenation conditions. The peak at around 500 K was attributed to hydrogen in the octahedral position of the TiNi hydride. The other peak at around 770 K was thought to arise from hydrogen evolution from grain boundary or defects, or decomposition of hydrides of the minor phases.

Finally, the results of hydrogen absorption in the alloys studied here demonstrated that these materials may be promising for hydrogen storage. Although desorption kinetics only occurs at high temperatures, the use of catalysts¹³ can help to reverse this undesired feature.

3. Conclusions

Hydrogen absorption studies on Ti-Ni based alloys indicate that these alloys can absorb a considerable amount of hydrogen. The Ti₅₃Zr₂₇Ni₂₀ sample absorbed 3.2 wt. % and Ti₅₀Ni₅₀ sample absorbed 2.4 wt. % of hydrogen making them potentially adequate materials for

hydrogen storage. The hydride formation in i-phase causes the alloy amorphization. Hydride formation was partial for the intermetallic compound TiNi and the alloy remained crystalline. Desorption of hydrogen from Ti-Ni based alloys is possible, although occurs at high temperatures. A complete determination of the pressure-composition isotherms will greatly aid to have better knowledge of these processes.

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