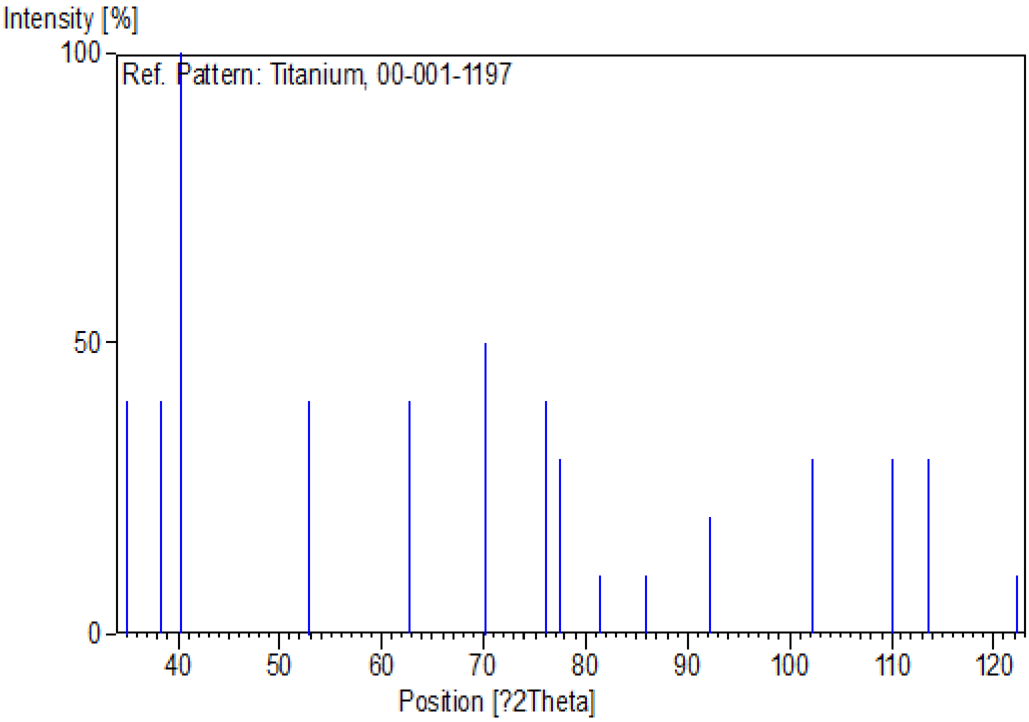
Appendix A
X-ray Data Cards

Ti

Crystallographic parameters

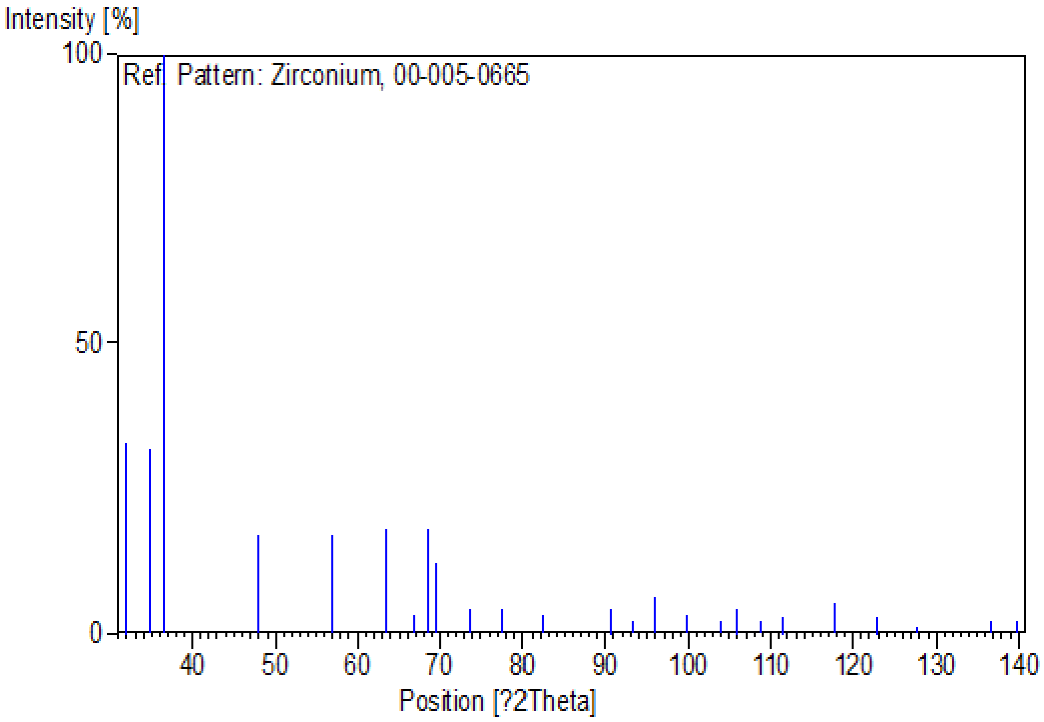
Crystal system:	Hexagonal
Space group:	$P6_3/mmc$
Space group number:	194
a (Å) :	2.9500
b (Å):	
c (Å):	4.6820
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	120.0000



