



Article Synthesis and Hydrogenation of the $Ti_{45-x}V_xZr_{38}Ni_{17}$ (5 $\leq x \leq$ 40) Mechanically Alloyed Materials

Joanna Czub^{1,*}, Akito Takasaki², Andreas Hoser³, Manfred Reehuis³ and Łukasz Gondek¹

- ¹ Faculty of Physics and Applied Computer Science, AGH University of Krakow, Mickiewicza 30, 30-059 Krakow, Poland; Igondek@agh.edu.pl
- ² Department of Engineering Science and Mechanics, Shibaura Institute of Technology, Toyosu, Kotoku, Tokyo 135-8548, Japan; takasaki@shibaura-it.ac.jp
- ³ Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz 1, 14109 Berlin, Germany; hoser@helmholtz-berlin.de (A.H.); reehuis@helmholtz-berlin.de (M.R.)
- * Correspondence: joanna.czub@agh.edu.pl

Abstract: The mechanically alloyed amorphous alloys of the $Ti_{45}Zr_{38}Ni_{17}$ composition are known for their ability to form a quasicrystalline state after thermal treatment. It is also known that the amorphous and quasicrystal alloys belonging to the $Ti_{45}Zr_{38}Ni_{17}$ family are able to store hydrogen and yield gravimetric densities above 2 wt.%. In this contribution, we report the results of research on the $Ti_{45}Zr_{38}Ni_{17}$ system with vanadium doped instead of titanium. We found that the amorphous samples with moderate doping (x < 20) show the ability to absorb hydrogen while maintaining the amorphous state and they transform into the novel glassy-quasicrystal phase during annealing. Those materials with higher vanadium concentrations do not form entirely amorphous structures. However, they still can absorb hydrogen easily. It was also confirmed that the in situ hydrogenation of the amorphous alloys is a straightforward process without decomposition of the alloy. In this process, hydrogen does not attach to any particular constituent of the alloy, which would lead to the formation of simple hydrides or nanoclusters. Therefore, we were able to confirm the fully amorphous nature of the deuterides/hydrides of the $Ti_{45-x}V_xZr_{38}Ni_{17}$ with moderate V doping.

Keywords: hydrogen-storage materials; amorphous alloys; quasicrystalline alloys; mechanical alloying; neutron diffraction; scanning electron microscopy

1. Introduction

Satisfying the rapidly and constantly growing need for green energy supplies is one of the main challenges for science these days. Efforts are aimed at so-called zeroemission energy resources to prevent environmental contamination, and for that reason, hydrogen seems to be a promising candidate as an energy carrier [1–3]. Therefore, hydrogen production and storage remain the main problems that need to be addressed [4].

Recently, amorphous hydrogen storage alloys have been widely studied, due to their relatively high hydrogen storage capacity and satisfactorily fast hydrogenation and dehydrogenation kinetics [5]. Among them, the amorphous and quasicrystalline alloys based on the Ti-Zr and the Ti-Zr-Ni stoichiometry have sparked an increased interest due to their possible applications. Shape memory alloys [6], coatings [7], and materials for biotechnology [8] could be named as examples. Even in the earlier years, those alloys were intensively investigated as targets for neutron generators and certainly for hydrogen storage (electrochemical and gaseous) [9–17].

Quasicrystalline Ti-Zr-Ni alloys [18] can be saturated with hydrogen up to 1.6 H/M (the hydrogen-to-metal ratio). However, problems with reversibility were reported for the icosahedral ribbons [19]. It was evidenced that the Laves phases, as well as the ZrH_2 , were formed during hydrogenation. Substantially better reversibility was achieved for the mechanically alloyed and subsequently annealed quasicrystalline $Ti_{45}Zr_{38}Ni_{17}$



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). powders, as only minor reflections from the Ti₂Ni phase were observed after hydrogen desorption [14,20]. An improvement in the reversibility of hydrogen absorption for the Pd-doped Ti-Zr-Ni quasicrystals was reported by Jo et al. [21]. However, it was established that the Pd addition decreases the thermal stability of the Ti-Zr-Ni quasicrystals [22]. Lee and Kim reported that the equilibrium vapor pressure of hydrogen increased for the replacement of Ti with Pd and V in the quasicrystals of the Ti-Zr-Ni composition [23]. The hydrogen storage properties of such quasicrystals were also studied theoretically and numerically [24].

