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ABSTRACT

Amorphous Ni-based alloy membranes show great promise as inexpensive, hydrogen-selective membrane materials. In this study, we developed membranes based on non-precious Ni-Nb-Zr alloys by adjusting the alloying content and using additives. Several studies on crystallization of the amorphous ribbons, in-situ x-ray diffraction, SEM and TEM, hydrogen permeation, hydrogen solubility, hydrogen deuterium exchange, and electrochemical studies were conducted. An important part of the study was to completely eliminate Palladium coatings of the NiNbZr alloys by hydrogen heat-treatment. The amorphous alloy (Ni_{0.6}Nb_{0.4})₈₀Zr₂₀ membrane appears to be the best with high hydrogen permeability and good thermal stability.

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Amorphous Alloy Membranes Prepared by Melt-Spin methods for Long-Term use in Hydrogen Separation Applications

Executive Summary

The objective of this program was to develop low cost amorphous membranes produced by melt spinning methods that have the potential of replacing Pd or Pd-Ag alloys. Several amorphous membranes were prepared in ribbon form of various compositions. Ni based alloys with additions of Nb-Zr. Adjustments in the compositions of these alloys were made to optimize the thermal stability and permeation of the alloy ribbons.

Amorphous Ni-based alloy membranes show great promise as inexpensive, hydrogen-selective membrane materials. One of the main barriers to the commercial uptake of these materials is their tendency to crystallize during long-term operation at elevated temperatures, a process which decreases strength, durability and permeability. In this study, a series of (1) binary base alloys of $\text{Ni}_{100-x}\text{Zr}_x$ ($x = 36.3$ or 70 at.%), (2) binary series $\text{Ni}_{60}\text{M}_{40}$ ($\text{M} = \text{Nb}, \text{V}, \text{Ta}$), (3) ternary series of $\text{Ni}_{60}\text{M}_{20}\text{Zr}_{20}$ ($\text{M} = \text{Nb}, \text{V}, \text{Ta}$), ternary series $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x = 0, 10, 20$ or 30), quaternary $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{100-x}\text{Zr}_x$ (where $x = 10, 20$ or 30), and $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.30})_{100-x}\text{B}_x$ ($x=1$, and 5) amorphous alloy membranes were prepared by melt spinning method. Several studies on crystallization of the amorphous ribbons, in-situ x-ray diffraction, SEM and TEM, hydrogen permeation, hydrogen solubility, hydrogen deuterium exchange, and electrochemical studies were conducted.

The glass transition and crystallization kinetics of the amorphous alloy membranes have been studied under non-isothermal and isothermal conditions using differential scanning calorimetry (DSC). The dependence of glass transition and crystallization temperatures on heating rates was analyzed by Lasocka's relationship. The activation energies (E_x) of crystallization were determined using Kissinger and Ozawa equations. A Johnson-Mehl-Avrami equation has also been applied for isothermal kinetics and corresponding time-temperature-transformation (TTT) diagrams have been made. Intermetallic phases and surface morphology after the thermal treatment have been identified by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The crystallization temperature, T_x , for the Ni rich-eutectic $\text{Ni}_{63.7}\text{Zr}_{36.3}$, $T_x=841.2$ K at 10K/min. , activation energy $E_x=374.1$ kJ/mol. For the near-eutectic Zr rich- $\text{Ni}_{30}\text{Zr}_{70}$ alloy, $T_x=668.9\text{K}$ at 10K/min , $E_x=353.3$ kJ/mol. We determined the activation energy of the ternary $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy using Kissinger and Ozawa equations (517 kJ/mol and 505 kJ/mol). In alloy series $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x = 0, 10, 20$ or 30 at.%) alloys, the T_x continuously decreased with increasing Zr concentration. The value of E_x increased up to 10 at.% Zr addition, then decreased, which is consistent with the decrease in T_x . In addition, the values of T_x and E_x increased with increasing Ta content in the $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{100-x}\text{Zr}_x$ alloys.

Hydrogen permeation properties of Ni-based amorphous alloy membranes were investigated over the $573\text{-}673$ K temperature range at different hydrogen partial pressures. The linear relationship between the hydrogen permeation flux and the hydrogen partial pressure difference across the membrane indicates that permeation was controlled by diffusion through the bulk membrane. The effect of Zr concentration on the hydrogen permeability, the thermal stability and hydrogen embrittlement was also investigated. The hydrogen permeability of the $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy was higher ($7.0 \times 10^{-9} \text{ mol.m}^{-1}.\text{s}^{-1}.\text{Pa}^{-0.5}$ with Diffusion

coefficient $D_x=4.91 \times 10^{-10} \text{ m}^2/\text{s}$) than those of the $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ and $\text{Ni}_{60}\text{Nb}_{40}$ alloys at 623 K (1.2×10^{-9} and $4.9 \times 10^{-11} \text{ mol.m}^{-1}.\text{s}^{-1}.\text{Pa}^{-0.5}$, respectively), but decreased with decreasing Zr concentration. The permeability of the alloy with Ta, $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{70}\text{Zr}_{30}$ at 623 K was slightly lower ($3.9 \times 10^{-9} \text{ mol.m}^{-1}.\text{s}^{-1}.\text{Pa}^{-0.5}$ with $D_x=3.99 \times 10^{-10} \text{ m}^2/\text{s}$) than $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ alloy, but resulted in improved thermal stability and hydrogen embrittlement.

Thermodynamic properties, such as, solubility of hydrogen in amorphous $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x=10, 20, 30$) alloy series were measured using a Sieverts apparatus; hydrogen solubility increased with decrease in temperature. Also the hydrogen solubility increased with the increase in Zr content across all the temperatures. The highest hydrogen solubility obtained amongst all the amorphous alloys studied in this study was found to be 0.6521 moles at an H/M=1.66 with highest solubility in alloys with $x=30$, but long term durability was best in alloys with $x=20$. Gibbs energies of hydrogenation were also determined. Results show that a trade-off between permeation and durability need to be made for the final selection of the alloy.

In the later part of the program we used membranes without any Pd coatings, achieved that due to hydrogen heat treatment that precipitated nanoscale Ni clusters on the surfaces of the ribbons. Gas phase $\text{H}_2\text{-D}_2$ exchange reaction has been carried out on the membrane surface and the exchanges were determined which provided a measure of catalytic activity of the above mentioned membranes. More studies included the crystallographic phase change determination, bulk hydrogen solubility measurements, surface conduction measurements and surface morphological studies. It was observed that crystalline materials provide more surface activity for hydrogen than their amorphous counterparts. Micro-kinetic analysis was performed to determine the heat of hydrogen absorption and desorption on the alloy surface. Electrochemical Impedance Spectroscopy was conducted on the membranes to determine the surface resistance and it was found that $\text{Ni}_{64}\text{Zr}_{36}$ as-spun ribbon displayed highest resistance while $\text{Ni}_{60}\text{Ta}_{20}\text{Zr}_{20}$ showed lowest resistance. Absorption studies on $\text{Ni}_{60}\text{V}_{40}$ binary alloy and $\text{Ni}_{60}\text{V}_{20}\text{Zr}_{20}$ ternary alloy indicated that the addition of Zr to these non-coated alloys increased the hydrogen solubility in the bulk. Microstructural analyses showed nano-crystalline phases in $\text{Ni}_{64}\text{Zr}_{36}$ membrane. XRD and SEM studies conducted on post treated samples showed the possible phase segregation of Ni and ZrO_2 .

Publications and Presentations and national/International Meetings

The results obtained from this research program have been presented at National/international meetings, and also published in peer-reviewed Journals/proceedings that are listed below:

JOURNAL ARTICLES

1. S.-M. Kim, W.-M. Chien, D. Chandra, N.K. Pal, A. Talekar, J. Lamb, M.D. Dolan, S.N. Paglieri, and T.B. Flanagan, “Phase Transformation and Crystallization Kinetics of Melt-Spun $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ amorphous alloy,” *Journal of Non-Crystalline Solids*, v358 (2012) 1165-1170.
2. Steve Paglieri, Narendra Kumar Pal, Michael Dolan, Sang-Mun Kim, Wen-Ming Chien, Joshua Lamb, Dhanesh Chandra, Kevin M. Hubbard, David P. Moore; “Hydrogen Permeability, thermal stability and hydrogen embrittlement of Ni-Nb-Zr and Ni-Nb-Ta-Zr amorphous alloy membranes” *Journal of membrane Science*, 378 (2011) 42-50.

3. S.-M. Kim, D. Chandra, W.-M. Chien, N.K. Pal, M.D. Dolan, A. Talekar, J. Lamb, S.N. Paglieri and T.B. Flanagan, "*Hydrogen Permeability and Crystallization Kinetics in Amorphous Ni-Nb-Zr Alloys*," International Journal of Hydrogen Energy, (2011) (in press, doi:10.1016/j.ijhydene. 2011.04.220).

CONFERENCE PAPER/POSTER/PROCEEDING

4. S. N. Paglieri, N. K. Pal, M. D. Dolan, S.-M. Kim, W.-M. Chien, J. Lamb, D. Chandra, "*Ni-Nb-Zr-(Ta, Co) Amorphous Alloy Membranes for Hydrogen Separation*," *Proc. of the 242nd ACS Natl. Mtg.; Denver, Colorado, Aug. 28-Sept. 1, 2011 (Conference Proceedings)*
5. S.-M. Kim, N.K. Pal, D. Chandra, M.D. Dolan, W.-M. Chien, J. Lamb, A. Talekar, S.N. Paglieri, and T.B. Flanagan, "*Effect of tantalum substitution on the crystallization kinetics and hydrogen permeability of Ni-Nb-Zr amorphous alloys*," TMS 2011 Annual Meeting, San Diego, California, USA (Feb 27-March 3, 2011).
6. Steve Paglieri, Michael Dolan, Narendra Kumar Pal, Sang-Mun Kim, Wen-Ming Chien, Joshua Lamb, Anjali Talekar, Dhanesh Chandra, Moore, Hubbard; "*Ni-Nb-Zr-(Ta, Co) Amorphous Alloy Membranes for Hydrogen Separation*," North American Membrane Society Mtg., June 5-8, 2011, NAMS Annual Meeting, June 4-8, 2011, Las Vegas, Nevada.
7. S. N. Paglieri, M. D. Dolan, N. K. Pal, S.-M. Kim, W.-M. Chien, J. Lamb, A. Talekar, D. Chandra, "*Amorphous Membranes for Hydrogen Separation Based on Ni-Nb-Zr Alloys*," AIChE Annual Mtg., Oct. 16-21, 2011, Minneapolis, Minnesota.
8. S. N. Paglieri, N. K. Pal, M. D. Dolan, S.-M. Kim, W.-M. Chien, J. Lamb, D. Chandra, "*Ni-Nb-Zr-(Ta, Co) Amorphous Alloy Membranes for Hydrogen Separation*," Presented at the 242nd ACS Natl. Mtg.; Denver, Colorado, Aug. 28-Sept. 1, 2011.
9. N. K. Pal, D. Chandra, S.N. Paglieri, J. Lamb, S.-M. Kim, W.-M. Chien, A. Talekar, T.B. Flanagan, and M.D. Dolan, "*Effect of Ta substitution on hydrogen solubility and permeability of $Ni_{42}Nb_{28}Zr_{30}$ amorphous alloy*," NAMS Annual Meeting, Las Vegas, Nevada, USA (June 4-8, 2011).
10. S.-M. Kim, M.D. Dolan, N.K. Pal, W.-M. Chien, J. Lamb, A. Talekar, D. Chandra, S.N. Paglieri, and T.B. Flanagan, "*Effect of hydrogen pressure on hydrogen permeability of Ni-based amorphous membranes*," ICOM 2011, July 23-29, 2011, International Congress on Membranes and Membrane Processes, July 23-29, 2011, Amsterdam, The Netherlands.
11. Poster: S. N. Paglieri, N. K. Pal, M. D. Dolan, S.-M. Kim, W.-M. Chien, J. Lamb, D. Chandra, Kevin M. Hubbard, David P. Moore, "*Ni-Nb-Zr-(Ta, Co) Amorphous Alloy Membranes for Hydrogen Separation*," North American Membrane Society Mtg., Las Vegas, Nevada, June 5-8, 2011.
12. Sang-Mun Kim, Narendra K. Pal, Wen-Ming Chien, Joshua H. Lamb, Anjali Talekar, Dhanesh Chandra, Michael D. Dolan and Stephen N. Paglieri, "*Crystallization Kinetics and Hydrogen Solubility in Ni-based Amorphous Alloys for Hydrogen Permeability*" NAMS/ICIM 2010 Conferences, July 17-22, 2010, Washington, D.C., USA
13. Stephen N. Paglieri, Michael D. Dolan, David P. Moore, Kevin M. Hubbard, Sang-Mun Kim, Narendra K. Pal, Wen-Ming Chien, Joshua H. Lamb, Anjali Talekar, Dhanesh Chandra, Sarah J. DeVoss and Gokhan O. Alptekin, "*Ni-Nb-Zr Amorphous Alloy Membranes for Hydrogen Separation*" 2010 AIChE Annual Meeting, November 7-12, 2010, Salt Lake City, UT, USA

14. Stephen N. Paglieri, Sarah J. DeVoss, Gökhan O. Alptekin, Tyler B. Gleditsch, Michael D. Dolan, Kevin M. Hubbard, David P. Moore, Sang-Mun Kim, Narendra K. Pal, Joshua H. Lamb, Wen-Ming Chien, and Dhanesh Chandra, “*Ni-Nb-Zr and Ni-Nb-Zr-Ta Amorphous Alloy Membranes for Hydrogen Separation*” *NAMS/ICIM 2010 Conference*, July 17-22, 2010, Washington, D.C., USA
15. Dhanesh Chandra, M. Dolan, S. Paglieri, T. Flanagan, J. Reilly,” Amorphous Alloy Membranes Prepared by Melt-Spin methods for Long-Term use in Hydrogen Separation Applications” International Energy association Meeting , International Energy Agency Task 22 – Workshop, IEA Task-22 Death Valley California April 11-15, 2010. Topic No.2
16. Dhanesh Chandra, M. Dolan, S. Paglieri, T. Flanagan, J. Reilly, “Amorphous Alloy Membranes for Hydrogen Separation Applications” International Energy association Meeting , International Energy Agency, – Workshop, IEA Task-22, Copenhagen, Denmark, Sept. 4-8, 2011.

OTHERS

1. INTERNATIONAL ENERGY AGENCY MEETING in GREECE. Dhanesh Chandra, , M. Dolan, S. Paglieri, T. Flanagan, Hydrogen separation Membranes, IEA Meeting, Crete, Greece, April 21-25, 2013. (Presentation)
- THREE Ph.D DISSERTATION FROM THIS PROJECT**
2. Dr. S-M Kim, Ph.D , Material Science and Engr. 2011, Uni. of Nevada, Reno,
  3. Dr. N. Pal, Ph.D Material Science and Engr. May 2012, University of Nevada, Reno.
  4. Dr. A. Adibhatala, Ph.D, Material Science and Engr. Dec. 2012, at University of Nevada, Reno.

Amorphous alloy ribbon membranes of Ni-Nb with 20 at.% Zr appears to be the best so far from this study, because this membrane has a high hydrogen permeability and good thermal stability. For long-term use the amorphous alloy (Ni_{0.6}Nb_{0.4})₈₀Zr₂₀ membrane may be used for hydrogen separation from carbon dioxide; permeability of this (0.063 μm thick) membrane was measured as 8.3×10⁻⁹ at 400°C.

REPORT DETAILS

I. Introduction

Alternative fuels and renewable energy technologies are being emphasized due to importance of an energy carrier and global energy systems transition as shown in Figure 1.1. Hydrogen is an ideal candidate for energy conversion systems such as fuel cells, hydrogen turbines, and IC engines using hydrogen fuel emit only water as the exhaust. Hydrogen can be produced from primary energy feedstocks, such as coal, natural gas as well as biomass, by gasification followed by processing the synthesis gas (syngas). Coal gasification is one of the routes considered for hydrogen production to provide affordable electricity in a safe and environmentally clean manner. There are various gas separation and purification technologies that could separate constituents of the syngas. Among them, hydrogen-selective membrane via the water-gas-shift (WGS) reaction has been recognized as a desirable technique that will reduce operating costs and improve thermal efficiency and environmental performance.

Figure 1.1. Global energy systems transition, 1850-2150. The world has been slowly shifting from one form of energy to another—from solids to liquids to gases [1.1].

Based on current existing technology, the coal is first gasified with oxygen and steam to produce a syngas consisting a mixture of hydrogen (H_2), carbon monoxide (CO), some CO_2 , and other chemical compounds. The carbon monoxide (CO) of the syngas reacts with steam to form H_2 via the water-gas shift (WGS) reaction (based on the equilibrium $CO + H_2O \rightarrow H_2 + CO_2$) as shown in Figure 1.2. This process is mildly exothermic reaction which is achieved at a high and low temperature controlled by the addition of steam, two-stage WGS reaction at around 400 and 250°C, respectively. Finally, separation of the CO_2 and H_2 streams is achieved using a low-temperature pressure-swing process at around 50°C. Syngas in the coal gasifier would then undergo further processing to separate and purify hydrogen as needed to satisfy industry product quality standards.

Metallic membranes can be used for the coal gasification application at high temperatures compatible to the WGS reaction because of their high hydrogen permeabilities and good mechanical properties. Another advantage of metallic membranes is that high-purity hydrogen (up to 99.9999%) can be obtained as a result of the solution-diffusion transport mechanism [1.3]. Crystalline Pd and Pd-based alloy membranes are commonly used metallic membrane materials for hydrogen separation and purification [1.4-1.8]. However, Pd is expensive for large-scale applications and not suitable for low temperature operation due to hydrogen embrittlement [1.5].

Furthermore, the presence of the α - β hydride phase transition [1.9, 1.10] below the critical temperature can lead to fracture of the membrane. Body centered cubic (BCC) metals including Nb, V, and Ta are cost-effective materials having high hydrogen permeability [1.11-1.15] as shown in Figure 1.3.

Figure 1.2: Major gasification reactions [1.2].

Figure 1.3: Hydrogen permeability as a function of temperature for the metals [1.13].

In case of Nb, V, and Ta, hydrogen permeability decreases with increasing temperature. This phenomenon is due to the decrease of hydrogen solubility more rapidly than the increase of the diffusion coefficient [1.11]. Although Nb, Ta, and V have higher permeability than that of Pd, it is difficult to use these metals as hydrogen separation materials. As the hydrogen solubility is high in these materials, they develop internal strains in the grains that will cause membrane failure [1.16-1.19].

Amorphous alloy membranes, however, can be inexpensive alternatives to Pd-based alloys for hydrogen separation membranes, although much development is still needed [1.20]. Amorphous alloy ribbons can be prepared with a wide composition range by the rapid solidification technique. A major advantage of this process is that thin foils can be obtained rather quickly. Considering that hydrogen flux through the membrane is inversely proportional to thickness, this gives the possibility to obtain high permeation flux. These membranes also, generally exhibit excellent mechanical strength, high thermal stability, and soft magnetic property [1.19-1.21].

Figure 1.4: Hydrogen from coal RD&D Program Milestones [1.2].

Table 1-1. Hydrogen separation technical targets.

Performance Criteria	Units	Current Status (Pd-based metallic or composite)	2010 Target	2015 Target
Flux ^a	ft ³ /hour/ft ²	~200-300	200	300
Temperature	°C	300-500	300-600	250-500
S tolerance	Ppmv	Tbd	20	>100
Cost	\$/ft ²	Tbd	100	<100
WGS activity	—	N/A	Yes	Yes
ΔP Operating capability	Psi	Tbd	Up to 400	Up to 800 to 1000
Carbon monoxide tolerance	—	Some	Yes	Yes
Hydrogen purity	%	>99.5	99.5	99.99
Stability/durability	Years	0.9 (tested)	3	5

^a For 100 psi ΔP (hydrogen partial pressure basis). ΔP=total pressure differential across the membrane reactor.

The goal of this study is to develop the amorphous alloy membranes for hydrogen separation and other advanced concepts such as process intensification that provide high purity hydrogen. Figure 1.4 summarizes the activities and technologies associated with hydrogen production and the performance criteria are shown in Table 1-1.

1.1. Hydrogen separation process

The solution-diffusion model has been most widely accepted transport model for permeation in membrane [1.3]. The mechanism for hydrogen separation through a metal membrane is often referred to as the solution-diffusion mechanism. It has been also known that these membranes play a catalytic role to perform hydrogen permeation. Therefore, the solution-diffusion model is mainly divided into three steps: 1) absorption and dissociation of H_2 on the high-pressure (or high chemical potential) surface of the membrane, 2) diffusion of atomic H through bulk metal, and 3) recombination of atomic H to form H_2 and desorption of H_2 from the low-pressure (or low chemical potential) surface of the membrane.

In contrast, other gases are almost chemically frozen on the membrane surface. High purity hydrogen is thus obtained at the permeate side of the membrane, whereas the concentrations of other gases are extremely low compared to hydrogen. The performance of a membrane can be discussed in terms of flux and selectivity. The flux of hydrogen is the product of the diffusion coefficient and the concentration gradient through the membrane, and can be expressed as mass or mole per unit time per unit area. The basic concept of a membrane permeation process is schematically depicted in Figure 1.5. The permeability coefficient (ϕ) is defined by the ratio between the hydrogen flux (J) of the membrane and its concentration gradient (Δc) through the membrane thickness (l)

$$J = \phi \frac{\Delta c}{l} \quad (1.1)$$

Fick's first law describes the atomic permeation flux of hydrogen through a homogeneous metal phase as a function of the concentration gradients and a diffusion coefficient, D_{H_2} (cm^2/s), which is the concentration gradient resulting from ΔP across the membrane. Permeation of hydrogen through a metal membrane is a function of the solubility and diffusion of hydrogen in the membrane in addition to the membrane thickness and temperature. When the downstream pressure is much less than the upstream pressure, permeability can be expressed by the product of the diffusion coefficient (D) and a solubility factor (S)

$$\phi = DS \quad (1.2)$$

For alloy membranes, the solubility of H varies with the exponent (n) of partial pressure. Under typical operating conditions, n of 0.5 reflects the dissociation of a single molecule of H_2 to form two dissolved H atoms that diffuse into the metal, where an ideal solution of hydrogen atoms in membrane is formed. The solubility-pressure relationship is defined as the following Sieverts' law:

$$C = kP^n \quad (1.3)$$

Figure 1.5: Hydrogen permeation mechanism through a membrane according to solution-diffusion model.

where k is Sievert's constant and P is the hydrogen partial pressure in the hydrogen-metal system. Because of this square root relationship (i.e., $n=0.5$), the permeation flux is typically proportional to the difference in the square roots of the pressure at the high-pressure surface (P_1) and the low-pressure surface (P_2). The flux divided by this pressure term is referred to as permeance (δ),

$$\delta = \frac{J}{(P_1^n - P_2^n)} \quad (1.4)$$

For a given membrane, permeance will be constant regardless of the H_2 partial pressures at each surface, as J changes in proportion to $(P_1^n - P_2^n)$. Permeance is applied as the primary performance characteristic for thin, surface-limited membranes.

As can be seen from Equation (1.1), flux is inversely proportional to the thickness (l) of a membrane. Factoring this in gives the permeability (ϕ):

$$\phi = \delta l = \frac{Jl}{(P_1^n - P_2^n)} \quad (1.5)$$

Permeability is independent of thickness and H_2 partial pressure, and thus offers the best means of comparing the intrinsic transport properties of different bulk materials. This assumes that H transport is limited by bulk diffusion, not the association or dissociation reactions. Furthermore, permeability is temperature dependent and can be represented by the Arrhenius equation

$$\phi = K \exp\left(\frac{-E}{RT}\right) \quad (1.6)$$

where K is the pre-exponential factor constant, E is the activation energy, R is the gas constant, and T is the absolute temperature. Similarly, the ability of a membrane to separate gases is characterized by the selectivity of the membrane [1.13]. Ideal selectivity (or separation factor) is defined as the ratio of the permeability of the penetrants of interest. The selectivity of hydrogen over mixed gas can be expressed as

$$\alpha_{H_2/mixed} = \frac{P_{H_2}}{P_{mixed}} \quad (1.7)$$

where $\alpha_{H_2/mixed}$ is the ideal selectivity of the hydrogen to the mixed gas.

1.2. Hydrogen separation membranes

Hydrogen separation membranes may be categorized into following four types:

- Polymer Membranes
- Carbon Membranes
- Ceramic Membranes
- Metallic Membranes

Key parameters for hydrogen selective membranes are high flux rates, thermal stability, chemical stability in the presence of contaminants (i.e., CO_2 , CO , CH_4 , H_2O , H_2S), high selectivity, ease of fabrication and low cost.

1.2.1. Polymer Membranes

Hydrogen separation process from polymer membranes has been used industrially from mixed gas. The permeation of hydrogen through the membrane is achieved through a solution-diffusion mechanism. However, it does not require the H_2 dissociation and recombination steps unlike metallic membrane for hydrogen separation [1.22]. The typical temperature for operation of polymer membranes is ~ 373 K although in certain cases this may extend up to ~ 473 K [1.23]. Good ability to cope with high pressure drops and low cost are key advantages of polymer membranes. However, there is limited information on their mechanical strength, relatively high sensitivity to swelling and compaction, and low selectivity factor over CO_2 make polymer membranes less attractive. In addition, these membranes have restricted applications due to their limited stability at temperature greater than 473 K.

1.2.2. Carbon Membranes

Carbon membranes have been prepared in both unsupported and supported forms of materials. They can be used in nonoxidizing environments with temperatures in the range of 773-1173 K. Carbon membranes are very brittle and fragile. Therefore, it is difficult to package if the membrane surfaces become large. Furthermore, carbon membranes are still expensive to fabricate. The performance of the membranes will deteriorate severely if feed streams contain organic traces or other strongly adsorbing vapors such as H_2S , NH_3 , or chlorofluorocarbons (CFCs). The performance of the carbon membrane is dependent on pyrolysis temperature. The gas permeance decreased with an increase in temperature because membranes became denser and their pore size decreased [1.24].

1.2.3. Ceramic Membranes

Ceramic membranes are chemically inert and can be used at high temperatures. Ceramic membranes can be made by combining metals with nonmetals in the form of nitride, carbide, or oxide. They can be either dense or porous. Porous ceramic membranes generally have a two-layer structure: the separation membrane and a porous ceramic supporting layer. Supporting material could be Vycor, alumina, or glass. Ceramic membranes can be prepared either by CVD, sol-gel, or electroless techniques. The mechanism for hydrogen transfer is via dissociation of hydrogen to protons and electrons on the high partial pressure side, migration of both electrons and protons through the dense membrane and re-association on the low partial pressure side. The membrane surface must have capability for charge transfer reactions to take place at both external surfaces or alternatively catalytic layers or electrodes are required to facilitate H₂ dissociation and re-association reactions. Similar to metal membranes, the H₂ selectivity is very high (>99%) and no secondary purification of the separation H₂ is required. Major shortcoming of perovskites based on Sr and Ba is that these materials are not chemically stable in coal syngas environments, which contain high concentrations of CO₂ and steam [1.25].

1.2.4. Metallic Membranes

High-purity hydrogen production could be possible through dense metallic membranes. The permeation properties and ΔH formation of pure metals for H₂ separation membranes are summarized in Table 1-2. Crystalline alloy membranes, typically Pd and its alloys, can be used to provide infinite selectivity and high flux at high temperatures (573-873 K); however they have several major limitations. Firstly, these membranes are not suitable for operation when the temperature is below 573 K, the Pd-H phase transition between α and β hydrides is a result of changes in structure and unit cell which can lead to produce eventual failure of the membrane [1.26-1.28]. Secondly, sintering at grain boundaries can cause failure, especially in nanocrystalline structures. Group IV and V metals such as Nb, Ta, and V are known to exhibit high H₂ permeabilities. However, the formation of stable oxides on the surface consequently hinders H₂ molecule dissociation, dissolution, and H absorption reaction. Therefore, the oxide surfaces of hydrogen-selective membranes based on BCC metals need to be removed or modified.

Amorphous membranes are generally more attractive than crystalline alloys because they typically exhibit improved mechanical and structural properties. These membranes are presently reported to exhibit decreased hydrogen embrittlement, high H₂ solubility, low cost, while still providing hydrogen permeance comparable to palladium.

Table 1-2. Hydrogen permeability and ΔH formation (of hydrides) data for selected metals [1.23]

Metal	Crystal structure	H ₂ permeability at T=500 °C (mol/m s Pa ^{1/2}) [29]	ΔH formation (of hydrides) (KJ/mol) [11]
Nb	bcc	1.6×10^{-6}	-60 (Nb-H ₂)
Ta	bcc	1.3×10^{-7}	-78 (Ta-H _{0.5})
V	bcc	1.9×10^{-7}	-54 (V-H ₂)
Fe	bcc	1.8×10^{-10}	+14 (Fe-H)

Cu	fcc	4.9×10^{-12}	—
Ni	fcc	7.8×10^{-11}	-6 (Ni-H _{0.5})
Pd	fcc	1.9×10^{-8}	+20 (Pd ₂ -H) ^b
Pt	fcc	2.0×10^{-12}	+26 (Pt-H)

^aNotation: bcc, body-centred cubic; fcc, face-centred cubic/cubic close packed; hcp, hexagonal close packed.

