New Studies of the Physical Properties of Metallic Amorphous Membranes for Hydrogen Purification

Oriele Palumbo 1, Francesco Trequattrini 1,2, Suchismita Sarker 3, Madhura Hulyakar 3, Narendra Pal 3, Dhanesh Chandra 3, Michael Dolan 4 and Annalisa Paolone 1,*

1 Consiglio Nazionale delle Ricerche, Istituto dei Sistemi Complessi, U.O.S. La Sapienza, Piazzale A. Moro 5, 00185 Roma, Italy; oriele.palumbo@roma1.infn.it (O.P.); francesco.trequattrini@roma1.infn.it (F.T.)
2 Department of Physics, Sapienza University of Rome, Piazzale A. Moro 5, 00185 Roma, Italy
3 Department of Chemical and Materials Engineering, University of Nevada, Reno, NV 89557, USA; suchismita13994@gmail.com (S.S.); hulyalkar.madhura@gmail.com (M.H.);
narendrapal@gmail.com (N.P.); dchandra@unr.edu (D.C.)
4 Commonwealth Scientific and Industrial Research Organisation, Queensland Centre for Advanced Technologies, Energy, 1 Technology Court, Pullenvale, QLD 4069, Australia; Michael.Dolan@csiro.au

* Correspondence: annalisa.paolone@roma1.infn.it; Tel.: +39-06-4991-4400

Academic Editor: Palmiro Poltronieri
Received: 22 December 2016; Accepted: 7 February 2017; Published: 10 February 2017

Abstract: Amorphous metallic membranes display promising properties for hydrogen purification up to an ultrapure grade (purity > 99.999%). The hydrogen permeability through amorphous membranes has been widely studied in the literature. In this work we focus on two additional properties, which should be considered before possible application of such materials: the propensity to crystallize at high temperatures should be avoided, as the crystallized membranes can become brittle; the hydrogen solubility should be high, as solubility and permeability are proportional. We investigate the crystallization process and the hydrogen solubility of some membranes based on Ni, Nb, and Zr metals, as a function of Zr content, and with the addition of Ta or B. The boron doping does not significantly affect the crystallization temperature and the thermal stability of the membrane. However, the hydrogen solubility for $p \approx 7$ bar is as high as $H/M \approx 0.31$ at $T = 440$ °C and $H/M \approx 0.27$ at $T = 485$ °C. Moreover, the membrane does not pulverize even after repeated thermal cycles and hydrogenation processes up to 485 °C and 7 bar, and it retains its initial shape.

Keywords: amorphous membranes; hydrogen purification; hydrogen solubility; crystallization

1. Introduction

Hydrogen purification by using membranes is needed in many industrial applications [1]. In some fields, such as the electronic industry or for feeding fuel cells, a hydrogen gas of an ultrapure grade (purity > 99.999%) is needed. At present, the most mature technology for hydrogen purification to such a grade is based on Pd or Pd-Ag alloy membranes [1]. In this hydrogen purification system, hydrogen molecules are ionized catalytically to obtain $H^+$ ions, on one of the surfaces of the membrane. $H^+$ ions solubilize in the material and, due to the gradient of pressure and concentration, they diffuse through the membrane towards the other surface, where they recombine to form ultrapure $H_2$ molecules. Metallic alloys, both crystalline and amorphous, display high selectivity for hydrogen and this characteristic allows to obtain the ultrapure grade of the hydrogen gas permeated through the metallic membranes [1].

