Commissioning Of An Arc-melting/vacuum Quench Furnace Facility For Fabrication Of Ni-ti-fe Shape Memory Alloys, And The Characterization

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COMMISSIONING OF AN ARC-MELTING / VACUUM QUENCH FURNACE
FACILITY FOR FABRICATION OF Ni-Ti-Fe SHAPE MEMORY ALLOYS,
AND THEIR CHARACTERIZATION

by

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ABSTRACT

Shape memory alloys when deformed can produce strains as high as 8%. Heating results in a phase transformation and associated recovery of all the accumulated strain, a phenomenon known as shape memory. This strain recovery can occur against large forces, resulting in their use as actuators. The goal of this project is to lower the operating temperature range of shape memory alloys in order for them to be used in cryogenic switches, seals, valves, fluid-line repair and self-healing gaskets for space related technologies. The Ni-Ti-Fe alloy system, previously used in Grumman F-14 aircrafts and activated at 120 K, is further developed through arc-melting a range of compositions and subsequent thermo-mechanical processing.

A controlled atmosphere arc-melting facility and vertical vacuum quench furnace facility was commissioned to fabricate these alloys. The facility can create a vacuum of $10^{-7}$ Torr and heat treat samples up to 977 °C. High purity powders of Ni, Ti and Fe in varying ratios were mixed and arc-melted into small buttons weighing 0.010 kg to 0.025 kg. The alloys were subjected to solutionizing and aging treatments. A combination of rolling, electro-discharge machining and low-speed cutting techniques were used to produce strips. Successful rolling experiments highlighted the workability of these alloys. The shape memory effect was successfully demonstrated at liquid nitrogen temperatures through a constrained recovery experiment that generated stresses of over 40 MPa. Differential scanning calorimetry (DSC) and a dilatometry setup was used to characterize the fabricated materials and determine relationships between composition, thermo-mechanical processing parameters and transformation temperatures.
Dedicated

to my

Late Grandfather Pritam Singh Sidhu,

Grandparents and Parents
ACKNOWLEDGEMENTS

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CHAPTER 1: INTRODUCTION

1.1 Motivation

Space technology encompasses an incredibly broad spectrum of engineering and scientific disciplines. The prime movers for placing payloads into orbits or sending missions into deep space use rockets which require controls, seals, joints, coupling and actuators of a broad variety. Shape memory alloys (SMAs) have potential application in these devices. The satellites themselves involve passive and active components which can exploit the unique properties of SMAs.

SMA actuators are particularly advantageous for space applications as they [1]:

(i) Offer high power to weight and stroke-length to weight ratios

(ii) Integrate sensory and actuation functions

(iii) Function in a clean, debris-less and spark free manner

(iv) Possess the ability to function in zero-gravity environments

(v) Offer design flexibility, i.e., function in a linear or rotary manner.

The behavior of SMAs largely depend on the alloy composition and thermo-mechanical processing. Addition of new elements, as well as variation in the original alloy composition, produces drastic shifts in the transformation temperatures of SMAs. The development of a new system of SMAs, for cryogenic applications, required a facility with the capability to melt and heat treat varying compositions. The motivation for this project comes from the need to commission such a facility for the development of SMAs. A controlled atmosphere arc melting and vertical vacuum quench furnace facility was commissioned. Arc-melting offers a way of making small volumes of varying compositions in a clean and controlled environment. The
vertical quench furnace facility offers heat treatment up to 1200 °C in high vacuum (~10⁻⁷ Torr). This facility was used to successfully fabricate Ni-Ti-Fe SMAs with sub-ambient transformation temperatures.

The immediate application of these alloys is in a cryogenic thermal conduction switch. Also there is potential for application in seals, valves, debris-less separation mechanisms, latch and release mechanisms, fluid line repair, and self healing gaskets.

1.2 Martensitic Transformation

Martensitic transformation (MT) is defined as a lattice transformation involving shear deformation resulting from the cooperative movement of atoms until the parent lattice transforms into martensite (named after the eminent German metallurgist Adolf Martens). The transformation has the following properties:

(i) It is a displacive transformation and is formed by cooling from a higher temperature phase called the parent phase or austenite.

(ii) It is accompanied by shape change. The shape change plays an important role in the deformation mechanism responsible for the shape memory effect (SME).

(iii) The martensite crystal has a specific “habit plane”. This is the interface between the parent and martensite phases.

MT is a first order transformation, i.e., it proceeds by nucleation and growth. Martensite formation is associated with liberation of heat, a hysteresis and a temperature range over which austenite and martensite co-exist. As the transformation is associated with a shape change, large
strains arise as the martensite starts to form in the parent phase. The reduction in strain is for the nucleation and growth of martensite. This is attained either by undergoing slip or by introducing twins [2] (Figure 1.1). This is called lattice invariant shear (LIS), since neither process changes
the structure of the martensite. The traces of LIS such as dislocations and stacking or twinning faults have been observed by electron microscopy [3]. Slip is a permanent process. Twinning is unable to accommodate volume changes but can accommodate shape changes. For the SME to occur, the accommodation should be fully reversible; hence twinning is introduced as LIS in SMAs [2]. Martensite in steel involves both a volume and a shape change, whereas SMAs only undergo a shape change.