^bData from K.F. Kelton, T.K. Croat, A.K. Gangopadhyay, L.Q. Xing, A.L. Greer, M. Weyland, X. Li, K. Rajan, J. Non-Cryst. Solids 317 (2003) 71.

Amorphous alloys containing low-cost elements such as Ni, Cu, Zr and Al are inherently resistant to embrittlement since they absorb hydrogen without hydride formation. The variety of hydrogen-permeable elements for amorphous structures is available and there have been many attempts to develop hydrogen permeation property. Recently, it has focused on Ni-based and additional elements of V, Nb, Ta, or Zr having relatively high H₂ permeability. Binary Ni-Zr alloys have been investigated and shown to have stable permeability, relatively good mechanical and thermal stability. The hydrogen permeability in the Ni-Zr alloys was found to decrease with increasing Hf or Ti content [1.30]. The ternary Ni-Nb-Zr alloys have also been studied, and they have been shown to have permeability comparable to pure palladium membrane [1.31]. It has been reported that the (Ni_{0.6}Nb_{0.4})₅₀Zr₅₀ membrane has a hydrogen permeability ($1.59 \times 10^{-8} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$) exceeding that of pure palladium ($0.95 \times 10^{-8} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$). However, the mechanical strength of the Ni-Nb-Zr amorphous alloys decreases with Zr addition. To efficiently optimize amorphous alloys for hydrogen-selective membranes, multiple physical and chemical characteristics must be known and ideally understood.

Table 1-3 presents the general properties of the different classes of materials for hydrogen separation membranes. The major properties listed are operating temperature range, hydrogen selectivity, hydrogen flux, stability, poisoning issues, and transport mechanism. On the basis of the membrane's operating temperature, polymer membranes are mainly suitable for temperatures <373 K, whereas porous carbon and dense ceramic membranes are suitable for a higher temperature range (773-1173 K). Metallic membranes would be suitable somewhere around 573-873 K. The dense metallic and ceramic membranes are highly selective for H₂ permeation.

1.3. Preparation of amorphous materials

Amorphous alloys combining metallic atomic bonding and the lack of long-range order have unique and useful properties not found when the same alloy is in a crystalline state: low magnetic losses, high corrosion resistance, low degradation of mechanical, electrical, and superconducting properties in irradiation environments, high strength, and improved catalytic properties. In addition, these alloys can be prepared from relatively inexpensive elements over broad composition ranges.

Table 1-3: Properties of the selected hydrogen separation membranes [1-13]

	Membrane type				
	dense polymer	microporous ceramic	dense metallic	porous carbon	dense ceramic
temp. range	<373 K	473-873 K	573-873 K	773-1173 K	873-1173 K
H ₂ selectivity	low	5-139	>1000	4-20	>1000
H ₂ flux ^a	low	60-300	60-300	10-200	6-80
stability issue	swelling, compaction	stability in H ₂ O	phase transition	brittle	stability in CO ₂
poisoning issues	HCl, SO _x		H ₂ S, HCl, CO	strong adsorbing vapors	H ₂ S
materials	polymers	silica, alumina, zirconia, titania, zeolites	palladium and its alloys	carbon	proton-conducting ceramics
transport mechanism	solution-diffusion	molecular sieving	solution-diffusion	surface diffusion, molecular sieving	solution-diffusion

^a10⁻³ mol m⁻² s⁻¹ at pressure diff. = 1 bar.

Solidification of molten alloys is the process of formation of solid. The process of melt spinning is widely practiced to fabricate thin metallic ribbons, in which a stream of molten alloy is ejected onto a rotating wheel surface. A molten alloy puddle forms on the wheel substrate resulting from continued impingement of the melt jet serves as a local reservoir from which ribbon is continuously formed and chilled. Figure 1.6 shows a schematic diagram of the melt spinning process.

The method of chill block melt-spinning (CBMS) has been most widely used for the fabrication of rapidly quenched materials because of its practicality for making uniform, continuous ribbons. In standard CBMS, the molten stream forms a single-phase amorphous ribbon typically 10 to 100 μm thick and a few millimeters in width by impingement onto a single roll rotating. Thin strips up to 500 mm in width can be cast by reducing the distance from the nozzle orifice to the wheel surface in order to eliminate formation of the melt pool and associated instabilities. Rapid solidification can be achieved with rapid cooling rates in the range of 10⁵ to 10⁶ K/s. However, the microstructure of melt-spun ribbons may consist of a variety of microstructures. The

variation in local cooling rate from the molten state on the resulting solidification micro structure is illustrated in Figure 1.7

Figure 1.6. Melt spinning apparatus, in which the molten metal alloy is ejected into the copper wheel to produce a long amorphous alloy ribbon [1.32].

It is noted that the micro structure changes from equiaxed chill crystal to highly columnar to branched dendrite solidification with distance from the substrate contact side of the ribbon. The region nearest the sample-substrate interface is the chill zone and is comprised of fine equiaxed grains of random orientation. A region of columnar crystals grows out of the chill zone and ultimately become dendritic. The presence or absence of each zone illustrated will largely depend on local cooling rate, this being related to the local velocity of the solid-liquid interface during CBMS [1.33].

Figure 1.7: Schematic representation of solidification microstructures which may be found in CBMS ribbons [1.33].

Figure 1.8 shows an example of the unique and complex microstructures generated by the melt spinning process. It is found that the micro morphology varies with the position relative to the

roller as shown in Figure 1.8(a). Between the contact surface and the free surface, the dramatically different cooling rates and the resulting distinct nucleation/crystal growth rates can account for the observed microstructure variation. There is essentially an amorphous phase near the contact surface (Figure 1.8(c)) while it gradually crosses over to the 5-10 nm fine nanocrystal regime with coherent grain boundary (Figure 1.8(d)).

Figure 1.8. Diagram of the melt spinning process indicating the free surface (FS) and the contact surface (CS) of the resulting melt-spun ribbon is shown. (b) TEM images of ribbon's cross section. (c)-(e) show the TEM images in different areas in (b). (f) shows TEM image of free surface of ribbon sample [1.34].

1.4. Glass-Forming Ability (GFA)

It is necessary to the formation of an amorphous phase by rapid solidification to suppress the nucleation and growth reaction of a crystalline phase in the supercooled liquid region between melting temperature (T_m) and T_g [1.35]. The critical cooling rate necessary to form a glass is determined by the position of the “nose” of the C-curve in the T-T-T (Time-Temperature-Transformation) diagram. For a pure metal, the critical rate is estimated to be over 10^{12} K/s, while for many oxide systems it is only about 1-10 K/s [1.36]. In comparison, the cooling rate attainable with the rapid cooling apparatus such as the one used by Duwez's group or the ones used in industries producing metallic glasses is of the order of 10^6 K/s. Thus, only certain alloys systems over a certain composition range can be quenched into a glass. The T-T-T diagram is the plot of t on a logarithmic scale against temperature which is on a linear scale as shown in Figure 1.9. It also shows the estimation of the critical cooling rate, R_c , for glass formation with a melt-quenching method from the T-T-T curve calculated by Equation (1.8). R_c can be approximated as follows:

$$R_c = \frac{T_m - T_n}{t_n} \quad (1.8)$$

where T_n and t_n are the temperature and the time at the nose of the T-T-T curve, respectively. Many criteria have been proposed to reflect relative GFA on the basis of the characteristic temperatures measured by differential thermal calorimetry or differential thermal analysis. The most extensively used are the reduced glass transition temperature T_{rg} (glass transition temperature T_g over liquidus temperature T_l) and the supercooled liquid region ΔT_x (the temperature difference between the onset crystallization temperature T_x and the glass transition temperature T_g) [1.37]. Lu et al reported that the reduced glass transition temperature T_g shows a better correlation with GFA than that given by T_g/T_m for bulk metallic glasses [1.38, 1.39]. The large glass-forming ability is obtained with higher reduced glass transition temperature (T_g/T_m)

and large ΔT_x . The R_c tends to decrease with increasing ΔT_x , the temperature difference between crystallization temperature (T_x) and glass transition temperature (T_g).

Figure 1.9. Schematic diagram of a T-T-T (Time-Temperature-Transformation) curve for liquid to crystal transformation. By circumventing the nose of the C-curve by rapid cooling a glass can be obtained.

When a liquid is cooled from above the liquidus temperature T_l to a temperature below T_g at a constant cooling rate R , the time-dependent volume fraction of crystalline phase X can be given based on the non-isothermal crystallization kinetics [40,41]:

$$X(T) = \frac{4\pi}{3R^4} \int_{T_l}^{T_g} I(T') \left[\int_{T'}^{T_g} U(T'') dT'' \right]^3 dT' \quad (1.9)$$

Here I and U are the steady-state nucleation frequency and the crystal growth rate, respectively. If one selects $X < 10^{-6}$ as a criterion for glass formation, then the critical cooling rate R_c can be derived from Equation (1.9) as:

$$R_c^4 = \frac{4\pi}{3 \times 10^{-6}} \int_{T_l}^{T_g} I(T') \left[\int_{T'}^{T_g} U(T'') dT'' \right]^3 dT' \quad (1.10)$$

According to the common crystallization theory, the nucleation frequency and crystal growth rate can be estimated by the following equations [42,43]:

$$I = \frac{10^{35}}{\eta} \exp \left[\frac{-16\pi}{3} \frac{\Delta S_f \alpha_m^3 T^2}{N_A k (T_l - T)^2} \right] \quad (1.11)$$

and

$$U = \frac{kT}{3\pi a_0^2 \eta} \left[1 - \exp \left(\frac{(T_l - T) \Delta S_f}{R_g T} \right) \right] \quad (1.12)$$

Here η , k , α_m , a_0 , N_A , ΔS_f and R_g are viscosity, the Boltzmann constant, a constant of 0.86, mean atomic diameter, Avogadro's number, the molar fusion entropy and the gas constant,

respectively. From Equations (1.10), (1.11) and (1.12), one can know that the critical cooling rate R_c decreases with increasing viscosity of the supercooled liquid, activation energy for viscous flow, fusion entropy, and with decreasing liquidus temperature T_l . When a glass is reheated with a constant heating rate β from a certain temperature T_0 up to a temperature T , as is the case with differential scanning calorimetry (DSC) heating experiments, the fraction $X(T)$ of precipitated phases in amorphous solids could also be calculated from crystallization kinetics based on the non-isothermal transformation theory [44,45]:

$$X(T) = \frac{4\pi}{3\beta^4} \int_{T_0}^T I(T') \left[\int_{T'}^T U(T'') dT'' \right]^3 dT' \quad (1.13)$$

The nucleation frequency I and crystal growth rate U can also be computed based on Equation (1.11) and (1.12), respectively.

As discussed above, GFA of metallic glasses associates with two factors, T_x/T_g and T_x/T_l , from the perspective of crystallization processes during both reheating and cooling of the undercooled liquid. Their relationship can be expressed as follows:

$$GFA \propto \left(\frac{T_x}{T_g}, \frac{T_x}{T_l} \right) \quad (1.14)$$

The above correlation can be rewritten as:

$$GFA \propto \left(\frac{T_x}{T_g + T_l} \right) \quad (1.15)$$

For simplicity, we introduce a single parameter, which is an average of the two factors T_g/T_x and T_l/T_x , i.e. $1/2[(T_g + T_l)/T_x]$. Then equation (1.15) predicts:

$$GFA \propto \left(\frac{T_x}{T_g + T_l} \right) \quad (1.16)$$

Hence, a new parameter γ for inferring the relative GFA among metallic glasses as:

$$\gamma = \frac{T_x}{T_g + T_l} \quad (1.17)$$

The ratio in equation (1.17) is the simplest and most reliable based on experimental data [1.37].

The glass-forming ability of metallic glasses can be described by Inoue's empirical rules [1.46]. Generally, the large glass-forming ability is obtained in the condition of low free energy $\Delta G(T)$ for the transformation of liquid to crystalline phase. In the relation of $\Delta G = \Delta H_f - T\Delta S_f$ for Gibbs free energy, the low ΔG value is obtained in the cases of low ΔH_f and large ΔS_f . Here, the ΔH_f and ΔS_f are enthalpy of fusion and entropy of fusion, respectively. The large ΔS_f is expected to be obtained in multicomponent alloy systems because ΔS_f is proportional to the number of microscopic states. The free energy at a constant temperature also decreases in the cases of low chemical potential caused by the low enthalpy and high reduced glass transition temperature as well as of large interface energy between liquid and solid phases. Based on these thermodynamical aspects, it is concluded that the multiplication of alloy components leading to the increase in ΔS_f causes the increase in the degree of dense random packing which is favorable for the decrease in ΔH_f and the increase in solid/liquid interface energy.

The amorphous alloys consist of the elements with significantly different atomic radii and the ratios ($\Delta r/r$) among the main constituents exceed 10%. The atomic radii of the main constituents (i.e., in ternary amorphous alloys) can be classified into the three groups of larger, intermediate

and smaller. Such a significant difference in the atomic sizes is expected to cause the increase of packing density in the supercooled liquid which enables the achievement of a large liquid/solid interfacial energy.

The change in free energy of nucleation is also dependent on the contribution of volume and surface effects,

$$\Delta G_r = \frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma \quad (1.18)$$

where ΔG_r is the free energy change upon nucleation, ΔG_V is the gain in the free energy per unit volume due to a liquid transforming into a solid, r is the radius of the nucleus, and γ is the energy per unit area of the interface between the liquid and the solid. The radius, r^* , of the critical nucleus size is determined by differentiating ΔG_r with respect to r and setting equal to zero: $d\Delta G_r/dr = 4\pi r^2 \cdot \Delta G_V + 8\pi r \gamma$ when $r=r^*$.

Figure 1.10: Gibb's free energy of a crystalline nucleus in a liquid as a function of the radius of the nucleus.

As shown in Figure 1.10, the critical nucleus size occurs when the free energy of nucleation is greater than zero. Below this critical size, the nucleus is unstable, while above this size, the nucleus continues to grow. The critical radius is proportional to the interfacial energy:

$$r^* = \frac{-2\gamma}{\Delta G_V} \quad (1.19)$$

As summarized in Figure 1.11 [1.46], these rules lead to structural and thermodynamic properties that have high glass-forming ability of the glass: (i) Increase in the degree of dense randomly packed atomic configurations; (ii) Formation of liquid with new atomic configurations (different to corresponding crystalline system) and multi-component interactions on a short-range scale; (iii) Homogeneous atomic configuration of the multi components on a long-range scale. The supercooled liquid which satisfies the three empirical rules can have high solid/liquid interfacial energy which suppresses the nucleation of a crystalline phase.

Recently, molecular dynamics (MD) simulations are carried out to predict the composition range, in which the metallic glasses can be obtained. Such composition range is often called the glass-forming range (GFR), which reflects the glass-forming ability (GFA) of a system in a quantitative manner [1.47]. Dai and Li proposed a long-range empirical potential for body-centered cubic (bcc) and face-centered cubic (fcc) metals and their alloys with interatomic interaction [48,49]. The total potential energy E_i of atom i can be calculated by

Figure 1.11. Mechanisms for the stabilization of supercooled liquid and the high glass-forming ability for the multicomponent alloys which satisfy the three empirical rules.

$$E_i = \frac{1}{2} \sum V(r_{ij}) - \sqrt{\sum \phi(r_{ij})} \quad (1.20)$$

where $V(r_{ij})$ is the pair term and $\phi(r_{ij})$ is the electron density term. r_{ij} is the distance separated by atoms i and j . The pair and electron density terms can be expressed respectively as

$$V(r_{ij}) = (r_{ij} - r_{c1})^m (c_0 + c_1 r_{ij} + c_2 r_{ij}^2 + c_3 r_{ij}^3 + c_4 r_{ij}^4) \quad 0 < r_{ij} \leq r_{c1} \quad (1.21)$$

and

$$\phi(r_{ij}) = \alpha (r_{c2} - r_{ij})^n \exp \left[-\beta \left(\frac{r_{ij}}{r_0} - 1 \right) \right] \quad 0 < r_{ij} \leq r_{c2} \quad (1.22)$$

Here, r_{c1} and r_{c2} are cutoff radiuses for pair term and electron density, respectively. r_0 is the atomic distance between the nearest neighbors in the ground state. The exponent m and n are two integers and adjustable according to the specific metals. α is a parameter. β is a constant which is proven to be relevant to describe the atomic interactions for the three metals and their alloys.

1.5. Glass transition and Crystallization

1.5.1. Glass transition

Glass transition range describes the temperature interval over which a given system gradually transforms upon cooling from a supercooled liquid state into the glassy state. Figure 1.12 shows the specific volume V_{sp} as a function of temperature for a typical liquid [1.50]. Upon cooling from high temperatures, a liquid may crystallize at T_m . Crystallization occurs if there are a sufficiently large number of nuclei present in the mass and a large enough crystal growth rate

exists [51]. This phase transition usually results in a decrease in the specific volume. If crystallization does not occur below T_m , the liquid moves into the supercooled liquid state, in which a liquid manages to get below T_m without crystallization. The smooth curve between the onset of the supercooled liquid line and the completion to a seemingly glass condition is referred to as the glass transition range [1.51].

Figure 1.12. Schematic representation of the specific volume as a function of temperature for a glass-forming liquid [1.50].

The thermodynamic properties of a glass depend on the cooling rate: glass 1 was formed with a faster cooling rate than glass 2. The glass transition temperature T_g can be defined by extrapolating V_{sp} in the glassy state back to the supercooled liquid line. Glass transition temperature also depends on the cooling rate. A glass is defined as any solid formed by the continuous cooling of a liquid such that detectable crystallization is avoided.

1.5.2. Crystallization kinetics

The crystallization of metallic glasses occurs by a nucleation and growth process in liquids just below the melting point. As shown in T-T-T diagram (Figure 1.9), crystallization begins at a temperature, T_x , if the liquid is cooled slowly. The devitrification of metallic glasses has a number of practical implications. In the first place, the loss of many of the desirable properties on crystallization imposes a strict limit on the operating times at elevated temperatures. Secondly, it is becoming increasingly clear that the partial or full crystallization of metallic glasses can be used to produce novel and useful microstructures unobtainable by other means.

The temperatures of transformations as well as the thermodynamics and kinetics of a process may be determined using DSC results. Figure 1.13 shows an example of a DSC curve of the heating of a glass. The material initially underwent a glass transition, then an exothermic transformation corresponding to crystallization from the glass, and finally an endothermic transformation representing the melting of the crystalline phase.

Figure 1.13. Typical non-isothermal DSC plot [1.52].

The crystallization temperature is represented by the onset of the peak. The convention for determining the melting temperature is to extend the straight line portions of the baseline and the linear portion of the upward slope, marking their intersection. The convention is similar for locating T_g , the glass transition temperature.

Thermodynamic constants, such as the heat released or absorbed in a phase transformation (latent heat), may be determined by DSC. A DSC plot of dQ/dt versus temperature may be translated to a plot of dQ/dt versus time, using the heating rate. The heat released/absorbed in a reaction is simply the area under the peak:

$$Q = \int_{-\infty}^{\infty} \left(\frac{dQ}{dt} \right) dt \quad (1.23)$$

Recalling the first law of thermodynamics and further recalling that work is defined as force through a distance:

$$dU = dQ - dW \quad (1.24)$$

$$dW = Fdx = \frac{R}{A} dx A = p dV \quad (1.25)$$

where p is pressure and V is volume, thus:

$$dU = dQ - p dV \quad (1.26)$$

If a sample is sealed in a gas-tight container that does not deform and allows no mass exchange with the outside world, then the transformations that are measured in the instrument are under the conditions of constant volume. Hence, $dV=0$ and $dU=dQ$ or $\Delta U=Q$.

On the other hand, if the sample is placed in an open crucible, the volume of the system is no longer constant. For example, if the sample decomposes during a transformation, releasing a gas, the gas spreads throughout the room and the volume of the system increases. However, the pressure to which the system is exposed is constant, that is, whatever atmospheric pressure is-

generally 1 atm. Another energy function, the “enthalpy”, has been constructed for these conditions, which is defined as:

$$H = U + pV \quad (1.27)$$

The total differential of this function has the form:

$$dH = dU + pdV + Vdp \quad (1.28)$$

Inserting the expression for dU :

$$dH = dQ - pdV + pdV + Vdp = dQ + Vdp \quad (1.29)$$

Thus under the conditions of constant pressure, $dH=dQ$ or $\Delta H=Q$. Since enthalpy is the sum of state functions (U and pV), it too is a state function.

As a short aside, we can use the above equations to define “heat capacity”, the ability of a substance to hold thermal energy (via atomic vibration, rotation, etc.). The constant volume heat capacity is defined:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{dQ_V}{dT} \quad (1.30)$$

The constant pressure heat capacity is defined:

$$C_P = \left(\frac{\partial H}{\partial T} \right)_p = \frac{dQ_p}{dT} \quad (1.31)$$

The importance of heat capacity will become apparent throughout the discussion of these instruments. When heat capacity is expressed on a per gram rather than per mole basis, it is referred to as the “specific heat.”

Information with respect to the kinetics of a reaction may be established from DSC output by determining the fraction of reactant transformed and then fitting these data to reaction kinetics models. Modeling will be dealt with in later sections; for now, we will only show how to determine the fraction of material transformed, based on a DSC trace. If we assume that the heat released per unit time is proportional to the rate of the reaction, then the partial area swept under the peak divided by the entire peak area is the fraction transformed:

$$F = \frac{\text{Partial Area}}{\text{Total Area}} \quad (1.32)$$

As shown in Figure 1.14, by determining the fraction transformed over successive times (or temperatures), the standard “S” -shaped fraction transformed versus time curve can be generated.

1.5.3. Calculation of activation energy

There are many methods to calculate the activation energy from kinetic data [1.53]. As is shown below equations, this parameter can hardly be ascertained by analyzing the kinetic data taken only at one heating rate. This is because of the strong mutual interdependence of parameters E_a and A . Hence it is more suitable to apply so called multiple scan methods using several sets of kinetic data taken at various heating rates.

Probably the most popular in this family is the Kissinger method, where the activation energy is calculated using a plot of $\ln (\beta/T_p^2)$ versus $1/T$, the slope of which is $-E_a/R$. Another calculation method was introduced by Ozawa and is based on a plot of $\ln (\beta)$ versus $1/T$, with slope $-1.0516 E_a/R$. The parameter T is the temperature of the maximum of the DSC peak.

Figure 1.14. Fraction transformed via partial area integration of a DSC peak. A partial area divided by the area under the entire endotherm contributes one datum to the fraction transformed versus temperature plot [1.52].

Johnson-Mehl-Avrami (JMA) transformation equation

The kinetics of phase transformations involving nucleation and growth processes under isothermal conditions is the Johnson-Mehl-Avrami (JMA) equation [1.54-1.56]. This model is written in the following form:

$$F = 1 - \exp(-kt^n) \quad (1.33)$$

where F is fraction of the transformation complete at time t . k is a time independent but temperature dependent rate constant, and n is referred to as the parameter which reflects the nucleation rate and the growth morphology.

An isothermal experiment on the DSC can be run in which the sample temperature is quickly brought up into a temperature regime of interest and held during the crystallization transformation. The above equation can be rearranged in to equation of a line:

$$\ln(1 - F) = -kt^n \quad (1.34)$$

$$\ln[-\ln(1 - F)] = \ln k + n \ln t \quad (1.35)$$

From fraction transformed versus time data, the values of F and t can be inserted into this function, to generate a plot which should take the form of a straight line. By crystallizing samples at various isothermal temperatures, a series of fraction transformed traces and corresponding JMA traces can be generated, as shown in Figure 1.15. The slopes of the lines in the JMA plot represent the mechanism constant; each slope should be the same, presuming that the mechanism of the reaction has not changed for crystallization at various isothermal temperatures. The rate constant is generally taken to have an Arrhenius with respect to temperature during the crystallization process:

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \quad (1.36)$$

where k_0 is a pre-exponential constant and E_a is the activation energy of the transformation. The activation energy is an important descriptive factor of the extent of the exponential temperature dependence of a transformation and is the compared value for the kinetics of reactions.

For each JMA trace in Figure 1.15, a value of $\ln k$ corresponding to each isothermal temperature can be determined from the y -intercept. These values can then be put into the logarithmic form of the Arrhenius equation ($\ln k = \ln k_0 - E_a/RT$). The best fit line to these points would establish the activation energy of the reaction as the slope (after multiplying by $-R$), as illustrated in Figure 1.16.

Figure 1.15. Illustration of a transformation of fraction transformed plot to a JMA plot [1.49].

Kissinger method

It is well known that the characteristic temperatures of the metallic glasses, such as glass transition temperature, onset crystallization temperature, and crystallization peak temperature, show strong dependence on the heating rate. The dependence of the characteristic temperatures on the heating rate is important in calculating activation energy of glass transition and crystallization of the metallic glasses under continuous heating transformation condition. Kissinger method has been widely used to determine the activation energy of solid state reaction that leads to the transformation. Kissinger equation can be written as [1.57]

$$\ln\left(\frac{\beta}{T^2}\right) = \frac{-E_a}{RT} + \ln A \quad (1.37)$$

Where A is the frequency factor and β is the heating rate, which is expressed as $\beta = dT/dt$. Activation energy, E_a can be obtained by plotting $\ln(\beta/T^2)$ as function of $1/T$, where T is the characteristic temperature.

Figure 1.16. Arrhenius plot to determine the activation energy of crystallization [1.52].

Ozawa method

This method is an integral method which is also independent of the degradation mechanism. It involves the measurement of the temperature T , corresponding to a fixed value of conversion degree α , from the experiments at different heating rates β . By using Doyle's approximation this method provides the following equation [1.58, 1.59]:

$$\ln(\beta) = -1.0516 \frac{E_a}{RT} + K \quad (1.38)$$

The plot of $\ln \beta$ vs $1/T$ provides the slope $-1.0516 E_a/R$ from which the activation energy is obtained. If the determined activation energy is the same for the various values of α , the existence of a single-step reaction can be assumed with certainty. On the contrary, a change of E_a with increasing degree of conversion is an indication of a complex reaction mechanism that invalidates the separation of variables involved in the OFW analysis.

1.6 Hydrogen solubility in amorphous alloys

Amorphous materials decompose into multiple crystalline phases when heated to the crystallization temperature, as amorphous alloys are thermodynamically meta-stable. Therefore, it is essential not to raise the temperature above crystallization temperature T_{cryst} during hydrogen absorption of amorphous alloys [1.60]. In the case of amorphous alloy samples, the surface is activated by abrading with emery paper and cleaning ultrasonically in acetone and ether. Coating with a Pd over layer after cleaning by argon-ion sputtering has also been known to be effective [1.61].

In pressure-concentration isotherms of crystalline alloys, the pressure of hydrogen remains constant within the two phase region (if a phase transformation occurs in the metal-hydrogen system) although the total hydrogen concentration increases. As evident from Figure 1.17 for a $\text{Zr}_{50}\text{Ni}_{50}$ alloy [1.62], the disappearance of the plateau in the pressure-concentration isotherms is one of the characteristic change in going from crystalline to amorphous alloys [1.61, 1.63-1.65]. The absence of plateau in the pressure-concentration isotherms of Ni (Zr, Ti) amorphous alloys has also been reported by Spit et al. [1.66, 1.67].

where they have related it either to a rather low critical temperature of the amorphous hydride or to an absence of phase separation, even at low temperatures.

The absence of plateau has also been observed in other cases, though, it cannot be said to be a general property because it was not observed in a few other amorphous alloys. Hydrogen solubility is defined as the hydrogen concentration in a particular metal / alloy-hydrogen system at a given hydrogen pressure. The hydrogen solubility for crystalline metals is usually described by Sieverts' law which is valid mainly at sufficiently low pressures ($p < 1$ MPa):

$$C = K_s \sqrt{p} = K_0 \exp(-E_k / RT) \sqrt{p}$$

where C is the atomic hydrogen concentration in the metal, K_s is the hydrogen solubility in the metal, p is the partial pressure of H_2 in the gaseous phase, K_0 is the solubility constant, E_k is the activation energy of solution, R is the constant of ideal gases and T is the absolute temperature.