Despite the very good performances of Pd and Pd-Ag alloy membranes, it must be considered that Pd is an expensive (about $24,000 USD/kg) and strategic metal. Moreover, in some conditions Pd...
can suffer from embrittlement. Therefore, a large effort in the research of alternative membranes have
been conducted in the last years.
Separation of gases by means of polymeric membranes is already used in industrial processes,
such as the production of technical-grade nitrogen, the hydrogen separation in refineries and the
petrochemical industry, and the separation of CO₂ from CH₄ or N₂ [2–4]. However, this type of
membrane, which is relatively cheap, can found applications only when gas separation can occur
in the temperature range below 100 °C. Moreover, their selectivity is relatively low (not exceeding
100 [3]) and, therefore, they can be used only when the purity of the permeated gas is not a primary
concern [1]. Polymeric membranes suffer from swelling and poisoning [1]. Another concern about
polymer membranes is the need to recover the toxic by-products for their production [5].
Metallic membranes based on chemical elements different from Pd can be a valid alternative,
as they show high selectivity (>1000) and an operational temperature range between 300 °C and
600 °C [1]. Indeed, some metals show a permeability comparable to, or even higher than, Pd [6]. Many
of them, such as Ni, Co, Nb, and Zr cost in the range of $5–40 USD/kg and, therefore, are considered
as possible alternatives to palladium. However, crystalline materials usually become brittle when they
are hydrogenated. In this framework, in the last years, an important effort has been devoted to the
study of metallic amorphous membranes [7,8]. Indeed, the pioneering research of Hara et al. [9–11]
reported that the hydrogen permeability of Ni₆₄Zr₃₆ is of the order of 10⁻⁹ mol m⁻¹ s⁻¹·Pa⁻⁰·₅. These
amorphous membranes do not become brittle and are stable at least up to 350 °C [9–11]. Since these
initial studies about amorphous membranes for hydrogen purifications, many chemical compositions
have been investigated (see [1,8]). The review of Ockwig and Nenoff [1] reported different types of
hydrogen separation membranes and reported hydrogen permeability of Ni-Al, V-Al, V-Ni-Al, Nb-Mo,
Nb-Pd, Nb-Ti-Ni, V-Ti, V-Co, Zr-Ti-Ni, and other alloys, in the temperature range between 475 K
and 673 K and of V-Cr-Ti from 793 K to 923 K. Ni-Nb-Zr alloys are the most widely studied system
from the perspective of hydrogen separation. In some cases, doping with other alloying elements,
such as Ta, Co, Hf, Ti, Ta, Sn, Si, Pd, Cu, Co, and Al, has been investigated [8,12]. In general, the
addition of Nb to Ni-Zr alloys, similar to those initially proposed by Hara et al. [9–11], produces
effective benefits: it increases the crystallization temperature and the fracture strength and reduces the
hydrogen embrittlement [13]. Moreover, it has been shown that some Ni-Nb-Zr membranes (such as
Ni₈₀Nb₂₀Zr₀, Ni₆₀Nb₂₀Ti₀, and the presently-investigated (Ni₁₀₀₋ₓNbₓ)₃₀·Zrₓ membranes) display a
hydrogen permeability higher than that of Ni₆₀Zr₃₀, of the order of 10⁻⁸ mol m⁻¹·s⁻¹·Pa⁻⁰·₅, a value
comparable to, or even higher than, that of the Pd-based alloys [8].
One of the main concerns about the amorphous membranes is their propensity to crystallize when
heated to temperatures close to those ones (400–450 °C) needed for hydrogen purification. Indeed,
crystalline phases are usually more brittle than the amorphous ones. For this reason, a preliminary
investigation of the crystallization process is needed for each new composition.
Although the permeation rates of the membranes are very important, one should consider that
solubility and diffusion rates are strictly mathematically linked. If one assumes the diffusion coefficient
to be constant, the relationship between the diffusion coefficient, D, the permeation coefficient, P,
and the solubility coefficient, S, simplifies to P = D × S. Moreover, the hydrogen flux through a
membrane is linked to the shape of the pressure composition isothermal curves of the material [14].
Therefore, a deep knowledge of the hydrogen solubility of membranes is strategic to characterize their
potential applicative use. The mechanical stability of amorphous membranes during operation at high
temperatures is another important concern in view of their application. In fact, the sample should not
become brittle or present faults due to thermal treatments and/or hydrogenation. Finally, the evolution
of the physical properties of membranes with increasing temperature in the presence of hydrogen
should also be considered. In fact, quite recently it has been reported the occurrence of an abrupt
expansion induced by hydrogenation of the amorphous structure of a Ni₃₂Nb₃₂Zr₃₀Cu₁₁₀ membrane
between 240 and 300 °C. Correspondingly, also the sorption properties are drastically changed and the
solubility strongly decreases [15].
In this work, we report some new investigations of the physical properties of amorphous membranes based on Ni, Nb, and Zr metals. In particular, the dependence of the crystallization temperature and of the hydrogen solubility at 400 °C on the Zr content in \((\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x\) (\(x = 0, 10, 20, \) and 30) are measured. Upon partial replacement of Nb by Ta, no major changes in the crystallization process or the sorption properties are observed. Moreover, we compare the solubility of amorphous and crystallized \((\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}\). The crystallized samples are not useful for applications, because they pulverized upon hydrogenation, but, to the best of our knowledge, their solubility properties have not been measured until now. Finally, for the first time, the sorption of a boron containing Ni-Nb-Zr membrane is studied as a function of temperature. The motivation behind the choice of doping with B resides in the recent observation [16] that the addition of 1–5 at% of B to amorphous \(\text{Zr}_{66.7-x}\text{Ni}_{33.3}\) membranes increases their thermal stability, the microhardness, and resistance to corrosion. Moreover, boron can form a large variety of complexes with metals [17] and, therefore, it is expected to increase the hydrogen solubility.