Zr

Crystallographic parameters

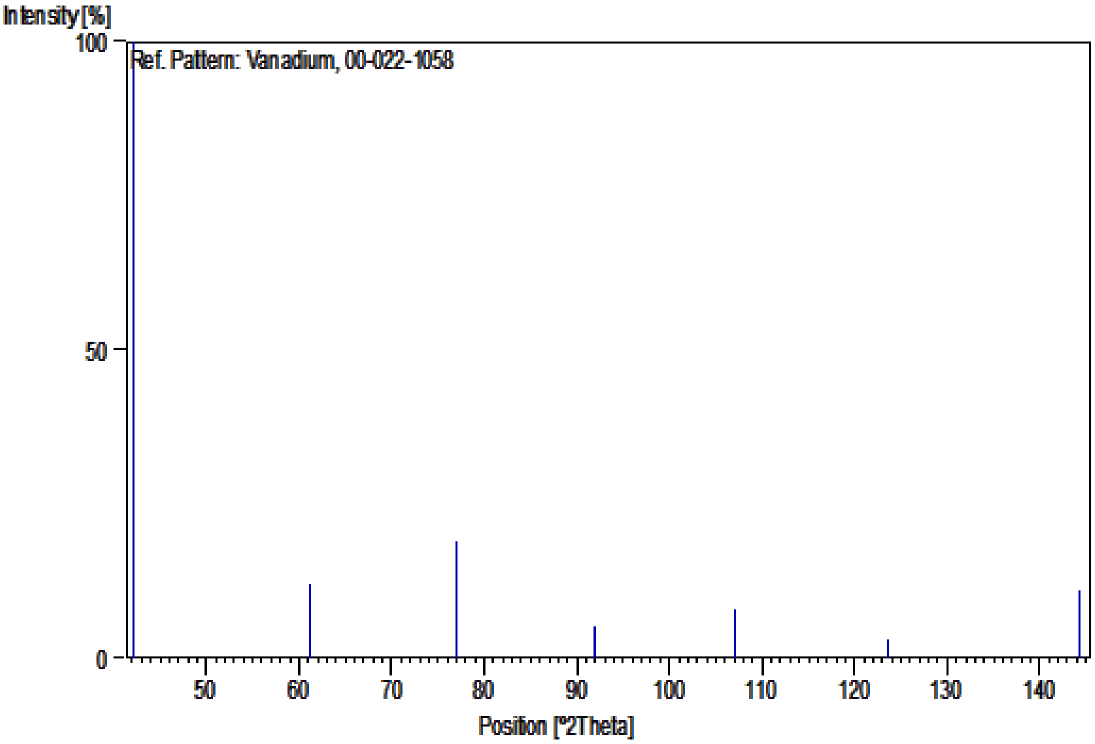
Crystal system:	Hexagonal
Space group:	P63/mmc
Space group number:	194
a (Å) :	3.2320
b (Å):	
c (Å):	5.1470
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	120.0000



V

Crystallographic parameters

Crystal system:	Cubic
Space group:	Im3m
Space group number:	229
a (Å):	3.0274
b (Å):	3.0274
c (Å):	3.0274
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	90.0000