Atomic hydrogen concentration, C is given in number of moles per mole of metal and is generally represented as H/M . The H/M can further be converted to weight percentage of metal.

$$C = H / M$$

$$\begin{aligned} \text{Weight \%} &= \left(\frac{\text{weight of hydrogen}}{\text{weight of metal} + \text{weight of hydrogen}} \right) \times 100 \\ &= \left(\frac{C \times M_{H_2}}{M_m + C \times M_{H_2}} \right) \times 100 \\ &= \left(\frac{C}{\frac{M_m}{M_{H_2}} + C} \right) \times 100 \end{aligned}$$

Here,

$$M_{H_2} = \text{molecular weight of hydrogen} = 2.016 \text{ g/mol}$$

$$M_m = \text{molecular weight of metal}$$

Hydrogen absorption capacities in amorphous alloys are mostly higher than the corresponding crystalline alloys [3, 1.63, 1.64, 1.70] which may be explained with much less restricted sites for hydrogen in the amorphous structure. However, some contradictory results may also be found in the literature [1.71] where this behavior has been explained by the inherent structural disorder in the amorphous phase, which might restrict the number of interstitial sites favorable for hydrogen occupancy. The physical differences between amorphous and crystalline metals of similar chemical composition for application as hydrogen separation / permeation membranes are summarized by Ockwig et.al. [1.72] in Table 1.4.

For amorphous Zr-Ni alloys. This plot shows the strong positive deviation from Sievert's law mostly at higher hydrogen concentration. This effect has also been observed in other cases and is believed to be a general feature of amorphous alloys and can be related to the successful entry of hydrogen atoms into higher-energy states [1.61].

Figure 1.17. Pressure-composition isotherms for hydrogen in amorphous and crystalline $Zr_{50}Ni_{50}$ [1.62].

Figure 1.18. Sieverts' law plots of the pressure-composition isotherms in amorphous $Zr-Ni$ alloys[1.62, 1.68]

Table 1.4. Distinctions between Crystalline and Amorphous Metallic Membranes with Comparable Compositions[1.72]

Crystalline	Amorphous
Plateau in pressure-concentration isotherms Sieverts' law obeyed at elevated hydrogen concentration Arrhenius H ₂ diffusion behavior H ₂ embrittlement from dislocation Constant diffusivity with dissolved hydrogen	No plateau in pressure-concentration isotherms Positive deviation from Sieverts' law No Arrhenius H ₂ diffusion behavior H ₂ embrittlement from free volume filling No constant diffusivity with dissolved hydrogen
Stable at high temperatures Mechanically weak	Potential crystallization at high temperatures Mechanically strong

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II. Background

2.1. Desired membrane characteristics

For hydrogen separation membrane to be commercially viable for reforming reactors or handling syn-gas should have high permeation flux and good long-term chemical, thermal, and mechanical stability under high temperatures and pressures[2.1]. The draft technical targets set by the U.S. Department of Energy are shown in Table 2.1. As per the targets, the required long-term stability (durability) ranges from 3 years at 2007 to greater than 10 years by 2015. So far, the longest tested time for composite Pd and Pd-alloy membranes reported in the literature is around 6000 hours carried out at 350 and 450°C under pure hydrogen [2.2], and at 500°C under steam reforming reaction conditions [2.3]. Before putting it up for commercial application, it is imperative that long-time tests be carried out to evaluate the long-term stability of the membrane.

Though the hydrogen permeability in composite Pd and Pd-alloy membranes reported in the literature from different investigators varied widely, a generalized equation to estimate the hydrogen permeability in the temperature range of 200–500°C was provided based on the various values for the hydrogen permeability on Pd foils and activation energy reported in the literature [2.4].

Physical adsorption by CO and CO₂ reduces the area for hydrogen absorption and contaminates the membranes which can readily be regenerated by passing pure hydrogen over the membrane surface at a high temperature for a short period of time.

Table 2.1: DOE's Hydrogen Separation Technical Targets[2.5]

Performance Criteria	Units	Current Status (Pd-based metallic or composite)	2010 Target	2015 target
Flux ^a	Ft ³ /hour/ft ²	~200-300	200	300
Temperature	°C	300-500	300-600	250-500
S tolerance	ppmv	tbd	20	>100
Cost	\$/ft ²	tbd	100	<100
WGS activity	-	N/A	Yes	Yes
ΔP Operating capability ^b	psi	tbd	Up to 400	Up to 800 to 1000
Carbon monoxide tolerance	-	Some	Yes	Yes
Hydrogen purity	%	>99.5	99.5	99.99
Stability / durability	Years	0.9	3	5

^aFor 100 psi ΔP (hydrogen partial pressure basis).

^b ΔP = total pressure differential across the membrane reactor.

For both Pd and Pd–Cu membranes, H₂S, could block the surface sites for hydrogen absorption, causing the hydrogen flux to deteriorate at low H₂S concentrations. For high H₂S concentrations, membrane failure occurred due to the formation of micron-size pores resulting from the sulfidation of Pd and Cu [2.6].

Due to the exorbitantly high cost of palladium, there have been major concerns for large-scale process applications of composite Pd and Pd–alloy membranes in the past. On rational view, the Pd cost is a factor necessary to consider, but it is not the dominant element in the overall cost of the Pd membrane reactors or separators as long as a thin layer of Pd membrane is used (e.g., ~ 5 µm) as the cost of the support may be high and may contribute significantly to the overall cost of the membrane module. However, when a large quantity is needed, the cost of the support is expected to drop. In addition, the process intensification afforded by the membrane reactor will further reduce the capital cost, making the membrane reactor process competitive to the current conventional steam-reforming process. The high-pressure CO₂ produced from the membrane reactor will not only add economical value to the process but also is beneficial to the environment[2.1].

2.2. Palladium and palladium alloys

Palladium and its alloys are the most commonly used materials for the preparation of dense metal membranes for hydrogen separations because of their high hydrogen permeability relative to other hydrogen-permeable inorganic materials (e.g., silica, tantalum, and nickel) and excellent chemical resistance to oxidation and corrosion.

The permeation of hydrogen through a palladium layer is by the solution and diffusion mechanism. For the case of low H concentrations in the Pd–H phase, no a-to-b phase transformation, and the permeation controlled by the hydrogen diffusion through the bulk of palladium layer, the hydrogen flux can be expressed as;

$$J = kD \frac{P_{retentate}^{1/2} - P_{permeate}^{1/2}}{d} \quad (2.1)$$

where J is the hydrogen flux, m³/m² s or mol/m² s, k the absorption or Henry's law constant, kmol/m³ Pa^{1/2}, D the diffusivity, m²/s, and d the thickness of the membrane, m. Subscripts retentate and permeate designate the high- and low-pressure side of the membrane, respectively, and kD is the permeability, which is temperature dependent. Since the membrane thickness is often unknown or difficult to determine accurately, $P = kD/d$, defined as permeance, is frequently used to characterize the permeation property of the membrane.

The Eq. (2.1) can be expressed in a more general form as

$$J = P(p_{retentate}^n - p_{permeate}^n) \quad (2.2)$$

where $1 \geq n \geq 1/2$. When $n = 1/2$, Eq. (2.2) reduces to Eq. (2.1), which is known as the Sieverts law.

Pd and Pd-alloy have mostly been used as dense metallic membranes for hydrogen separations, with early work concentrated on Pd and Pd-alloy foils[2.7]. Palladium foils are not suitable for large chemical process applications, especially membrane reactor applications, because of the difficulties of using plane geometry in large chemical processes. In the case of tubular geometry, in order to have sufficient mechanical strength for high-pressure applications, the diameter of the thin pure Pd tube has to be small in order to have the needed mechanical strength which results in large pressure drop prohibiting them from large-scale applications.

Although foils as thin as 25 μm or less are available commercially, the Pd cost for the tube is too high for large-scale chemical process applications because there are limits on how thin the tube wall can be practically made. To overcome the lack of mechanical strength due to the tube wall thickness constraint as well as the cost problem, thin Pd layers are formed on a porous support. This results in a decrease in Pd cost and at the same time increase the hydrogen flux.

Figure 2.1 shows the phase diagram of the palladium-hydrogen system which shows the existence of a two-phase region below the critical temperature of 295°C[2.8]. A limitation to the use of pure palladium for hydrogen diffusion has its basis in the pressure-concentration isotherms for palladium-hydrogen system. The problem of hydrogen embrittlement can be minimized by forming palladium-rich alloys such as Pd/Ag and Pd/Cu to lower the critical temperature. Furthermore, a number of palladium-rich alloys have higher hydrogen fluxes than pure palladium, as shown in Table 2.2[2.8]. This has added benefit of reduction of the needed amount of Pd by using Pd-alloy membranes, thereby further reducing the total cost of the membrane. However, temperature has varying effect on hydrogen flux which may sometimes offset the benefit of using palladium-rich alloys to improve the hydrogen permeation flux[2.9].

Figure 2.1. Absorption relationships in the palladium-hydrogen system. Unalloyed palladium undergoes an α - β transition on low temperature hydrogenation leading to gross distortions[2.8].

Pd and Pd–alloy membrane layers can be supported on either porous ceramic or metallic tubes or plates which have their own advantages and disadvantages. Porous ceramic supports have the advantages of small pore sizes, uniform pore size distributions, and excellent chemical stability. The small pore size and uniform pore size distribution allow the formation of thinner and uniform membrane layers, but at the same time ceramic supports are brittle and prone to cracking. Also, connecting ceramic material to metallic elements in a process presents a considerable challenge. However, in the case of porous metallic supports, such as porous stainless steel and other porous specialty alloys, can easily be connected to other metallic elements in the process, making the process of integrating the membrane module to a specific process relatively easy[2.1].

TABLE 2.2 Improvement in Hydrogen Permeability of Various Binary Pd Alloys at 350°C[2.8]

Alloy Metal	wt% for Maximum Permeability	Normalized Permeability ($P_{\text{alloy}} / P_{\text{Pd}}$)
Y	10	3.8
Ag	23	1.7
Ce	7.7	1.6
Cu	40	1.1
Au	5	1.1
Pure Pd	--	1.0

Large pore sizes and wide pore size distributions of porous metallic supports make the formation of thin and uniform membrane layers a real challenge in spite of having good mechanical strength. Also, at high temperatures, inter-metallic diffusion between the metal elements in the support and the membrane layer can cause the hydrogen flux to deteriorate which can be managed to some extent by inserting an inter-metallic diffusion barrier layer between the support and the membrane layer.

Long-time hydrogen permeation data have been reported in the literature. The length of the long-term stability tests varied widely. Most of these were in the hundreds of hours or less except the work of Ma et al. [2.2], who showed their membrane with inter-metallic diffusion barrier prepared by the in situ oxidation method to be stable for over 6000 h in the temperature range of 350–450°C. In order for membranes to be viable for large-scale industrial applications, the membrane must be tested for long-term stability in thousands of hours.

2.3. Group IV and V metals

Conventionally, crystalline Pd alloy membranes have been used as state of the art in alloy membranes by virtue of their high H_2 permeation rates and stability in hydrocarbon and synthesis gas streams [2.10]. However, high cost of Pd limits their use and forces industry to find alternative membranes. Amorphous alloy membranes composed primarily of inexpensive elements such as Ni and early transition metals (ETMs-Group IV and V), are of considerable interest as a low cost alternative[2.11]. In addition, these materials can be produced in large quantities using planar flow casting[2.12], an established technique used in the production of

other rapidly solidified alloys. Given these favorable characteristics, these amorphous alloy membranes are of particular interest for the large scale production of H₂ from coal-gasification.

The first reported amorphous alloy membranes Ni₆₄Zr₃₆[83], demonstrated a hydrogen permeability of approximately $1 \times 10^{-9} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$ at 300 °C, and provided a significant performance/ cost saving over Pd based alloys. However, these Ni based amorphous alloy membranes still require the presence of a thin (~500 nm) Pd alloy catalyst layer at each surface to promote hydrogen dissociation and prevent inhibition by CO, H₂S and steam. Even then it reduces the cost of membrane significantly mainly because of reduction in high cost Pd use. Ni based amorphous alloys can be divided into two main classes: (i) based on eutectic compositions, and (ii) based on off eutectic compositions. Ni forms binary eutectics with the approximate composition of Ni₆₀–70ETM₄₀–30 with Ti, Zr, Nb, Hf and Ta, with melting points in the range (Table 2.3). The low melting point of these alloys, allow them to be formed in the amorphous state using a suitable rapid solidification technique. Departures from eutectic compositions reduce the glass forming ability of these alloys[2.13].

Table 2.3 Physical and chemical properties of typical components of hydrogen-selective amorphous alloy membranes[2.13]

Element	Atomic radius (nm)[85]	Melting point (°C)[86]	Bond valence[87]	Ni-ETM eutectic	Eutectic melting point (°C)[88]
Pd	0.1246	1455	2.83		
Ni	0.1375	1555	3.15		
Ta	0.1430	3017	4.51	Ni ₆₄ Ta ₃₆	1350
Nb	0.1429	2477	4.14	Ni ₆₀ Nb ₄₀	1175
Hf	0.1578	2233	3.97	Ni ₆₄ Hf ₃₆	1190
Zr	0.1603	1855	3.75	Ni ₆₄ Zr ₃₆	1070
Ti	0.1462	1688	3.20	Ni ₆₉ Ti ₃₁	1118

The bond valence (BV), a measure of the number of electrons a given metal atom contributes to the overall metallic bonding [87], of the ETM components[2.11] (Table 2.3), governs the thermal stability of amorphous alloys. It is also closely related to the melting point of the metal. It has been reported that the partial substitution of Zr (BV= 3.75) by Nb (BV= 4.14) improves the thermal stability of the aNi₆₄Zr₃₆ membrane[89]. Several groups have also investigated Ni based, off-eutectic amorphous alloys through the addition of Zr to a thermally stable binary eutectic such as Ni₆₀Nb₄₀ [2.13-2.15]. These alloys have higher reported permeabilities than the binary eutectic alloys, but the thermal stability and durability of these alloys has not been reported in detail.

2.4. Cost Savings in using Ni-Nb-Zr based amorphous alloy membrane

Under similar conditions of temperature and pressure, some metallic glass alloys can absorb more hydrogen than their crystalline counterparts [2, 32.16, 2.17]. This fact and the ductility of the amorphous alloys, suggests that they may be more promising than crystalline inter-metallic compounds as a medium for hydrogen storage. Under the present circumstances, Ni-Nb-Zr amorphous alloy membranes are considered to be prospective candidate for separation membranes as they possess permeability close to Pd. Apart from better performance, these amorphous alloy membranes also provide considerable cost benefits compared to Pd and Pd-alloy based membranes. The cost benefit ratio have been calculated assuming the Ni-Nb-Zr based amorphous alloy membrane having thin layer of palladium on its surface.

$$\text{Cost Benefit Ratio} = \frac{\rho_{pd} \times (2d_{pd} + d_{alloy}) \times P_{pd}}{(\rho_{pd} \times 2d_{pd} \times P_{pd}) + (\rho_{alloy} \times d_{alloy} \times P_{alloy})} \quad (2.3)$$

If we ignore the price of alloy as compared to cost of palladium, then the cost benefit ratio will be maximum;

$$\text{Maximum Cost Benefit Ratio} = \frac{(2d_{pd} + d_{alloy})}{2d_{pd}} \quad (2.4)$$

ρ_{pd} = density of palladium

ρ_{alloy} = density of alloy

d_{pd} = thickness of pd coating

d_{alloy} = thickness of alloy

P_{pd} = price of palladium, USD / kg

P_{alloy} = price of alloy, USD / kg

Example:

P_{alloy} = 40 USD / kg, for $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy considering the costs of Ni=31 USD/kg, Nb=60 USD/kg and Zr=30 USD/kg

P_{pd} = 20,000 USD / kg

d_{alloy} = 70 μm

d_{pd} = 500 nm

Maximum cost benefit ratio = $(1000 \text{ nm} + 70 \mu\text{m}) / (1000 \text{ nm}) = 71$ times.

If we could reduce the thickness of palladium coating to 100 nm on each side, then the maximum cost benefit ratio will be 351 times.

2.5. BACKGROUND ON H₂-D₂ EXCHANGE STUDIES

Basics of a plug flow reactor are shown in Figure 2.2. Material balance on this system yields a relationship between the flow rate of reactant A, the conversion and the rate of the equation.

$$F_{A0} dX_A = -r_A dV \quad (2.5)$$

A packed bed of catalyst can be used to carry out reactions between two gases to produce a product gas. It is a well-known process that is used in chemical laboratories for highly flammable gases. Catalysts are used to enhance the reaction rate by not affecting either the reactants or the products. Although catalysts can enhance the rate of reaction by manifold, the most important

property of catalyst is its selectivity. Selection of catalyst for a particular reaction is mostly achieved by trial and error. In terms of transition state theory, the catalyst reduces the potential energy barrier that is needed for the reactants to overcome to make products.

It has been pointed out by L. Schlappbach et al [2.18] that the difference in activation treatment of metals and poisoning depends on the surface of the metal. Surface plays an important role for the absorption and desorption of hydrogen in a metal or metal hydride. The hydrogen needs to be dissociated to hydrogen atoms at the surface in order to get absorbed and the H atoms recombine to form H_2 molecules in the desorption process. The heat of dissociation has very high energy barrier that reduces the rate of the reaction. Lennard-Jones calculated curves of potential energy

Figure 2.2. A schematic of a steady state plug flow reactor [2.17].

Figure 2.3. Potential energy curves for activated and non-activated chemisorption of hydrogen on a clean metal surface and endothermic and exothermic solution in the bulk [2.17].

as a function of distance from metal surface for a H_2 molecule and for 2 H atoms. This is depicted in Figure 2.2.

Away from the surface, the two curves are separated by dissociation energy, E_D . the chemisorbed H is represented by deep minimum in the $2H+M$ curve, denoted by E_c . If the two curves $2H+M$

Figure 2.4. Block diagram of the apparatus used to determine the catalytic activity of Ni. DP- Mercury diffusion pump, Ω - omegatron, T- cold trap, MV- metal valves, IG- Ion gauge, R- Reaction chamber [2.19].

and H_2+M are above the zero line that means that the chemisorption needs activation energy, E_A to occur. Intersection of the lines below the zero energy level means that the process occurs non-activated. H_2 molecule can either be chemisorbed or physisorbed on a metal surface based on the potential energy well and its kinetic energy. The H atoms are absorbed into the bulk and they then diffuse into the bulk. It has also been pointed out that the diffusion into the bulk needs activation energy or diffusion.

It has been shown by Speiser [2.17] that W, Mo, Ti, Zr, Fe, Ni, Pd, Rt, Ba, Nb and Cr adsorb hydrogen without an activation energy. It has also been shown by Charlot and Kahn [2.18] that the H-H bond weakens because of charge transfer from the Ni clusters favoring the chemisorption process.

Jewell. L. L and Davis B. H [2.19] have presented a review on the extensive study of H_2 adsorption and absorption behavior studied by various researchers on palladium. An extensive amount of study is being done experimentally and computationally to determine the nature of the process and to determine a mechanism of transport. However, there is not clear trend that is observed from one author to the other for heats of adsorption, E_{ads} , with change in surface coverage, although it has been observed that the energy of adsorption increases as the surface coverage increases.

Removal of surface contaminants in gas phase is an important step for the study of effectiveness of heterogeneous catalysts. D. Shooter et al [2.21] developed a reaction chamber for measuring the catalytic activity of small samples cleaned by Ar ion bombardment. Activity of Ni was

determined by reaction of hydrogen- deuterium on the surface that was cleaned by Ar ion bombardment [2.20]. The reaction rate was measured by omegatron mass spectrometer. Figure 2.3 shows the experimental setup that was used to measure the activity of Ni.

A polycrystalline Ni was used with a surface area of 6cm^2 . For the omegatron mass spectrometer, it was found that the mechanism that was followed by $\text{H}_2\text{-D}_2$ reaction involved dissociation and chemisorption at the surface. Adjacent H and D atoms can then evaporate as HD. Proportions of H_2 , D_2 and HD leaving the surface is the equilibrium proportions of the mixture. It was also found that very high activity was observed after ion bombardment process. This however, diminished very rapidly. It was concluded that decent activity measurements were made using the equipment made for cleaning the Ni surface and measure the mass spectrometer signals [2.20].

Cavalier J. C and Chornet E, attempted to quantify the reactivity associated with (110), (100), (111) and polycrystalline surfaces of iron [2.22]. Kato and Kobayashi have found out that the topmost layers in iron atoms (111) and (110) are displaced from the bulk of the system by about 1.5% of the interatomic spacing [2.21]. It has been shown that on (110), (111) and (100) faces of tungsten that adsorption bonds are directional and specific to surface structure [2.22]. It was also found out from the sticking probability results that adsorption kinetics operates differently on the three planes.

A possible distortion and /or penetration of the lattice in Ni on (001) and (110) could be associated with two adsorption states, surface and subsurface which have been determined by Demuth and Rhodin [2.21]. This work by Cavalier [2.22] shows that hydrogen adsorption is specific to the crystal face on substrates like W, Fe, Ni and Pd. The presence of dissolved hydrogen is considered to be an important factor in determination of the overall surface activity of Fe. Quantitative determination of reactivity on [110], [100] and [111] polycrystalline of Iron has been performed. A typical recorder plot for $\text{H}_2\text{-D}_2$ reaction is shown in Figure 2.4.

$\text{H}_2\text{-D}_2$ exchange reaction has been carried out at 294 K on defined iron surfaces and it was found out that the polycrystalline surfaces are more reactive than any of the oriented single crystal. An exponential relationship between reactivity and surface atomic density was developed.

Figure 2.5 shows the plot of reactivity versus the pressure. The polycrystalline sample is shown to have highest reactivity. It was also concluded that dissolved hydrogen or deuterium had negative effects on the reactivity to reach equilibrium.

A series of investigations have been carried out to study chemisorption on palladium surface, but it has been a challenge to separate the surface and the bulk effects. Adsorption and absorption studies were carried out using molecular beam scattering from Pd (111) surface by Engel and Kuipers [2.23]. Ordering of an adlayer was observed. Langmuir- Hinshelwood mechanism of hydrogen adsorption was observed. On Pd (111) surface, the $k_{\text{DD}} = k_{\text{HD}} = k_{\text{HH}}$ and it can be assumed that the total coverage, θ , is the sum of the coverage by hydrogen and deuterium, $\theta_{\text{H}} + \theta_{\text{D}}$. The rate of HD production is given by

$$\frac{D[\text{HD}]}{dt} = v \theta^2 \exp \left[\frac{-E(\theta)}{RT} \right] \quad (2.6)$$

where v is the pre-exponential factor in the desorption rate.

It can be summarized that the H₂-D₂ kinetics were found to follow Langmuir-Hinshelwood mechanism and the HD is backscatter coefficient and the activation energy for desorption result in the variation of HD exchange with temperature.

Consider a surface catalyzed reaction of species A converting to B. Gaseous A is sorbed on the surface, liberating sorption energy. The surface reaction surpasses the energy barrier and forms the chemisorbed product B, releasing the energy ΔH . Chemisorbed B is released from the surface with the sorption of energy Q_b [2.23].

The mechanism that follows is

The rate law is given by

d into the gas phase with a cosine function. Sticking

$$r = kC_s^2 \frac{K_1 K_2 C_A C_B}{(1 + K_1 C_A + K_2 C_B)^2}$$

Figure 2.5. Time course of H₂, HD and D₂ peaks during equilibration onto Fe(100) at 294K [2.17]

Sticking probability of hydrogen on palladium and palladium hydride was studied at 1 bar [2.24]. Since hydrogen and deuterium are similar in electronic structure, the potential encountered by hydrogen molecule when approaching the metal surface is independent of relative amounts of H and D on the metal surface at a fixed total coverage. They took into consideration that if H or D

Figure 2.6. Summary of equilibration experiments that were carried out at 294 K. plot of reactivity versus pressure [2.17].

have different sorption properties, then the equilibrium coverage at a fixed pressure is going to be different for H_2 and D_2 . Thus the adsorption potential will become a function of gas composition. Later it was assumed that the coverage on Pd for H_2 , D_2 and HD is the same.

In terms of sticking probability and molecular flux, the rate of the reaction is given by

$$R_i = F_i \cdot S - r_i \quad (2.7)$$

Where F_i is the molecular flux and S is the sticking coefficient. r_i is the rate of desorption of the species i from the surface. The molecular flux is given by

$$F_i = \frac{p_i}{\sqrt{2\pi m_i kT}}, \quad i = H_2, HD, D_2 \quad (2.8)$$

Where p_i is partial pressure, m_i molecular mass of species i and k is the Boltzmann constant.

A technique to measure the sticking probability on the metal was demonstrated by defining equilibrium conditions that were integrated into a model that was developed. The sticking probability of Ni was found to be really low like Pd and Pt. isotope effects were considered in the model used. It has also been found that below $298^\circ C$, two phases exist; α phase is a solid solution of hydrogen in Pd and β phase is the Pd hydride [2.25] that affects the sticking

probability. To describe the net HD production, a model was developed that assumed that the sticking probability for all species, H₂, HD and D₂ were the same [2.25].

They studied the heat of absorption of H₂, the rate of H₂-D₂ exchange and the rate of exchange between adsorbed D and gaseous H₂ on Ni-SiO₂ catalysts. It has been mentioned that there two mechanisms may occur for hydrogen deuterium exchange [2.26].

The first mechanism was given by Bonhoeffer and Farkas that connected the exchange kinetics with the adsorption-desorption process.

S is the empty site and H or D are the adsorbed atoms. The second mechanism that was proposed by Eley and Rideal is given by [2.25]

Isotopic exchange between H₂S and D₂ on molybdenum disulfide and manganese sulfide was studied. The measurements were taken between 420 °C and 500°C. Two mechanisms have been proposed to be possible for the formation of H₂ and HD. The first mechanism H₂ and HD formed by [2.27]

In the second mechanism, H₂S directly is converted to H₂,

and then the H₂ reacts with D₂

It was found from the experiments that the process took place by the second mechanism [2.27].

Figure 2.7. Total methane production versus time at 1680°C on 14.3% Ru-Pd [2.29]

Microkinetic modeling studies have been done to understand the hydrogen dissociation on the catalyst surface [2.28]. Palladium- ruthenium catalyst has been studied at temperatures between 90° C and 120° C using the method of methane-deuterium exchange reaction [2.29]. Methane and deuterium exchange is an easy measure for determining catalytic activity of an alloy since its easily measurable using mass spectroscopy. The sample preparation method was similar to our sample preparation. The sample was heated and hydrogen stream was passed over it to reduce the surface of the oxides. The sample was then exposed to excess quantities of deuterium to get it to condition to D₂, after which the mixture of methane-deuterium was passed over the sample. The measurements were made of the rate of formation of CD₄ – H₂ and CH₄ –D₂. Rate constants were calculated for both exchange processes. The overall rate of exchange is the combination of the rate constants for formation of the both compounds. Measurements done at 168°C showed the effect as shown in Figure 2.7 on 1.687g 14.3wt % Ru-Pd , 40mmD₂ + 80mm CH₄. Activation energies and pre-exponential factors were calculated for the process. For a catalyst composition of about 40 wt % Ru-Pd, the catalytic activity was measured to be the highest. It was found to be about 37 times higher than pure Pd and 43 times higher than pure Ru at 100°C [2.29].

Kinetic and thermodynamics aspects of H₂/D₂ isotope exchange was studied on films of Sc, Y, La and all lanthanides at temperature range of 77-230 K [2.30]. The films of these materials were deposited on the inner surface of the glass reactor under high-vacuum. Gas mixture was detected for its composition using a heat-conductivity detector. The specific catalytic activity of the materials were determined by the equation,

$$K_g = \frac{k_0 N}{S_H} \quad (2.9)$$

k_0 is the first order rate constant. N is the number of hydrogen molecules in the reaction volume, S_H is the active surface area of the catalyst film measured by hydrogen chemisorption at 77 K. The reason for the study at such low temperatures is because at such low temperatures, the hydrogen dissolution in the metals is very low and the interaction is only due to the surface chemisorption. Elay and Rideal mechanism of isotope exchange has been proven to occur in this work [2.30]. It has been suggested that the interaction between an atoms and molecule of hydrogen chemisorbed on the neighboring sites according to the Langmuir-Hinshelwood mechanism determines the rate of the process.

The Figure 2.8 shows a Lennard Jones Potential plot to demonstrate the contribution of both factors of heat of formation of hydrides and the adsorption of molecular hydrogen, q_{H_2} . The Figure 2.8 shows the activation energies of various metals, at an arbitrary scale.

An extensive study on the kinetics and mechanisms of the hydrogen-

Figure 2.8. Lennard-Jones potential curves for hydrogen chemisorption on transition metals [2.33]

deuterium equilibration and the conversion of orthodeuterium and parahydrogen conversion was performed by Scholten and Konvalinka [2.34]. The catalyst was palladium that underwent phase transitions during the process. Various kinetic mechanisms have been established for the exchange of H_2 and D_2 .