The hydrogen storage behaviors of the Ti-Zr-Ni and the Zr-Ti-V melt-spun ribbons synthesized through rapid solidification have been investigated as well [25–27]. The hydrogen concentration of 3.2 wt.% was achieved for the $Ti_{53}Zr_{27}Ni_{20}$ and the formation of the hydride led to amorphization of the alloy [25]. Shahi et al. reported that the increased hydrogen storage capacity of the Ti-Zr-Ni ribbons is related to the increasing content of Ti [26]. It was shown for the Zr-Ti-V ribbons that such materials can be easily activated and are characterized by fast hydrogen absorption kinetics [27]. On the other hand, the increasing Ti content causes a decrease in the initial hydrogen absorption rate.

Besides, the high entropy alloys of the Ti-Zr-Cr-Mn-Fe-Ni, the Ti-Zr-V-Cr-Ni, and the Zr-Ti-V-Fe compositions have been studied in recent years [28–30]. The hydrogen storage properties of those alloys seem promising due to the effect of the lattice distortion and the content of the C14 Laves phase.

The hydrogen storage properties of the Ti- and V-based alloys of the various compositions synthesized using the arc-melting and mechanical alloying techniques have been widely studied in recent years, namely, the $Ti_{0.72}Zr_{0.28}Mn_{1.6}V_{0.4}$ [31]; the Ti-V-Mn alloys with Zr, Ni, and Zr₇Ni₁₀ addition [32,33]; the Ti-V-Fe-Zr with various contents of V [34]; and the Ti-V-Mn-Cr with Zr addition [35]. The aim of those investigations was to establish the effect of the alloy composition on increasing or decreasing hydrogen sorption. In this paper, the $Ti_{45-x}V_xZr_{38}Ni_{17}$ ($5 \le x \le 40$) material synthesized by mechanical alloying is investigated for the first time.

It was established in our previous studies that hydrogen concentrations around 2.5 wt.% can be achieved for the Ti-Zr-Ni and the related alloys with the addition of Mn, Fe, and Co [36–39]. The main evidenced problem was the decomposition of the amorphous alloys into simple hydrides during hydrogenation [37]. Recently, that problem has been surpassed by tailoring the course of the sample activation and the thermodynamics of hydrogenation [36,38,39]. As a result, amorphous hydrides and deuterides with high hydrogen concentrations reaching 1.4 H/M can be routinely synthesized for the Ti-Zr-Ni and the related families [38,39].

The aim of the present work is to study the hydrogenation process for the $Ti_{45-x}V_xZr_{38}Ni_{17}$ alloy and to track its transition from the amorphous to the novel glassyquasicrystalline phase by the in situ neutron diffraction technique. Moreover, the main goal is to obtain the fully amorphous deuterides/hydrides of the investigated alloys.

2. Experimental Process

The amorphous $Ti_{45-x}V_xZr_{38}Ni_{17}$ alloys were prepared by mechanical alloying using the Frisch Pulverisette 7 planetary mill. The commercial pure powders of Ti, V, Zr, and Ni (of at least 99.9% purity) with stoichiometric ratios were placed in stainless steel milling bowls (the volume of 45 mL) with grinding balls (stainless steel, 15 mm); the ball to material ratio was 8:1. The milling was conducted in the protective high-purity Ar (99.9999%) atmosphere, as even a small content of spurious oxygen hampers the amorphization of the alloys. Milling with the balls' acceleration of 15 g and the corresponding motor speed of 3200 rpm lasted for 40 h 30 min, and it was followed by 30 min of resting in order to avoid overheating of the alloy. The obtained powders were examined by X-ray powder diffraction (XRD) to assess the amorphicity ratio. The sample with x = 40 was found to be crystalline (decomposed into simple phases), similar to the V₄₅Zr₃₈Ni₁₇. Therefore, those samples were not a subject of further studies. Additionally, scanning electron microscopy (SEM) with microprobe X-ray analysis (EDS) was employed to investigate the microstructure and the homogeneity of the obtained powders. Those studies were performed using a Jeol 5900 LV microscope with the NORAN System SIX microprobe.