### 1.2.1 Transformation Thermodynamics

The martensite transformation occurs when the chemical free energy of the martensite phase is lower than the parent phase. The free energy curves for both the parent and the martensite phases as a function of temperature are shown in Figure 1.2. The thermodynamic equilibrium temperature between the two phases is represented by $T_o$ and $\Delta G^{p\rightarrow m}$ represents the driving force for the nucleation of martensite. The same argument applies for the reverse transformation. The Gibbs free energy of a system upon MT may be written as

$$\Delta G = \Delta G_c + \Delta G_s + \Delta G_e = \Delta G_c + \Delta G_{nc}$$

where $\Delta G_c =$ chemical free energy term originating from parent to martensite

$\Delta G_s =$ surface energy term between parent and martensite

$\Delta G_e =$ elastic energy term around the martensite

$\Delta G_{nc} =$ non-chemical energy term.
In most martensitic transformations, $\Delta G_c$ is almost equal to $\Delta G_{nc}$. Hence a driving force is required for the transformation, i.e., the specimen has to be supercooled to a suitably low temperature, $M_s$ (martensite start temperature) below the equilibrium temperature $T_o$ for the transformation to occur. Same holds true for the reverse transformation, i.e., the specimen has to be superheated to a suitably high temperature above $T_o$. The difference between $T_o$ and $M_s$ is called the degree of supercooling. The degree of supercooling for martensitic transformations in ferrous alloys and steels can be as much as 200 °C, but for shape memory alloys it is 5~30 °C [3].
1.2.2 Thermoelastic Martensitic Transformation

Martensitic transformations can be classified into two categories, thermoelastic and non-thermoelastic transformation.

When a specimen is cooled below $M_s$, the martensite crystal starts to grow. However, after reaching a certain size the growth is arrested as the sum of the decrease in the thermal, chemical free energy and the increase in the elastic, non-chemical free energy has approached a certain minimum value. This equilibrium between thermal and elastic effects is defined as thermoelasticity. The equilibrium is disrupted by the application of thermal or mechanical energy to the specimen. The stabilized martensite crystals then start to grow or shrink again. This transformation is termed a thermoelastic martensitic transformation. It is characterized by a transformation hysteresis as small as 15 °C [3] and a crystallographically reversible transformation. It has been experimentally observed that in thermoelastic martensitic transformations, the martensite crystals first formed at the temperature $M_s$ are the last to undergo the reverse transformation at temperature $A_f$ (austenite finish temperature) [3].

In non-thermoelastic martensite transformations, single martensite crystals grow instantaneously to their final size and do not grow further as the temperature falls. For the reverse transformation, the martensite crystals do not shrink and revert to the parent phase; instead the parent phase crystals nucleate and grow within the martensite phase. The transformation is characterized by transformation hysteresis as large as ~400 °C [3].
1.3 **Shape Memory Alloys**

Shape memory alloys refer to a unique class of alloys that remember their original shape or pre-deformation shape when heated from a relatively low temperature. After deformation in the low temperature phase (martensite phase), the alloys stay deformed until heated, whereupon they spontaneously return to their original, pre-deformation shape. One of the important aspects of SMAs is their ability to experience large and reproducible shape recovery.

![Figure 1.3: Shape memory effect described with the characteristic transformation temperatures; martensite start (M_s), martensite finish (M_f), austenite start (A_s) and austenite finish (A_f) temperatures.](image)

Figure 1.3: Shape memory effect described with the characteristic transformation temperatures; martensite start (M_s), martensite finish (M_f), austenite start (A_s) and austenite finish (A_f) temperatures.
The first recorded observation of the shape memory transformation was by Chang and Read in 1932 [4]. They noted the reversibility of the transformation in AuCd by metallographic observations and resistivity changes. In 1938, the transformation was seen in brass (Cu-Zn) and the shape memory effect was observed in a bent bar of AuCd in 1951 [4]. Before the identification of the shape memory effect in Au-Cd, Ölander reported a rubbery feel in this alloy. Buehler observed that warm nickel-titanium gave a sharp ring when struck whereas the cooled alloy gave a dull thud [5]. The discovery of the NiTi system in 1963, at the Naval Ordinance Laboratory (hence the name Nitinol) led to the rapid growth of interest in the shape memory phenomenon. In 1970, the same phenomenon was observed in Cu-Al-Ni and it became clear that this behavior was common to alloys which underwent a thermoelastic martensite transformation. Table 1.1 lists alloy systems exhibiting shape memory effect.

When an SMA is cooled from the austenite phase, the martensite phase starts at $M_s$ and finishes at $M_f$ (martensite finish temperature). Upon heating, martensite transformation to austenite begins at $A_s$ (austenite start temperature) and at $A_f$ martensite completely transforms to austenite. Martensite is completely unstable above $A_f$. Composition variation and thermo-mechanical treatments significantly influence these transformation temperatures.

### 1.3.1 Shape Memory Effect

Shape memory effect (SME) is the phenomena where the alloys are easily deformed in the low temperature phase (martensitic phase) and return to its pre-deformation or original shape when heated from the low temperature. Figure 1.3 displays these transformation temperatures.
Table 1.1: Alloys exhibiting shape memory effect with their parent structure [6].