In a more recent paper of interest, Casey O' Brian et al, have studied the catalytic activity of Pd and Pd-Cu alloys [2.37]. H_2 and D_2 were exchanged over the catalyst that was cut into small pieces in the quartz reactor. The gases were analyzed at the end of the reactor. The activation energies and preexponential factors for adsorption and desorption were calculated by modeling the flow rate of HD out of the reactor. Pd, $Pd_{47}Cu_{53}$, $Pd_{70}Cu_{30}$ and Cu were studied as possible catalyst for the reaction. The results showed that the phase transitions in Pd ($\alpha \rightarrow \beta$) and in $Pd_{47}Cu_{53}$ have an impact on the hydrogen adsorption and desorption energies, which directly relate to the catalytic activity. It was also established that Pd can be alloyed with as much as 50% Cu with compromising much on the activation energies for adsorption and desorption processes for hydrogen. As can be seen in the Figure 2.9, HD flow rates are plotted against temperature at various flow rates of H_2 and D_2 . Plot (a) shows a phase transition occurring in Pd that is missing in Cu in plot (b). The flow rates have been modeled to a kinetic rate expression to determine the values of preexponential factors and activation energies.

Figure 2.9. (a) Experimental (points) and modeled (lines) HD flow rate versus temperature for Pd foil at various flow rates (b) Total coverage of H&D atoms over Pd foil [2.37]

The results obtained in this paper show that there may be a link between increasing Cu content in Pd-Cu alloys and reduced H_2 dissociation activity in the presence of H_2S . This study is useful in understanding the behavior of effect of absorption of H_2 in presence of impurity for separation

membranes. The model used for the fitting of experimental HD flow rate was derived from the rate kinetics equations that are described in the experimental section.

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III. Experimental methods

3.1 Preparation of Alloy Ingots for Melt Spinning Experiments

The binary and ternary alloy ingots were first arc melted for all the alloy compositions, and these were made at U.S. DOE Ames laboratory in Iowa. These alloy ingots were used to make the ribbons using an induction furnace in the melt spin apparatus. Experimental procedures will be described in the following sections.

The category of membranes made for this DOE project can be broadly categorized as follows:

- A. Binary Ni-Zr alloys: $\text{Ni}_{64}\text{Nb}_{36}$ (eutectic alloy), $\text{Ni}_{30}\text{Nb}_{70}$ (XRD and $\text{H}_2\text{-D}_2$ tests)
- B. Binary Ni-Zr, and Ni-V and Ni-Ta, to test effect of alloy element Nb, V, and Ta in Ni. (XRD and $\text{H}_2\text{-D}_2$ tests)
- C. Ternary $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$, $\text{Ni}_{60}\text{V}_{20}\text{Zr}_{20}$, $\text{Ni}_{60}\text{Ta}_{20}\text{Zr}_{20}$, (to test effect of alloying element in $\text{Ni}_{60}\text{Zr}_{20}$ alloys. (XRD and $\text{H}_2\text{-D}_2$ tests)
- D. Ternary $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x=10, 20, 30$) amorphous alloy membranes (Kinetic (DSC) tests, Permeation tests, XRD, and Solubility tests)
- E. Quaternary $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{100-x}\text{Zr}_x$ (where $x=10, 20, 30$) amorphous alloy membranes (Permeation tests, XRD, and Solubility tests)
- F. Quaternary $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.30})_{100-x}\text{B}_x$ (where $x=2, 5$) amorphous alloy membranes (Permeation tests, XRD, and Solubility tests)

A. Ingot Preparation at US DOE Ames Laboratory

High purity alloy ingots were fabricated at the DOE-AMES laboratory in Iowa. Reagent grade Ni, Nb, Ta, Zr and V were mixed in Vacuum arc melting equipment under argon atmosphere. Ni-Nb-Zr, Ni-Nb-Zr-Ta and Ni-Nb-Zr-B ingots with a weight of 100 g were fabricated at AMES Laboratory by Vacuum Arc Melting of a mixture of pure reagent grade nickel, zirconium, niobium, tantalum and boron in a purified argon atmosphere. Each arc-melted ingot was flipped over and re-melted multiple times to obtain a homogeneous composition. A schematic of arc melting process is shown in Figure 3.1. Vacuum arc melting (VAR) is a secondary melting process for production of metal ingots with elevated chemical and mechanical homogeneity for highly demanding applications[3.1]. The VAR process has made it possible to make alloys rather quickly, procedures are very well standardized.

A homogeneous composition was obtained by re-melting the metals several times. Nickel based alloys are made using vacuum arc melting method. It is an extra step to improve the purity of the alloy. For metals like titanium the vacuum arc melting is carried out even thrice. This method reduces the segregation in the ingot. Melt spinning equipment was used to make ribbons from the ingots that were obtained from AMES labs.

Melt spinning process is used for making ribbons of the alloys; these could be several feet in length, depending on the amount alloy melted. It is well known that low cooling yields crystalline materials, whereas amorphous alloy ribbons require rapid cooling of the order of 10^5 to 10^6 K s^{-1} to avoid crystallization. To achieve this one of the method is to use a Melt-Spinning

apparatus that allows alloys to cool at very high cooling rate resulting in amorphous alloy membrane of desired thickness. One way to do this is by single-roller melt spinning as shown in Figure 3.2

Figure 3.1. Vacuum arc melting furnace
(Source: <http://www.phys.ufl.edu>)

3.2 Fabrication of membranes by Melt Spinning process

The $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x= 10, 20, 30$), $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{100-x}\text{Zr}_x$ (where $x= 10, 20, 30$) and $(\text{Ni}_{0.42}\text{Nb}_{0.28})_{100-x}\text{Zr}_x$ (where $x= 2, 5$) amorphous alloy membranes were fabricated, from alloy ingots fabricated, by using single wheel melt-spinning process at CISRO, Brisbane, Australia facility (Figure 3.2) under argon atmosphere. Membranes fabricated were ~ 25 mm wide and thickness varied from $50\text{ }\mu\text{m}$ to $90\text{ }\mu\text{m}$.

Figure 3.2. Melt Spinner at CISRO, Brisbane, Australia

A melt-spinning apparatus made by Buhler GmbH, Germany is now available in our laboratory at University of Nevada, Reno . A schematic of the apparatus is shown in Figure 3.3 (a) along with a close up image of the spinning wheel of the melt spin apparatus (Figure 3.3b). The cooling rates of 10^5 and 10^6 K/s are used to avoid crystallization of the alloy.

Figure 3.3 (a) Melt Spinner at University of Nevada, Reno

Figure 3.3 (b) Schematic and close-up image of a melt spinning apparatus, where molten alloy in crucible is ejected onto the copper wheel which forms foils at high RPM and cooling rates [3.2-3.3]

Photographs of rolls of amorphous ribbons produced by the melt spin method are shown in Figure 3.4 (a,b). Before examining these membranes for hydrogen solubility and permeability, the samples were examined for amorphicity by means of X-ray diffraction. All the samples were found to be amorphous. These samples were also tested by X-ray diffraction after permeation/hydrogen solubility testing to be sure that they are amorphous even after exposure to hydrogen.

Figure 3.4 (a) . Sample amorphous alloy membranes fabricated under the DOE program.

Figure 3.4(b). An as-spun $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ amorphous ribbon used for H_2 - D_2 experiments.

3.3 Palladium Coating on Membranes

When we started the program, the alloy ribbons of NiNbZr were coated with palladium films on both the surfaces of amorphous alloys that served two purposes. (1) Palladium prevents oxidation of zirconium, which can block the membrane surface to hydrogen. (2) Palladium catalyzes the dissociation of molecular hydrogen to atomic hydrogen. However, later in the project, we found that Pd coating were not needed if we hydrogen heat treat the ribbons, these are discussed later. Please note that all hydrogen-deuterium experiments and the associated in-

situ x-ray diffraction did not require the Pd coating (towards the end of the project) as we were able to precipitate Ni on the surfaces; *thus eliminating the need of any precious metals*.

Typically, a 500 nm Pd film applied to both sides of a membrane requires 12 g of palladium per square meter, which, at the current palladium price of about US\$ 600/oz, equates to US\$ 255/m² (excluding the cost of the coating process). It is desirable to minimize or avoid the use of palladium, through the incorporation of inexpensive metals with high catalytic activity considering cost along with potentially-limited availability of palladium in the future [3.4]. Palladium layer of ~ 500 nm was deposited on both sides of the ribbons using Physical Vapor Deposition (PVD) - magnetron sputtering process partly at *CISRO, Brisbane, Australia*, and some at *Southwest Research Institute (SwRI), San Antonio, USA*. A schematic of the sputtering apparatus commonly used for thin-film deposition, etching and analytical techniques is shown Figure 3.5. Note that the Ni-Nb-Zr, Ni-Nb-Zr-Ta and Ni-Nb-Zr-B amorphous alloy membranes were fabricated at CISRO, Australia by single-wheel melt-spinning process.

Figure 3.5. Schematic of Sputtering process
(Source: <http://en.wikipedia.org/wiki/File:Sputtering.gif>)

3.4 Hydrogen Permeation Tests on Amorphous Ribbons

Permeation tests of amorphous alloy membranes are conducted to measure the efficiency and effectiveness under close to practical conditions. These tests are also conducted to see the durability of membranes by running the tests continuously for many hours (say 100 or 200 hrs). The permeation test apparatus also tests the hydrogen selectivity of the membranes. These permeation tests were carried out at two different locations that discussed below.

A. Experiments Performed at TDA Research (USA)

After characterizing the samples, the permeation tests were performed in an automatic permeation test apparatus at TDA Research Inc., Wheat Ridge, Colorado, USA at temperatures 400°C and 450°C. The apparatus had integrated safety monitoring system. All the parameters like N₂, H₂, CO, and CO₂ etc. were monitored and recorded on real-time basis. The tests were performed not only for measuring permeation of

Figure.3.6. Permeation Test Apparatus at TDA Research Inc., Wheat Ridge, Colorado.

Membrane in test cell

2.2 cm² permeable area

Test cell in the Furnace

Figure 3.7. Details of Membrane Sample Holder at TDA Research Inc.

the samples but also for long-term durability. Figure 3.6 shows the permeation test apparatus at TDA Research Inc.; this apparatus is also used for testing of catalyst used in petroleum refining industry.

The Pd coated amorphous alloy membranes were cut into 25 mm diameter discs. An amorphous alloy membrane disc was then sandwiched between porous stainless steel frit along with alumina felt and graphite gasket and positioned in the fixture and tightened (Figure 3.7) . While porous stainless steel frit supports membrane, porous alumina felt prevents metallic inter-diffusion between membrane and porous stainless steel frit. The mated fixture was tightened roughly one-quarter turn. The Pd coated amorphous alloy membranes were cut into 25 mm diameter discs. A amorphous alloy membrane disc was then sandwiched between porous stainless steel frit along with alumina felt and graphite gasket and positioned in the fixture and tightened. While porous stainless steel frit supports membrane, porous alumina felt prevents metallic inter-diffusion between membrane and porous stainless steel frit. The mated fixture was tightened roughly one-quarter turn. The membrane module was placed in a furnace and connected to a gas supply and measurement system.

Helium pressurization tests were performed to confirm the absence of leaks. Helium and argon were nominally 99.9995% pure and hydrogen was 99.99995% pure and both gases were used without further purification. Mass flow controllers metered the gas flows while 0– 1330, 0–13.3 and 0–1.33 kPa pressure transducers measured upstream (retentate) and downstream (permeate) pressures.

The membrane module was heated in the absence of hydrogen with an argon purge on the retentate side and argon purge or vacuum (provided by an oil free turbo-molecular pump backed by a scroll pump) on the permeate side of the membrane. The hydrogen feed pressure ranged between 101 and 700 kPa and the permeate pressure ranged between 0.5 and 103 kPa. Pressures were controlled using backpressure regulators. Sweep gas was not used during the permeation experiments. Hydrogen flux was measured using calibrated flow meters[3.5].

Table 3.1. Operating conditions for hydrogen permeation tests

Effective membrane area		2.2 cm ²
Membrane thickness		50-90 μm
Introducing gas		Hydrogen, Hydrogen+Nitrogen
Pressure	retentate side	1 - 7 Bar (abs)
	permeate side	0.83 Bar (abs)
Temperature		773 - 823 K

A condition of a typical membrane after hydrogen flux testing is shown in Figure 3.8 (a and b) . It can be seen that there bulging on one side to the differential pressure exerted on the membrane.

Figure 3.8(A). Typical Ni-Nb-Zr amorphous alloy membrane after permeation test.

Figure 3.8(b). Example of a $\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ and $\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{70}\text{Zr}_{30}$ amorphous alloy membrane after permeation test sandwiched between two copper gaskets.

B. Experiments Performed in Australia:

Some of the tests were also performed at the CSIRO facilities in Brisbane, Australia by our University of Nevada, Reno graduate students. These tests were performed at a constant pressure in a temperature range of 573-673 K the CSIRO apparatus as shown in Figure 3.9. In these experiments membranes were also circular in shape, diameter 30 mm. These membranes were mounted in between two copper gaskets (1 mm thick, 10 mm inside diameter and 30 mm outside diameter) in the membrane module.

The gasket surfaces were smoothed before use with 1200 grit sandpaper and the inner edge which comes into contact with the membrane was also smoothed with a suitable file. The membrane module and resistance heater were insulated with ceramic fiber insulation and housed inside a stainless steel containment vessel that was continuously purged with nitrogen. The containment vessel was used to ensure that any hydrogen escaping from the membrane apparatus would be diluted, cooled, and vented.

In the experiments performed in Australia, H₂, N₂, and CO₂ mixtures were introduced to the feed side of a membrane at 0.8 MPa while the pressure on the permeate side was maintained at 0.9 MPa using Ar sweep gas at a constant flow rate of 200 mL/min. The feed and sweep gas flow rates were controlled by Brooks mass flow controllers. The process feed and sweep pressures were regulated by pneumatic, stainless steel Badger Research control-valves. The hydrogen partial pressure gradient across the membrane was in the range of 0.2 to 0.76 MPa. To make sure that there were no pin-holes and ruptured areas in the membrane due to hydrogen reactions, tests were performed to observe if N₂ or CO₂ were present in the sweep stream during the permeation testing. The hydrogen-containing permeate stream was carried to a gas chromatograph. The hydrogen permeation flux through the membranes was calculated based on the sweep gas flow rate and the concentration of hydrogen in the permeate. The hydrogen permeation flux reported here were taken after stabilizing the permeation rate at different temperatures and hydrogen partial pressures.

The Pd coated amorphous alloy membranes were cut into 25 mm diameter discs. A amorphous alloy membrane disc was then sandwiched between porous stainless steel frit along with alumina felt and graphite gasket and positioned in the fixture and tightened. While porous stainless steel frit supports membrane, porous alumina felt prevents metallic inter-diffusion between membrane and porous stainless steel frit. The mated fixture was tightened roughly one-quarter turn.

3.5 Hydrogen solubility Tests performed at University of Nevada, Reno

Solubility tests are integral part of permeation studies as they give pressure-concentration isotherms (H/M) values of these materials at different temperatures and pressures. Permeability depends on hydrogen concentration / solubility (atomic H/M) and diffusion coefficient of the material at particular condition. Permeability (P) is the product of solubility (K_s) and diffusivity (D) of hydrogen in the metal.

$$P = K_s D$$

A simple schematic of the apparatus is shown in Figure 3.10. In Sievert's apparatus, the sample is exposed to hydrogen under incremental pressures and allowed to absorb hydrogen at fixed temperature. The absorbed hydrogen is then measured by measuring the pressure drop in each step. The test rig also calculates the hydrogen desorbed during reverse process called desorption. For crystalline metals / alloys at sufficiently low pressures ($p < 1$ MPa), the solubility is usually described by Sieverts' law:

$$c = K\sqrt{p} = K_0 \exp\left(-\frac{E_k}{RT}\right)\sqrt{p}$$

where c is the atomic hydrogen concentration in the solid, K is the hydrogen solubility in the metal, p is the partial pressure of hydrogen in the gaseous phase, K_0 is the solubility constant, E_k is the activation energy of solution, R is the ideal gas constant and T is the absolute temperature.

Figure 3.9. (A) Membrane testing system, showing (top) furnace control, furnace and gas inlet system, (B) gas control panel, PC with LabView display and gas chromatograph, (C) Alloy membrane module for hydrogen permeation test.

Figure 3.10. Schematic of simple Sievert's Apparatus
(Source: <http://www.sciencedirect.com>)

Figure 3.11 shows an automated Sievert's apparatus at University of Nevada, Reno. This Sievert's apparatus can test hydrogen solubility in any solid metal or powder up to 9250 torr hydrogen pressure. Before each test, the system is calibrated with helium to ensure the experimental repeatability. Also, the samples were heated to 400°C for at least 24 hours every time under vacuum before starting test on any sample at a particular temperature (200-400°C) to maintain the uniform testing conditions. I also did hydrogen solubility tests on palladium in between the tests on amorphous alloy membranes to compare these data with published data; my data on palladium matched with published data on palladium-hydrogen system[80]. We performed hydrogen solubility tests on these Pd coated (~ 500nm each side) amorphous alloy membranes at five different temperatures (200°C, 250°C, 300°C, 350°C and 400°C) in automatic Sievert's apparatus at University of Nevada, Reno laboratory.

Hydrogen solubility tests on Ni-Nb-Zr amorphous alloy membrane were conducted at five different temperatures (200°C, 250°C, 300°C, 350°C and 400°C) by exposing the samples under incremental hydrogen pressure up to maximum of ~ 12bar. The temperature of the sample holder was controlled with an accuracy of within $\pm 1^\circ\text{C}$. The tests included absorption and desorption cycles at each temperature. The pressure-composition isotherms of the hydrogen absorption were then plotted for Ni-Nb-Zr amorphous alloy membranes at five different temperatures. In a typical pressure-composition isotherm, the horizontal axis represents the hydrogen content, H/M, expressed by the number of hydrogen atoms per metal atom and longitudinal axis represents the pressure in bar or MPa. The pressure-concentration isotherms were then used to draw the Van't Hoff plots to calculate the enthalpy of individual amorphous alloy samples.

Figure 3.11. Automatic Sievert's apparatus at University of Nevada, Reno.

3.6 Differential scanning Calorimetry (DSC)

The kinetic of phase transformation such crystallization temperature were measured by differential scanning calorimetry. A *Setaram Synses calorimeter* was used for this purpose. An example of the supercooled region developed during rapid cooling is given in the Figure 3.12.

Binary Ni-Zr and a series of Ni-Nb-Zr crystalline alloy ingots were prepared by arc melting in a purified Ar atmosphere. The eutectic and near-eutectic points with Ni composition of 30 and 63.7 at.% in the Ni-Zr binary system were selected to provide a comprehensive picture for the thermal property. Amorphous ribbons of 50-70 μm thick and 30 mm wide made by using melt spin method.

The crystallization kinetics of these amorphous alloys was determined by using isothermal and non-isothermal techniques. Experiments were performed by using a Sensys TG-DSC with flowing ultra high purity Ar. For isothermal analysis, sample sizes were 3 ± 0.1 mg. These samples were placed in an Al_2O_3 crucible in the TG-DSC. The samples were heated from room temperature to just below the crystallization temperature with a heating rate of 20 K/min. The parameters, such as, scanning rate and temperature ranges were determined by preliminary examination of these samples.

3.7 Hydrogen- Deuterium Exchange Experiments

Amorphous ribbons for these studies were fabricated at CSIRO, Australia. The $\text{H}_2\text{-D}_2$ experiments were carried out by passing hydrogen- deuterium through a 4mm ID quartz tube reactor. The membrane was cut into pieces $\sim 1\text{mm}^2$ and the reactor was filled with the membrane pieces. The $\text{Ni}_{64}\text{Zr}_{36}$, $\text{Ni}_{60}\text{Nb}_{40}$, $\text{Ni}_{60}\text{V}_{40}$, $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$, $\text{Ni}_{60}\text{V}_{20}\text{Zr}_{20}$ alloys. For reference a pure crystalline Ni foil was also examined.

Figure 3.12 Schematic showing melting of the alloy (left). The glass transition and crystallization temperature are shown in the Figure on the right. (Sang-Mun Kim Ph.D. Dissertation 2011)

A packed bed reactor was placed in a furnace connected to a temperature controller. The experimental setup is shown in Figure 3.13. The outlet of the reactor is connected to a mass spectrometer by European Spectroscopy Systems Bronkhorst mass flow controllers were used for H₂, D₂ and N₂ gases to the catalyst bed. Teflon piping was used to connect the reactor to the mass spectrometer. The membranes were cleaned ultrasonically in acetone before using them in the reactor. Approximately 10 cm² area was used for the membranes at the flow rate of 10 mL/min for the gases. The catalyst was heated to about 300°C and subsequently cooled. Then the catalyst was heated to about 550°C, held overnight and cooled the next day. During this operation, the outlet gas from the reactor was constantly analyzed. The HD data was recorded in % HD production. At each temperature, enough time was given to the HD formation to stabilize before recording the reading. Hysteresis was observed on plotting the outlet HD flow rate versus temperature for heating and cooling of samples. The laboratory setup for the HD exchange experiment is shown in Figure 3.14. The Figure 3.15 shows the experimental setup of the reactor with the mass spectrometer for the scrambling apparatus. Figure 3.16 shows the H-D reaction to form HD gas. The background experiments were conducted by passing the H₂ and D₂ through the reactor without the presence of catalyst. Nickel was used for baseline experiments.

After heating a sample to 300°C and cooling it to room temperature, a change in the HD % conversion was observed. This can be attributed to reduction of the surface of catalyst due to hydrogen exposure. Due to the cleaning of the catalyst surface, the HD production was improved. This is a more real value to consider. Mass spectrometer signals for HD were collected at certain temperatures, which minimized the bulk absorption effects.

Figure 3.13. A schematic of H₂-D₂ scrambling rig setup.

The rate of the HD formation can be given by

$$k = \frac{p_{HD}^2}{p_{H_2} \cdot p_{D_2}}$$

Where P_{HD} is the partial pressure of HD, P_{H_2} is the partial pressure of H_2 and P_{D_2} is the partial pressure of D_2 in the outlet gases. The flow rate and the partial pressure relationship is given by :

Figure 3.14. Experimental setup of the H_2 - D_2 scrambling apparatus showing the MFC and reaction chamber.

Figure 3.15. Experimental setup for H_2 - D_2 exchange reaction, showing mass spectrometer at outlet.

Figure 3.16 Schematic of the H_2 - D_2 Exchange

$$F_i = \frac{F_{total} \cdot P_i}{P_{total}}$$

F_i is the flow rate for individual species, F_{total} is the total flow rate, P_i is the partial pressure of the individual species. A microkinetic analysis model for kinetics was used to model the HD flow rate [3.7]. It can be assumed that the isotopic effects don't play a major role in the kinetics of the reactions. Also, it can be assumed the Arrhenius relationship constant and activation energies are constant. The coverage of the catalyst material can be defined as the fraction of active sites occupied by hydrogen and deuterium on the catalyst surface, it is represented by θ . Langmuir Hinshelwood kinetics can be assumed for this process. An equal coverage for H_2 and D_2 atoms can be assumed, so, the total coverage is twice the coverage of these individual species.

$$\frac{\theta}{2} = \theta_{H_2} = \theta_{D_2}$$

The Langmuir isotherm gives the coverage as

$$\theta = \frac{P_{H_2} B}{1 + P_{H_2} B}$$

where B is the adsorption constant.

The rate equation for the formation of the HD is given by

$$r_{HD} = 2k_{des}\theta_H\theta_D - k_{ads}P_{HD}(1 - \theta_H - \theta_D)^2$$

Given that chemically the hydrogen and deuterium are similar, the isotope effects are neglected assumed that surface area coverage is same for both the species, the rate equation from above can be written as

$$r_{HD} = 2k_{des}\left(\frac{\theta}{2}\right) - k_{ads}P_{HD}(1 - \theta)^2$$

The mass balance on HD can be given as

$$\int_0^{F_{HD\_out}} \frac{dF_{HD}}{r_{HD}} = A$$

dF_{HD} is the differential HD flow rate and r_{HD} is the rate of formation of HD. A is the area of the catalyst. The rate of HD formation is given by

$$r_{HD} = 2k_{des}\theta_H\theta_D - k_{ads}P_{HD}(1 - \theta_H - \theta_D)^2$$

k_{des} is the rate constant for desorption of HD, k_{ads} is the rate constant for adsorption, θ_H is the catalyst coverage for hydrogen atoms, while θ_D is the catalyst coverage for deuterium atoms. Because it can be assumed that isotope effects can be neglected, the coverage by hydrogen and deuterium will assumed to be equal. Hence, the rate equation for HD formation becomes

$$r_{HD} = 2k_{des}\left(\frac{\theta}{2}\right)^2 - k_{ads}P_{HD}(1 - \theta)^2$$

where θ is the overall coverage of the catalyst material.

The partial pressure of HD can be converted to the flow rates by,

$$P_{HD} = \frac{F_{total} P_{HD}}{P_{total}}$$

Hence, the integral rate law becomes

$$\int_0^{F_{HD\_out}} \frac{dF_{HD}}{2k_{des}\left(\frac{\theta}{2}\right)^2 - k_{ads}\frac{P_{total}F_{HD}}{P_{total}}(1 - \theta)^2} = A$$

On integration

$$F_{HD,out} = \frac{k_{ads}F_{total}\theta^2}{2k_{ads}P(1-\theta)} \left[1 - \exp\left(-\frac{k_{ads}PA(1-\theta)^2}{F_{total}}\right) \right]$$

At steady state of coverage

$$\frac{d\theta_H}{dt} = 0 = 2k_{ads}P_{H_2}(1-\theta_H-\theta_D)^2 + k_{ads}P_{HD}(1-\theta_H-\theta_D)^2 - 2k_{ads}\theta_H^2 - 2k_{ads}\theta_H\theta_D$$

Since, it is assumed that the coverage of H and D atoms are equal, the above equation becomes

$$\frac{d\theta_H}{dt} = 0 = 2k_{ads}P_{H_2}(1-\theta)^2 + k_{ads}P_{HD}(1-\theta)^2 - k_{ads}\theta^2$$

On solving for θ , we get the expression for coverage of H or D atoms on the catalyst

$$\theta = \frac{\sqrt{2 \frac{k_{ads}}{k_{des}} P_{H_2,feed}}}{1 + \sqrt{2 \frac{k_{ads}}{k_{des}} P_{H_2,feed}}}$$

This is an expression obtained from the Langmuir- Hinshelwood kinetics.

The final HD flow rate model can be deduced from the equations for coverage above and substituting it into mass balance equation,

$$F_{HD,out} = F_{H_2,feed} \left[1 - \exp\left(\frac{-k_{ads}p_{total}A}{F_{total} \left(1 + \sqrt{1 + \frac{k_{ads}}{k_{des}} P_{H_2,feed}}\right)^2}\right) \right]$$

3.8 In-situ X-ray Diffraction

The amorphous ribbons were heated to observe recrystallization temperature by performing in-situ X-ray diffraction method by PANalytical X'Pert PRO X-ray machine at University of Nevada, Reno. This powder diffractometer has a theta–theta configuration, a Cu X-ray source operated at 45 kV and 40 mA and an X'Celerator detector with a monochromator was used to determine crystalline phases present in the membranes and changes resulting from flux testing. PANalytical X'Pert PRO offers high-speed, high-quality phase identification and quantification of polycrystalline materials in an affordable package. It can be equipped with a sample changer to add high throughput to your high-speed data collection. There is a wide variety of holders to handle many different types of sample, and also a standard clip stage is provided for flat samples or slides. A photo of the X-ray diffractometer and the Anton Parr XRK 900 heating stage are shown in Figures 3.17 (a and b)

The structure of the amorphous alloy samples before and after hydriding was characterized by X-ray diffraction using monochromatic Cu K α radiation. The samples were characterized before Pd coating as well as after coating by removing coating on one side of alloy membranes. Removal of Pd coating on one side was important otherwise only Pd peak was observed. X-ray diffraction test were performed on few of these samples at different temperatures and pressures to examine the behavior of these samples at high temperature and also at high pressures.

Figure 3.17 (top) PANalytical X'Pert Pro X-ray diffraction machine at University of Nevada, Reno

Figure 3.17 (bottom) In-situ high temperature XRK 900 (left). The sample holder that in the In the XRK 900 heating stage (right).

In-situ X-ray diffraction was carried out on the samples at various temperatures under hydrogen. The diffractometer used is as PANalytical X'Pert PRO X-ray diffraction system. Cu-K α beams were obtained by using a Ni- filter at 40kV and 40mA. Each scan ranged from 10° to 90° angles in steps of 0.02° and 2 seconds counts at each step. For calibration Si was used for initial measurements. The Figure IV-7 shows the setup of the instrument in the X-ray machine.

The membrane was cut into small pieces and placed on the stage XRK-900 by Anton Paar as shown in Figure 3.17 b. It was done because the membrane by itself curled on placing on the stage at high temperature. Figure IV-8 shows the stage XRK-900 with sample on the top. Before each experiment, the chamber was vacuumed and flushed with He and H₂ thrice. This stage is a unique tool for in-situ XRD investigations of solid state and solid-gas reactions at temperatures

from room temperature to 900 °C [3.7]. The special arrangement of the electrical heater inside the furnace guarantees the absence of temperature gradients within the sample bulk.