Hydrogenation and deuteriding were performed using the Sieverts-type PCT-PRO Setaram automated sorption analyzer. The known sample mass was loaded into an Inconel steel reactor connected to the apparatus. The reactor was flushed several times with high-purity helium (99.9999%), followed by evacuation. Then, the reactor volume was estimated by the expansion of pure helium (99.9999%) from the calibrated volumes of the apparatus. The samples were not activated prior to the experiments, as it was established that the effect of activation is marginal for the sorption properties. For precise estimation of the maximum hydrogen load, the powders were exposed to 40 bar of H₂ pressure at the temperature of the instrument (30 $^{\circ}$ C); then, the reactor was heated up to 200 $^{\circ}$ C with constant pressure reading. Typically, the pressure drop related to the uptake of the H₂ was observed above 100 °C. After 6 h of annealing at 200 °C the reactor was cooled down to 30 °C again to evaluate the amount of absorbed hydrogen (the results are gathered in Table 1). Then, pressure was set to an atmospheric value to observe potential desorption at ambient conditions. The desorption was negligibly small, which was also confirmed by the XRD studies after 1 week from the samples' preparation. The samples for the neutron experiments were prepared in the same way but using deuterium because hydrogen exhibit a very high incoherent scattering cross section for neutrons. The samples were prepared shortly before the neutron diffraction experiments (less than 5 days). The kinetic measurements were conducted at a constant temperature of 120 °C. After reaching that temperature and stabilizing hydrogen was applied to the sample at pressure of 40 bar to track the kinetics. The Pressure-Concentration Isotherm (PCI) was collected as well for the selected samples. The PCI measurements at different temperatures were performed on the new bed of the investigated alloys, to avoid biasing the data by changing the morphology of the samples during desorption at elevated temperatures.

 $\begin{tabular}{|c|c|c|c|c|c|} \hline Compound & Concentration [wt.%] \\ \hline Ti_{40}V_5Zr_{38}Ni_{17} & 2.4 \\ \hline Ti_{35}V_{10}Zr_{38}Ni_{17} & 2.3 \\ \hline Ti_{30}V_{15}Zr_{38}Ni_{17} & 2.1 \\ \hline Ti_{25}V_{20}Zr_{38}Ni_{17} & 1.5 \\ \hline Ti_{15}V_{30}Zr_{38}Ni_{17} & 0.8 \\ \hline \end{tabular}$

Table 1. The maximum hydrogen concentrations after 6 h of hydrogenation at 200 $^{\circ}$ C and 40 bar obtained for the synthesized samples.

The neutron diffraction measurements were performed at the E6 focusing powder diffractometer (BENSC-Berlin, Berlin, Germany) and the E2 diffractometer using the incident neutron wavelength of 2.45 Å. The in situ measurements were performed up to 800 °C using a high-temperature HTF1 furnace (AS Scientific Products, Abingdon, UK). The samples were placed in a quartz tube under flow of inert high-purity argon gas. The background from the furnace and the quartz tube was estimated in the full temperature range, so it was possible to extract the sample signal from the other contributions. Also, in situ deuteriding experiments were conducted for the chosen samples. The powders were placed into an Inconel steel tube connected to the Sieverts apparatus. During the in situ synthesis, the initial pressure of deuterium was set to 30 bar at 150 °C. The low-temperature neutron diffraction experiment was performed in the range of -271.65 °C-26.85 °C (1.5–300 K) using the helium cryostat by AS Scientific. The sample was sealed in a vanadium container of 5 mm diameter under 1 bar of He pressure in order to avoid deuterium release during cooling of the sample.