<table>
<thead>
<tr>
<th>Alloy systems</th>
<th>Austenite structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-Cd</td>
<td>B2</td>
</tr>
<tr>
<td>Cu-Zn</td>
<td>B2</td>
</tr>
<tr>
<td>In-Tl</td>
<td>FCC</td>
</tr>
<tr>
<td>Ni-Ti</td>
<td>B2</td>
</tr>
<tr>
<td>Cu-Zn-Al</td>
<td>B2, DO$_3$</td>
</tr>
<tr>
<td>Ti-Nb</td>
<td>BCC</td>
</tr>
<tr>
<td>Au-Cu-Zn</td>
<td>-</td>
</tr>
<tr>
<td>Cu-Zn-Sn</td>
<td>B2</td>
</tr>
<tr>
<td>Cu-Zn-Si</td>
<td>B2</td>
</tr>
<tr>
<td>Cu-Al-Ni</td>
<td>DO$_3$</td>
</tr>
<tr>
<td>Ag-Cd</td>
<td>-</td>
</tr>
<tr>
<td>Cu-Sn</td>
<td>B2</td>
</tr>
<tr>
<td>Cu-Zn-Ga</td>
<td>B2</td>
</tr>
<tr>
<td>Ni-Al</td>
<td>B2</td>
</tr>
<tr>
<td>Fe-Pt</td>
<td>Li$_2$</td>
</tr>
<tr>
<td>U-Nb</td>
<td>BCC (disordered)</td>
</tr>
<tr>
<td>Ti-Pd-Ni</td>
<td>B2</td>
</tr>
<tr>
<td>Fe-Mn-Si</td>
<td>FCC (disordered)</td>
</tr>
</tbody>
</table>

The shape recovery due to the SME is completed by heating the specimen above $A_f$. The driving force for the shape recovery is the difference in chemical free energy between the parent and the
martensite phase upon the reverse transformation. However, the reverse transformation does not always restore the specimen's shape. For complete SME the following two conditions have to be met:

(i) The martensite transformation must be crystallographically reversible, i.e., the alloy must undergo a thermoelastic martensitic transformation.

(ii) The deformation process should not involve slip as it induces permanent deformation.

The shape memorized in the SME is the shape of the specimen in the parent phase. When the alloy remembers only the parent phase (austenite phase) shape, it is called the one-way shape memory effect. However, by heavily deforming the specimen in the martensite state or by heating the specimen under constraint after deforming it in the martensite state, the shape of the martensite phase can be partially memorized. This phenomenon is termed as the two-way shape memory effect.

### 1.3.2 Superelasticity

Another unique property of SMAs is superelasticity or pseudoelasticity. The driving force for this transformation is mechanical as opposed to thermal. Superelasticity occurs when a material is deformed above $A_s$ and below $M_d$ (martensite desist). In this range martensite is made stable with the application of stress, but becomes unstable as the stress is removed. Large strains are possible due to the formation of stress-induced martensite. Strains are completely recovered on unloading. Strains up to 8% are recoverable in Ni-Ti SMAs. The increase in difficulty to stress induce martensite continues to increase with temperature until $M_d$. 


1.4 **SMA Actuators**

An SMA actuator utilizes the shape memory effect to generate force and motion. They act both as a temperature sensor and a work-generating element. The electrical actuators are generally used to do work, replacing solenoids, servomotors, hydraulics, pneumatics devices etc.

![Figure 1.4: A biased two-way actuator [7].](image)
They are simpler in design, quieter, compact and often less expensive [8]. The thermal actuator detects a change in temperature where upon they actuate. Compared to other actuation methods, SMA actuators are generally simpler, less expensive, and compact. They provide very large and sudden motion. The electrical actuators are heated by passing current directly through the SMA, while thermal actuators are heated by changes in ambient temperature. Figure 1.4 illustrates a simple model of a biased spring two-way actuator. The bias spring opposes the SMA spring for actuation in either direction. When the temperature of the SMA element rises above a set temperature, \( A_t \), the SMA element becomes stronger, as it undergoes a phase transformation, and forces the bias spring into compression. As the temperature of the SMA element drops below a certain temperature, \( M_s \), the bias spring force overcomes the SMA element force, thus acting in the opposite direction.

### 1.5 Cryogenic Thermal Conduction Switch

Krishnan [7] discusses the design, fabrication and testing of a SMA based cryogenic thermal conduction switch. He has successfully demonstrated the actuation of this switch between two cryogenic reservoirs. Figure 1.5 shows a schematic of a generalized cryogenic thermal conduction switch. The switch is shown initially in contact with the environment and is in the low temperature phase. As the temperature of environment B increases, heat is transferred to the SMA springs. These springs then undergo a phase transformation to the high temperature phase and expand by an amount ‘a’ and come in contact with environment A. This creates tension in the bias spring. As the temperature in environment B decreases below \( M_s \) the SMA spring transforms to the low temperature phase and is weakened. The bias spring loses its tension.
and compresses along with the SMA springs. This breaks the heat transfer contact. The cycle repeats itself maintaining the two environments at the desired temperatures.