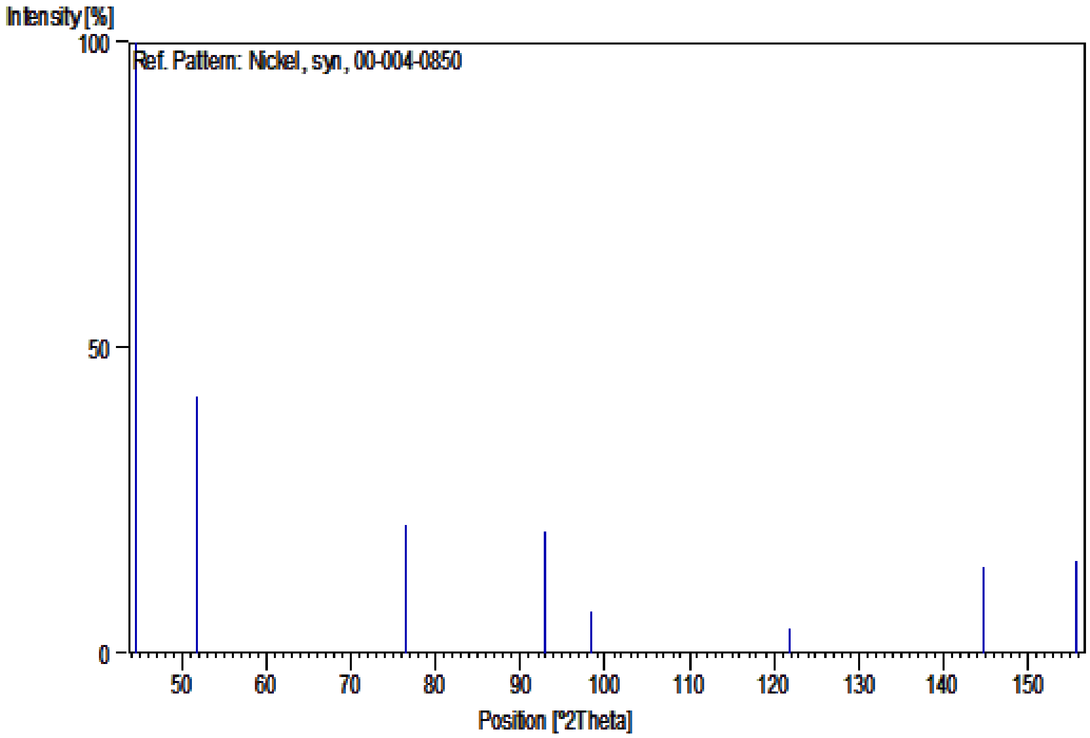


Ni

Crystallographic parameters

Crystal system: Cubic
Space group: Fm-3m
Space group number: 225

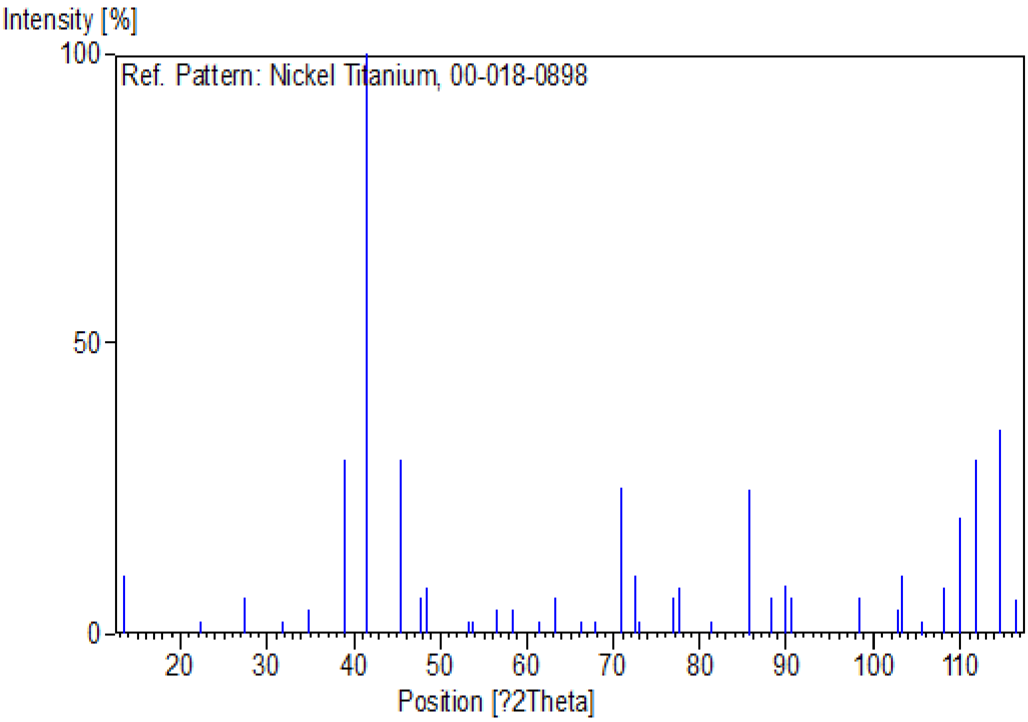
a (Å): 3.5238
b (Å): 3.5238
c (Å): 3.5238
Alpha (°): 90.0000
Beta (°): 90.0000
Gamma (°): 90.0000



Ti$_2$Ni

Crystallographic parameters

Crystal system:	Cubic
Space group:	Fd3m
Space group number:	227
a (Å) :	11.2780
b (Å):	
c (Å):	
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	90.0000

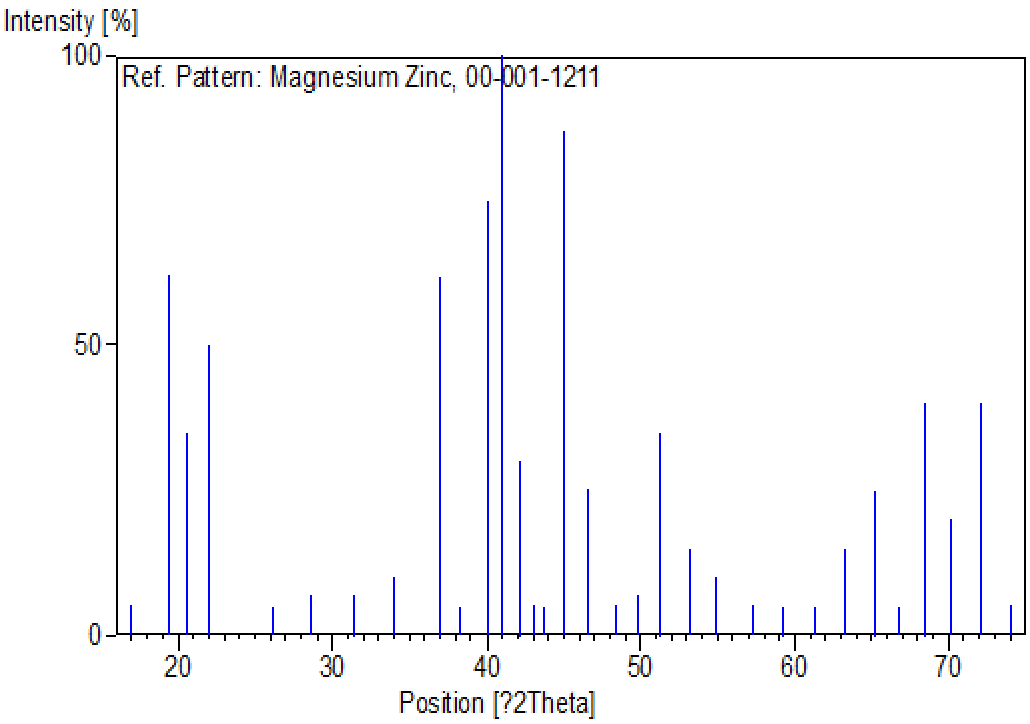


Laves phase ($MgZn_2$)