2. Results and Discussion

2.1. Changes of the Physical Properties as a Function of the Zr Content

The occurrence of crystallization upon heating is observed from differential thermal analysis (DTA) measurements. Figure 1 shows DTA curves of various samples of \((\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x\) with different concentrations of Zr (\(x = 0, 10, 20, \) and 30). In order to properly compare the effects of Zr concentration, the temperature scanning rate is fixed at 10 °C/min. All samples display exothermic peaks above 500 °C, corresponding to the crystallization process. Consistently with previous partial measurements, it is well evident that the peaks shift to lower temperature as the Zr content increases [18]. A similar decrease in the crystallization temperature with increasing Zr content was reported for Ni-Nb-Zr alloys, with the addition of Co [19]. Table 1 shows the temperature at which crystallization starts, \(T_{c,\text{onset}}\), defined as the temperature at which one observes the deviation from the linear background displayed by the DTA curves at low temperature.
Table 1. Onset temperature for crystallization, \( T_{\text{onset}} \), in (Ni\(_{0.6}\)Nb\(_{0.4}\))\(_{100-x}\)Zr\(_{x}\) membranes as a function of Zr content, \( x \).

<table>
<thead>
<tr>
<th>( x )</th>
<th>( T_{\text{onset}} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>648 ± 2</td>
</tr>
<tr>
<td>10</td>
<td>591 ± 3</td>
</tr>
<tr>
<td>20</td>
<td>547 ± 3</td>
</tr>
<tr>
<td>30</td>
<td>506 ± 2</td>
</tr>
</tbody>
</table>

Figure 1 also shows that only in the case of (Ni\(_{0.6}\)Nb\(_{0.4}\))\(_{90}\)Zr\(_{10}\) the crystallization seems to occur in a single step, giving rise to a single peak in the DTA measurements. For all other samples, crystallization is present as a multistep process, corresponding to three peaks in the DTA curves.

Crystallization of the amorphous membranes is usually a thermally-activated process, as the DTA peaks shift to higher temperatures when measured with higher temperature rates [18]. The activation energy of the crystallization, \( E_a \), occurring in the samples with \( x = 20 \) and 30 have been already reported [18]: \( E_a \) is \(~549\) kJ/mol for \( x = 20 \) and \(~542\) kJ/mol for \( x = 30 \). In the present work, we extend such a study to the case \( x = 10 \). To determine the activation energy, DTA curves are obtained at various scanning rates (Figure 2). It is quite evident that the peaks shift to higher \( T \) as the scan rates increase. The inset of Figure 2 shows the Kissinger plot for the crystallization process and the best-fit line. The activation energy is obtained from the slope of the linear fit, which in the present case is \( 640 ± 60 \) kJ/mol. This value, obtained for \( x = 10 \), is higher than those reported in the case of samples with \( x = 20 \) and 30 [18].

![Figure 2](image-url)

**Figure 2.** DTA curves of sample (Ni\(_{0.6}\)Nb\(_{0.4}\))\(_{90}\)Zr\(_{10}\), measured at various temperature rates. The inset shows the Kissinger plot for the crystallization peak and the best fit line.

Figure 3 shows the comparison of the solubility measured at 400 °C for the three membranes with \( x = 10, 20, \) and 30, and of one ribbon with the composition (Ni\(_{0.6}\)Nb\(_{0.3}\)Ta\(_{0.1}\))\(_{70}\)Zr\(_{30}\). The last three compounds were also investigated as a function of temperature in [20]. For \( x = 10 \), investigated here for the first time, the kinetics of hydrogen absorption is so slow that we could not measure pressure-composition isotherm at temperatures lower than 400 °C (it took almost one day to observe pressure equilibration for each experimental point reported in Figure 3). The hydrogen solubility reported in Figure 3 and subsequent ones is expressed as H/M, i.e., the number of hydrogen atoms per atom of metal of the alloy (see section Materials and Methods for definition). It is quite evident from Figure 3 that the hydrogen solubility increases with increasing Zr content; for a pressure of ~7 bar,
which is the maximum applied pressure in the present study, we obtained a value of H/M equal to
~0.16 for x = 10, ~0.24 for x = 20 and ~0.36 for x = 30.