Figure 1.5: A shape memory alloy based cryogenic thermal conduction switch.
CHAPTER 2: LITERATURE REVIEW

2.1 NiTi Shape Memory Alloy

The equiatomic ordered intermetallic NiTi alloy exhibits a phase transformation between a low temperature, monoclinic B19′, martensite phase and a high temperature, cubic B2, parent austenite phase. The phase transformation from martensite to austenite is accompanied by a shape change which is employed for various applications. The transformation characteristics of NiTi are modified by changing composition, i.e., either deviating from equiatomic NiTi or substituting a small amount of Ni or Ti with another metal, cold working and heat treating. The modified characteristics include one or more combinations of shifts in transformation temperatures, appearance of an intermediate phase (R-phase) and change in hysteresis. These modifications result in a change in the shape memory and superelastic response of NiTi. Excess nickel, in amounts up to about 1 at.%, is the most common alloying addition. Table 2.1 lists selected properties of NiTi alloys. For applications that require \( M_s \) to be below room temperature, NiTi shows instability or an \( M_s \) dependence on prior thermal history [4]. Furthermore, they tend to have poor ductility.

2.1.1 Phase Transformations

Phase transformation in NiTi alloys can follow different paths, i.e., \( B2 \rightarrow B19' \), \( B2 \rightarrow R \rightarrow B19' \), \( B2 \rightarrow B19 \rightarrow B19' \) and \( B2 \rightarrow R \rightarrow B19 \rightarrow B19' \) [7]. The conditions for the above transformation paths is determined by variations in Ni content, alloying, aging after solution treatment, thermo-mechanical treatments and thermal cycling [7].
Table 2.1: Selected properties of NiTi alloys [4].

<table>
<thead>
<tr>
<th>Property</th>
<th>Austenite</th>
<th>Martensite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>1300 °C</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>6.45 g/cubic cm</td>
<td></td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>100 micro-ohms cm</td>
<td>70 micro-ohms cm</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>18 W °C /cm</td>
<td>8.5 W °C /cm</td>
</tr>
<tr>
<td>Corrosion resistance</td>
<td>Similar to 300 series Stainless Steel</td>
<td></td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>83 GPa</td>
<td></td>
</tr>
<tr>
<td>Yield strength</td>
<td>195 to 690 MPa</td>
<td>70 to 140 MPa</td>
</tr>
<tr>
<td>Ultimate tensile strength</td>
<td>895 MPa</td>
<td></td>
</tr>
<tr>
<td>Transformation temperature</td>
<td>-50 °C to 110 °C</td>
<td></td>
</tr>
<tr>
<td>Latent heat of transformation</td>
<td>5.78 cal/g</td>
<td></td>
</tr>
<tr>
<td>Hysteresis</td>
<td>30 °C to 50 °C</td>
<td></td>
</tr>
<tr>
<td>Transformation strain</td>
<td>Single cycle</td>
<td>8% (max)</td>
</tr>
<tr>
<td></td>
<td>100 cycles</td>
<td>6%</td>
</tr>
<tr>
<td></td>
<td>100,000 cycles</td>
<td>4%</td>
</tr>
</tbody>
</table>

2.1.2 Effect of Thermo-Mechanical Treatments

Ni rich alloys aged at lower temperatures (less than 500 °C) or slowly cooled decompose to a Ti-rich matrix with a finely dispersed Ni-rich phase [7]. This causes an elevation in the transformation temperature. Hence aging of Ni-rich alloys are done between 500 °C and 700 °C to preserve the lower transformation temperatures. Additionally, aging at higher temperatures suppresses the R-phase transformation. Selective work hardening, exceeding 50% reduction in some cases, and proper heat treatment greatly improve the ease with which the martensite
deforms. This gives austenite greater strength and results in the two-way shape memory effect being exhibited.

2.1.3 Effect of Alloying Elements

The moderate solubility of NiTi facilitates alloying with different elements. This helps to modify the mechanical properties and change the transformation characteristics. The addition of a third or fourth element to NiTi alloys is used to [9]:

(i) Control the transformation temperatures
(ii) Increase the stability of $M_s$ with respect to the thermal history
(iii) Control the hysteresis
(iv) Increase the austenitic strength
(v) Decrease or increase the martensitic strength
(vi) Improve the corrosion resistance
(vii) Suppress the R-phase.

Common contaminants such as oxygen and carbon can shift the transformation temperature and degrade the mechanical properties. Oxygen forms a NiTi complex, Ti$_4$Ni$_2$O$_x$, which tends to deplete titanium in the matrix, lower $M_s$, retard grain growth and increase the strength [10].

Niobium and copper are used to control hysteresis and martensitic strength. Niobium addition increases the hysteresis, desirable for coupling and fastener applications. Copper addition reduces the hysteresis to about 15 °C, desirable for actuator applications. Copper also improves the processing ability, makes the transformation less sensitive to processing and
improves the fatigue resistance. Most benefits are seen up to 10 at.% of copper addition [11]. Further addition show only marginal improvement in the alloy properties. Ni-Ti-Cu alloys are used in cell-phone antennae.

![Figure 2.1: Effect of 3d transition metal additives on the martensite start temperature (M_s) [12].](image)

The changes in transformation temperatures of NiTi alloys, when Ti is replaced by V, Cr, Mn and Ni is replaced by Fe and Co are shown in Figure 2.1 [12]. The depression of the martensitic start temperature is strongest with the addition of Cr and weakest with V and Co. Their additions
have practical importance in creating cryogenic SMAs, stiffening a superelastic alloy, or increasing the separation of the R phase from the martensite phase [10].