Crystallographic parameters

Crystal system: Hexagonal
Space group: $P6_3/mmc$
Space group number: 194

a (Å) : 5.233
b (Å):
c (Å): 8.566
Alpha (°): 90.0000
Beta (°): 90.0000
Gamma (°): 120.0000



Appendix B

1. Icosahedral Quasicrystal Diffraction Indexing Scheme

A natural way of representing the quasicrystal diffraction pattern is by means of projecting an ordinary higher dimension reciprocal lattice. Since there are six axes with non-crystallographic 5-fold symmetry in an icosahedron, six lattice vectors will produce an indexing with 6 integer indices. Following Bancel et al. [74], the six reciprocal basis vectors, which point to the vertices of an icosahedron, are defined as:

$$\vec{q}_1 = (1, \tau, 0) \qquad \vec{q}_2 = (1, -\tau, 0) \qquad \vec{q}_3 = (0, 1, \tau)$$

$$\vec{q}_4 = (0, 1, -\tau) \qquad \vec{q}_5 = (\tau, 1, 0) \qquad \vec{q}_6 = (-\tau, 0, 1)$$

Where τ is the golden mean = 2 cos 36^0 = $(1 + \sqrt{5})/2 = 1.618034$. The golden mean is the distance that separate quasicrystal diffraction spots. The q-vector represent the diffracted beam intensity can be expressed as a linear combination of these vectors,

$$\vec{q} = Q_0 * \sum_{i=1}^{6} \vec{ni}\; qi$$

Where Q_0 is determined by choosing of a fundamental reciprocal vector (100000). The fundamental peak is taken to be the most intense peak. With the choice of the fundamental reciprocal vector made, other peaks can be indexed by calculating their q-values and comparing them to experimental data. As an example, the (110001) peak is found at $\vec{q}_{(110001)} = Q_0 * (\vec{q}_1 + \vec{q}_2 + \vec{q}_6)$ or $\vec{q}_{(110001)} = Q_0 * (2-\tau, 0, 1)$. Then q-value could be calculated as: $q_{(110001)} = Q_0 * \sqrt{(2-\tau)^2 + 1^2}$.

$Q_0 = 1 / d_0 * \sum_{i=1}^{6} ni\ \ qi$, for the (100000) peak $Q_0 = 1 / (d_0 * \sqrt{\tau^2 + 1^2})$. Where d_0 is the spacing between the planes in the atomic lattice for the most intense peak, it could be calculated using Bragg's law:

$$d = \frac{\lambda}{2 \sin \theta}$$

Notice that q-value is for the reciprocal lattice. Then d spacing for any peak will be:

$$d_{peak} = \frac{1}{q}$$

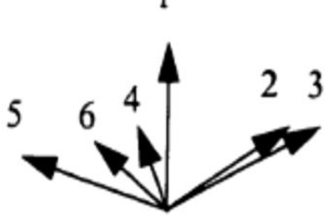


Figure B.1 Six basis vectors used for describing an icosahedral quasicrystal.

To test our calculation to solve this indexing model, we used it to verify the indexing of icosahedral quasicrystalline phase of $Ti_{45}Zr_{38}Ni_{17}$ powders [55], Figure B.2.