3.9 Electrochemical Impedance spectroscopy (EIS)

This technique is used to determine the proton conductivity of a membrane by an in-plane measurement. BekkTech conductivity system (Figure 3.18) was used to place the sample and to measure the conductivity of the sample. Figure 3.19 shows the BekkTech conductivity cell. It contains four platinum electrodes. These electrodes are connected to the potentiostat /impedance analyzer using alligator clips. The potentiostat was purchased from Princeton Applied Research and its model number is PARSTAT 2273. The EIS is capable of testing a sample from 10μHz to 1MHz. 2A current can be applied with a 100V. It possesses 10¹³ Ohms input impedance. The electrochemical potentiostat is synchronized to a computer that has the PARSTAT software, Power Suite, installed. This software has a capability to measure Bode plots and Nyquist plots. This software can also be used to model the Nyquist plots obtained.

Electrochemical impedance is measured by applying an AC potential to the electrochemical cell and measuring the current through the cell. Electrochemical impedance is normally measured by applying a small excitation signal. This is done so that the cell's response is pseudo-linear. In a linear system, the current response to a sinusoidal potential will be sinusoidal at the same frequency but shifted in phase [3.8].

The excitation signal is expressed as a function of time, has a form,

$$E(t) = E_0 \sin(\omega t)$$

The expression for $Z(\omega)$ is composed of a real and imaginary part. If the real part is plotted on the X-axis and the imaginary part is plotted on the Y-axis of a chart, we get a "Nyquist plot". The points on Y-axis are negative and each Nyquist point on the plot is the impedance at one frequency.

The impedance Nyquist plot (Figure 3.20) can be represented as a vector of the length $|Z|$. The angle between this vector and the X-axis is called the "phase angle". The circuit in Figure 3.19 resulted in the Nyquist plot above. Every Nyquist plot is generated from an electrical circuit.

Membranes were cut into small pieces and placed in the conductivity cell. The upper Teflon block was screwed tight on the conductivity cell and it was connected to the electrochemical testing device. The dimensions of the membrane were measured and the conductivity was measured in 100% humidity at room temperature. The Nyquist plot gave the resistance values and the reciprocal of that resulted in conductivity. The conductivity can be calculated by the following equation:

$$\sigma = \frac{l}{t * w * R}$$

Here, σ = conductivity in S/cm

t = thickness of the membranes in cm

w = width of the membrane in cm, and

R = resistance of membrane in kΩ.

Figure 3.18. XRD sample holder with sample cut into pieces after heat treatment process.

Figure 3.19 BekkTech sample holder for testing the impedance of samples using 4-probe method [3.8-3.9].

Figure 3.20. A Typical Nyquist plot and a R-C circuit that corresponds to the plot [3.8]

3.10 Hydrogen Solubility Measurements using Sieverts apparatus

Hydrogen solubility in metals is an important property to determine since it directly relates to the diffusion and the permeability of hydrogen through the membrane. Solubility of hydrogen in the samples is determined by Sieverts method. The method is based on making several measurements of known amount of hydrogen gas over a known amount of material. Sequential pressure drop evaluated to the amount of absorbed hydrogen. Dehydriding of the sample is also performed after the end of absorption process.

It was observed by Sieverts that hydrogen absorption over wide range temperatures and pressure is proportional to the square root of gas-phase hydrogen pressure. This is expressed in terms of Sieverts Law given by

$$C_H = K_s \cdot P_{H_2}^{1/2}$$

It is assumed that dissolved hydrogen in metal behaves like ideal solution and makes Sieverts law only applicable when hydrogen is a dilute solute in metal.

Figure 3.21. Sievert's apparatus that is used at UNR to determine hydrogen absorption in the bulk membranes.

The apparatus used for these experiments is shown in Figure 3.21. The setup reaches a highest pressure of 9250 torr. Calibration of volumes was performed before each sample. Isotherms were obtained at 250° C, 300° C and 350° C. Membranes were conditioned under small quantities of hydrogen at 300° C overnight under vacuum before performing the measurements.

Approximately 1 g of sample was used in each measurement. Leak tests were also performed to ensure complete sealing of the pressure transducers and sample holder.

3.11 Scanning Electron Microscopy/ Energy Dispersive Spectroscopy (SEM/EDS) and Transmission Electron Microscope (TEM).

An FE SEM was used to study the surface morphology of the membranes before and after heat treatment with hydrogen. EDS was used to determine the surface compositions on the membranes and has proven to be a very useful tool. Scanning Electron Microscopy (SEM) provides the ability to magnify an image from 10X – 100,000X [3.10]. The SEM is a famous method because it is not only simple in term of using and sample preparation but also offers a better performance than optical microscopy. It is a high resolution surface imaging method. SEM provides information related to the crystal orientation, crystal structure, phase distribution, compositional differences, and presence and location of electrical defects. EDS provides both quantitative and qualitative information of the sample. To observe and characterize the composite polyurethane-microspheres and surface coated of iron particles, SEM/EDS are used. The SEM Hitachi S-4700 equipped with an Oxford EDS system is provided by the Chemical/Metallurgy Engineering Department, University of Nevada, Reno.

A transmission electron microscope provides morphologic, compositional and crystallographic information of the samples. The maximum resolution can go upto 1nm scale producing high resolution, two-dimensional images, allowing for a wide range of applications. TEM produces a very high-resolution black and white image that takes place between prepared samples and energetic electrons in the vacuum chamber. Pumping of air into the vacuum chamber creates a medium for the electron movement. The electrons then pass through multiple electromagnetic lenses with solenoids wrapped around them. Figure 3.22 shows thwe phot and schematic of the Field Emission, JEOL 2100F microscope.

The lighter areas of the image represent the place where a greater number of electrons were able to pass through the sample and the darker areas reflect the dense areas of the object. The difference provides information on the structure, texture, shape and size of the sample. The sample preparation is different than SEM for TEM. The samples need to be thinly sliced thin enough for electrons to pass through, hence higher electron transparency. The SEM used at UNR is JEOL 2100 coupled with EELS capability.

This is an advanced Field Emission Electron Microscope featuring ultrahigh resolution and rapid data acquisition. The JEOL 2100 F is capable of achieving high image quality in 200kV class analytical TEM with a probe size under 0.5nm. The resolution is 0.23nm with ZrO/ W (110) as the electron gun. The accelerating voltage is 200kV and the magnification rages from 2000X to 1,500,000X. The length of the diffraction camera is 8 to 200cm. The high temperature diffraction camera length is 8 to 80m [3.12].

The use of TEM has been of use to determine the phases present in the binary Ni-Zr alloy before and after treatment for comparison purposes. The use of TEM has been of use to determine the phases present in the binary Ni-Zr alloy before and after treatment for comparison purposes. The sample was first cut to a disk of 3mm and then in Fischione 150 Dimple grinder, the sample is ground to 5-10micron thickness. The final thinning is performed in Fischione 1010 Low Angle Ion mill till a tiny hole is made in the center of the sample. The sample is then plasma cleaned to remove all the contaminants. The edge of the hole is tested under TEM to ensure that it is less than 100 nm. Figure 3.23 shows the pictures of the equipment at the University of Nevada, Reno, to prepare sample for TEM.

Figure 3.22. Schematic of TEM and JEOL 2100F [3.11].

Figure 3.23. Equipment used to prepare samples for TEM [3.13].

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IV. Results and Discussions

4.1 Crystallization and Surface Kinetics Studies on Ni-based Binary Alloys

Binary Ni-Zr glasses are typical examples of amorphous alloys having their wide composition ranges [4.1]. It has been reported that zirconium-based Zr-Ni amorphous alloys absorb considerable quantity of hydrogen [4.2-4.3]. Since these materials are generally used in the presence of hydrogen at elevated temperatures, it is important to evaluate the thermal stability and crystallization behavior of amorphous alloys. Hara et al. [4.4-4.6] investigated the hydrogen permeability and embrittlement of the Ni-Zr alloy system. It was found that the Ni-Zr based alloys were stable in the range of 473-623 K and the hydrogen permeability of Ni₆₄Zr₃₆ alloy was in the order of 10⁻⁹ (mol m⁻¹ s⁻¹ Pa^{-0.5}). Considering technological applications of glassy alloys, information of thermal property of glasses is of considerable importance. Since the crystallization behavior is also dependent on alloy composition, the alloys with two different compositions (Ni₃₀Zr₇₀ and Ni_{63.7}Zr_{36.3}) were examined.

4.1.A Phase Transformation on Amorphous Ni-Zr Binary Alloys

4.1.A.1 Crystallization Kinetics: Isothermal Experiments

The crystallization kinetics of Ni-Zr, Ni_{63.7}Zr_{36.3} and Ni₃₀Zr₇₀ was determined as the baseline experiments for the ternary alloys. The analyses were based on Chen et al. [4.1]. Kinetic analyses performed by isothermal experiments are reported first. Isothermal data was obtained at four different temperatures for Ni_{63.7}Zr_{36.3} and Ni₃₀Zr₇₀ as shown in Table 4-1, and results are shown in Figures 4.1(a-1) and 4.1(b-1). The incubation time was taken as the time period between the specimen reaching the annealing temperature and the start of the transformation. Thus the incubation time increases with the decrease in annealing temperature. These are listed in Table 4-1.

The kinetics of isothermal devitrification of amorphous alloys can be described by the Johnson-Mehl-Avrami (JMA) isothermal analysis [4.2-4.4]:

$$\alpha(t) = 1 - \exp[-(kt)^n] \quad (4.1)$$

Thermal characteristics associated with the crystallization temperature (T_x) and the activation energy (E_x) were examined at various heating rates. The crystallization temperature during the process was determined by intersection of the base line and extrapolation of the rise in heat flow signal. where, α is the volume fraction of transformation at time t , n is the Avrami exponent that reflects the mechanism of crystallization. The volume fraction of transformation at any temperature was determined as the ratio $A(t)/A(\text{total})$; where $A(t)$ and $A(\text{total})$ are the area and the total area of the isothermal exotherm, respectively.

The plots for crystallized volume fraction against time display a classical sigmoid shape, shown in Figures 4.1(a-2) and 4.1(b-2). The activation energy was evaluated from Arrhenius relation during crystallization process:

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \quad (4.2)$$

Figure 4.1. Comparison of amorphous alloys: (a) $\text{Ni}_{67.3}\text{Zr}_{36.3}$ and (b) $\text{Ni}_{30}\text{Zr}_{70}$ alloy; (-1) Isothermal DSC curves; (-2) crystallized volume fraction $[\alpha]$ as a function of time at different temperatures; (-3) the JMA plot from which the Avrami exponent $[n]$ is calculated; (-4) plot of $[\ln k]$ versus $[1/T]$, from which the activation energy for crystallization is obtained.

where, k is the rate constant, which is a function of the temperature (T) and the activation energy (E). From the rewritten Eq. (1), the values of k and n can be determined:

$$\ln[-\ln(1-\alpha)] = n \ln(k) + n \ln(t-\tau) \quad (4.3)$$

Table 4-1: Incubation times of amorphous Ni-Zr alloys at different annealing temperatures.

Ni-Zr alloy	Temperature, T (K)	Incubation time, τ (min)
Ni _{63.7} Zr _{36.3}	843	3.33
	838	4.47
	828	10.80
	823	17.72
Ni ₃₀ Zr ₇₀	653	2.41
	648	4.76
	638	8.87
	633	11.96

Table 4-2: Values of n in diffusion controlled growth.

Conditions	n
All shapes growing from small dimensions, increasing nucleation rate	>2.5
All shapes growing from dimensions, constant nucleation rate	2.5
All shapes growing from small dimensions, decreasing nucleation rate	1.5-2.5
All shapes growing from small dimensions, zero nucleation rate	1.5
Growth of particles of appreciable initial volume	1-1.5
Needles and plates of finite long dimensions, small in comparison with their separation	1
Thickening of long cylinders (needles) (e.g. after complete end impingement)	1
Thickening of very large plates (e.g. after complete edge impingement)	0.5
Precipitation on dislocations (very early stages)	~0.67

The plot of $\ln[-\ln(1-\alpha)]$ versus $\ln(t-\tau)$ yields a straight line with slope of n . where, τ is the incubation time. Such plots for amorphous Ni_{63.7}Zr_{36.3} and Ni₃₀Zr₇₀ alloys are shown in Figures 4.1(a-3) and 4.1(b-3) and the values of Avrami exponent, n at different temperatures are also described in the Figures. The value of n lies between 2.56 and 3.03 for eutectic Ni_{63.7}Zr_{36.3} alloy and the average value of n was calculated to be 2.82.

For near-eutectic Ni₃₀Zr₇₀ alloy, Avrami exponent was between 1.87 and 2.51 with an average value of $n = 2.24$. This indicates that most of the crystallization growth of both alloys is governed by three-dimensional growth. The Avrami exponent $n > 2.5$ for Ni_{63.7}Zr_{36.3} alloy indicates the growth of small particles with an increasing nucleation rate and $1.5 < n < 2.5$ for Ni₃₀Zr₇₀ alloy reflects growth of small particles with a decreasing nucleation rate [4.7]. Table 4-2 summarizes the values of Avrami exponent which may be obtained in various experimental situations.

The activation energies for transformation were evaluated by plotting $\ln k$ versus $1/T$. It is found that the activation energy ($E_x = 411.9$ kJ/mol) of the Ni_{63.7}Zr_{36.3} alloy is higher than that of the Ni₃₀Zr₇₀ alloy ($E_x = 383.7$ kJ/mol), implying easier crystallization transformation of Ni₃₀Zr₇₀ alloy than that of Ni_{63.7}Zr_{36.3} alloy.

4.1.A.2 Crystallization Kinetics: Non-isothermal Experiments

Non-isothermal crystallization experiments were also performed on $\text{Ni}_{63.7}\text{Zr}_{36.3}$ and $\text{Ni}_{30}\text{Zr}_{70}$ amorphous alloy samples to compare the activation energies. In this case DSC curves were obtained eight different heating rates, and the results are shown in Figure 4.2. For the eutectic $\text{Ni}_{63.7}\text{Zr}_{36.3}$ alloy, the onset temperatures of primary and secondary crystallization peaks were observed at $T_{x1}=852\text{ K}$ and $T_{x2}=867\text{ K}$, respectively, at a heating rate of 20 K/min . The primary crystallization peak of the alloy showed clearly at heating rates exceeding 2 K/min .

Table 4-3: Crystallization products of glassy Ni-Zr [4.8].

Initial alloy composition	Intermediate stages (if any)	Final products (900 K)
$\text{Ni}_{20}\text{Zr}_{80}$	$\omega\text{-Zr} + \text{glassy phase}$	$\alpha\text{-Zr} + \text{NiZr}_2$
$\text{Ni}_{24}\text{Zr}_{76}$		$\alpha\text{-Zr} + \text{NiZr}_2$
$\text{Ni}_{29}\text{Zr}_{71}$		$\alpha\text{-Zr} + \text{NiZr}_2$
$\text{Ni}_{33}\text{Zr}_{67}$		NiZr_2
$\text{Ni}_{36.5}\text{Zr}_{63.5}$	1. glassy phase 2. NiZr_2	$\text{NiZr}_2 + \text{NiZr}$
$\text{Ni}_{40}\text{Zr}_{60}$	1. glassy phase + NiZr_2 2. NiZr_2	$\text{NiZr}_2 + \text{NiZr}$
$\text{Ni}_{45}\text{Zr}_{55}$		$\text{NiZr}_2 + \text{NiZr}$
$\text{Ni}_{50}\text{Zr}_{50}$		NiZr
$\text{Ni}_{55}\text{Zr}_{45}$		$\text{Ni}_{11}\text{Zr}_9$
$\text{Ni}_{60}\text{Zr}_{40}$		$\text{Ni}_{10}\text{Zr}_7$
$\text{Ni}_{63.7}\text{Zr}_{36.3}$	$\text{Ni}_{10}\text{Zr}_7$	$\text{Ni}_{10}\text{Zr}_7 +$ Ni_2Zr
$\text{Ni}_{67}\text{Zr}_{33}$		Ni_2Zr
$\text{Ni}_{70}\text{Zr}_{30}$		Ni_2Zr

Altounian et al [4.8] reported the intermediate and final phases of Ni-Zr alloys and the results are summarized in Table 2-3. The first exotherm corresponds to the formation of $\text{Ni}_{10}\text{Zr}_7$ and the final crystallization products include $\text{Ni}_{10}\text{Zr}_7$ and the new Ni_2Zr structure. The near-eutectic $\text{Ni}_{30}\text{Zr}_{70}$ alloy clearly crystallizes by a two-stage process. Crystallization starts at a temperature (T_{x1}) of 676 K leading to second exothermic peaks (T_{p2}) at 688 K . The near-eutectic $\text{Ni}_{30}\text{Zr}_{70}$ alloy crystallizes directly into hexagonal $\alpha\text{-Zr}$ and NiZr_2 phases. Crystallization kinetics was examined, from obtained DSC curves at different heating rates using the Kissinger equation [4.9];

$$s = AT^2 \exp\left(\frac{-E}{kT}\right) \quad (4.4)$$

where s is the heating rate, and T is the characteristic temperatures, defined as T_x or T_p . Such The s/T^2 vs $1/T$ plots yield the activation energy at T_{x1} , T_{x2} , and T_{p2} ; these are shown in Figure 2.4 for the two alloys. The Arrhenius plot obtained for the near-eutectic $\text{Ni}_{30}\text{Zr}_{70}$ alloy the slope of the line yielded, $E_{x1}=353.3\text{ kJ/mol}$, which is lower than the value for the eutectic $\text{Ni}_{63.7}\text{Zr}_{36.3}$ alloy of $E_{x1}=374.1\text{ kJ/mol}$. The characteristic temperatures and activation energies for crystallization of the alloys are listed in Table 4-4. Generally, the onset crystallization temperature is strongly associated with the nucleation process and the peak temperature is related to the growth process. The values of activation energies for primary and secondary crystallization of $\text{Ni}_{63.7}\text{Zr}_{36.3}$ alloy are very close each other ($E_{x1}=374.1\text{ kJ/mol}$ and $E_{x2}=373.5\text{ kJ/mol}$, respectively).

Table 4-4: Characteristics temperatures for the crystallization of the binary Ni-Zr amorphous alloy and the corresponding activation energies obtained from Kissinger method

Ni-Zr alloys	Temperature T (K)	Heating rate, s (K/min)								E (kJ/mol)
		0.5	1	2	3	4	5	10	20	
Ni _{63.7} Zr _{36.3}	T _{x1}	-	-	818. 1	822. 8	827. 7	830. 3	841. 2	852. 0	374.1
	T _{x2}	810. 9	826. 7	835. 1	842. 9	846. 9	849. 8	858. 7	866. 6	373.5
Ni ₃₀ Zr ₇₀	T _{x1}	639. 0	647. 0	654. 2	657. 9	660. 5	662. 4	668. 9	676. 0	353.3
	T _{p2}	-	-	-	-	666. 4	669. 0	678. 1	688. 4	267.1

On the other hand, the value of activation energy for peak temperature of Ni₃₀Zr₇₀ alloy is much lower than that of onset crystallization temperature as listed in Table 4-4, implying that the nucleation process is more difficult than the growth process. The activation energies obtained through isothermal analysis are somewhat higher than the values obtained by the Kissinger equation although the two different equations reflected the same tendency for both alloys. This crystallization study of Ni-Zr alloys with different compositions has allowed us to obtain correlation in glass forming ability (GFA) and thermal property. As we observed, high crystallization temperature was obtained at eutectic composition in Ni-Zr system. Moreover, it was found that the activation energy is also higher than that of near-eutectic composition. These results indicate that the GFA can be improved by selecting eutectic compositions where nucleation rates are faster.

Higher values of crystallization temperature (T_x) and activation energy (E_x) of crystallization are observed at eutectic composition (Ni_{63.7}Zr_{36.3}) in case of binary Ni-Zr system. The values of E_x obtained from Johnson-Mehl-Avrami (JMA) analysis were slightly higher than those of alloys calculated by Kissinger method. The Avrami exponent *n* indicates that the main crystallization process of the binary Ni-Zr alloys is governed by three dimensional growth.

4. 1.B X-Ray Diffraction of Binary Alloy Membranes

4.1.B.1 XRD of Ni₆₄Zr₃₆ Amorphous Alloy Membrane

In-situ XRD was performed on the membrane to determine any prominent phase changes that occurred in the membrane while heating or cooling. XRD of the amorphous membrane was first carried out in-situ by heating quickly to 650 °C and then cooling to room temperature. Amorphicity of the membranes have been confirmed by the XRD measurements. These scans are shown in Figure 4.4 in which significant phase changes have been observed. The room temperature XRD has been compared to the high temperature XRD pattern. This is shown in Figure 4.5. At room temperature, an amorphous bump is observed. At 650°C, after treating with hydrogen, the material has crystallized and the shows peaks.

Figure 4.2. DSC curves of amorphous (a) $\text{Ni}_{63.7}\text{Zr}_{36.3}$ and (b) $\text{Ni}_{30}\text{Zr}_{70}$ alloys at different heating rates.

In-situ XRD was performed exactly as the H-D experiments were carried out. Figure V-6 shows the first heating cycle of the membrane sample to 300°C. Measurements were done at various temperatures and at each temperature, the sample was held for 10 minutes before heating again. The XRD pattern shows a slight transformation at 300 °C. The sample was then held at 300°C overnight and cooled to 100°C next day. The FigureV-7 shows the transformations observed during the cooling cycle. As is seen from the XRD partial crystallization of the membrane seems

Figure 4.3: Plot of s/T^2 against $1/T$ for the onset (T_x) and peak (T_p) temperatures of crystallization of amorphous (a) $\text{Ni}_{63.7}\text{Zr}_{36.3}$ and (b) $\text{Ni}_{30}\text{Zr}_{70}$ alloys.

Figure 4.4. (a) XRD scans of Ni-Zr binary at room temperature and 650°C (b) phase analysis of the XRD pattern at 650°C. Red lines indicate Ni (FCC) and blue lines indicate ZrO2 (FCC).

to occur. The peak was identified to belong to ZrO_2 . It shows the early formation of ZrO_2 . The

Figure 4.5. Heating (top) and cooling (bottom) cycles for $\text{Ni}_{64}\text{Zr}_{36}$ alloy.

Figure 4.6 shows the XRD pattern obtained during the heating cycle of the membrane. The membrane was held overnight at 400° C and then heated to 450° C. It was held overnight there to allow full transformation to occur. Peaks were more dominant after holding the membrane overnight at 450° C. The peaks were identified to be ZrO_2 and Ni. This could mean that Zr was preferentially oxidized. The Ni phase became more prominent and that may have increased catalytic activity. SEM and EDS was carried out to look at the surface of the material. The sample was then cooled to 25° C and the phases seem to have retained. Figure 4.6 shows the cooling cycle of the sample from holding overnight at 450° C to room temperature.

Figure 4.6. Heating and cooling cycle -2 for the $\text{Ni}_{64}\text{Zr}_{36}$ membrane.

The peak identification showed the presence of Ni and ZrO_2 phases in the sample. The identification was performed on the sample that was held overnight at 450° C. This is shown in Figure 4.4.

4.1.B.2 XRD of $\text{Ni}_{60}\text{Nb}_{40}$ Amorphous Alloy Membrane

XRD was carried for sample of $\text{Ni}_{60}\text{Nb}_{40}$ membrane. The membrane was confirmed to be amorphous. The initial heating and cooling showed amorphous phase. Figure 4.8 shows the heating cycle of the sample from room temperature to 400°C. The membrane was then cooled to room temperature. XRD pattern was obtained while no phase changes observed while heating or cooling. The membrane was then heated up to 550° C. The sample was then cooled to room temperature.

Heating to 550°C did not induce any phase transitions either. There may be minor re-orientation of atoms due to the temperature but that cannot be detected by XRD. Other surface methods like XPS should be used to detect those changes. There is a possibility of amorphous to amorphous transition in the sample. Further work in this aspect can be carried out. The sample was then cooled to 25°C and the XRD of the process is shown in Figure 4.9.

Figure 4.7. Highlights of XRD trend with change in temperature for $\text{Ni}_{64}\text{Zr}_{36}$ in a 3-D plot.

4.1.B.3. XRD of $\text{Ni}_{60}\text{V}_{40}$ Amorphous Alloy Membrane

In-situ XRD of the membrane was carried out by heating the alloy from room temperature to 650°C. The patterns were recorded while the heating was performed. The alloy was cooled to room temperature while recording the XRD pattern every 50°C interval

The cooling and heating XRD have not shown any change in the phases. However, a peak appears at low temperature that seems to disappear at 650°C. This is shown in Figure 4.10. The possible explanation of that could be that a residual phase exists at low temperature when the alloy was fabricated. There is a chance that there is residual nickel that could be remaining during the quench process. It is known to be common to observe non-equilibrium structures in a fast quench process like melt spinning. During processes like this, the atoms form non-stoichiometric phases, like Ni_3V and some residual phase. When the XRD pattern was fitted, Ni was found to be well matched as shown in Figure 4.11. This can be seen in the Ni-V phase diagram

Figure 4.8. Heating and cooling cycles for $\text{Ni}_{60}\text{Nb}_{40}$ membrane.

Figure 4.9. Cooling of $\text{Ni}_{60}\text{Nb}_{40}$ from 550° C to RT.

Figure 4.10. In-situ XRD pattern of heating (left) and cooling (right) of $\text{Ni}_{60}\text{V}_{40}$ alloy.

Figure 4.11. RT and 650° C comparison of XRD pattern. Ni pattern overlay on Ni-V XRD pattern.

A closer look at the phase diagram till 40% V section is shown in Figure 4.12. It shows that there is a good possibility that the path followed by the atoms while quenching might have been to

form Ni_3V and Ni. The fabrication of membranes is done in few minutes and there is a good chance that the atoms do not get enough time to make stable compositional phases. It is possible that the Ni has formed a solid solution with V atoms. Since, Ni is more in content than V, in RXD only Ni peaks are shown in the pattern. An overlay of the peaks on the XRD pattern shows that the peaks match. The extra peak that is visible at low temperatures disappears on heating. This could be associated with low temperature Ni that mixes itself with solid solution at high temperature, merging with the peak next to it at $42^\circ 2\theta$.

Figure 4.12. Phase diagram for Ni-V system and a schematic of melt spinning apparatus [4.10-4.11].

4.1.C Hydrogen-Deuterium (H-D) Exchange Studies on Ni and Ni-based Binary Alloy Membranes

Experiments were carried out to understand the surface phenomena of the membranes. Series of experiments were carried out where the H_2 and D_2 gases were reacted on the membrane surface in a packed bed and the production of HD was measured. The measured parameters were then used to develop a kinetic model to for the determination of energy barriers of chemisorptions on the surface. To complement the HD interaction studies, In-Situ XRD was carried out to determine the possible phase transitions during the process. SEM and TEM images were gathered to clearly determine the phase transitions. Supplementary tests were carried out on Ni-V and Ni-V-Zr alloys for hydrogen absorption in the bulk. The characteristics of bulk are also very important to consider when surface studies are performed. The results have been discussed based on each material. Ni was used as a standard before the amorphous membranes were run in the scrambling rig.

4.1.C.1 Hydrogen-Deuterium Exchange Studies on Ni

Pure Ni foil was cut into small pieces and filled in the reactor, as discussed in the experimental section. Hydrogen and deuterium gases were passed through the mass flow meters at 10mL/min. The reactor was purged with nitrogen before and after each run to ensure there was no oxygen or other impurity gases present. Before introducing deuterium, the reactor was flushed with hydrogen to ensure all the nitrogen had been flushed out. The purpose of using Ni was to conduct a baseline experiment. The sample was heated to 425° C where full conversion was observed. Then the reactor was cooled to room temperature and the HD flow rate flowing out of the reactor was measured. The mass spectrometer measured the HD production as a % in the total gas stream which is then converted to partial pressure followed by volumetric flow rates. Figure 4.13 shows the variation of HD flow rate as a function of temperature for Ni.

The trend of the plot obtained by Ni is comparable with the plots obtained by O'Brien et al [4.12] for Pd and Pd-Cu based alloys. Hence, a similar method for modeling was taken to determine the adsorption energy barrier for Ni and other materials. As is expected, as the temperature is reduced, the HD production rate decreases.

Eutectic shows the phase diagram of Ni-Zr system. The alloy composition of Ni₆₄Zr₃₆ was chosen to study for its surface and bulk properties. Amorphous ribbons compositions from rapid solidification techniques. Moving away from the eutectic is more convenient to make around eutectic compositions.

Figure 4.13. Experimental HD flow rate vs Temperature of Ni as the temperature is decreased.

Eutectic composition of Ni₆₄Zr₃₆ was chosen to study for its surface and bulk properties. Amorphous ribbons are more convenient to make around eutectic compositions from rapid

solidification techniques. Moving away from the eutectic compositions makes it harder for the alloys to become glassy.