Figure 3. Pressure-composition isotherms measured at 400 °C for (Ni_{0.6}Nb_{0.4})_{100−x}Zr_{x} samples as a function of the Zr content. For comparison, also the isotherm of sample (Ni_{0.6}Nb_{0.4}Ta_{0.1})_{70}Zr_{30} is reported.

Conversely, the Ta content in the compounds seems to play only a marginal effect on the absorption properties, although substitution of Nb with Ta causes a slight increase of the crystallization temperature and does not vary the permeability significantly [21]. In Figure 3, one can observe that the pressure-composition isotherms of (Ni_{0.6}Nb_{0.4})_{70}Zr_{30} and (Ni_{0.6}Nb_{0.4}Ta_{0.1})_{70}Zr_{30} are close one to the other. Further details on solubility as a function of temperature of (Ni_{0.6}Nb_{0.4−y}Ta_{y})_{100−x}Zr_{x} membranes with y = 0, 0.1 and x = 20, 30 can be found in [20].

2.2. Hydrogen Sorption Properties in the Amorphous and in the Crystalline State

To the best of our knowledge, a comparison of the solubility properties of amorphous and crystalline materials is not available. For this reason, the pressure composition isotherms of amorphous and crystalline (Ni_{0.6}Nb_{0.4})_{70}Zr_{30} are here measured. Figure 4 displays both the absorption and desorption isotherms of (Ni_{0.6}Nb_{0.4})_{70}Zr_{30}, measured at 300 °C and 350 °C for the amorphous membrane and at 280 °C and 350 °C for the crystalline sample. The latter one was obtained as reported in section Materials and Methods. In the amorphous sample, one observes that the solubility decreases at higher temperature, while the hydrogen concentration at fixed temperature smoothly increases as pressure increases. Additionally, the desorption curves are smooth and do not present pressure plateaus. However, it is worth noting the occurrence of a clear hysteresis between the absorption and desorption curves. The occurrence of hysteresis during hydrogenation/dehydrogenation is a well-known property of metal powders, discussed in previous literature [22]. Due to the fast kinetics, it was possible to measure an entire absorption/desorption isotherm in 1 day for the amorphous sample.

The crystallized membrane isotherms show sorption curves with a shape different from that of the amorphous sample: the crystallized sample displays the presence of a “slopy” pressure plateau, as, indeed, expected for crystalline compounds [23]. Additionally, the crystalline membranes show a hysteresis between absorption and desorption. The kinetics of the crystallized sample is extremely slow when dealing with the low pressure part of the curve: it took about 10 days to measure the absorption/desorption curve for P < 5 bar, whereas the phase that forms at P ~6 bar for T = 280 °C is able to absorb/desorb in a few minutes, possibly due to the formation of new sites due to lattice
expansion. However, the amount of hydrogen stored in that phase is quite low ($\Delta H/M\approx 0.06$, from the width of the pressure plateau around $H/M \approx 0.34$ in Figure 4). To measure the two isotherms of the crystallized sample, it took one month and a half. Such a long time of acquisition limited the possibility to measure crystallized samples with different elemental composition.

Another aspect that needs to be highlighted is the fact that in the crystalline material one observes a near vertical trend of the pressure-composition isotherm for low $H/M$ values, while in the amorphous ribbons the tangent of the curve forms an acute angle with the horizontal axis. Such a behavior indicates that it is more difficult to remove hydrogen from the crystalline material than from the amorphous sample, i.e., one should reduce the pressure values to a much lower values in the crystalline membrane than in amorphous samples to have a complete dehydrogenation, starting from the same initial pressure value.