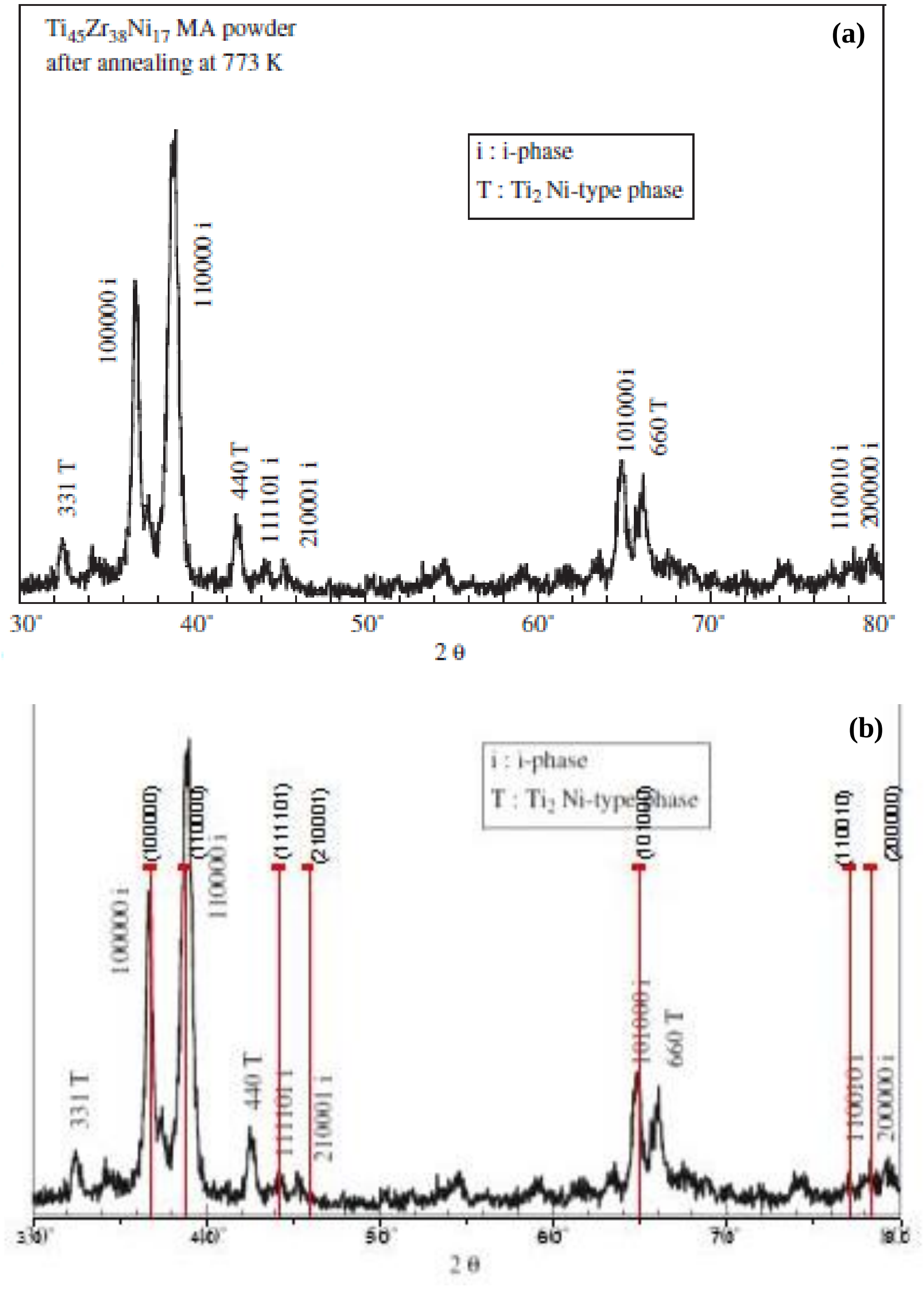


Figure B.2 X-ray diffraction patterns for $Ti_{45}Zr_{38}Ni_{17}$ powders, (a) after MA for 20 h and subsequent annealing at 773 K for 2h [55], (b) indexing of icosahedral quasicrystalline phase.

2. Williamson-Hall Equation

The crystallite size and lattice strain in the annealed $Ti_{41.5}Zr_{41.5}Ni_{17}$ sample was determined by measuring the width (breadth) of the XRD peaks and using Williamson-Hall Equation as follows:

$$\beta \cos\theta = 4\,\epsilon \sin\theta + \frac{K\,\lambda}{D}$$

Where β is the peak width at half maximum height after subtracting the instrument broadening, $\mathcal{E}$ is the strain, K is the shape factor taken as 0.9, λ is the wave length (0.154 nm), and D is the crystallite size. Comparing this to the standard equation for a straight line (m = slope = $4\mathcal{E}$ and c = intercept = $K\lambda/D$):

$$y = mx + c$$

$\beta\cos\theta$ was plotted versus $\sin\theta$ at 2θ of 36.4°, 39°, 67.85°. Strain and crystallite size were calculated from the slope and y-intercept of the fitted line respectively, see Figure B.3.From the plot the crystallite size was measured to be around 25 nm with lattice strain of 0.07%.