### 2.1.4 Applications

(i) **Actuators**: SMA actuators integrate both sensory and actuation functions. Another advantage is the small size.

(ii) **Thermostatic mixing valve**: The valve supplies water at a temperature which is controlled by mixing cold water with hot water [13]. A NiTi spring is exposed to mixed currents of hot and cold water. The spring controls the temperature of the mixed water in real time.

(iii) **Muscle wires**: SMA wire has the ability to replicate biological muscle fibers. The actuation of these wires can occur either by external or internal passage of electric current. This makes them suitable for use in robots and toys.

(iv) **Couplings**: Couplings of NiTi alloys provide a secure connection at room temperatures and can be easily removed by cooling.

(v) **Eyeglass frames**: Frames made of superelastic NiTi can withstand severe deformation.

(vi) **Vascular stents**: The biocompatibility of NiTi alloys makes them suitable to expand clogged blood vessels.

(vii) **Orthodontic wire**: NiTi wires are used in orthodontic operations to adjust irregular teeth lines. The constant correcting force they provide gives both doctors and patients a great advantage. In addition, Ti-Ni-Cu-Cr and Ti-Ni-Pd alloys, with small
differences in the installation force and the correction force, are under development for future use [13].

2.2 Ni-Ti-Fe Shape Memory Alloys

Wang investigated changes in transformation temperatures in NiTi when Ni is partially replaced by Co and Fe. He determined the transformation temperatures by monitoring the changes in the elastic wave propagation of the specimen; therefore his results were not accurate. However, he demonstrated that substitution with Fe (more than Co) remarkably lowers the transformation temperature [12].

Ni-Ti-Fe based shape memory alloys have been widely used to connect titanium hydraulic coupling in Grumman F-14 aircrafts [1]. The couplings were deformed and stored in liquid nitrogen (-196 °C). It was then introduced to join two tubes at room temperature, at the time of application. The increase in temperature resulted in a phase transformation (at around -153 °C) and the shape change associated with the phase transformation decreased the coupling diameter [1]. This decrease in diameter exerted a stress on the tubes and resulted in a secure joint. The couplings were advantageous in that:

(i) There was no thermal damage to surrounding materials as welding was not required
(ii) Overhauls were streamlined as the couplings could be removed simply by freezing them in liquid nitrogen.

More than one hundred thousand of these couplings have been successfully used, free from oil leaks. This type of coupling has also been used in the plumbing of atomic submarines, warships
and in the maintenance and repair of pipes (diameters ~150 mm) laid on the ocean floor to transport oil from oil fields [14].

The wide transformation hysteresis Ni-Ti-Nb shape memory alloys (about 145 °C versus 30 °C of NiTi) are advantageous over Ni-Ti-Fe alloys as they avoid storing and installing at cryogenic temperature after deformation in the martensitic state. By over deforming Ni-Ti-Nb alloys in the martensitic condition, the $A_s$ temperature is temporarily increased to $A_s'$ ($A_s' - M_s \sim 145 °C$), thus permitting pipe coupling and fasteners, to be stored at ambient temperature and not necessarily in liquid nitrogen [15]. Since Ti, Ni and Nb possess quite different melting points, compositional deviation often occurs. However NiTiFe alloys are easily controlled in terms of composition, processing and to obtain precise transformation temperatures.

2.2.1 Phase Transformations

Addition of Fe in place of Ni in NiTi suppresses the martensitic transformation. This third element substitution gives rise to an intermediate phase (R phase) in both the forward and reverse transformation [16, 17, 18]. The transformation now proceeds by a two stage process:

High temperature, austenite phase (B2)

↓↑

Intermediate/premartensite phase (R-phase)

↓↑

Low temperature, martensite phase (B19').
Pushin et al. have demonstrated that finely grained Ni-Ti-Fe alloys containing 4 at.% Fe and ultra fine grained alloys containing 3 at.% Fe undergo a two step transformation, i.e., B2 ↔ R ↔ B19′. Also fine grained Ni-Ti-Fe alloys with 4-5 at.% Fe and ultra fine grained alloys with 3-5 at.% Fe are characterized by a single martensitic transformation R ↔ B19′ [19]. The fine grained alloys and the ultra fine grained alloys were measured in the temperature ranges of -173 °C to 127 °C and -268.8 °C to 127 °C, respectively.

### 2.2.2 Transformation Temperature Variation with Fe Addition

NiTi alloys with addition of Fe show distinct separated transformations, first between the B2, cubic phase to a rhombohedral R-phase and next to the B19’, martensite phase.

![Figure 2.2: Effect of Fe substitution upon the existing phases of NiTi [12].](image)
Fe addition widens the temperature region in which the intermediate phase is stable (Figure 2.2) [12]. Table 2.2 gives the transformation temperatures of different Ni-Ti-Fe alloys as per different authors. The substitution of 3 at.% Fe for Ni in NiTi depresses the start of martensite transformation by 100 °C more than the corresponding decrease in the pre-martensitic/intermediate transformation [20, 21, 22].