2.3. Physical Properties of a Boron Containing Sample

In this study, the influence of the addition of a small concentration of boron in a Ni-Nb-Zr ribbon is investigated, studying a membrane with composition $(Ni_{0.4}Nb_{0.28}Zr_{0.30})_{98}B_{2}$. The crystallization process was firstly investigated, in order to check that the addition of boron did not significantly decrease the crystallization temperature with respect to the $(Ni_{0.4}Nb_{0.4})_{70}Zr_{30}$ sample. Figure 5 shows the DTA curves of the boron containing membrane, measured at various temperature scanning rates. An exothermic peak, corresponding to the crystallization, is visible above $500 \, ^\circ C$, possibly followed at higher temperatures by a broader peak. For the curve measured at 10 $^\circ C$/min, the departure from a linear background is revealed at $\pm 3 \, ^\circ C$, a value close to that $(506 \pm 2 \, ^\circ C)$ obtained for $(Ni_{0.6}Nb_{0.4})_{70}Zr_{30}$ and reported in Table 1. In view of these results, we can assert that the addition of boron does not significantly affect the crystallization temperature and the thermal stability of the membrane. However, the boron-containing membrane displays only one well-defined peak in the DTA curve, while other materials, without B, show multiple peaks (see Figure 1). Additional studies are needed in order to ascertain the origin of such an effect.

Figure 4. Pressure-composition isotherms at two temperatures for amorphous and crystalline $(Ni_{0.6}Nb_{0.4})_{70}Zr_{30}$.

![Pressure-composition isotherms](image-url)
The hydrogen solubility decreases as temperature increases, as already reported for other Ni-Nb-Zr amorphous membranes [15,20]. Indeed, the maximum concentration of hydrogen obtained on the other hand, the sorption properties of the sample containing boron are modified with respect to the corresponding membranes without boron. Figure 6 displays the absorption pressure-composition isotherms of (Ni0.42 Nb0.28 Zr0.30)98B2 measured between 440 °C and 485 °C. Indeed, as the kinetics of the boron-containing membrane is slow below 420 °C, we could not obtain absorption curves below 420 °C.

The activation energy, E_a, of the crystallization process is obtained from the Kissinger plot, reported in the inset of Figure 5. For the boron containing sample E_a = 500 ± 30 kJ/mol. This value is lower than that obtained for (Ni0.6 Nb0.4)70 Zr30, E_a = 540 kJ/mol.

The hydrogen solubility decreases as temperature increases, as already reported for other Ni-Nb-Zr amorphous membranes [15,20]. Indeed, the maximum concentration of hydrogen obtained...
for $p \sim 7$ bar decreases from $\sim 0.31 \text{H/M}$ at $T = 440 \, ^\circ\text{C}$ to $\sim 0.27 \text{H/M}$ at $T = 485 \, ^\circ\text{C}$. Moreover, the entire absorption curve is displaced towards lower solubility values as temperature increases.

From the pressure-composition isotherms, one can obtain the value of the hydrogenation enthalpy using the so called van’t Hoff plot. In crystalline materials, pressure plateau are observed in isotherms, at $p^*$, and the van’t Hoff plot reports $\ln(p^*)$ vs. $1/T$; the slope of the best fit lines provides the hydrogenation enthalpy, $\Delta H_{\text{hyd}}$. In amorphous materials, no pressure plateau can be observed. However, one can still construct a van’t Hoff plot reporting $\ln(p)$ vs. $1/T$, where $p$ is the pressure at a fixed value of $\text{H/M}$ at the various temperatures. Additionally, in this case, one can estimate the hydrogenation enthalpy, $\Delta H_{\text{hyd}}$, from the slope of the plot [24].

Figure 7 shows the van’t Hoff plot of the boron containing membrane, calculated at various $\text{H/M}$ ratios. In order to construct such a graph, the experimental pressure-composition isotherms were interpolated by means of beta splines, thanks to a program implemented with the Labview (National Instruments, Austin, TX, USA) routines. Table 2 reports the values of the hydrogenation enthalpy, calculated from the slope of the lines of Figure 7. A decrease of the hydrogenation enthalpy as the hydrogen concentration increases from 0.10 to 0.20 can be noted (see Table 2). Indeed, $\Delta H_{\text{hyd}}$ passes from $89 \pm 9 \, \text{kJ/mol H}_2$ at $\text{H/M} = 0.10$ to $43 \pm 3 \, \text{kJ/mol H}_2$ at $\text{H/M} = 0.20$. The decrease of the hydrogenation enthalpy with increasing hydrogen content was already reported for $(\text{Ni}_{0.6}\text{Nb}_{0.4-y}\text{Ta}_y)_{100-x}\text{Zr}_x$ with $y = 0, 0.1$ and $x = 20, 30$ [20], and for $\text{Ni}_{32}\text{Nb}_{28}\text{Zr}_{30}\text{Cu}_{10}$ [15].