H-D Modeling on Metallic Ni

When modeling was performed for Ni, a smooth plot was observed, matching with the trend observed by O'Brien et al [4.13] in their study of H₂ adsorption in Pd-Cu alloys. Figure 4.14 shows a comparison of modeled and experimental flow rate of HD obtained by Ni catalyst. The

Figure 4.14. Modeled and experimental HD flow rates for Ni.

Figure 4.15. Total coverage for pure Ni membrane.

catalyst coverage is plotted as a function of temperature (Figure 4.14), showing an increase in total coverage at lower temperature. The optimized values were obtained for the fitting parameters $\ln(\vartheta_{ads})$, $\ln(\vartheta_{des})$, E_{ads} and E_{des} . The optimized values for Ni are as follows:

$\ln(\vartheta_{ads}) = -2.9 \text{ mol/m}^2\text{/s/Pa}$, $\ln(\vartheta_{des}) = 8.5 \text{ mol/m}^2\text{/s}$, $E_{ads} = 0.04\text{eV}$ and $E_{des} = 0.55\text{eV}$. The total activation energy of adsorption is $\Delta E_{ads} = E_{ads} - E_{des} = -0.51\text{eV}$.

4.1.C.2 Hydrogen-Deuterium Exchange Studies on $\text{Ni}_{64}\text{Zr}_{36}$

The $\text{Ni}_{64}\text{Zr}_{36}$ membrane was cut into pieces after cleaning its surface in the sonic bath. The catalyst was packed into the quartz reactor tube and heated. Initial flushing of the reactor was done by using nitrogen. The reactor was flushed with nitrogen till the mass spectrometer showed strong peak for nitrogen and no peaks for oxygen. The sample was $\sim 7\text{cm}^2$ that was filled into the reactor. The reactor was flushed with nitrogen before and after the experiments. Then, 10mL/min of H_2 and D_2 were injected into the reactor. The temperature of the reactor was heated step-wise to 300°C and cooled to room temperature. A change in the HD formation was observed. This can be due to the cleaning of the surface that could have happened at high temperature under the presence of hydrogen.

Figure 4.16. Heating and cooling cycle of the $\text{Ni}_{64}\text{Zr}_{36}$ binary membrane. HD flow rate plotted against Temperature.

The sample was heated to 400°C and then to 450°C . It took 2 days for the stabilization in the HD formation rate. The sample was heated again and was held at 450°C overnight. After stability was reached, the temperature was ramped down in steps of 25°C . Readings were taken after stabilization. There was an impact of time on the final data obtained as well. The temperature was brought down and the following plot was obtained for HD flow rate versus temperature.

The Figure 4.17 shows the comparison between the HD flow rate obtained from amorphous alloy and crystalline alloy. The cooling cycles of the results have been plotted. Cooling data is more reliable than the heating data, since the surface has been cleaned and the results will be more appropriate. The change can be seen as a function of time when the heating of the sample was performed from 400°C to 450°C. This is of key importance to know how the transition has occurred overnight. Heating process has been shown in the Figure 4.17. This was a non-steady state process where the HD flow rate was constantly being recorded as the heating was being performed. As can be seen the HD flow rate increased by just holding the temperature at 400° C. This can be due to certain structural changes that could occur in the material. Full conversion was obtained at 450° C and as the temperature was reduced, the HD flow rate also reduced. The possible structural changes were determined by in-situ XRD.

Figure 4.17. HD flow rate versus temperature for Ni₆₄Zr₃₆ binary alloy.

4.1.C.3 Hydrogen-Deuterium Exchange Studies on Ni₆₀Nb₄₀

A 1200mm² amorphous alloy was cut into small pieces and was filled in the reactor tube. The membrane was heated to 400 °C and was left overnight. The sample was cooled to 150 °C before heating it directly to 550° C. The sample was left overnight at this temperature and then cooled. Figure 4.18 shows the HD flow rate versus the temperature plot.

The Figure 4.19 shows the comparison between the sample after it had been kept overnight at 550 °C to that of the sample when it was just heated to 300°C. This shows an improved HD flow rate when the sample was heated overnight at 550°C. Then the temperature was subsequently decreased and HD flow rate was measured. The HD flow rate seems to fluctuate when holding

the sample at certain intermediate temperature overnight. While cooling at 300 °C, there were few power failures in the lab that did not allow the HD flow rate to stabilize at that temperature. This is the last point on the cooling curve. It will not be unfair to neglect this point for modeling purposes. It can be seen that the HD flow rate at 550° C after conditioning of the membrane is almost full conversion.

Figure 4.18. HD data obtained by first cooling of $\text{Ni}_{60}\text{Nb}_{40}$ alloy after heating till 650K.

Figure 4.19. HD flow rate vs Temperature for a $\text{Ni}_{60}\text{Nb}_{40}$ alloy.

H-D Modeling of Ni₆₀Nb₄₀ Amorphous Membrane

We now discuss Ni₆₀Nb₄₀ alloy; HD flow rates (after the heat treatment) were modeled using the kinetic model developed. Figure 4.20 shows a comparison of these data with the model; the R^2 value for this fit is 0.97. Figure 4.21 shows the total surface coverage obtained for Ni₆₀Nb₄₀ versus temperature.

The fit was obtained by minimizing the error between the measured and the modeled flow rates

Figure 4.20. The modeled and experimental HD flow rate for Ni₆₀Nb₄₀ amorphous membrane.

Figure 4.21. Total coverage of the HD for Ni₆₀Nb₄₀.

by changing the fitting parameters $\ln(\vartheta_{ads})$, $\ln(\vartheta_{des})$, E_{ads} and E_{des} . The optimized values for Ni-Nb system are as follows: $\ln(\vartheta_{ads}) = -9.09$ mol/m²/s/Pa, $\ln(\vartheta_{des}) = 7.88$ mol/m²/s, $E_{ads} = 0.33$ eV and $E_{des} = 0.71$ eV. The total activation energy of adsorption is $\Delta E_{ads} = E_{ads} - E_{des} = -0.376$ eV.

The total coverage was determined by using the optimized values of the pre-exponential factors and the individual activation barriers. It is found that the coverage is the highest at 623 K that decreased as the temperature was increased, as is expected. It is also observed that the adsorption energy for H₂ on the surface of Ni-Nb alloy is lower is compared to desorption energies.

4.1.C.4. Hydrogen-Deuterium Exchange Studies on Ni₆₀V₄₀

Ni₆₀V₄₀ membrane was cut into small pieces and filled in the reactor. Hydrogen and deuterium gases were flown over the catalyst in the reactor. The catalyst was heated to 250° C and then cooled to 100° C. Then the sample was heated to 550° C and cooled to room temperature. HD measurements were taken during this process. As can be seen from Figure 4.20, the membrane was cooled from 250° C and then heated to 550° C and then cooled to room temperature. HD flow rates were recorded during the cooling process.

The results show that a lower HD production rate was observed at lower temperatures. When the membrane was heated and left overnight, the HD formation rate increased and almost full conversion was observed. This may be due to the reduction of oxide from the surface. The membrane was cooled and HD formation rates were measured. A nice trend was observed for the HD flow rate from 450 °C to 100°C. The high temperature points are not joined since leaving the membrane overnight in the reactor at 700 K caused changes that increased and then decreased the subsequent measurement. This phenomenon still needs to be explained.

Figure 4.20 HD exchange data for Ni₆₀V₄₀ alloy at low temperatures and high temperatures combined.

H-D Modeling of Ni₆₀V₄₀ Amorphous Membrane

The activation energies were comparable to that of Ni-Nb. The Figure 4.22 shows the comparison between the modeled and the experimentally measured flow rate of HD for Ni₆₀V₄₀ was used as a catalyst in the fluidized bed. The minimization of error between both the flow rates, resulted in the parameters as follows: $\ln(\vartheta_{ads}) = -4$ mol/m²/s/Pa, $\ln(\vartheta_{des}) = 8$ mol/m²/s, $E_{ads} = 0.3$ eV and $E_{des} = 0.7$ eV. The total activation energy of adsorption is $\Delta E_{ads} = E_{ads} - E_{des} = -0.4$ eV. The total energy change of adsorption was comparable to that of Ni-Nb system. The total surface coverage was determined by using the optimized values mentioned above. The plot for the surface coverage as a function of temperature is shown in Figure 4.22 below.

The highest coverage is approximately “one” at lowest temperatures, indicating H or D monolayer adsorption fully covered by the gas molecules.

Figure 4.21 Experimental and modeled of Ni₆₀V₄₀ membrane.

Figure 4.22 Total coverage of Ni₆₀V₄₀ membrane.

4.1.D SEM/ TEM Results of Ni₆₄Zr₃₆ Amorphous Membrane

The XRD data presented below helps to connect the phenomena of this change to material characteristics. From the XRD it was determined that the membrane crystallized after being heated to 450°C. It is possible that the rearrangement of atoms and preferential oxidation of Zr and possible cluster formation of Ni may have enhanced the catalytic activity of the sample. The TEM images have shown that the membrane sample is not entirely amorphous and some parts of the membranes are crystalline. These could be nanocrystals of ZrO₂ phase. Figure 4.25 shows the TEM image obtained on an as-spun Ni₆₄Zr₃₆ sample. TEM and SEM images were gathered for as spun ribbons and for the in-situ XRD treated membranes. This was done to replicate the effect the membrane had in the HD scrambling reactor. Another TEM image of the as-spun ribbon that was obtained showed the clusters of crystalline material in a possible amorphous matrix.

Scanning Electron Microscopy and EDS was carried out these samples to look at the surface morphology and to determine the chemical composition of the sample.

After the treatment of the sample, SEM images were gathered that are shown in Figure 4.23.

Figure 4.24 shows the image of the Ni₆₄Zr₃₆ sample after it was taken out of the XRD equipment

Figure 4.23 SEM image of the Ni₆₄Zr₃₆ sample after the H₂ treatment.

after being heated under hydrogen. Some possible plastic deformation is observed of the ribbons that can be due to rapid cooling of the membrane material causing residual stresses. Some more SEM images with line scan can be seen in Figure 4.25. Further TEM analysis was carried out to determine the crystal structure differences in the membrane after the treatment with hydrogen. It was compared with the TEM images obtained on the as-cast membrane. As can be seen in Figure 4.24, there are nano sized crystalline structures. But mostly the membrane is amorphous and hence the XRD pattern that showed an amorphous bump.

After the membrane was heated in XRD under hydrogen, crystallization had taken place. To determine the phases, this membrane was imaged using TEM as well. More crystalline nature was observed. Figure 4.26 shows the TEM diffraction pattern of a treated $\text{Ni}_{64}\text{Zr}_{36}$ sample. The images showed more crystallinity than before. More discussion about the crystal structure and correlation to XRD will be discussed in later sections.

Figure 4.24 SEM image and EDS line scan of Ni-Zr binary ribbon after H_2 treatment- Blue- Zr, Green – Ni and Red – O.

Figure 4.25 TEM images of after treatment of $\text{Ni}_{64}\text{Zr}_{36}$ sample. HCP structure and FCC structures are observed.

Figure 4.26 TEM image of the received Ni-Zr samples. Image shows crystalline clusters mostly amorphous background.

The results of the morphological studies (using SEM) on the ribbons show an interesting change in the structure after the crystallization; clusters were formed after the heating process (described in the experimental section). Figure 4.27 shows XRD before and after treatment. The SEM images show the ribbon (before treatment in amorphous condition) on left. The two images on the right are of the ribbons after hydrogenation a different morphology, with possible clusters of Ni and ZrO₂.

Figure 4.27 XRD, SEM and EDS correlation for Ni₄₄Zr₃₆ membrane as-spun and after treatment.

The TEM samples are thinned significantly by ion-milled/plasma cleaned; removing the oxide layer, thus, presence of metallic Ni and Zr is plausible. The TEM pattern in Figure 4.28 shows amorphous pattern with single crystal spots. We have superimposed Debye rings on the pattern to show different zones. The d- spacing match Ni (FCC) and Zr (HCP) for the selected area.

The d-spacing for Ni and Zr are given as follows:

Ni – $d_{111} = 0.203\text{nm}$, $d_{200} = 0.176\text{nm}$, $d_{020} = 0.176\text{nm}$, $d_{220} = 0.124\text{nm}$

Zr – $d_{0002} = 0.257\text{nm}$, $d_{1010} = 0.280$, $d_{0110} = 0.280\text{nm}$, $d_{0111} = 0.245\text{nm}$

The electron diffraction of the pre-treated $\text{Ni}_{64}\text{Zr}_{36}$ samples, as mentioned before showed scattered nano-crystalline structures. The electron diffraction patterns obtained are showed in Figure 4.29

Figure 4.28 TEM pattern of a small area of $\text{Ni}_{64}\text{Zr}_{36}$ sample.

The projection plane is (220). The d-spacing is well matched with d-spacing for Ni (FCC) on (220) projection plane. (002) and (00-2) are four-fold symmetry while (-111), (1-11), (-11-1) and (1-1-1) are three fold symmetry. It may be deduced that during the melt spinning process the alloy crystallized to some degree

Figure 4.29 TEM diffraction pattern for pre-treated $\text{Ni}_{64}\text{Zr}_{36}$ alloy showing amorphicity coexisting with some crystalline nature. Analysis of phase determination.

4.2 Crystallization, Permeation, and Surface Kinetic Studies on Ni-based Ternary Alloys

4.2.A Phase Transformation and Crystallization Kinetics Studies on $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$

The glass transition and crystallization kinetics of melt-spun $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ amorphous alloy ribbons have been studied under non-isothermal and isothermal conditions using differential scanning calorimetry (DSC). The dependence of glass transition and crystallization temperatures on heating rates was analyzed by Lasocka's relationship. The activation energies of crystallization, E_x , were determined to be 499.5 kJ/mol and 488.6 kJ/mol using the Kissinger and Ozawa equations, respectively.

The Johnson-Mehl-Avrami equation has also been applied to the isothermal kinetics and the Avrami exponents are in the range of 1.92-2.47 indicating a diffusion-controlled three-dimensional growth mechanism. The activation energy obtained from the Arrhenius equation in the isothermal process was calculated to be $E_x = 419.5$ kJ/mol. The corresponding three dimensional time-temperature-transformations (TTT) diagram of crystallization for the alloy has been drawn which provides the information about transformation at a particular temperature. In addition, the intermetallic phases and morphology after thermal treatment have been identified by X-ray diffraction (XRD) and scanning electron microscope (SEM).

4.2.A.1 Glass Transition and Crystallization of $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$

Figure 4.30 shows normalized DSC profiles obtained for amorphous $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy at various heating rates. Glass transition temperature (T_g) was determined from the intersection of

the extrapolated straight line of initial change in the baseline slope of the corresponding glass transition region [4.14-4.15]. The glass transition temperature shifts to higher temperatures with increasing heating rates and occurs at a temperature slightly below crystallization temperature (T_x) as shown in Figure 4.30.

Figure 4.30. DSC curves of the $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ amorphous alloy at different heating rates.

While the crystallization of amorphous $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy is detected at all heating rates, the glass transition shows only at heating rates exceeding 10 K/min. The experimental observation of T_g is reported to be difficult at low heating rates for some materials [4.14, 4.16]. On the other hand, the T_g can be estimated by Lasocka's relationship [4.17] with the dependences of T_g and T_x on the heating rates (s):

$$T_g = A_g \log(s) + B_g \quad (4.5)$$

and

$$T_x = A_x \log(s) + B_x \quad (4.6)$$

where, A_g , A_x , B_g and B_x are constants for a given glass composition. T_g and T_x can be expressed as a linear combination of equation (3.1) and (3.2):

$$T_g = \left(\frac{A_g}{A_x} \right) T_x + \left(\frac{A_x B_g - A_g B_x}{A_x} \right) \quad (4.7)$$

Therefore, the relation for $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy is obtained:

$$T_g(K) = 2.48T_x - 1369.65 \quad (4.8)$$

Figure 4.31 shows typical plots of T_g and T_x versus $\ln s$ for the amorphous $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy. It is clearly found that both T_g and T_x linearly increase with increasing heating rate. The glass transition kinetics can also be explained by evaluating the intersection of the two extrapolated curves. T_g is significantly raised by increasing heating rate than that of T_x , resulting in high value of s . The intersection temperature (T_c) is 925 K, indicating $T_x^* < T_c$ for $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy: T_x^* is the crystallization temperature at low heating rates (1-10 K/min). This is an indication of the kinetics of less-stable metallic glass, dominated mainly by atomic mobility or diffusion rather than viscous behavior [4.18].

Figure 4.31. Dependence of the glass transition (T_g) and crystallization (T_x) temperature for the $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ amorphous alloy as a function of the logarithm of scanning rate (s).

The supercooled liquid region of an amorphous alloy ($\Delta T_x = T_x - T_g$) is one of the parameters for GFA of the alloys. Although the ΔT_x is not a direct measure of the GFA of the alloy, alloys having large ΔT_x could lead to the satisfaction of high GFA. The $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy exhibits larger ΔT_x than 50 K, resulting in excellent atomic diffusivity and absorption rate in the supercooled liquid state. Table 4.5 lists the results of thermal analyses (T_g and T_x), supercooled liquid region ($\Delta T_x = T_x - T_g$) and the respective heat release (ΔH) for crystallization determined from the DSC curves at various heating rates.

Table 4.5. Characteristic temperatures and heat released for the crystallization of the $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ amorphous alloy at different heating rates.

Heating (K/min)	rate	1	2	3	4	5	10	15	20
T_g (K)		-	-	-	-	-	791.68	802.59	812.50
T_x (K)		844.18	851.71	856.44	859.97	862.83	871.63	876.24	879.77
ΔT_x (K)		-	-	-	-	-	79.95	73.65	67.27
ΔH (Jg ⁻¹)		-49.79	-55.35	-58.43	-59.10	-61.55	-57.23	-59.78	-51.06

4.2.A.2 Crystallization kinetics: Non-isothermal DSC Experiments of $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$

As seen from Figure 4.27, all DSC curves exhibit one exothermic peak corresponding to the single stage of crystallization in the $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy and this temperature shifts to higher temperatures with an increase in the heating rate. The activation energy of crystallization (E_x) of the $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy can be determined by using the Kissinger equation:

$$\ln\left(\frac{s}{T_x^2}\right) = -\left(\frac{E_x}{RT_x}\right) + \text{const.} \quad (4.9)$$

where s is the heating rate, E_x is the activation energy, R is the gas constant and T_x is the crystallization temperature. Figure 4.32 shows the plot of $\ln(s/T_x^2)$ vs $1/T_x$ and the value of the apparent activation energy is determined as 499.5 kJ/mol. It is generally known that the activation energies for the same alloy system exhibit different values if different analyses equations are utilized, which can be attributed to the different approximations in the models. To compare the activation energy with non-isothermal analysis, the widely used Ozawa's equation can be invoked, which is as follows:

$$\ln s = -1.0516 \frac{E_x}{RT_x} + \text{const.} \quad (4.10)$$

where s and E_x are the heating rate and activation energy, respectively. Similarly, a plot of $\ln s$ against $1/T_x$ yields an approximate straight line with a slope of $-E_x/R$. According to the Ozawa method, the activation energy for crystallization of amorphous $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy is estimated to be 488.6 kJ/mol. The apparent activation energy for crystallization obtained by Kissinger analysis is somewhat lower than the value of a binary $\text{Ni}_{60}\text{Nb}_{40}$ alloy [4.19] but, much larger than that of $\text{Zr}_{76}\text{Ni}_{24}$ alloy [4.20]. This indicates that the substitution of Zr in the Ni-Nb alloy system may reduce the thermal stability due to the chemical inhomogeneity related with positive mixing enthalpy between Nb and Zr [4.21].

Figure 4.32. Kissinger and Ozawa plots of the $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ amorphous alloy for crystallization.

4.2.A.3 Crystallization Kinetics: Isothermal DSC Experiments of $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$

In order to consider a crystallization mechanism, the isothermal kinetics of crystallization of $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ amorphous alloy was studied at different temperatures between T_g and T_x established from the non-isothermal analysis. The corresponding DSC curves are presented in Figure 4.33. Similar to previous results at continuous heating, all DSC curves exhibit a single

Figure 4.33. Isothermal DSC curve of melt-spun $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy at different temperatures.

exothermic peak after a certain incubation period. It shows that the incubation time (τ) increases with decrease in annealing temperature. The crystallized volume fraction is determined by measuring the partial area of the peak during crystallization procedure which can be plotted in terms of time as shown in Figure 4.34.

It is clearly seen that the curves display a classical sigmoid shape for crystallized volume fraction versus time under isothermal annealing condition. The isothermal solid-state transformation crystallization kinetics of amorphous alloys is generally studied by the Johnson-Mehl-Avrami (JMA) equation:

$$\alpha(t) = 1 - \exp[-k(t - \tau)^n] \quad (4.11)$$

where α is the crystallization fraction, n is the Avrami exponent, which reflects the mechanism of nucleation and growth process during crystallization, k is a reaction rate constant, which has Arrhenius behavior with respect to temperature during crystallization process:

$$k(T) = k_0 \exp\left(-\frac{E_x}{RT}\right) \quad (4.12)$$

where k_0 is the pre-exponential factor, E_x is the effective activation energy for crystallization, R is the universal gas constant, and T is the absolute temperature. The values of n and k can be determined using the relationship:

$$\ln[-\ln(1 - \alpha)] = n \ln k + n \ln(t - \tau) \quad (4.13)$$

The values of the Avrami exponent n and the reaction constant k are calculated from the plot of $\ln[-\ln(1 - \alpha)]$ versus $\ln t$ on the basis of the slope and intercept of the straight line.

Figure 4.34. The crystallized fraction α as a function of time at different annealing temperatures.

Figure 4.35. The JMA plot of $\ln[-\ln(1-\alpha)]$ versus $\ln t$ at different temperatures. The Avrami exponent n is calculated.

The variation of Avrami exponents at different annealing temperatures for $0.1 < \alpha < 0.9$ is from 1.93 to 2.47 as shown in Figure 4.35, which can be interpreted as transformation kinetics under isothermal conditions. The nucleation rate is found to be constant at $n=2.5$. But, as the value of n decreases between 1.5 and 2.5, the kinetics is diffusion-controlled with all shapes growing from small dimensions [4.22]. The plot of $\ln k$ versus $1/T$, which presents a straight line with a slope E_x/R , gives the value of the activation energy as shown in Figure 4.36. According to Eq. (3.8), the activation energy for crystallization is $E_x=419.5$ kJ/mol, which is smaller than those calculated by the Kissinger's (499.5 kJ/mol) and Ozawa's (488.6 kJ/mol) equations.

Figure 4.36. Plot of $\ln k$ versus $1/T$ for the isothermal crystallization in melt-spun $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy.

Figure 4.37 shows the time required at a given temperature for the peak of crystallization to occur for binary Ni-Zr and ternary $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloys, derived from isothermal measurements. Of those alloys examined, the $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ clearly has the highest temperature to crystallization, which is expected from the substitution of a refractory element. Moreover, the Nb addition on the Ni-Zr alloys improves the long-term resistance to crystallization. We have plotted isothermal transformation curves and TTT diagram for the $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy to summarize our results, as shown in Figure 4.37. TTT diagram is a plot of temperature versus the crystallization time of the membrane. It provides important information to estimate when transformations begin at a particular operating temperature and what percentage of crystallization is achieved.

Figure 4.37. Time-Temperature-Transformation (TTT) curves of Ni-Nb-Zr alloys, derived from isothermal differential scanning calorimetry measurements. Experimental points represent the peak of crystallization at each temperature.

The experimental points for the 5, 50, and 95% transformed crystallization at different annealing temperatures are shown in Figure 4.35(a). The solid lines represent optimal curve fittings of the data with an exponential decay formula ($T = T_0 + A_1 e^{-x/t_1} + A_2 e^{-x/t_2}$), where T_0 indicates the offset temperature which may be the maximum operating temperature of the membrane. The T_0 values for transformed crystallization of the $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy are 841, 840, and 839 K, respectively and the crystallization will start above these temperatures. The TTT diagram shows the amount of transformation as a function of temperature and time in Figure 4.38(b).

Figure 4.38. T-T-T diagram for the $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy; (a) T vs. t , (b) 3-D TTT diagram, and (c) t vs. α showing relationship between different parameters.

4.1.A.4 Phase Transformation of $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$

The amorphous structure of the $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy prepared by melt-spinning was investigated by X-ray diffraction. Phase transformations in the amorphous $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy induced by heat treatment were identified in XRD patterns of the ribbon after the crystallization process as shown in Figure 4.39. Results showed the amorphous to crystalline transformation was achieved. The XRD patterns of the amorphous ribbons before and after heating are shown in Figure 4.36(a) and 4.39(b), respectively.

The diffraction pattern of the amorphous ribbons in as-received condition mainly consists of a broad peak and no appreciable diffraction peaks corresponding to any crystalline phases are detected, indicating the amorphous nature of the melt-spun alloys as shown in Figure 4.36(a). The XRD pattern of the crystallized ribbon of $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ shown in Figure 4.36(b) matched the orthorhombic structure (space group $\text{C2}_1\text{na}$ and $Z=4$) of the $\text{Ni}_{10}\text{Zr}_7$ pattern with a small change in lattice parameter. It appears that $\text{Ni}_{10}\text{Zr}_7$ (JCPDS Card #: 47-1027) has an intermediate type compound structure which can vary in composition. Evdokimova's ternary Ni-Nb-Zr phase diagram at 800°C showed a single phase region with large solid solubility ~ 30 at.% Zr [4.23]; this phase diagram [4.23] is shown in Figure 4.40 for reference. The lattice parameters of $\text{Ni}_{10}\text{Zr}_7$ were reported by Kirkpatrick et al. [4.24] as $a_0 = 12.386 \text{ \AA}$, $b_0 = 9.156 \text{ \AA}$, $c_0 = 9.211 \text{ \AA}$, and $\text{vol} =$

1044.58 Å³. Our lattice parameters of the heated ribbon sample are: $a_0 = 12.42(0.03)$ Å, $b_0 = 9.09(0.02)$ Å, $c_0 = 9.19(0.02)$ Å, and $\text{vol} = 1037.53(4.07)$ Å³. This small change of 0.7% reflects partial substitution of the larger Zr atoms with smaller Nb atoms ($\text{Nb}_{\text{atomic radius}} = 1.429$ Å and $\text{Zr}_{\text{atomic radius}} = 1.6025$ Å) [4.25].

Also shown in the insets of Figure 4.39(a) and 4.39(b) are scanning electron micrographs (SEM) of the ribbons' microstructures, both before and after heating, indicating that the thermal treatment leads to the phase transformation and the morphology change of the amorphous Ni₆₀Nb₂₀Zr₂₀ alloy. The grain size of the crystallized orthorhombic structure is determined to be ~50 nm after the heat treatment.

Figure 4.39. X-ray diffraction patterns and SEM images (inset) of (a) the Ni₆₀Nb₂₀Zr₂₀ ribbons in as-received condition, (b) after temperature scans up to 800 °C with heating rate of 10 °C/min.

The activation energy for crystallization of melt-spun Ni₆₀Nb₂₀Zr₂₀ amorphous alloy is $E_x=419.5$ kJ/mol. The Avrami exponent n , between 1.92-2.47, indicates that the main crystallization process of this alloy is governed by three-dimensional growth. Whereas, using non-isothermal methods of Kissinger and Ozawa yielded activation energies of 499.5 kJ/mol and 488.6 kJ/mol, respectively. Thus, depending on the methodology of experiments and models used, the activation energy of amorphous Ni₆₀Nb₂₀Zr₂₀ alloy is in the range of 420-500 kJ/mol. Although glass transition in the alloy is only observed at higher heating rates, the T_g can be estimated by Lasocka's relationship. The final crystallization product of the amorphous Ni₆₀Nb₂₀Zr₂₀ alloy was an orthorhombic Ni₁₀Zr₇ type structure with a slightly smaller unit cell volume. Structural

analyses indicate that lattice parameters reduced slightly by the addition of Nb substituting for Zr site in this ternary alloy system

Figure 4.40. The ternary phase diagram of Ni-Nb-Zr [4.14]. The $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloy was fabricated by melt-spinning technique.

4.2.B Hydrogen permeability and crystallization kinetics in amorphous Ni-Nb-Zr amorphous alloy membranes

Amorphous Ni-based alloys show great promise as inexpensive, hydrogen-selective membrane materials. One of the main barriers to the commercial uptake of these materials is their tendency to crystallize during long-term operation at elevated temperatures, a process which decreases both strength and permeability. In this study, the crystallization kinetics of a series of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x = 0, 10, 20$ or 30 at.%) amorphous alloy membranes were examined by thermal analyses under isothermal and non-isothermal conditions. The activation energy of crystallization and the crystallization mechanism for ternary Ni-Nb-Zr alloys were investigated. The Kissinger and Ozawa methods were applied to the non-isothermal kinetics derived from the heating rate dependence of the crystallization temperature.