3.1. The Microstructure and the Composition

Figure 1 presents the microstructures of the $Ti_{45-x}V_xZr_{38}Ni_{17}$ powders along with the elemental distributions for different values of x. Additionally, the results of the EDS quantitative analysis listed in Table 2 confirm the chemical compositions of the powders. It can be seen in the figure that agglomerates formed and the particles' sizes are in the micrometer range. As far as the microstructure of the powder is concerned, the results of the experiment show that it is composition independent for each sample. What is more, the elemental distribution is very homogeneous for all the powders and the impurity phases are not clearly present in the images.



Figure 1. The scanning electron microscopy images and the maps of the elemental distribution for the selected compounds. The labels V0, V5, V10 and V30 correspond to the vanadium abundance in the samples.

Table 2. The compositions of the $Ti_{45-x}V_xZr_{38}Ni_{17}$ powders. The results were obtained from the EDS studies.

Compound:	Ti [at.%]	V [at.%]	Zr [at.%]	Ni [at.%]
$Ti_{40}V_5Zr_{38}Ni_{17}$	40.4	5.3	37.1	17.2
Ti ₃₅ V ₁₀ Zr ₃₈ Ni ₁₇	35.4	9.7	37.4	17.5
Ti ₃₀ V ₁₅ Zr ₃₈ Ni ₁₇	31.0	14.1	37.7	17.2
Ti ₂₅ V ₂₀ Zr ₃₈ Ni ₁₇	25.9	19.8	37.2	17.1
Ti ₁₅ V ₃₀ Zr ₃₈ Ni ₁₇	14.7	30.8	36.9	17.6

Although for the higher concentrations (x > 30) the addition of vanadium leads to disproportionation of the compound into the crystalline phases, it was observed that V atoms are distributed uniformly even for x = 30, and no tendency to agglomerate was noticed. Therefore, it seems that there is a threshold for the solubility of vanadium in the $Ti_{45-x}V_xZr_{38}Ni_{17}$ alloy and that a limit occurs for the x values around 30.

3.2. Structural Properties

The XRD patterns for the investigated alloys are presented in Figure 2. The parent $Ti_{45-x}V_xZr_{38}Ni_{17}$ compounds show typical amorphous patterns up to x = 20, while the signs of the appearing crystalline phases can be noticed for the higher V concentration. The feature at about 42° of 2 θ can be recognized as the 100 reflections of elemental vanadium. Therefore, it may be concluded that the solubility limit of V in the Ti-Zr-Ni system is about 20 at%. The other patterns seem to be very similar, with small shifts towards higher 2 θ , related presumably to the differences in the Ti and V metallic radiuses (1.47 and 1.34 Å, respectively).



Figure 2. The X-ray diffraction patterns for the parent $Ti_{45-x}V_xZr_{38}Ni_{17}$ alloys (**a**) and the corresponding hydrides at the maximum hydrogen concentration (**b**).

It can be noticed that the patterns that were observed for the fully hydrogenated alloys are moved towards lower 2 θ angles with an increase in the hydrogen content, which indicates an increase in the mean interatomic distances due to hydrogen insertion. The highest shifts can be noted for $x \le 10$, while they are less pronounced for the alloys with smaller hydrogen uptake. The volume expansion for x = 5, estimated on the basis of the center of gravity for the main reflection, is about 9%, while it is only 5% for x = 30. Interestingly, the hydrides show decent amorphicity, even for x = 30, which seems to be substantially better than for the raw alloy. Apparently, several minor reflections originating from the vanadium-rich hydrides are present at about 40–41° of 2 θ .

3.3. Hydrogen Sorption

The maximum hydrogen concentrations are given in Table 1. It was found that the alloys do not require activation (annealing at vacuum or cycling) and, once exposed to hydrogen, start to absorb it easily after reaching temperatures above 120 °C. Yet, the kinetics of hydrogenation are quite different, changing inhomogeneously with the vanadium concentration. Even small vanadium doping (x = 5) changes the shape of the curve significantly (Figure 3), and the initial (up to 60 min) exponential growth is diminished. Instead, the nearly linear behavior with the overall higher hydrogen concentration was evidenced up to 45 min. The character of the kinetic curve for x = 10 is similar to that with previous doping, yet the reaction is much faster. A further increase in the V content restores the exponential growths at the initial stages of the reaction, while the kinetic and the maximum concentrations are decreased. The Ti₁₅V₃₀Zr₃₈Ni₁₇ compound shows slow kinetics with the maximum hydrogen concentration decreased by a factor of 3.