As a comparison, in $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$, the hydrogenation enthalpy varies from $\sim 41 \, \text{kJ/mol}$ for $\text{H/M} = 0.34$ to $\sim 33 \, \text{kJ/mol}$ for $\text{H/M} = 0.42$; in $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{80}\text{Zr}_{20}$, $\Delta H_{\text{hyd}}$ decreases from $\sim 14 \, \text{kJ/mol}$ at $\text{H/M} = 0.10$ to $\sim 8 \, \text{kJ/mol}$ at $\text{H/M} = 0.16$ [20]. In $(\text{Ni}_{0.6}\text{Nb}_{0.4-y}\text{Ta}_y)_{100-x}\text{Zr}_x$ the decrease of $\Delta H$ as $\text{H/M}$ increases was attributed to the progressive occupation of interstitial sites available for hydrogen trapping during the absorption process [20]. In fact, at the beginning of the process, the deepest energy levels become occupied, leaving shallower energy levels empty. The former become occupied only at higher hydrogen concentrations and, therefore, the hydrogenation enthalpy decreases as $\text{H/M}$ increases [20]. Indeed, Jayalakshmi et al. [25] investigated the thermal desorption process of some Ni-Nb-Zr-Ta amorphous ribbons by means of thermal desorption spectroscopy. These authors [25] linked the dehydrogenation temperature to the energy of the sites occupied by hydrogen atoms: the strongly bonded interstitial sites desorbed at higher temperature than the weakly bonded sites. For samples containing less than 40 at% H, the dehydrogenation occurred above 500 °C, while at higher hydrogen content dehydrogenation started already at 200 °C. These facts suggest that at lower $\text{H/M}$ the deeper energy interstitial sites are occupied by hydrogen [25], while at higher $\text{H/M}$ also the shallower energy levels become populated. The absorption data presently reported [25] are consistent with this picture: at higher $\text{H/M}$ the hydrogenation enthalpy decreases because the absorption involves the shallower energy sites. In the presently-investigated $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.30})_{98}\text{B}_2$ membrane, no change of the hydrogenation enthalpy is observed above $\text{H/M} = 0.20$.

Finally, we want to point out that, despite the high temperatures reached during the sorption measurements, the boron-containing membranes used for the Sieverts measurements maintained their shape and did not pulverize after the hydrogenations and thermal cycles (in total, nine cycles, including the ones used for activating the membranes).

Table 3 reports a summary of the elemental composition, the crystallization temperature $T_C$ (defined as the maximum of the first peak in DTA measurements conducted with a temperature rate of $10 \, ^\circ\text{C/min}$), solubility at $T = 400 \, ^\circ\text{C}$ and $p = 7$ bar and dehydrogenation enthalpy of the investigated membranes.
The elemental composition of the alloys, as reported in the whole paper, corresponds to the initial concentration of elements used for the preparation of the materials. For each composition investigated at H/M ratios, the dehydrogenation occurred above 500 °C, while at higher H/M also the shallower energy levels become populated. The absorption data presently reported are of comparison, in Figure 7, are shown. Additionally, from the pressure—composition isotherms, one can obtain the value of the hydrogenation enthalpy, $\Delta H_{\text{hyd}}$, calculated for (Ni$_{0.42}$Nb$_{0.28}$Zr$_{0.30}$)$_{98}$B$_2$ at various H/M values.

<table>
<thead>
<tr>
<th>H/M</th>
<th>$\Delta H_{\text{hyd}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>89 ± 9</td>
</tr>
<tr>
<td>0.12</td>
<td>76 ± 5</td>
</tr>
<tr>
<td>0.14</td>
<td>69 ± 3</td>
</tr>
<tr>
<td>0.16</td>
<td>59 ± 3</td>
</tr>
<tr>
<td>0.18</td>
<td>49 ± 2</td>
</tr>
<tr>
<td>0.20</td>
<td>43 ± 3</td>
</tr>
<tr>
<td>0.22</td>
<td>43 ± 3</td>
</tr>
<tr>
<td>0.24</td>
<td>43 ± 3</td>
</tr>
<tr>
<td>0.26</td>
<td>43 ± 3</td>
</tr>
</tbody>
</table>

Table 3. Elemental composition, crystallization temperature $T_c$ (defined as the maximum of the first peak in DTA measurements conducted with a temperature rate of 10 °C/min), solubility at $T = 400$ °C and $p = 7$ bar and dehydrogenation enthalpy of the investigated membranes.