The shape recovery strain of 5.6% has been obtained with a total strain of 8% in the Ni$_{48}$Ti$_{50}$Fe$_2$ alloy [16]. The effect of rapid quenching and grain size on the transformation temperature from B2 to R-phase slightly decreases the temperatures (by 10 °C to 20 °C) whereas the start of B19′ is substantially decreased [19].

### 2.2.3 Heat Treatments

The biggest challenge in processing SMAs is the development of effective fabrication techniques to achieve the desired properties. Table 2.2 shows the different heat treatments done by respective authors on Ni-Ti-Fe. Heat treatment narrows down the temperature interval of the existence of the two phase region, weakly affects the onset temperature of R-phase and sharply increases the end of R-phase [27]. Annealing at 700 °C has no effect on the start of R-phase, but a notable effect on end of the phase. In alloys with 4 and 5 at.% Fe there is a wide temperature interval in which the R-phase occupies the entire volume of the material [27]. In Ni-Ti-Fe alloys with 2.5 and 5 at.% Fe annealed at 800 °C for one hour and subsequently oven cooled, there was no change in start of R phase. However the two phase region was preserved and it became narrower by 20 °C and 10 °C respectively [27]. Heat treatment of severely cold-worked materials
results in higher yield strength and ductility. Annealing of warm worked material does not significantly change its mechanical properties [28].

Table 2.2: Ni-Ti-Fe SMAs with their heat treatment and the transformation temperatures as reported by different authors.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Heat treatment</th>
<th>Transformation Temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni&lt;sub&gt;49&lt;/sub&gt;Ti&lt;sub&gt;50&lt;/sub&gt;Fe&lt;sub&gt;1&lt;/sub&gt; [19]</td>
<td>a</td>
<td>Martensite start (M&lt;sub&gt;s&lt;/sub&gt;)</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;48&lt;/sub&gt;Ti&lt;sub&gt;50&lt;/sub&gt;Fe&lt;sub&gt;2&lt;/sub&gt; [16, 17]</td>
<td>b</td>
<td>-13</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;48&lt;/sub&gt;Ti&lt;sub&gt;50&lt;/sub&gt;Fe&lt;sub&gt;2&lt;/sub&gt; [23]</td>
<td>c</td>
<td>-32</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;47&lt;/sub&gt;Ti&lt;sub&gt;50&lt;/sub&gt;Fe&lt;sub&gt;3&lt;/sub&gt; [23]</td>
<td>c</td>
<td>-88</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;47&lt;/sub&gt;Ti&lt;sub&gt;50&lt;/sub&gt;Fe&lt;sub&gt;3&lt;/sub&gt; [24]</td>
<td>d</td>
<td>-133</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;47&lt;/sub&gt;Ti&lt;sub&gt;50&lt;/sub&gt;Fe&lt;sub&gt;3&lt;/sub&gt; [20]</td>
<td>e</td>
<td>-98</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;46.5&lt;/sub&gt;Ti&lt;sub&gt;50&lt;/sub&gt;Fe&lt;sub&gt;3&lt;/sub&gt; [25]</td>
<td>f</td>
<td>-133</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;46.7&lt;/sub&gt;Ti&lt;sub&gt;50&lt;/sub&gt;Fe&lt;sub&gt;3&lt;/sub&gt; [20]</td>
<td>e</td>
<td>-127</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;45&lt;/sub&gt;Ti&lt;sub&gt;50&lt;/sub&gt;Fe&lt;sub&gt;5&lt;/sub&gt; [20]</td>
<td>e</td>
<td>&lt; -196</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;45&lt;/sub&gt;Ti&lt;sub&gt;50&lt;/sub&gt;Fe&lt;sub&gt;5&lt;/sub&gt; [26]</td>
<td>g</td>
<td>&lt; -196</td>
</tr>
</tbody>
</table>

a: Ultra fine grained (rapidly quenched at the rate of 10<sup>6</sup> K/s).
b: Annealed at 900 °C for 10 minute (evacuated quartz tube) and quenched in ice brine.
c: Homogenization at 1000 °C for 1440 minute, solutionizing at 1000 °C for 60 minute and quenched in water to room temperature.
d: Annealed to 900 °C for 10 minute in vacuum and water quenched.
e: Annealed at 800 °C for 60 minute (Vacuum 10<sup>-3</sup> Pa) and quenched in water.
f: Controlled quenching from 900 °C in water.
g: Homogenization at 900 °C for 1440 minute and quenching to room temperature. Solutionizing at 500 °C for 60 minute.
2.2.4 Mechanical Properties

Pushin et al. showed the mechanical properties of the rapidly quenched Ni$_{50}$Ti$_{50}$, Ni$_{49}$Ti$_{50}$Fe$_1$ and Ni$_{47}$Ti$_{50}$Fe$_3$ alloys measured in tension at room temperature. They characterized Ni$_{50}$Ti$_{50}$ and Ni$_{49}$Ti$_{50}$Fe$_1$ with a martensite yield strength of 150 MPa and 200 MPa, respectively. The proof stress of Ni$_{47}$Ti$_{50}$Fe$_3$ in the austenite state is equal to 650 MPa [19]. Also upon tensile loading, they observed no martensitic transformation until failure. Pushin et al. also demonstrated that the micro hardness of the rapidly quenched Ni-Ti-Fe SMAs is 3000-3500 MPa, which is higher than that of the similar fine grained alloys by 1.2 to 1.5 times. Table 2.2, Moberly W. J. et al., lists the yield strengths and ductility of fully annealed, worked and heat treated samples. The fully annealed alloy exhibits a yield strength of ~400 MPa and greater than 30% tensile elongation to failure [28]. Ti$_{50}$Ni$_{47}$Fe$_3$ has slightly greater strength than low-carbon steel and much greater strength than typical intermetallic (Ni$_3$Al, TiAl).