Figure 3. The kinetics of the hydrogenation reaction measured at 120 $^{\circ}$ C and with the H₂ initial pressure of 40 bars.

The PCI curves were measured for the $Ti_{35}V_{10}Zr_{38}Ni_{17}$ alloy, which showed the best hydrogenation kinetic. The data presented in Figure 4 shows quite typical plateau-like behavior. The van't Hoff plot, presented in the insert to Figure 4, revealed that the enthalpy of formation was -28.4 kJ/mole H₂. That value is much higher than -48 kJ/mole H₂ reported for the $Ti_{45}Zr_{38}Ni_{17}$ quasicrystalline icosahedral phase. The collected data corresponds well to the maximum loading capacity presented in Table 1. At each temperature, the PCI curves were recorded for the completely new sample. Such a procedure is essential in order to obtain reliable results, as the desorption of hydrogen is associated with the crystallization of the amorphous alloy, which will be discussed in the next section of this paper.

3.4. Desorption of the Deuterided Samples

Desorption of the deuterided amorphous specimens at an Ar pressure of 1 bar occurs at a temperature of 600 °C, as depicted in Figure 5. For the low concentrations of V (Figure 5a,b), the initial patterns have an amorphous nature consisting of two very broad peaks at 61° and 93° of 20. The first peak corresponds to the distribution of the metal–metal distances with the maximal value at 2.305 Å. The latter, which was not observed in the XRD measurements (Figure 2b), originates from the distribution of the deuterium–metal distances with the maximum at 1.621 Å. As deuterium is a good neutron scatterer, that feature can be exclusively observed by neutron diffraction, while a too-low electronic charge around deuterium/hydrogen hampers such observation for XRD. The occurrence of those two broad features is first-hand proof that deuterium is not associated with a particular element of the amorphous matrix but is an equal constituent of the alloy similar to the other elements. Moreover, those two reflections can be attributed to the occurrence of the novel glassy quasicrystalline phase that was previously observed for the deuterides of the Ti₄₅Zr₃₈Ni_{17-x}Co_x (x < 8) amorphous alloy [36]. The release of hydrogen is related to the crystallization of the amorphous alloy; therefore, any attempts to register the PCI curves for the same sample would bring false results, as only the first PCI curve is truly related to the amorphous material.



Figure 4. The Pressure-Concentration Isotherms (PCI) for the $Ti_{35}V_{10}Zr_{38}Ni_{17}$ alloy. The insert presents the van't Hoff plot.



Figure 5. The neutron diffraction patterns during desorption for the selected $Ti_{45-x}V_xZr_{38}Ni_{17}$ deuterides.

The sample decomposes into simple phases after desorption and transforms into the c-phase (cubic) at about 800 °C. Such behavior was previously observed for the similar alloys of the Ti-Zr-Ni-Fe composition [36].

3.5. In Situ Neutron Diffraction under High Deuterium Pressure

The problem of the amorphous hydride formation was addressed by the neutron diffraction experiment performed during the deuteriding of the amorphous Ti₃₀V₁₅Zr₃₈Ni₁₇ sample. The reaction was conducted at a relatively low temperature to extend its time span enough to collect the data with the appropriate statistics. The result is depicted in Figure 6. Only a weak broad reflection at 59° of 2θ can be noticed at the beginning of the reaction. This is a typical pattern for amorphous materials, which is consistent with the XRD data collected for that sample (Figure 2b). The reaction starts relatively slowly, which corresponds to the kinetic data from Figure 3. Then, quite rapid deuteriding occurs. This results in a fast appearance of the second broad reflection at 91° of 20. Additionally, the reflection at 59° of 2 θ moves towards lower angles at that stage of the reaction, which is indicative of an increase in the metal–metal mean distances. Only a slow, gradual increase in the peak intensities can be observed at the last stage of the reaction. The above three stages are very consistent with the kinetic curve, which shows the same characteristic. Apart from the appearance of the broad maximum related to deuterium, one can notice an increase in the background. This effect is related to hydrogen, which is the main impurity of the deuterium gas, typically 0.1%. Even a small amount of hydrogen absorbed by the sample originates from the background signal due to the H_2 large incoherent scattering cross section.