The hydrogen permeation properties of the Ni-Nb-Zr membranes were investigated over the 573-673 K temperature range at different hydrogen partial pressures. The linear relationship between the hydrogen permeation flux and the hydrogen partial pressure difference across the membrane indicates that permeation was controlled by diffusion through the bulk membrane. The effect of Zr concentration on the hydrogen permeability and the thermal stability was also investigated. The hydrogen permeability improved while the thermal stability decreases with the addition of Zr.

4.2.B.1. Crystallization Kinetics of Ni-Nb-Zr Amorphous Alloy Membranes

It is known that the thermal stability of the amorphous alloys can be improved by inclusion of refractory metals such as, Hf, Ta, Mo, W, Nb [4.23]. In this study, Nb was alloyed with Ni-Zr system and the crystallization behavior of amorphous $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ alloy ribbons were made with compositions ranging from, $x=0, 10, 20$ and 30 alloys and examined non-isothermal scanning DSC. DSC thermograms of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where 'x' ranges from 0 to 30) with heating rate of 10 K/min are shown in Figure 4.38 (middle diagram). The crystallization temperatures were determined by intersection of the base line and extrapolation of the rise in heat flow signal and the primary and secondary exotherms are marked with blue hatch and red cross patterns, respectively.

In $\text{Ni}_{60}\text{Nb}_{40}$ alloy ($x=0$), the crystallization starts at a temperature of 909 K leading to two distinct exothermic peaks and third almost no noticeable small peak. Therefore, only primary and secondary exotherms are marked with blue hatch and red cross patterns, respectively. The alloy $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ with the addition of 10 at% Zr exhibited two broad exothermic peaks. Similar results are obtained for the $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{80}\text{Zr}_{20}$ and $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ alloys, but the peaks appear sharp. The onset temperatures of primary (T_{x1}) and secondary crystallization (T_{x2}), decreased continuously with increasing Zr concentration. The decrease in the crystallization temperature of the $\text{Ni}_{60}\text{Nb}_{40}$ alloy on addition of Zr implies a definite loss in thermal stability. DSC thermograms that were obtained at different heating rates are shown Figure 4.38(a)-(d) surrounding the figure in the middle. It was observed that the increase in heating rates also correspondingly increased the crystallization temperature.

The apparent activation energies for primary crystallization were determined using Kissinger equation [4.25] as shown in Figure 4.39. The activation energy for the primary crystallization of $\text{Ni}_{60}\text{Nb}_{40}$ alloy ($E_x = 612.1$ kJ/mol) determined from Kissinger equation is in a good agreement with the previously reported data [4.26-4.27]. For verification this was also calculated according to the Ozawa method [4.28], which is as follows:

$$\ln s = -1.0516 \frac{E}{RT} + \text{const.} \quad (4.14)$$

where s and E are the heating rate and activation energy, respectively. Plotting of $\ln s$ against $1/T$ yields a straight line with a slope of $-E/R$.

The activation energies calculated by Ozawa method were in good agreement with the values obtained from Kissinger equation as shown in Figure 4.42. The value of E_{x1} decreases continuously, which is consistent with the decrease in T_{x1} although E_{x1} increased with 10 at.% Zr addition ($E_{x1} = 659.7$ kJ/mol). The crystallization temperature and the values of activation energy estimated from Kissinger and Ozawa equations are compiled in Table 4.6.

Figure 4.41. DSC curves of amorphous $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x=0, 10, 20$ or 30) alloys with heating rate of 10 K/min . DSC curves of amorphous alloys with different heating rates; (a) $\text{Ni}_{60}\text{Nb}_{40}$, (b) $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$, (c) $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{80}\text{Zr}_{20}$, and (d) $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$.

In this study, the thermal analysis of alloys was investigated under non-hydrogenated conditions, which is valuable for revealing composition stability. It will be impractical to repeat the measurements under hydrogen atmosphere, but the behavior observed under non-hydrogenated condition will be useful to predict thermal stability under hydrogen.

Table 4.6. Values of crystallization temperature and activation energy of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x=0, 10, 20$ or 30 at.%) estimated by the Kissinger and Ozawa equations.

Composition	Temperature T (K)	Activation energy (kJ/mol)	
		Kissinger	Ozawa
$\text{Ni}_{60}\text{Nb}_{40}$	909	612.1	602.6
$(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$	881	659.7	641.1
$(\text{Ni}_{0.6}\text{Nb}_{0.4})_{80}\text{Zr}_{20}$	856	549.0	535.7
$(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$	808	541.7	527.8

Figure 4.42. Kissinger and Ozawa plots of amorphous $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x = 0, 10, 20$ or 30) alloys.

4.2.B.2. Hydrogen Permeability of Ni-Nb-Zr Amorphous Alloy Membranes

Hydrogen permeation through the amorphous $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$, (where 'x' ranges from 10 to 30), alloy membranes was measured from 573 to 673 K and at pressure differential between 0.2 to 0.76 MPa. Figure 4.43 shows that the permeation fluxes increased with the temperature and the permeation flux of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ was higher than the $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$, when measured at the same hydrogen pressure. The flux value of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ reached $0.095 \text{ mol m}^{-2} \text{ s}^{-1}$ at 623 K.

The linear relationship between hydrogen flux and the square root of the pressure difference indicates that the permeability of hydrogen gas through the membranes is controlled by the diffusion of atomic hydrogen and not by the reaction on the membrane surface. In addition, the membranes' selectivities were confirmed by introducing 5 % CO_2 into the feed gas. Both the membranes are shown to have high selectivity for hydrogen based on the solution-diffusion transport mechanism since CO_2 was not detected on the permeate side during the permeation tests.

Figure 4.43. Hydrogen flux of amorphous (Ni_{0.6}Nb_{0.4})₇₀Zr₃₀ and (Ni_{0.6}Nb_{0.4})₉₀Zr₁₀ alloys as a function of the difference in the square-root of hydrogen pressures at different temperatures. The data of other membrane alloys are also shown for comparison: —: this study, ----: ref [4.30] and ref [4.20].

Generally, hydrogen permeability ($\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-0.5}$) can be determined by following equation:

$$k = \frac{J \cdot x}{P_F^{0.5} - P_p^{0.5}} \quad (4.15)$$

where J is the hydrogen flux ($\text{mol m}^{-2} \text{s}^{-1}$), x is the membrane thickness (m), and P_F and P_P are the hydrogen partial pressure of the feed side and permeate side of the membrane (Pa), respectively.

Figure 4.44 presents the hydrogen permeability of the $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x=0, 10$ or 30 at.%) amorphous alloys as a function of the inverse temperature. The permeability of the Pd membrane was also measured in this study and compared with the amorphous alloys. The permeability of Pd at 635 K was measured to be 1.2×10^{-8} ($\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-0.5}$) which was in good agreement with previously reported data [4.20, 4.29]. Permeation tests for the $\text{Ni}_{60}\text{Nb}_{40}$ and $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ alloy membranes was performed at higher temperature (~ 673 K) than that of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ alloy membrane (~ 623 K) since the alloys having low Zr content are thermally more stable.

Figure 4.44. Arrhenius plots of the hydrogen permeability of amorphous $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x=0, 10$ or 30) alloys. The data of other membrane alloys are also shown for comparison: —; this study, ----; ref [4.20] and ref [4.30].

The permeation flux through the $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ alloy membrane kept declining at high temperature (673 K) although the permeation flux data were successfully obtained at the same temperature with membranes having low Zr content (0, 10 at.%) such as $\text{Ni}_{60}\text{Nb}_{40}$ and $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ membranes. Nevertheless, the value of hydrogen permeabilities of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ alloys were higher (7.0×10^{-9} ($\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-0.5}$)) than those of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ and $\text{Ni}_{60}\text{Nb}_{40}$ alloys, but decreased with decrease in Zr concentration. For both

ternary alloy membranes, the hydrogen permeability increased linearly with the inverse temperature. However, the hydrogen permeability for $\text{Ni}_{60}\text{Nb}_{40}$ alloy tended to decrease with increasing temperature which is questionable. Hydrogen permeability decreases with increasing temperature in the case of BCC metals such as Nb, V, and Ta. This phenomenon may be attributable to the decrease of hydrogen solubility more rapidly than the increase of the diffusion coefficient [4.31]. The thermal stability and permeation rates data of the alloy membranes in this study are inversely related as depicted on the Ni-Nb-Zr ternary diagram (Figure 4.45). In this alloy system (yellow region), the crystallization temperature decreased with increasing Zr content (it consequently decrease in Ni and Nb contents) whereas the hydrogen permeation increases. The activation energy of crystallization increases with decreasing Zr content up to 10 at%. E_x for the binary $\text{Ni}_{60}\text{Nb}_{40}$ is higher than $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ and $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{80}\text{Zr}_{20}$ but lower than $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$.

Figure 4.45. Sketch of the crystallization temperature (T_x) and activation energy (E_x) for the primary crystallization in Ni-Nb-Zr (yellow region) and Ni-Zr (green region) systems. Dependence of hydrogen permeability as a function of the Zr concentrations in the Ni-Nb-Zr system is also described.

In the Ni-Zr binary alloy system (green region), the eutectic composition ($\text{Ni}_{63.7}\text{Zr}_{36.3}$) has higher values of crystallization temperature and activation energy of crystallization than those of near eutectic composition ($\text{Ni}_{30}\text{Zr}_{70}$).

The Avrami exponent n indicates that the main crystallization process of the binary Ni-Zr alloys is governed by three-dimensional growth. In $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where 'x' ranges from 0 to 30

at.%) alloys, T_x continuously decreased with increasing Zr concentration. The value of E_x increased up to 10 at.% Zr addition, then decreased continuously, which is consistent with the decrease in T_x . The hydrogen flux was found to increase proportionally with the square root of the hydrogen partial pressure difference, indicating dominance of the bulk diffusion transport controlling step. While the value of hydrogen permeability for $\text{Ni}_{60}\text{Nb}_{40}$ alloy was low, it was found to increase with the addition of Zr. It was found that the permeability and stability of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ ($0 < x < 30$) alloys have inverse relationship; therefore optimization between these two factors is necessary at operating temperatures.

4.2.C Hydrogen Solubility and Permeation in $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x=10, 20, 30$) Amorphous Alloy Membranes

$(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x=10, 20, 30$) amorphous alloy membranes were fabricated using melt-spinning process from ingots of these alloys, which were procured from AMES laboratory. These membranes were subsequently coated with very thin layer of Pd (approx 500 nm) on both sides by sputtering process at Southwest Research Institute.

4.2.C.1 Hydrogen Solubility

Hydrogen solubility tests were conducted on these alloy membranes at five different temperatures 200°C, 250°C, 300°C, 350°C and 400°C by volumetric method using automated Sievert's apparatus at University of Nevada, Reno laboratory. The details of Sievert's apparatus is given at Experimental session. At each temperature, pressure-composition isotherms (P-C isotherms) data were recorded, plotted and analysed.

Figure 4.46 shows the pressure-composition isotherms of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy membrane at five different temperatures (200-400°C). In this figure, the horizontal axis represents the hydrogen concentration (molar H/M ratio), expressed by the number of hydrogen atoms per metal atom and longitudinal axis represents the pressure in bar. The hydrogen pressure is found to increase gradually with hydrogen concentration (H/M). As can be seen from the figure, hydrogen concentration (H/M) increases with decrease in temperature.

Figure 4.46. P-C-isotherms of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ alloy.

It can also be seen from the plot that the plateau is absent which is common in case of pressure-concentration isotherms of all the crystalline metal / alloys. This behavior of amorphous alloys may be attributed to an absence of phase separation, even at low temperatures[4.32]. The formation of solid solution of hydrogen in the amorphous state is suggested from the shape of p-c isotherms[4.32].

Figure 4.47 shows plot of the square root of the equilibrium pressure vs the hydrogen concentration (atomic H/M ratio) of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy which is also called Sievert's plot.

Figure 4.47. Sievert's plots of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ alloy membrane

The results in this plot shows that overall there exist the linear relationship between square root of equilibrium pressure and hydrogen concentration, which implies that hydrogen absorption reasonably obeys the Sievert's law while positively deviating a little bit from ideal Sievert's law which should be straight proportional line. This can be related to the distribution of energy states in the amorphous structure, where H atoms enter successively higher-energy states[4.33]. The positive deviations from Sievert's law is observed with increase in hydrogen concentration at all the temperatures which is not a general behavior in case of crystalline metals / alloys. Similar positive deviations have been reported in p-c isotherms of Zr-Ni amorphous alloys[4.32, 4.34] and in some intermetallic compounds[4.35-4.37]. The deviation from Sievert's law, indicates H-H repulsive interaction which may be due to change in local environmental structure like coordination etc. around hydrogen.

As $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy membranes give permeability comparable to palladium membranes, I thought of comparing the solubility data of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy with palladium and therefore did hydrogen solubility tests on palladium (Pd) at 200°C, 250°C, 300°C, 350°C, 400°C and compared it with $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy hydrogen solubility data. Figure 4.48 shows the comparative pressure-concentration isotherms of Pd and $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy.

Figure 4.48. Comparative P-C-isotherms of Palladium and $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy.

Figure 4.49. Comparative Sievert's plots of Palladium and $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy.

The figure shows that across all the temperatures, hydrogen concentration, H/M is very high in $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy as compared to Pd. This means, considering the higher permeability of Pd compared to $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy, diffusion effect in Pd overtakes the solubility effect, which is higher in $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy. Also the Pd shows clear cut plateau which is missing in the case of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy because of the reasons discussed above.

Figures 4.50 and 4.52 show the pressure-composition isotherms of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{80}\text{Zr}_{20}$ and $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ amorphous alloys at five different temperatures (200-400°C). The

horizontal axis represents the hydrogen concentration (molar H/M ratio), expressed by the number of hydrogen atoms per metal atom and longitudinal axis represents the pressure in bar. The hydrogen pressure is found to increase gradually with hydrogen concentration (H/M). As can be seen from the figure, hydrogen concentration (H/M) increases with decrease in temperature. In this case also, it can be seen that the plateau is absent which is common in case of pressure-concentration isotherms of all the crystalline metal / alloys.

Figure 4.50. P-C-isotherms of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{80}\text{Zr}_{20}$ alloy.

Figures 4.51 and 4.53 show the plots of the square root of the equilibrium pressure vs the hydrogen concentration (atomic H/M ratio) of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{80}\text{Zr}_{20}$ and $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ amorphous alloy which is also called Sievert's plot. The results in these plots show strong deviation from the linear relationship between square root of equilibrium pressure and hydrogen concentration, which implies that hydrogen absorption positively deviates from the Sievert's law. As discussed in earlier section, this can be related to the distribution of energy states in the amorphous structure, where H atoms enter successively higher-energy states[4.33]. The positive deviations from Sievert's law is observed with increase in hydrogen concentration at all the temperatures which is not a general behavior in case of crystalline metals / alloys. The deviation from Sievert's law, indicates H-H repulsive interaction which may be due to change in local environmental structure like coordination etc. around hydrogen.

The solubility data of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{80}\text{Zr}_{20}$ and $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ alloys also show the reversal of hydrogen solubility beyond certain pressure which varies with temperature and composition of alloys. These membranes starts rejecting hydrogen at these pressures across all the temperature.

Figure 4.51. Sievert's plots of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{80}\text{Zr}_{20}$ alloy

Figure 4.52. P-C-isotherms of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ alloy membranes

Figure 4.53. Sievert's plots of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ alloy membrane

Figure 4.54. Effect of Zr content on hydrogen solubility of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x=10, 20, 30$) amorphous alloy membrane @ 400°C

Figure 4.54 shows the comparative hydrogen concentration vs equilibrium pressure data of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$, $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{80}\text{Zr}_{20}$ and $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ membranes. The plot clearly indicates that higher Zr content in these alloys results in higher hydrogen solubility (H/M) across all the temperatures. The higher hydrogen solubility in higher Zr content amorphous alloys may be attributed to higher hydrogen affinity of Zr compared to other constituents of alloy. The higher hydrogen solubility (H/M) of higher Zr content alloys have ultimately affected the overall permeation results discussed in latter section, though the durability was compromised.

4.2.C.2 Hydrogen Permeation

Permeation tests were conducted on these alloys at TDA Research Inc, Wheat Ridge, Colorado, USA. Automated permeation test rig was used for permeation tests on amorphous alloy membranes. The test rig has integrated safety interlocks and was able to monitor the gas leakage, excessive pressure or temperature. It also monitored the gases coming out at retentate side to see the hydrogen selectivity of the membrane.

Figure 4.55. Permeation durability plot of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ at 400°C

The permeation tests are performed to know the permeability and durability of these alloy membranes at 400°C and 450°C along with the hydrogen selectivity. During the tests many membranes broke even before starting the tests and many lasted for more than 100 hours.

Figure 4.55 show the permeation durability plot of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ at 400°C. The maximum permeability of this membrane was found to be $1.89 \times 10^{-8} \text{ mol H m} / \text{m}^2 \text{ s Pa}^{0.5}$.

As suggested by Hara et.al.[4.38], the following equation can be used to calculate the pressure-dependent permeability from plot of flux vs retentate side pressure of the membrane (Figure 4.13);

$$\frac{dJ}{dq^f} = \frac{\phi(q)_{q=q^f}}{d} \quad (4.16)$$

The pressure-dependent permeability can be evaluated by differentiating the permeation flux with respect to q^f which in this case is square root of p . The calculated value of permeability from this plot is found to be $2.24 \times 10^{-8} \text{ mol H m} / \text{m}^2 \text{ s Pa}^{0.5}$ which is higher but comparable with the directly measured value (maximum) of $1.89 \times 10^{-8} \text{ mol H m} / \text{m}^2 \text{ s Pa}^{0.5}$ for $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy membrane at 400°C .

The plot of hydrogen permeation flux vs feed (retentate) side pressure for $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy membrane at 400°C is shown in Figure 4.56.

Figure 4.56. Calculated hydrogen-dependent hydrogen permeability of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy membrane at 400°C

Figure 4.57 shows the comparative permeance and durability of the $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ and $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ amorphous alloy membranes. The permeation results of these amorphous membranes show that higher Zr content results in higher permeability. At the same time it was also found that higher Zr content alloy membrane deteriorated faster compared to lower Zr content alloy membrane. The higher Zr content alloys broke into pieces while testing within few hours of starting the test, probably because of hydrogen embrittlement. $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy membrane gave permeability of $1.89 \times 10^{-8} \text{ mol H m} / \text{m}^2 \text{ s Pa}^{0.5}$ at 400°C which

is highest amongst the alloys evaluated as part of this study and is comparable with Palladium based alloys.

Figure 4.57. Effect of Zr content on durability of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ amorphous alloy membranes

The other two membranes $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{80}\text{Zr}_{20}$ and $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ gave very low permeability as compared to $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ but the durability was very high compared to $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ membrane. These results show that there is trade-off between permeability and durability, so it needs to be optimized during designing robust permeation membrane. Perhaps Zr content between 20 and 30 might give improved durability alongwith higher permeability, which can be taken up as future study / research.

Temperature also affected the permeation of a particular membrane. It can be seen from Figure 4.58, that the normalized permeability of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ at 450°C is higher than the normalized permeability at 400°C but the membrane lasts longer when tested at lower temperature of 400°C compared to 450°C. Therefore it can be concluded that though temperature increases the permeability but compromises the durability. However, the lower temperature may sometimes negatively affect the membrane if the temperature is very low which allows membrane to absorb a lot of hydrogen and ultimately embrittle it.

Figure 4.58. Effect of Temperature on durability of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy membrane

4.2.C.3 Diffusion Coefficients

Steady-state hydrogen flux, J , through metal is defined by the Fick's first law,

$$J = -D \times \left(\frac{\partial C}{\partial x} \right) \quad (4.17)$$

where $\frac{\partial C}{\partial x}$ is the hydrogen concentration gradient. If the metal-hydride system obeys the

Sievert's law ($C = K\sqrt{P}$), the above equation can be written as,

$$J = D \cdot K \times \left(\frac{\sqrt{P_{\text{retentate}}} - \sqrt{P_{\text{permeate}}}}{d} \right) \quad (4.18)$$

where K is the Sievert's constant, $P_{\text{retentate}}$ is hydrogen pressure on retentate side and P_{permeate} is the hydrogen pressure on permeate side of membrane and d is the thickness of the membrane. The $(D \cdot K)$ term is defined as the permeability (ϕ) of membrane, used to measure the performance of the hydrogen permeable membrane.

from above equation, it is clear that the diffusion coefficient can be calculated by only measuring the hydrogen flux J , provided the Sievert's constant is known for the membrane material. However this method cannot be applied for the system which does not obey the Sievert's law.

Under these conditions where the hydrogen-alloy system does not obey the Sievert's law, the diffusion coefficient can be calculated by using the difference in hydrogen concentration between the retentate and permeate sides of the membrane estimated from p-c isotherms at pressures of retentate and permeate sides respectively.

Using p-c isotherms data and permeation data of these amorphous alloy membranes at 400°C, I calculated diffusion coefficients of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$, and $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$, amorphous alloy membranes. Permeation tests gave the steady-state hydrogen flux, J data across the amorphous alloy membrane. The difference of hydrogen concentration, $\Delta C = (C_{\text{retentate}} - C_{\text{permeate}})$, between the retentate and permeate sides of the sample is estimated from p-c isotherms of the sample by applying the retentate and permeate side hydrogen pressures for each permeation condition. The calculated diffusion coefficient for $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy membrane is $4.91 \times 10^{-10} \text{ m}^2/\text{s}$ and for $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ amorphous alloy membrane is $1.59 \times 10^{-10} \text{ m}^2/\text{s}$ (Table-5.3). Here the lattice expansion due to the thermal heating [4.39] and the hydrogen uptake into the metals have not been taken into account for estimating the hydrogen volumetric molar concentration, $\text{mol H} / \text{m}^3$, instead of simple atomic ratio (H/M) as was done by Zhang et. al. who calculated the diffusion coefficients for niobium and palladium alloys using similar procedure for calculations[4.40].

4.2.C.4 Thermodynamics

The thermodynamic quantities which are determined from pressure-composition-temperature relations (isotherms) are called relative partial molar quantities and they refer to the formation of MH_r at a constant H content, r .

At equilibrium,

$$\mu_{H(\text{solid})} = (1/2)\mu_{(H_2, g)} = (1/2)\mu_{(H_2, g)^o} + RT \ln p_{(H_2)}^{1/2} \quad (4.19)$$

and therefore,

$$RT \ln p_{(H_2)}^{1/2} = \mu_{H(\text{solid})} - (1/2)\mu_{(H_2, g)^o} = \Delta\mu_H = \Delta H_H - T \Delta S \quad (4.20)$$

Therefore plots of $\ln p^{1/2}$ against $1/T$ give $\Delta H_H / R$ and $-\Delta S / R$ as slope and intercept. The relative partial molar enthalpy is:

$$\Delta H_H = H_H - (1/2)H_{H_2^o} \quad (4.21)$$

Where, H_H is the partial molar enthalpy of H in the solid at a given H/M and $H_{H_2^o}$ is the enthalpy of hydrogen gas at 1 bar. The Δ indicates that the enthalpy is relative to $(1/2)\text{H}_2$ and the sub H indicates a partial quantity. A partial molar quantity is defined as $H_H = (\partial H / \partial n_H)_{H/M}$ which indicates that ∂n_H moles of H are added to the solid at essentially constant H/M.

For the relative partial molar entropy the same symbolism holds. The entropy can be divided into a standard change and the ideal partial configurational entropy, i.e.,

$$\Delta S_H = \Delta S_{H^o} - R \ln(r / \beta - r) \quad (4.22)$$

where β is the number of interstices per metal atom and r is the H-to-metal atom ratio and

$$\Delta S_H = S_H - (1/2)S_{H_2^o} \quad (4.23)$$

From P-C isotherms, the enthalpy of formation ΔH and also ΔS of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ ($x=10, 20, 30$) amorphous alloys were calculated. Figure 4.59 and 4.60 show the isochors, plot of natural log of equilibrium pressure vs. inverse of temperature ($1/T$) for $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ and $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ amorphous alloys. Fairly good straight lines are obtained for these isochors which implies that the values of ΔH and ΔS are independent of temperature. The calculated values of ΔH and ΔS for these alloys are listed in Figure 4.59 and 4.60.

Figure 4.59. Van't Hoff Plots of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloys

Figure 4.60. Van't Hoff Plots of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{90}\text{Zr}_{10}$ amorphous alloys

4.2.D. Hydrogen-Deuterium Exchange Studies on Ni-based Ternary Alloys

4.2.D.1 Hydrogen-Deuterium (H-D) Exchange Studies of $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$

A $\sim 22\text{cm}^2$ $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ membrane was cut into pieces, and was tested in the HD scrambling rig. The membrane was heated 723K and then cooled. Later, the membrane was held overnight at 550° C. The sample was cooled at definite intervals and HD flow rates were measured. The Figure 4.61 shows the HD flow rate versus temperature for cooling process in amorphous state and the cooling process in crystalline process. A decrease in the HD flow rate is seen as the temperature is reduced and this can be due to the Arrhenius relation between reaction rate and temperature. Higher HD flow rates are obtained after the membrane has been held at 550°C overnight. This could be due to structural changes that occur due to heating under hydrogen environment. The points that are not joined by the dotted line are the ones that were obtained after holding the reactor overnight at 550K. The measurements were taken the following day. Holding the membrane at that temperature may have caused few structural changes. XRD has not detected them. This system is being studied in detail. Further experiments were performed by varying the inlet flow rates of H_2 and D_2 to 20mL/min, 25mL/min and 30mL/min. Measurements of HD outlet flow rate were taken at three temperatures of 500° C, 400° C and 300° C. Data from H_2 inlet flow rate of 10mL/min was superimposed on the data obtained at various flow rates, as shown in Figure 4.62.

It is observed that the experiments show repeatability of data since the trend observed by various flow rates remains unchanged. This may suggest that the property of the material remains unchanged as the flow rates change.

Figure 4.61. HD exchange data combined -crystalline and amorphous for $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$.

Figure 4.62. Outlet HD flow rate observed by varying inlet H_2 flow rate on $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$.

H-D Flow Modeling for $\text{Ni}_{60}\text{Nb}_{40}\text{Zr}_{20}$

The H-D flow rate of the $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ membrane was also modeled and a comparison is shown Figure 4.63 shows a relatively good fit. Similar approach, as above, was used to determine the

Modeling and experimental HD flow rates v/s Temperature for $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$

Figure 4.63. Modeled and experimental HD flow rates vs temperature for $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$

kinetic parameters of pre-exponential factors and activation energies.

Figure 4.64. Total coverage for Ni₆₀Nb₂₀Zr₂₀ membrane

The values for this system are as follows: $\ln(\theta_{ads}) = -9.8$ mol/m²/s/Pa, $\ln(\theta_{des}) = 4$ mol/m²/s, $E_{ads} = 0.36$ eV and $E_{des} = 0.51$ eV. The total activation energy of adsorption is $\Delta E_{ads} = E_{ads} - E_{des} = -0.15$ eV. The desorption energy is observed to be slightly higher than the adsorption energies for the system. There is a significant difference in the overall adsorption energies when the binary and the ternary alloys of Ni-Nb and Ni-Nb-Zr are compared. Figure 4.64 shows the total surface coverage changing with respect to temperature for the Ni-Nb-Zr alloy. Again, the coverage is much higher at lower temperatures. It can also be inferred that the overall coverage obtained by Ni-Nb-Zr is much lower than Ni-Nb alloy at a given temperature. This leads to a conclusion that Ni-Nb is more catalytically active than Ni-Nb-Zr. However, more studies need to be performed to validate this hypothesis.

4.2.D.2 Hydrogen-Deuterium (H-D) Exchange Studies on Ni₆₀V₂₀Zr₂₀

The Ni₆₀V₂₀Zr₂₀ sample was cut into pieces and was filled in the reactor. Approximately 32cm² of sample was used. The sample was heated to 650K and then was cooled down. 5mL/min of H₂ and D₂ gases were flown into the reactor. It was found that halving the flow rate did not change the kinetics of the material. The sample was heated to 550° C and was held overnight there. HD conversion data was recorded as the sample was cooled down to 200° C. Almost full conversion was obtained at 550° C (Figure 4.65). This can be due to the phase transitions that may have occurred during the heating of the sample. This is studied by conducting in-situ XRD experiments.

Figure 4.65. HD flow rate vs temperature for $\text{Ni}_{60}\text{V}_{20}\text{Zr}_{20}$ sample amorphous and crystalline

H-D Flow Modeling for $\text{Ni}_{60}\text{V}_{40}\text{Zr}_{20}$

Ternary composition, $\text{Ni}_{60}\text{V}_{20}\text{Zr}_{20}$ was studied and the HD flow rates were modeled by using the

Figure 4.66. Total coverage of H_2 on $\text{Ni}_{60}\text{V}_{20}\text{Zr}_{20}$

kinetic equation of the HD flow rate. The fitting was performed by optimizing the values of the kinetic parameters. This is shown in Figure 4.67.