2.3 R-Phase

Shape memory effect as well as superelasticity is associated with the R-phase transformation. The formation of the R-phase is attributed to the presence of coherent particles in the alloy matrix [29, 30]. These particles offer strong resistance to the large lattice variant transformation associated with the formation of B19'. Hence a transformation through the R-phase produces a significantly less lattice variant transformation and is much less affected by particles [29]. R-phase transformation can be achieved by suppressing the martensitic transformation relative to R-phase.
Table 2.3: Mechanical properties of worked and annealed Ti$_{50}$Ni$_{47}$Fe$_{3}$ shape memory alloy [28].

<table>
<thead>
<tr>
<th>Work condition</th>
<th>Heat treatment</th>
<th>Yield strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fully annealed</td>
<td>120 minutes at 875 °C</td>
<td>410</td>
<td>30-50</td>
</tr>
<tr>
<td>10% cold swage</td>
<td>Nil</td>
<td>690</td>
<td>13</td>
</tr>
<tr>
<td>10%</td>
<td>10 minutes at 400 °C</td>
<td>650</td>
<td>26</td>
</tr>
<tr>
<td>10%</td>
<td>10 minutes at 450 °C</td>
<td>560</td>
<td>25</td>
</tr>
<tr>
<td>10%</td>
<td>1 minutes at 500 °C</td>
<td>555</td>
<td>32</td>
</tr>
<tr>
<td>10%</td>
<td>10 minutes at 500 °C</td>
<td>510</td>
<td>26</td>
</tr>
<tr>
<td>10%</td>
<td>100 minutes at 500 °C</td>
<td>500</td>
<td>30</td>
</tr>
<tr>
<td>30% cold swage</td>
<td>Nil</td>
<td>1030</td>
<td>7</td>
</tr>
<tr>
<td>30%</td>
<td>10 minutes at 350 °C</td>
<td>840</td>
<td>17</td>
</tr>
<tr>
<td>30%</td>
<td>10 minutes at 400 °C</td>
<td>800</td>
<td>13</td>
</tr>
<tr>
<td>30%</td>
<td>10 minutes at 450 °C</td>
<td>750</td>
<td>20</td>
</tr>
<tr>
<td>30%</td>
<td>1 minutes at 500 °C</td>
<td>740</td>
<td>25</td>
</tr>
<tr>
<td>30%</td>
<td>10 minutes at 500 °C</td>
<td>700</td>
<td>22</td>
</tr>
<tr>
<td>30%</td>
<td>100 minutes at 500 °C</td>
<td>660</td>
<td>25</td>
</tr>
<tr>
<td>30%</td>
<td>1000 minutes at 500 °C</td>
<td>640</td>
<td>30</td>
</tr>
<tr>
<td>30%</td>
<td>10 minutes at 550 °C</td>
<td>630</td>
<td>31</td>
</tr>
<tr>
<td>30%</td>
<td>10 minutes at 600 °C</td>
<td>580</td>
<td>31</td>
</tr>
<tr>
<td>40% cold swage</td>
<td>Nil</td>
<td>1090</td>
<td>4</td>
</tr>
<tr>
<td>40%</td>
<td>10 minutes at 400 °C</td>
<td>850</td>
<td>29</td>
</tr>
<tr>
<td>40%</td>
<td>10 minutes at 500 °C</td>
<td>730</td>
<td>24</td>
</tr>
</tbody>
</table>
This can be achieved by:

(i) Introducing rearranged dislocations, produced by cold working and then annealing at temperatures between 400 °C and 500 °C

(ii) Introducing precipitates by solution-treated and aging NiTi alloys (at.% > 50.5) between 400 °C and 500 °C

(iii) Addition of certain third elements that suppresses the martensitic transformation (e.g., Fe or Al) [31].

An alloy aged after solution-treatment, has low critical stresses whereas an alloy annealed after cold working has higher critical stresses. This implies that the dislocations have a stronger effect on the mechanical properties associated with the R-phase transformation [31].