<table>
<thead>
<tr>
<th>Elemental Composition</th>
<th>$T_c$ (°C)</th>
<th>Solubility (H/M)</th>
<th>$\Delta H$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ni$<em>{0.6}$Nb$</em>{0.4}$)$<em>{90}$Zr$</em>{10}$</td>
<td>615</td>
<td>0.16</td>
<td>–</td>
</tr>
<tr>
<td>(Ni$<em>{0.6}$Nb$</em>{0.4}$)$<em>{80}$Zr$</em>{20}$</td>
<td>567</td>
<td>0.24</td>
<td>14 (H/M = 0.10) [20]</td>
</tr>
<tr>
<td>(Ni$<em>{0.6}$Nb$</em>{0.4}$)$<em>{70}$Zr$</em>{30}$</td>
<td>540</td>
<td>0.36</td>
<td>41 (H/M = 0.34) [20]</td>
</tr>
<tr>
<td>(Ni$<em>{0.42}$Nb$</em>{0.28}$Zr$<em>{0.30}$)$</em>{98}$B$_2$</td>
<td>526</td>
<td>0.31 (T = 440 °C)</td>
<td>89 (H/M = 0.10)</td>
</tr>
</tbody>
</table>

3. Materials and Methods

Buttons of the investigated alloys were obtained by arc melting the pure elements (Ni, Nb, Zr, Ta, B) in an argon atmosphere at AMES Laboratory, Ames, Iowa, USA, in the proper weight proportions. The elemental composition of the alloys, as reported in the whole paper, corresponds to the initial concentration of elements used for the preparation of the materials. For each composition investigated.
in the paper, one ingot of crystalline material was produced. These initial alloys are crystalline and need further processing to become amorphous. Indeed, subsequently, the buttons were used to fabricate the amorphous membranes by means of a melt spinning apparatus at the CSIRO laboratory, Brisbane, Australia [26]. In the melt spinning apparatus, the alloys are melted and are, subsequently, extruded onto a copper wheel, cooled by water. The rapid solidification, occurring with a temperature rate of the order of $\Delta T / \Delta t = 10^5 \degree \text{C} \cdot \text{s}^{-1}$, produces an amorphous state for the alloys. These amorphous ribbons have typical thickness of ~30–70 µm and a width of ~30 mm [26], and are those investigated throughout the paper. Only in the case of a specimen of (Ni$_{0.6}$Nb$_{0.4}$)$_{70}$Zr$_{30}$, recrystallization was obtained by means of a thermal treatment of an amorphous sample in a thermogravimetric apparatus, a Setaram Sensys Evolution 1200 TGA system (Setaram Instrumentation, Caluire, France), heating to 700 °C in a pure argon atmosphere (60 mL/min), using a temperature scanning rate of 10 °C/min. Previous X-Ray Diffraction measurements indicated that this treatment induces the occurrence of crystallization and Bragg peaks due to a Ni$_{48}$Zr$_{52}$ phase and possibly to a Ni$_{10}$Zr$_7$ phase can be detected [27].

DTA curves were measured by means of a Setaram Sensys Evolution 1200 TGA system [28] under a high purity argon flux (60 mL/min). For each temperature scan, a piece of a sample with a mass of ~10 mg was measured. For each specimen, acquisitions with various temperature rates, ranging between 4 °C and 30 °C/min, were used in order to calculate the activation energy of the crystallization process.

Pressure-composition isotherms were recorded by a homemade Sieverts apparatus described elsewhere [27, 29]. For each sample, measurements were conducted with a mass of 300–500 mg. In all graphs of the pressure-composition isotherms, pressure is referred to the molecular hydrogen in equilibrium with the solid, while the concentration is expressed as H/M, i.e., the number of hydrogen atoms per atom of metal composing the dehydrogenated alloy. During the acquisition of pressure-composition isotherms, the variation of the number of gaseous molecular hydrogen due to a change in the applied pressure is measured, $\Delta n(H_2)$. Consequently, the number of moles of atomic hydrogen absorbed or desorbed from the solid can be calculated as $\Delta n(H) = 2 \cdot \Delta n(H_2)$. The number of moles of the dehydrogenated alloy, $n_{\text{alloy}}$, is obtained by the measure of the initial mass of the sample ($m_{\text{alloy}}$): $n_{\text{alloy}} = m_{\text{alloy}} / M_{\text{alloy}}$, where $M_{\text{alloy}}$ is the mass of a formula unit. Consequently, the variation of the number of hydrogen atoms per metal atom can be calculated as $\Delta n(H) / n_{\text{alloy}} = 2 \cdot \Delta n(H_2) / M_{\text{alloy}} / m_{\text{alloy}}$. Adding contributions due to subsequent change of pressure, one can easily obtain $\Delta n(H) / n_{\text{alloy}}$, which is the ratio of the number of moles of atomic hydrogen and the number of moles of metal at a certain pressure and temperature or, equivalently, the number of hydrogen atoms per metal atom, which is usually called H/M [30].