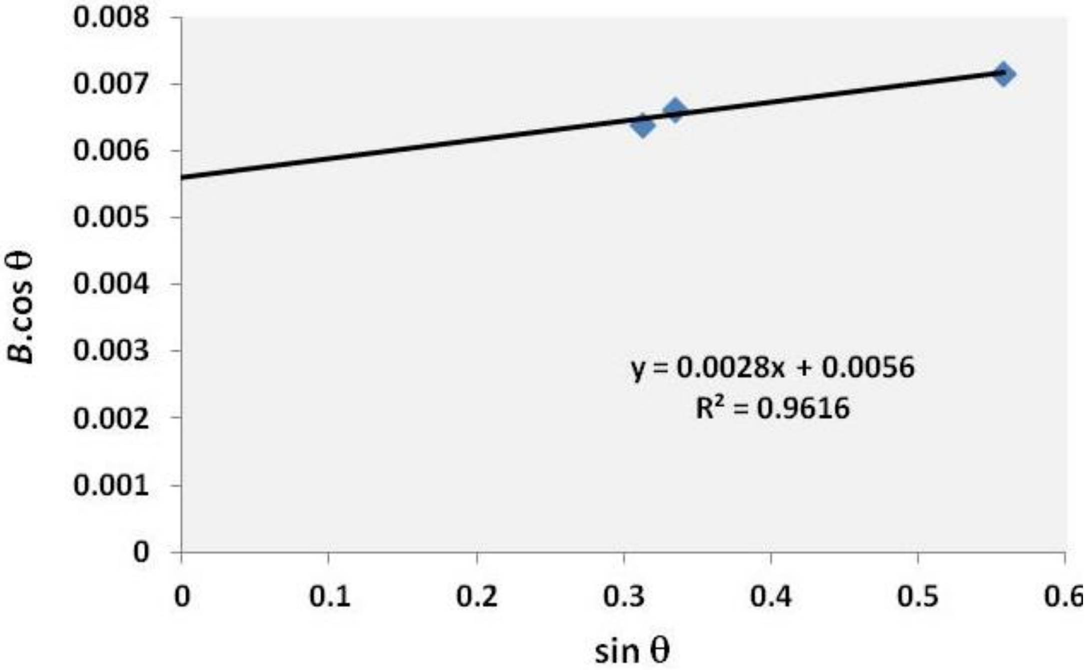


Figure B.3 Williamson-Hall Plot for calculating the crystallite size and lattice strain in the annealed $Ti_{41.5}Zr_{41.5}Ni_{17}$ sample.

Appendix C

Beattie-Bridgeman Equation of State

The amount of hydrogen that was absorped by the sample was calculated using Beattie-Bridgeman equuation of state as follows [136]:

$$Pv^2 = RT\left(1 - \frac{c}{vT^3}\right)\left(v + B_0 - \frac{bB_0}{v}\right) - A_0\left(1 - \frac{a}{v}\right)$$

Where:

P = hydrogen gas pressure in the vial (atm).
v = specific volume (L.mol^{-1})
T = temperature (K).
R = universal gas constant = 0.08206 (L.atm.mol^{-1}.K^{-1}).

The constants A_0, B_0, a , b, and c are characteristic of a gas and for hydrogen it given as:

A_0 = 0.1975, B_0 = 0.02096, a = - 0.00506,b = - 0.04359, c = 504.

A Visual Basic program was constructed and used to obtain the specific volume values using this equation as the following:

```
Public Function Calculate (Pv As Double, Tv As Double) As Double()
Dim result (0 To 4) As Double

Dim P As Double 'pressure (atm)
Dim T As Double 'tempreture (K)
Dim vr As Double 'specific volume for real gas (L/mol)
Dim Ao, Bo As Double
Dim R As Double
Dim a, b, c As Double


Ao = 0.1975
Bo = 0.02096
a = -0.00506
b = -0.04359
c = 0.0504 * 10 ^ 4
R = 0.08206
T = Val(Tv + 273.13) 'variable
P = Val(Pv / 1.01325) 'variable
```

```
  For vr = 0.0001 To 10 Step 0.0000001
 If CDbl(((R * T * (1 - (c / (vr * (T ^ 3)))) / (vr ^ 2)) * (vr + (Bo * (1 - (b / vr))))) - ((Ao * (1 - (a / vr))) / (vr ^ 2)) - P) <= 0 Then
     result(0) = Round(vr, 7) 'txtvr
     Calculate = result
    Exit For
End If
```

Using try and error to calculate the correct specific volume values when the right side of the equation reached 2-6*10^{-6}.

Comparing the calculated specific volume using Beattie-Bridgeman Equation with that calculated using Ideal-Gas Equation showed a pressure-dependant deviation as the following:

Deviation in the specific volume = $$\frac{v_{real} - v_{ideal}}{v_{ideal}} * 100$$