The parameters obtained for the fit are as follows: $\ln(\vartheta_{ads}) = -7.7 \text{ mol/m}^2\text{/s/Pa}$, $\ln(\vartheta_{des}) = 10 \text{ mol/m}^2\text{/s}$, $E_{ads} = 0.43\text{eV}$ and $E_{des} = 0.89\text{eV}$. The total activation energy of adsorption is $\Delta E_{ads} = E_{ads} - E_{des} = -0.46\text{eV}$. This is comparable to the values obtained by the other alloys. The total coverage is plotted against temperature as shown in Figure 4.66.

Figure 4.67. Modeled and experimental flow rate vs temperature for $\text{Ni}_{60}\text{V}_{20}\text{Zr}_{20}$

The results are summarized in the Table 4.7 given below. Statistical mechanics can be used to predict the pre-exponential factors for the adsorption and desorption of H_2 on a catalyst surface. The values of adsorption and desorption factors and energies for hydrogen interaction on Ni-based alloys have not been reported before as per our knowledge.

It can be concluded that based on adsorption energies that Ni-V-Zr alloy is most catalytically active in dissociating H_2 on its surface followed by Ni-V, Ni-Nb and Ni-Nb-Zr. Based on Figure 4.70 (all HD together plot) the above hypothesis can be confirmed. The most catalytic surface however would be $\text{Ni}_{64}\text{Zr}_{36}$

Table 4.7. Pre-exponential factors and activation energies for Ni-based alloys

Alloy	$\ln(v_{\text{ads}})$ mol/m ² /s/Pa	E_{ads} eV	$\ln(v_{\text{des}})$ mol/m ² /s	E_{des} eV	ΔE_{ads} eV
Ni	-2.9	0.04	8.5	0.55	-0.51
Ni ₆₀ Nb ₄₀	-9.09	0.33	7.88	0.71	-0.376
Ni ₆₀ Nb ₂₀ Zr ₂₀	-9.8	0.36	4	0.51	-0.15
Ni ₆₀ V ₄₀	-4	0.3	8	0.7	-0.4
Ni ₆₀ V ₂₀ Zr ₂₀	-7.7	0.43	10	0.89	-0.46

4.2.D.3. H-D Data Comparisons Charts and Modeling to Determine Activation Energies of Adsorption and Desorption

To determine the effect of Zr addition to the Ni-Nb system we plot the experimental outlet HD flow rates against temperatures for Ni₆₀Nb₄₀ and Ni₆₀Nb₂₀Zr₂₀ in Figure 4.68. The HD flow rate for both alloys increase with the temperature. The flow rates for Ni₆₀Nb₄₀ are greater than for Ni₆₀Nb₂₀Zr₂₀; noting that the Ni₆₀Nb₄₀ is amorphous in nature throughout the entire process, as indicated in the results section.

Figure 4.68. HD flow rate comparison between Ni₆₀Nb₄₀ binary and Ni₆₀Nb₂₀Zr₂₀ ternary.

In the case of Ni-V alloys, when we add Zr, the HD flow rate increases; noting that the $\text{Ni}_{60}\text{V}_{40}$ is crystalline in nature. Figure 4.69 shows that $\text{Ni}_{60}\text{V}_{20}\text{Zr}_{20}$ has higher HD flow rates at higher temperature as compared to $\text{Ni}_{60}\text{V}_{40}$. During cooling, there is a sudden drop at 723K in the HD flow rates for $\text{Ni}_{60}\text{V}_{20}\text{Zr}_{20}$. Comparing the binary and ternary flow rates, it appears that above a critical temperature the ternary exhibits more surface activity (catalytic) than the $\text{Ni}_{60}\text{V}_{40}$ alloy. The $\text{Ni}_{60}\text{V}_{40}$ on the other hand seems to have better stability/HD flow rate over the lower range of temperatures.

Figure 4.69. HD comparison data between Ni-V and Ni-V-Zr alloys.

Consolidating all the $\text{H}_2\text{-D}_2$ exchange, it can be inferred that $\text{Ni}_{64}\text{Zr}_{36}$ is most stable over the temperature range with highest HD output flow rate. Ni has almost as high as of the HD flow rate as Ni-Zr over a large temperature range. If one specific temperature of 550°C is to be considered, then $\text{Ni}_{60}\text{V}_{20}\text{Zr}_{20}$ has the second highest HD output flow rates. This is followed by $\text{Ni}_{60}\text{V}_{40}$, $\text{Ni}_{60}\text{Nb}_{40}$ and $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$. These are plotted in Figure 4.71.

Comparing just binary compositions, Ni-Zr has the highest HD flow rate vs. temperature data at a given temperature, followed by $\text{Ni}_{60}\text{V}_{40}$ and then $\text{Ni}_{60}\text{Nb}_{40}$. In ternary compositions, V-based ternary, $\text{Ni}_{60}\text{V}_{20}\text{Zr}_{20}$, has higher HD output flow rate as compared to $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$. In the plot (Figure 4.70), Ni-Zr almost has the same HD flow rates at high temperature as that of pure Ni. A possible explanation for can be, during crystallization, the Ni clusters separated from the Zr due selective formation of ZrO_2 . The presence of metallic Ni clusters could have resulted in higher HD production rate. Vanadium is well known to have high catalytic activity, this can be a

possible reason for Ni-V alloys have high surface activity. It can be seen that at high temperatures Ni-V-Zr (initially amorphous, but partially crystal to Ni_2V , and during this process an additional ZrO_2 layer forms) has higher HD production rate than Ni-V due to enhanced surface activity. In the final application of these membranes with the temperatures at which these membranes operate, the Ni-Zr and Ni-V-Zr alloys seem to be good candidates. Figure 4.71 is the plot of all the membranes plotted together in their amorphous state. Except for $\text{Ni}_{60}\text{V}_{40}$ that was crystalline to begin with. These measurements were taken at temperatures below the crystallization temperatures of all the membranes.

$\text{Ni}_{60}\text{V}_{40}$ seems to have the highest surface activity before the heat treatment at a given temperature. A trend that can be set here is that $\text{Ni}_{60}\text{V}_{40}$ and $\text{Ni}_{60}\text{V}_{20}\text{Zr}_{20}$ have higher surface activity than the rest. $\text{Ni}_{64}\text{Zr}_{36}$ has the next highest surface activity. Nb-based alloys have lower surface activity in their amorphous state as well as crystalline state. $\text{Ni}_{64}\text{Zr}_{36}$ increase the surface activity as it crystallizes.

Figure 4.70. HD production flow rate as a function of temperature for alloys below the crystallization temperature.

Figure 4.71. Combined HD flow rate of all alloys in after holding at high temperature.

4.3 Electrochemical Impedance Spectroscopy (EIS) of the Ni-based Binary and Ternary Alloys

The electrical properties of the seven alloys examined show different trends at low and high frequencies in the Bode plot; these are summarized in Figure 4.72 for all the membranes. The $\text{Ni}_{60}\text{Ta}_{20}\text{Zr}_{20}$ alloy has highest resistance, where the bulk effects are more predominant than the surface effects at lower frequencies. We found that resistance of $\text{Ni}_{60}\text{V}_{20}\text{Zr}_{20} > \text{Ni}_{64}\text{Zr}_{36} > \text{Ni}_{60}\text{Ta}_{40} > \text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20} > \text{Ni}_{60}\text{V}_{40} > \text{Ni}_{60}\text{V}_{40}$ between frequencies of 1-10,000 Hz. On the other hand, at frequencies greater than 10,000 Hz. the surface effects are more predominant than the bulk effects, thus an increased resistance is observed. We show the Nquist plots for reference in Figure 4.73. As can be seen from the Figures 4.73, the trend observed is similar to each other proving a consistency. This trend observed can be due to the conductive nature of the membranes that do not provide any capacitive resistance. The only resistance that is encountered is due to the inductive effect. In order to calculate the surface resistance ($|Z|$) of the ribbons we used the following formula:

$$|Z| = \sqrt{(Z_I^2) + (Z_{Re}^2)} \quad (4.24)$$

Figure 4.72. Bode plots for all as cast-membranes plotted together.

Figure 4.73. Nyquist plot of all as-cast membranes plotted together.

where, Z_L is the inductive resistance and Z_{Re} is the real resistance obtained from the Nyquist plot. Table 4.8 shows the list of surface resistances observed for the membranes.

Table 4.8. List of membrane and the surface resistance measured by EIS

Membrane Composition	Surface resistance value from Bode plot (Ω)
$Ni_{64}Zr_{36}$	0.9080
$Ni_{60}Nb_{40}$	0.7727
$Ni_{60}Nb_{20}Zr_{20}$	0.6116
$Ni_{60}V_{40}$	0.5752
$Ni_{60}V_{20}Zr_{20}$	0.5762
$Ni_{60}Ta_{40}$	0.4575
$Ni_{60}Ta_{20}Zr_{20}$	0.5093

Now we compare the resistances of the binaries at 1 MHz; the Ni-Zr has more resistance than Ni-Nb followed by Ni-V and Ni-Ta. Similar trends of resistances were observed for the ternary alloys; at 1 MHz, the resistance of $Ni_{64}Zr_{36} > Ni_{60}Nb_{40} > Ni_{60}Nb_{20}Zr_{20} > Ni_{60}V_{20}Zr_{20} > Ni_{60}V_{40} > Ni_{60}Ta_{40} > Ni_{60}Ta_{20}Zr_{20}$. The high resistance of $Ni_{64}Zr_{36}$ could be due to a stable oxide layer of Zr.

4.4 Hydrogen Solubility and Permeation Studies on Ni-based Quaternary Alloys

4.4.A Hydrogen Solubility and Permeation in $(Ni_{0.6}Nb_{0.3}Ta_{0.1})_{100-x}Zr_x$ (where $x=10, 20, 30$) Amorphous Alloy Membranes

$(Ni_{0.6}Nb_{0.3}Ta_{0.1})_{100-x}Zr_x$ ($x=10, 20, 30$) amorphous alloy membranes were fabricated using melt-spinning process from ingots of these alloys, which were procured from AMES laboratory. These membranes were subsequently coated with very thin layer of Pd (approx 500 nm) on both sides by sputtering process at Southwest Research Institute.

4.4.A.1 Hydrogen Solubility

Hydrogen solubility tests were conducted on $(Ni_{0.6}Nb_{0.3}Ta_{0.1})_{100-x}Zr_x$ ($x=10, 20, 30$) amorphous alloy membranes at temperatures 200, 250, 300, 350 and 400°C by volumetric method described in details in the previous chapter using automated Sievert's apparatus at University of Nevada, Reno laboratory. At each temperature, pressure-composition isotherms (P-C isotherms) data were recorded, plotted and analysed. Results show that hydrogen concentration (molar H/M ratio) increases with decrease in temperature. The highest hydrogen solubility (H/M) of $(Ni_{0.6}Nb_{0.3}Ta_{0.1})_{70}Zr_{30}$ amorphous alloy membrane is found to be 0.62 (Figure 4.74). The H/M vs $\sqrt{\text{Pressure}}$ data (Sievert's plot) data for this membrane at different temperatures (200-400°C) were plotted (Figure 4.75) and it was found that none of the plots follow Sievert's Law, deviation of which is considered to be a general rule in case of amorphous alloy.

Figure 4.74. P-C-isotherms of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{70}\text{Zr}_{30}$ amorphous alloy membrane.

Figure 4.75. Sievert's plots of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{70}\text{Zr}_{30}$ amorphous alloy membrane

Figure 4.76. P-C-isotherms of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{80}\text{Zr}_{20}$ amorphous alloy

The solubility data of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{100-x}\text{Zr}_x$ ($x=10, 20, 30$) alloys also show the reversal of hydrogen solubility beyond certain pressure across all the temperatures. These membranes start rejecting hydrogen at these pressures across all the temperatures. Figure 4.76 shows the hydrogen pressure-concentration isotherms of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{80}\text{Zr}_{20}$ amorphous alloy.

The highest hydrogen solubility of this alloy was found to be 0.21 (H/M) at 200°C. Figure 4.77 shows the plot of square root of pressure vs hydrogen concentration of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{80}\text{Zr}_{20}$ amorphous alloy, and it can be seen from figure that in general the Sieverts' law is not obeyed and also this alloy starts rejecting hydrogen after certain pressure.

Similarly, the hydrogen pressure-concentration isotherms were also plotted for $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{90}\text{Zr}_{10}$ amorphous alloy which are shown in Figure 4.78. Figure 4.79 shows the plot of square root of pressure vs hydrogen concentration of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{90}\text{Zr}_{10}$ amorphous alloy, and it can be seen from figure that in general the Sieverts' law is not obeyed and also this alloy starts rejecting hydrogen after certain pressure.

The comparative solubility data of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{70}\text{Zr}_{30}$, $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{80}\text{Zr}_{20}$ and $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{90}\text{Zr}_{10}$ membranes were also plotted, which show that higher Zr content results in very high hydrogen solubility across all the temperatures compared to lower ($x=20$ or 10) Zr content. This trend / effect of Zr content on hydrogen solubility is higher than without Ta addition.

Figure 4.77. Sievert's plots of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{80}\text{Zr}_{20}$ amorphous alloy

Figure 4.78. P-C isotherms of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{90}\text{Zr}_{10}$ amorphous alloy

Figure 4.79. Sievert's plots of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{90}\text{Zr}_{10}$ amorphous alloy

4.4.A.2 Hydrogen Permeation

Permeation tests were conducted on these alloys at TDA Research Inc, Wheat Ridge, Colorado, USA. Automated test rig was used for permeation tests. The test rig has integrated safety interlocks and was able to monitor the gas leakage, excessive pressure or temperature. It also monitored the gases coming out at retentate side to see the hydrogen selectivity of the membrane. I did permeation tests to know the permeability and durability of these alloy membranes at 400°C and 450°C along with the hydrogen selectivity. During the tests many membranes broke even before starting the tests and many ran for more than 100 hours.

Similar to $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ ($x=10, 20, 30$) amorphous membranes the permeation results of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{100-x}\text{Zr}_x$ ($x=10, 20, 30$) amorphous membranes also show that higher Zr content results in higher permeability (Figure 4.80). At the same time it was found that higher Zr content alloy membrane deteriorated faster compared to lower Zr content alloy membrane. Although $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{80}\text{Zr}_{20}$ amorphous membrane also lasted almost for same time as $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{70}\text{Zr}_{30}$ amorphous membrane did, but the permeability of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{80}\text{Zr}_{20}$ was less than half of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{70}\text{Zr}_{30}$ at 450°C.

Figure 4.80. Effect of Zr content on durability of $(\text{Ni}_{0.6}\text{Nb}_{0.4}\text{Ta}_{0.1})_{70}\text{Zr}_{30}$ amorphous alloy membrane

Temperature also affected the permeation of a particular membrane. Higher temperature gave higher permeability but with lower durability as can be seen from Figure-4.81. The $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{70}\text{Zr}_{30}$ amorphous membrane when tested for permeation at 400°C lasted for more than 100 hrs and permeability did not deteriorate as fast as at 450°C where the membrane deteriorated completely within 60 hrs of operation. Therefore it can be concluded that though temperature increases the permeability but compromises the durability.

Figure 4.81. Effect of Temperature on durability of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{70}\text{Zr}_{30}$ amorphous alloy membrane

4.4.A.3 Diffusion Coefficients

As discussed in section 4.2.C.3, the diffusion coefficients of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{70}\text{Zr}_{30}$ and $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{90}\text{Zr}_{10}$ were calculated. The diffusion coefficients of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{70}\text{Zr}_{30}$, and $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{90}\text{Zr}_{10}$ amorphous alloy membranes were calculated using p-c isotherms data and permeation data of these amorphous alloy membranes at 400°C. Permeation tests gave the steady-state hydrogen flux, J data across the amorphous alloy membrane as given in Table 5.3. The difference of hydrogen concentration, $\Delta C = (C_{\text{retentate}} - C_{\text{permeate}})$, between the retentate and permeate sides of the sample is estimated from p-c isotherms of the sample by applying the retentate and permeate side hydrogen pressures for each permeation condition. The calculated diffusion coefficient for $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{70}\text{Zr}_{30}$ amorphous alloy membrane is $3.99 \times 10^{-10} \text{ m}^2/\text{s}$ and for $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{90}\text{Zr}_{10}$ amorphous alloy membrane is $3.10 \times 10^{-10} \text{ m}^2/\text{s}$ (Table 5.3). Here also the latic expansion due to the thermal heating [4.39] and the hydrogen uptake into the metals have not taken into account for estimating the hydrogen volumetric molar concentration, $\text{mol H} / \text{m}^3$, instead of simple atomic ratio (H/M) as was done by Zhang et. al. who calculated the diffusion coefficients for niobium and palladium alloys using similar procedure for calculations[4.40].

4.4.A.4 Thermodynamics

From P-C isotherms, The enthalpy of formation ΔH and also ΔS of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{100-x}\text{Zr}_x$ ($x=10, 20, 30$) amorphous alloys are calculated. Figures 4.82 and 4.83 show the isochors, plot of natural log of equilibrium pressure vs. inverse of temperature ($1/T$) for $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{70}\text{Zr}_{30}$ and $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{80}\text{Zr}_{20}$ amorphous alloys. Fairly good straight lines are obtained for these isochors which implies that the values of ΔH and ΔS are independent of temperature and listed in Figures 4.82 and 4.83.

Figure 4.82. Van't Hoff Plots of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{70}\text{Zr}_{30}$ amorphous alloys

Figure 4.83. Van't Hoff Plots of $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{80}\text{Zr}_{20}$ amorphous alloys.

4.4.B Hydrogen Solubility and Permeation in $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.3})_{100-x}\text{B}_x$ (where $x=2$ and 5) Amorphous Alloy Membranes

Similar to other amorphous alloy membranes, $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.30})_{100-x}\text{B}_x$ (where $x=2, 5$) amorphous alloy membranes were also fabricated using melt-spinning process from ingots of these alloys, which were procured from AMES laboratory. These membranes were subsequently coated with very thin layer of Pd (approx 500 nm) on both sides by sputtering process at Southwest Research Institute.

4.4.B.1 Hydrogen Solubility

Hydrogen solubility tests were conducted on these $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.32})_{100-x}\text{B}_x$ (where $x=2, 5$) alloy membranes at temperatures 200, 250, 300, 350 and 400°C by volumetric method described in details in the previous chapter using automated Sievert's apparatus at University of Nevada, Reno laboratory. At each temperature, hydrogen concentration (atomic H/M ratio) vs equilibrium pressure data were recorded and p-c isotherms were plotted and analysed.

In both the cases, B addition has resulted in increase in hydrogen solubility of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy. Figures 4.84 & 4.85 show that temperature has very little effect on the hydrogen solubility in case of alloy with higher B as compared to lower B content alloy. Therefore, the membrane with higher B content can be used where temperature varies a lot without varying the solubility.

Figure 4.84. Comparative P-C isotherms of amorphous $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.32})_{98}\text{B}_2$ alloy membrane with $\text{Ni}_{42}\text{Nb}_{28}\text{Zr}_{32}$ alloy membrane.

Figure 4.85. Comparative P-C isotherms of amorphous $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.32})_{95}\text{B}_5$ alloy membrane with $\text{Ni}_{42}\text{Nb}_{28}\text{Zr}_{32}$ alloy membrane.

Figure 4.86 shows the p-c isotherms of amorphous $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.32})_{98}\text{B}_2$ alloy membrane at five different temperatures. the pressure plateau in the p-c isotherms is not found and the capacity for desolving hydrogen increases with decrease in temperature. Figure 4.87 shows plot of the square root of the equilibrium pressure vs the hydrogen concentration (atomic H/M ratio) of $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.32})_{98}\text{B}_2$ amorphous alloy.

Figure 4.86. P-C isotherms of $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.30})_{98}\text{B}_2$ amorphous alloy membrane

Figure 4.87. Sievert's plots of $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.30})_{98}\text{B}_2$ amorphous alloy membrane.

The results in this plot shows that in the relatively very low hydrogen concentration region, there exist the linear relationship between square root of equilibrium pressure and hydrogen concentration, which implies that hydrogen absorption in this region obeys the Sievert's law. The positive deviations from Sievert's law is observed with increase in hydrogen concentration at all the temperatures which is not a general behavior in case of crystalline metals / alloys. Similar positive deviations have been reported in p-c isotherms of Zr-Ni amorphous alloys[4.32, 4.34] and in some intermetallic compounds[4.35-4.37]. The deviation from Sievert's law, indicates H-H repulsive interaction which may be due to change in local environmental structure like coordination etc. around hydrogen.

Figure 4.88. P-C-isotherms of $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.30})_{95}\text{B}_5$ amorphous alloy membrane

Similarly, Figure 4.88 shows the p-c isotherms of amorphous $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.30})_{95}\text{B}_5$ alloy membrane at five different temperatures. The pressure plateau in the p-c isotherms is not found and the capacity for desolving hydrogen increases with decrease in temperature. Figure 4.89 shows plot of the square root of the equilibrium pressure vs the hydrogen concentration (atomic H/M ratio) of $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.30})_{95}\text{B}_5$ amorphous alloy.

Figure 4.89. Sieverts' plots of $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.30})_{95}\text{B}_5$ amorphous alloy membrane

4.4.B.2 Thermodynamics

As discussed in previous sections, from p-c isotherms, the enthalpy of formation ΔH and also ΔS of $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.32})_{100-x}\text{B}_x$ (where $x=2, 5$) amorphous alloys were calculated. Figure 4.90 shows the isochors, plot of natural log of equilibrium pressure vs inverse of temperature ($1/T$) for $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.32})_{98}\text{B}_2$ amorphous alloy. Fairly good straight lines are obtained for these isochors which implies that the values of ΔH and ΔS are independent of temperature. The calculated value of enthalpy of formation of metal- H_2 (ΔH) for $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.32})_{98}\text{B}_2$ amorphous alloy is found to be $-42.17 \text{ kJ / mol H}_2$. ΔS for $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.32})_{98}\text{B}_2$ amorphous alloy is found to be $-60.22 \text{ J / K mol H}_2$.

Figure 4.91 shows the isochors, plot of natural log of equilibrium pressure vs inverse of temperature ($1/T$) for $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.32})_{95}\text{B}_5$ amorphous alloy. The calculated value of enthalpy of formation of metal- H_2 (ΔH) for $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.32})_{95}\text{B}_5$ amorphous alloy is found to be $-15.56 \text{ kJ / mol H}_2$. ΔS for $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.32})_{95}\text{B}_5$ amorphous alloy is found to be $-15.22 \text{ J / K mol H}_2$.

Figure 4.90. Van't Hoff plots of $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.32})_{98}\text{B}_2$ amorphous alloys.

Figure 4.91. Van't Hoff plots of $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.30})_{95}\text{B}_5$ amorphous alloys.

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V. Summary and Conclusions

Amorphous Ni-based alloy membranes show great promise as inexpensive, hydrogen-selective membrane materials. In this report, progress towards understanding crystallization kinetics and hydrogen permeation properties of Ni-based amorphous alloy has been described. In this program, we addressed key issues associated with hydrogen separation membranes, such as effect of alloying elements in the nickel-based amorphous alloy ribbons, recrystallization temperatures and permeation rates, hydrogen solubility in the amorphous alloys, role of nano-crystalline Ni surface precipitation by hydrogen heat treatment, determination surface properties of these amorphous ribbons by hydrogen-deuterium exchange experiments. Several experimental methods were used to characterize these ribbons, such as melt spinning fabrication system, permeation measurement equipment, differential scanning calorimetry, electrochemical impedance spectrometry, scanning and transmission electron microscopy, in-situ x-ray diffraction.

One of the main barriers to the commercial uptake of these materials is their tendency to crystallize during long-term operation at elevated temperatures, a process which decreases strength, durability and permeability. In this study, a series of (1) binary base alloys of $\text{Ni}_{100-x}\text{Zr}_x$ ($x = 36.3$ or 70 at.%), (2) binary series $\text{Ni}_{60}\text{M}_{40}$ ($\text{M} = \text{Nb}, \text{V}, \text{Ta}$), (3) ternary series of $\text{Ni}_{60}\text{M}_{20}\text{Zr}_{20}$ ($\text{M} = \text{Nb}, \text{V}, \text{Ta}$), ternary series $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x = 0, 10, 20$ or 30), quaternary $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{100-x}\text{Zr}_x$ (where $x = 10, 20$ or 30), and $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.30})_{100-x}\text{B}_x$ ($x=2, \text{and } 5$) amorphous alloy membranes were prepared by melt spinning method. Several studies on crystallization of the amorphous ribbons, in-situ x-ray diffraction, SEM and TEM, hydrogen permeation, hydrogen solubility, hydrogen deuterium exchange, and electrochemical studies were conducted.

Addressing the devitrification temperatures we found that binary amorphous alloys have higher crystallization temperature (T_x) and activation energy (E_x) of crystallization; for example, $E_x = 602.6$ kJ/mol. When Zr is added to Ni-Nb alloys as in series $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x = 0, 10, 20$ or 30) ribbons, the higher the Zr content the lower the recrystallization temperature, and the associated activation energies are lower with higher Zr; as calculated by Kissinger and Ozawa plots. For example the $E_x = 541.7$ kJ/mol for the above ternary at $x=30$. The activation energy of amorphous $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$, with higher Ni and lower Nb content, yielded E_x in the range of 420-500 kJ/mol depending on the methodology of experiments and models used. Crystal structural analyses indicate that lattice parameters reduced slightly by the addition of Nb substituting for Zr site in this ternary alloy system.

The permeation rates, hydrogen flux was found to increase proportionally with the square root of the hydrogen partial pressure difference, indicating dominance of the bulk diffusion transport controlling step. It was found that the permeability and stability of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ ($0 < x < 30$) alloys have inverse relationship; therefore optimization between these two factors is necessary at operating temperature. Hydrogen permeability is affected significantly by adjustment of the composition of Ni-based amorphous alloys, first by adding the third alloying element; this illustrated in the permeation plots in Figure 5.1. The development of amorphous alloy materials to improve thermal and hydrogen properties is left as future research to be done.

With the addition of Ta, the primary crystallization temperature of $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ amorphous alloy decreases slightly, but the secondary crystallization temperature increases significantly. In addition, the crystallization temperature and activation energy of membranes increased with increasing Ta content in quaternary $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{100-x}\text{Zr}_x$ whereas the hydrogen permeation decreased.

Figure 5.1: Summary and comparisons of Arrhenius plots of the hydrogen permeability of the amorphous Ni-based membranes. * S.-i. Yamaura et al., Acta Mater. 53 (2005) 3703-3711. [†]M. Dolan et al., J. Membr. Sci., 326 (2009) 549-555.

Hydrogen solubilities in the amorphous alloys, such as, $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x=10, 20, 30$) series of amorphous alloys, show that higher Zr content results in higher hydrogen solubility (with higher permeability), but the durability of these membranes are compromised compared to lower Zr content alloy membranes. The amorphous alloy $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$ gave highest hydrogen solubility and also the highest hydrogen permeability. In order to improve the thermal stability and permeation, additions of Ta and B were made to the base amorphous alloys, $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ (where $x=10, 20, 30$). Tantalum added $(\text{Ni}_{0.6}\text{Nb}_{0.3}\text{Ta}_{0.1})_{100-x}\text{Zr}_x$ alloys reduced the H-solubility and permeability. The Boron added $(\text{Ni}_{0.42}\text{Nb}_{0.28}\text{Zr}_{0.30})_{100-x}\text{B}_x$ alloys increased the H-solubility due to high affinity of hydrogen to Boron. Increasing Boron concentration yielded an anomalous result; there was hydrogen release at a critical pressure which we call “Hook effect,” during the absorption cycle at constant temperature; the only exception was the alloy $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}\text{Zr}_{30}$.

The surface catalytic effects, evaluated by H₂-D₂ exchange methods, for the Ni-based amorphous alloy of the binaries showed that the catalytic activity of Ni-Zr > Ni-V > Ni-Nb (non-Pd coated foils); supported by micro kinetic modeling. Comparing the ternaries, we report that the surface kinetics of $\text{Ni}_{60}\text{V}_{20}\text{Zr}_{20}$, > $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$. It can be concluded that hydrogen heat treated alloys show the following trend in the decreasing order of adsorption energies: Ni > $\text{Ni}_{64}\text{Zr}_{36}$ > $\text{Ni}_{60}\text{V}_{20}\text{Zr}_{20}$ > $\text{Ni}_{60}\text{V}_{40}$ > $\text{Ni}_{60}\text{Nb}_{40}$ > $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$. In the case of Ni-Zr alloys, Ni (~200nm) precipitation on the surface of the ribbons resulted in increased catalytic activity during hydrogen heat treatment. Associated with this, large micron sized bubbles with higher Zr content interpreted to be ZrO₂ phase. In conclusion, we suggest replacing Pd coating on the Ni-based ribbons with nanocrystalline Ni or alloy particles for hydrogen molecule dissociation.

GRAPHICAL MATERIALS LIST

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