Figure 6. The in situ neutron diffraction patterns for the $Ti_{30}V_{15}Zr_{38}Ni_{17}$ amorphous alloy under D_2 pressure.

3.6. Lattice Expansion for the Amorphous Deuteride

The low-temperature studies for the $Ti_{30}V_{15}Zr_{38}Ni_{17}$ amorphous deuteride are presented in Figure 7. Apparently, no structural changes due to deuterium release were noticed. Only the shift of the broad reflections towards low angles associated with the lattice expansion can be observed. The changes in the interatomic distances were estimated by the calculation of the centers of gravity for two reflections corresponding to the mean metal–metal and metal–deuterium distances. It was found that the distances show a tendency similar to that for the crystalline phases, with a plateau at low temperatures and the quasilinear behavior above -123.15 °C. However, the changes are very small yielding less than 0.2% between -271.65 °C and 26.85 °C. The analysis of the distances using the Debye formula for the lattice expansion [40] provides a very rough estimation of the Debye temperature as equal to 465(25) K (191.85 °C).



Figure 7. The low-temperature studies for the $Ti_{30}V_{15}Zr_{38}Ni_{17}$ amorphous deuteride. The mean distances between the metal and deuterium atoms were estimated on the basis of the center of gravity for the corresponding maxima.

4. Concluding Remarks and Summary

Firstly, it can be deduced from the results of the XRD studies that the solubility of V in the mechanically alloyed $Ti_{45-x}V_xZr_{38}Ni_{17}$ material is limited and equal to about 20 at%. Aside from this, it was shown that the hydrogen concentration varies with the x value. The maximum hydrogen concentration can be obtained for the $Ti_{40}V_5Zr_{38}Ni_{17}$ alloy and is equal to 2.4 wt.%. For those reasons, an important conclusion can be drawn that the parent alloy $Ti_{45}Zr_{38}Ni_{17}$ can be successfully doped with vanadium in order to tailor its hydrogen storage properties. Another significant accomplishment is the fact that the stability boundaries for the amorphous phase in the Ti-V-Zr-Ni system were determined.

Secondly, it was presented that the mean interatomic distances increase during hydrogenation. The effect caused by hydrogen insertion into the structure is the most prominent for the samples with $x \le 10$. The volume expansion varies from 9% for x = 5 to 5% for x = 30. It should be also mentioned that the hydrides are amorphous for all the alloys within the complete x range.

It was established that the kinetics of hydrogenation depend strongly on the vanadium concentration. The best result was achieved for the $Ti_{35}V_{10}Zr_{38}Ni_{17}$ alloy with the enthalpy of formation equal to $-28.4 \text{ kJ/mole H}_2$. Therefore, another important conclusion is that the kinetics of hydrogenation is significantly increased if a moderate amount of V (around 10 at%) is introduced to the $Ti_{45}Zr_{38}Ni_{17}$ alloy.

It can be concluded from the results of the desorption experiments for the deuterided samples that deuterium is an equal constituent of the alloy not associated with any particular element of the amorphous matrix. Desorption leads to the sample decomposition into the simple phases and transformation into the c-phase (cubic) at about 800 °C. What is more, in addition to the course of deuteriding, an increase in the metal–metal mean distances was confirmed by the in situ neutron diffraction experiment under high deuterium pressure. The results of the low-temperature studies for the $Ti_{30}V_{15}Zr_{38}Ni_{17}$ amorphous deuteride point to the conclusion that the mean metal–metal and metal–deuterium distances behave in a similar manner to those of the crystalline phases at low temperatures and present quasilinear behavior above -123.15 °C. The Debye temperature was estimated from the lattice expansion, giving the value of 465(25) K (191.85 °C).

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