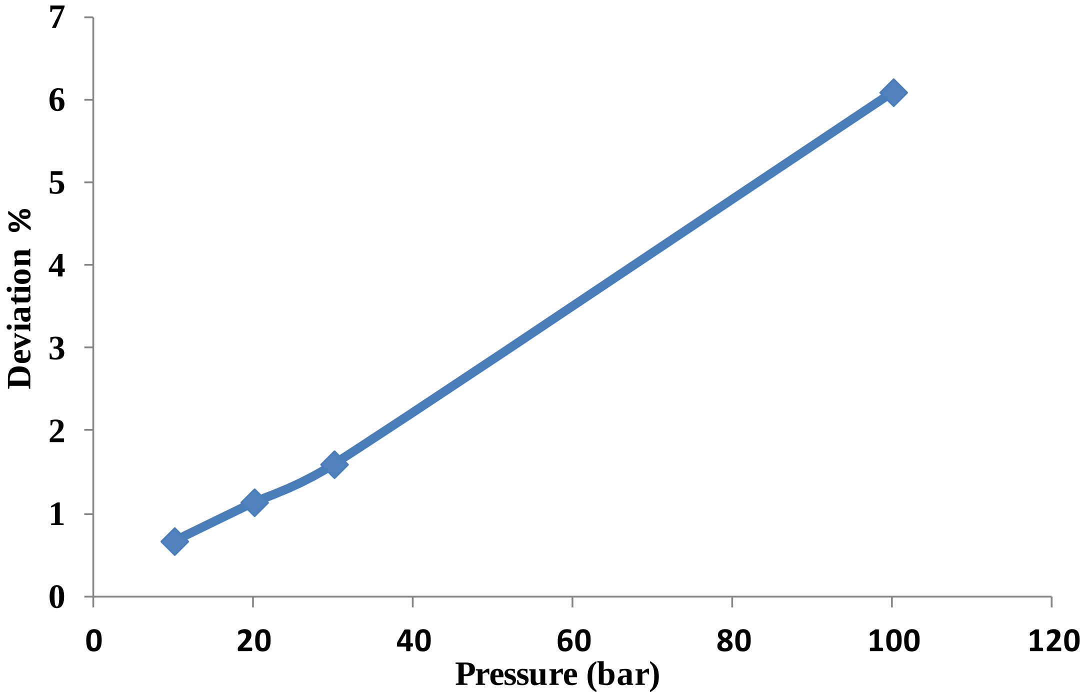


Figure C.1 Calculated specific volume deviation percentage from ideal gas.

CHAPTER 1

Introduction

The rapid technical and industrial development all over the world has increased the demand on energy sources. Enlarged dependency on fossil fuel emerged dreads regarding to its depletion and its destructive effect on the environment. The best alternative to fossil fuel is renewable clean energy sources which have minimal effect on environment. Hydrogen is the simplest naturally occurring element that can be found in numerous materials. When it burnt with oxygen the only product is water vapor, making hydrogen gas an environment-friendly fuel. Hydrogen contains more chemical energy per weight than any hydrocarbon fuel. Hydrogen has nearly three times the energy content of gasoline (120 MJ/kg for hydrogen versus 44 MJ/kg for gasoline) [1]. Due to these physical and chemical advantages, and the successful use of hydrogen fuel in space technology, scientists in general as well as some companies, governmental agencies, and financial institutions believe that hydrogen will be a globally important synthetic fuel in the near future. As a matter of fact, automobile companies like BMW have already started to develop and test cars that run on hydrogen.

Hydrogen can be produced from abundant sea water by electrolysis using the renewable solar energy. Other renewable energy sources such as: wind power, tides and falling water can also be used to create electricity for water electrolysis. Hydrogen also can be produced from many waste streams that contain hydrogen-containing compounds such as: sewage, garbage, landfill accumulations, agricultural biomass, and paper. Flexible use of hydrogen as an energy carrier requires means to store excess product in hydrogen production sites for later use, to overcome daily and seasonal inconsistencies, and to overcome geographical inconsistencies.

One of the key challenges for the establishment of a hydrogen economy is the development of a feasible hydrogen storage system. Unfortunately hydrogen is the lightest element with the lowest volumetric energy density (8 MJ/liter for liquid hydrogen versus 32 MJ/liter for gasoline), see Table 1.1. If we consider a modern commercially available car optimized for mobility with a range of 400 km will burn about 24 kg of gasoline in a combustion engine [2]. To cover the same range, 8 kg of hydrogen will be needed by the direct combustion of hydrogen. At room temperature and atmospheric pressure, 8 kg of hydrogen occupies a volume of 90000 lit. Which means that to store a substantial amount of hydrogen large volumes and high pressures would be required. Solid-state storage is the most efficient long-term alternative for those measures.

Table 1.1 Properties of hydrogen compared to some fossil fuels [1]

	Fuel Oil	**Natural Gas**	**Hydrogen**
Density as Gas, kg/m3	4.4	0.65	0.084
Density as Liquid, kg/m3	740	422.5	70.8

Higher Heating Value, MJ/kg	47.4	50	141.9
Energy Density, MJ/m3 at NTP	35076	32.5	11.92
Normal Boiling Point, K	310-478	111.6	20.3
Limits of Flammability in Air, Vol%	1-7.6	5-15	4-75
Limits of Detonation in air, Vol%	1.1-3.3	6.3-13.5	18.3-59
Autoignition Temperature, K	501-744	813	858

In this thesis, an effort was made to demonstrate the preparation and the characterization of some of Ti-based alloys as hydrogen storage materials. In addition an attempt to enhance the alloys storing performances at ambient temperature by reactive hydrogenation during reactive high energy mechanical milling were done. The experimental work presented here provides significant insight into the hydrogen storage performance characteristics of those intermetallic hydrides.

The thesis starts in its first and second chapters with the introduction of the basic requirement behind storing hydrogen energy and hydrogen storage technologies. Then it focuses on theory and mechanism of hydrogen absorption/desorption processes in metals and alloys, in addition to their reaction kinetics and thermodynamics aspects. Finally, it provides a discussion about the research goals.

The third chapter of this thesis covers the experimental techniques that were used for samples preparation, characterization and hydrogenation. Some of the aspects discussed in this chapter are: samples preparation using mechanical alloying and annealing techniques; samples characterization using scanning electron microscopy/x-ray dispersive spectrometry (SEM/XEDS), Differential Scanning Calorimeter (DSC), X-ray Diffraction (XRD) and High Resolution Transition Electron Microscopy (HRTEM); as well as samples hydrogenation technique.

The fourth chapter discusses the results of samples preparation by mechanical alloying and by subsequent annealing. The chapter starts by a short characterization of the raw materials, followed by the characterization results of the mechanically alloyed sample. Investigation of the prepared powders thermal stability is then presented. Finally, annealing effect on the samples structure and the produced phases for each alloy are discussed.