4. Conclusions

In this work we investigated a series of amorphous membranes based on Ni, Nb, and Zr metals. In (Ni$_{0.6}$Nb$_{0.4}$)$_{100-x}$Zr$_x$, the onset crystallization temperature decreases from ~590 °C for x = 10 to ~510 °C for x = 30. Concomitantly, the activation energy of the crystallization decreases from ~640 kJ/mol for x = 10 to ~550 kJ/mol for x = 30. The hydrogen solubility measured at 400 °C increases for increasing Zr content.

A hysteresis between the adsorption and desorption pressure-composition isotherms is observed both in amorphous and in crystallized (Ni$_{0.6}$Nb$_{0.4}$)$_{70}$Zr$_{30}$. However, the crystalline sample shows multiple pressure plateaus, due to the hydrogenation of various crystalline phases. A slow kinetics of the sorption processes in the crystalline state is observed. Conversely, in the amorphous state, a smooth behavior of the p-c isotherms is visible and the sorption kinetics are much faster.

Finally, the addition of a small amount of boron to (Ni$_{0.6}$Nb$_{0.4}$)$_{70}$Zr$_{30}$ is investigated. The crystallization temperature is not significantly affected, while the activation energy of the crystallization process decreases. The sorption properties are measured above 440 °C, showing a good hydrogen solubility. The hydrogenation enthalpy passes from $89 \pm 9$ kJ/mol H$_2$ at H/M = 0.10 to $43 \pm 3$ kJ/mol H$_2$ at H/M = 0.20. This behavior, similar to that observed in similar membranes,
is attributed to the fact that, at the beginning of hydrogenation, the lowest energy sites become populated, while lately only shallower energy levels become occupied, with a consequent change in the energy requested for hydrogenation. It should be noted that the boron-containing membrane does not pulverize even after repeated thermal cycles and hydrogenation processes up to 485 °C and 7 bar.

Acknowledgments: This research is supported by U.S. DOE-NNSA grant, (U.S. DE-NA0002004) at University of Nevada, Reno.

Author Contributions: Michael Dolan produced the melt spun membranes; Oriele Palumbo and Francesco Trequattrini performed the DTA measurements and analysis; Narendra Pal, Madhura Hulyakar, Suchismita Sarker and Dhanesh Chandra conducted preliminary solubility measurements; Annalisa Paolone wrote the paper; all authors discussed the data and shared the conclusions.

Conflicts of Interest: The authors declare no conflict of interest.

References
2. Budd, P.M.; McKeown, N.B. Highly permeable polymers for gas separation membranes. Polym. Chem. 2010, 1, 63–68. [CrossRef]
16. Xu, J.; Niu, J.; Zhang, Z.; Ge, W.; Shang, C.; Wang, Y. Effects of B addition on glass formation, mechanical properties and corrosion resistance of the Zr66.7-xNi33.3Bx (x = 0, 1, 3, and 5 at%) metallic glasses. JOM 2016, 68, 682–691. [CrossRef]
17. Li, H.-W.; Yan, Y.; Orimo, S.-I.; Züttel, A.; Jensen, C.M. Recent Progress in Metal Borohydrides for Hydrogen Storage. Energies 2011, 4, 185–214. [CrossRef]
20. Palumbo, O.; Trequattrini, F.; Pal, N.; Hulyalkar, M.; Sarker, S.; Chandra, D.; Flanagan, T.; Dolan, M.; Paolone, A. Hydrogen absorption properties of amorphous (Ni_{0.6} Nb_{0.4-y} Ta_y)_{100-x} Zr_x membranes. Prog. Nat. Sci. 2017. [CrossRef]
27. Palumbo, O.; Brutti, S.; Trequattrini, F.; Sarker, S.; Dolan, M.; Chandra, D.; Paolone, A. Temperature dependence of the Elastic Modulus of (Ni_{0.6} Nb_{0.4})_{1−x} Zr_x Membranes: Effects of Thermal Treatments and Hydrogenation. Energies 2015, 8, 3944–3954. [CrossRef]

© 2017 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 (http://creativecommons.org/licenses/by/4.0/).