The fifth chapter presents the results for the hydrogenation/dehydrogenation process of the prepared alloys before and after annealing. Absorption/desorption kinetic rate measurements and Pressure Composition Isotherms (PCT) properties of the samples at high and at cryogenic temperatures are also presented.

The sixth chapter studies the attempt to enhance the alloys storing performances at room temperature by hydrogenation during reactive high energy mechanical milling. Accelerated hydrides formation during reactive mechanical milling, are presented. The influence of milling conditions on hydrogenation rate and extent are also discussed.

The seventh chapter summarizes the main conclusions from this study. After that the references consulted during this work are given.

CHAPTER 2

Literature Survey

2.1 Requirements of Hydrogen Storage Systems

Hydrogen storage systems could be used for stationary or transportation applications. Stationary applications can occupy a large area, operate at high temperatures and pressures, and have slow kinetics. In contrast; transportation applications must operate within minimum volume and weight specifications, operate at moderate temperatures and pressures, and have sufficient hydrogen capacity with fast rates. Hence, the requirements for stationary applications are more flexible and easy to achieve than those for transportation applications. So, one of the major challenges in achieving the hydrogen economy is to find suitable hydrogen storage systems for transportation applications. The main storage criteria to any fuel storage are explained in the following subsections:

2.1.1 Volumetric Density/Capacity

There are two capacities commonly used in discussion of gas storage. One is the volumetric capacity and the other is the gravimetric capacity. The volumetric capacity is the amount of hydrogen stored divided by the total volume occupied by the container. For applications with limited space, the volumetric capacity is more dominant.

$$\text{Volumetric Density} = \frac{\text{mass of hydrogen stored}}{\text{total volume occupied by the container}} \left(\text{kg H}_2 / m^3\right)$$

2.1.2 Gravimetric Density/Capacity

The gravimetric capacity is often defined as the weight percentage of hydrogen divided by the total weight of storage system, including the weight of hydrogen.

$$\text{Gravimetric Density} = \frac{\text{weight of hydrogen stored}}{\text{total weight of storage system} + \text{hydrogen}} \times 100 \ \left(\text{wt\%}\right)$$

For applications with limited weight, the gravimetric capacity is more dominant. Low weight is essential for all mobile applications, in particular larger vehicles and hand-held devices, but not as important for stationary applications such as filling stations. Small volume is critical for small vehicles and hand-held devices but less so for stationary applications and larger vehicles.

2.1.3 Ease of Storage and Retrieval

Hydrogen storage system should work near ambient temperature with high hydrogen storage capacity in a small volume; have fast kinetics, mechanical stability towards intrusions in collisions or inflammable when penetrated. Other desirable property is the possibility to operate at near ambient pressure with low thermal losses.

2.1.4 Energy Consumption and Storage Cost

The energy losses during charging and discharging the hydrogen decrease the efficiency of the storage system. The way of storing hydrogen must be cost-effective.

2.1.5 Safety

Like any other fuel, improper storing or handling of hydrogen could present risks. The physical properties of hydrogen are quite different from those of common fuels. Some of those properties make hydrogen potentially less dangerous, while in certain theoretical situation it could be more hazardous. Of course, all the precautions necessary for the safe handling of any flammable fuel must be taken with hydrogen.

Since hydrogen has the lightest density, it has a greater tendency to escape through leaks than do other common fuels. Though, since the other fuels have higher energy densities per unit volume than hydrogen, their leak would result in more energy release than a hydrogen leak. In addition in case of hydrogen leak; hydrogen will disperse much faster than any other fuel, which would reduce the risk level. Hydrogen detonation in the open atmosphere is highly unlikely. If an explosion should occur, hydrogen has the least explosive energy per unit stored energy among the fuels.

Hydrogen flame is nearly invisible, which could be dangerous because people in the vicinity of a hydrogen flame may not even know there is a fire. However, the low emissivity of hydrogen flames means that materials and people in the close proximity will be much less likely to ignite and be hurt by the radiant heat transfer. Also, Hydrogen fires produce only water vapor [3].

Hydrogen is nontoxic but it can act as a simple asphyxiate by displacing the oxygen in the air. Inhaling sufficiently large amount of hydrogen can cause unconsciousness without any warning symptoms such as dizziness. Still the lower flammable limit of hydrogen in air, which is only some four percent by volume, would make it flammable before it could lead to unconsciousness [4].

2.2 Hydrogen Storage Targets

Specific performance targets are specified by the USA Department of Energy (DOE) for a successful transition to hydrogen-fueled transportation as follows [5]:

- Appropriate thermodynamics (Operating temperature and pressure -20/50 °C, and up to 2.5 bar respectively).
- Fast kinetics (Refueling rate 1.5 kg H_2/min).
- High storage capacity (6 wt %).
- High gravimetric and volumetric densities (7.2 MJ/kg, 5.4 MJ/L respectively).
- Long cycle lifetime for hydrogen absorption/desorption.
- Effective heat transfer, high mechanical strength and durability.
- Like any fuel, safety during normal use and acceptable risk under abnormal conditions.