Table 2.4: Transformation temperatures for the R-phase transformation as reported by different authors.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Heat Treatment</th>
<th>Transformation Temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cooling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R-phase (M_s)</td>
</tr>
<tr>
<td>Ni_{45}Ti_{50}Fe_{5} [26]</td>
<td>g</td>
<td>--</td>
</tr>
<tr>
<td>Ni_{48}Ti_{50}Fe_{2} [18]</td>
<td>h</td>
<td>5</td>
</tr>
</tbody>
</table>

g: Homogenization at 900 °C for 1440 min and quenching to room temperature. Solutionizing at 500 °C for 60 min.
h: Solutionizing at 900 °C for 60 min in argon atmosphere and quenching in ice water.
With increasing Fe content, the B2 to R-phase transformation decreases gradually but the transformation temperatures from the R-phase to B19' are more strongly suppressed [26]. The R-phase transformation is associated with a small temperature hysteresis (1.5 °C) as compared with the martensite transformation of more than 10 °C [30]. An important application of this small temperature hysteresis is in thermal actuators. However, there is a limitation to the application of load. At small loads (80 g) the temperature hysteresis is small, characteristic of R-phase transformation, but under larger loads (320 g), the temperature hysteresis is large, indicative of the inducement of martensite [30]. The shape memory effect of the R-phase (NiTi alloy) under cyclic conditions, at constant load (62 MPa), is essentially unchanged after 500,000 cycles [30]. This also indicates a better fatigue life for the R-phase as compared to martensite. However the recoverable strain is limited to ~1% [30].

### 2.4 Transformation Temperature Measurement Techniques

Although pseudoelasticity and recovery of strain are the most observed occurrences of the shape memory alloys, there are also other changes occurring simultaneously. One of the prime measurement techniques, with direct applicability, is the observation of shape change during cooling and the subsequent recovery during heating. Table 2.3 lists different characteristic changes associated with the shape memory effect.
Table 2.5: Changes associated with the shape memory effect [5].

<table>
<thead>
<tr>
<th>Feel</th>
<th>Ring</th>
<th>Bend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Expansion</td>
<td>Yield strength</td>
</tr>
<tr>
<td>Young’s Modulus</td>
<td>Damping</td>
<td>Internal friction</td>
</tr>
<tr>
<td>Acoustic emission</td>
<td>Electrical resistance</td>
<td>Magnetic properties</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>Latent heat of transformation</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td></td>
<td>Lattice spacing</td>
<td></td>
</tr>
</tbody>
</table>

2.5 Differential Scanning Calorimetry

Thermal analysis is a name applied to a group of techniques having a common operating principle, i.e., as the sample is heated or cooled according to a pre-determined program, some physical property of the sample is recorded as a function of the temperature on the thermal analysis curve. The interpretation of the thermal analysis curve consists of relating the changes (peaks, discontinuities, change of slope etc) in the property–temperature curve to the possible thermal events in the sample. In Differential Scanning Calorimetry (DSC) the energy difference (enthalpy) between the sample and the reference is measured. The equipment essentially consists of two chambers with independent heating/cooling elements, which are heated at exactly the same rate. One chamber contains the test material crimped in a pan, while the other contains the empty crimped pan (Figure 2.3). The amount of energy, required to heat or cool the two chambers, at the same rate is monitored. The energy difference between the two chambers is plotted against the temperature. DSC analysis of the fabricated Ni-Ti-Fe samples was initially
done at Kansas Polymer Research Center and later a DSC was commissioned at the university itself.

Figure 2.3: Schematic of a differential scanning calorimeter (DSC).
CHAPTER 3: VACUUM TECHNOLOGY

3.1 Introduction

The processing of Ni-Ti-Fe shape memory alloys requires a facility operating under vacuum/inert atmosphere. A good understanding of the degrees of vacuum, vacuum creation, vacuum equipments and vacuum metallurgy is thus needed. This chapter is a review of vacuum technology from References 32 - 36.

The Latin word ‘vacuum’ means emptiness. In engineering, vacuum is considered as a state of gas with pressure less than the atmospheric pressure. Differential manometers or vacuum gauges are employed to measure this difference in pressure. Vacuum is classified by purpose into ultra-high, high, medium and low levels, and by the principle of action into mechanical and physico-chemical. The low, medium and high degrees of vacuum are classified using the Knudsen criterion. Ultra-high vacuum is treated as a special state of gas which satisfies the conditions of high vacuum as well as low surface coverage with adsorbed gas molecules. Surface properties of pure metals are only studied under ultra-high vacuum. Advanced vacuum engineering techniques can achieve and measure absolute pressures up to $10^{-8}$ Torr for conventional industrial equipment and $10^{-12}$ Torr for unique laboratory instruments. These pressures correspond to $10^8$ and $10^4$ molecules per one cubic centimeter, respectively, at room temperature.
3.2 **History of Vacuum Technology**

The development of vacuum engineering as a science has its roots in the research of Italian scientist Galileo (1564-1642), who measured the atmospheric pressure. In 1654 O. Guericke (1602-1686), in Madgeburg, conducted experiments with rarefied gases and developed a design of a vacuum piston-drive pump, with water sealing. Experiments with electric charge in vacuum led to the discovery of X-ray radiation (1895) and the electron (1897). The first vacuum electric device, incandescent lamp with a coal electrode, was invented by Russian scientist A. N. Lodygin (1847-1923). The early 20th century saw the invention of presently used vacuum pumps, i.e., rotary pumps (Gaede, 1905), adsorption pumps (D. Dewar, 1906), molecular pumps (Gaede, 1912), and diffusion pumps (Gaede, 1913). Vacuum measurement techniques were simultaneously developed, i.e., mercury compression manometer (G. Mcleod, 1874), the thermal manometer (M. Pirani, 1909), and ionization manometers (O. Buckley, 1916). Pressure below $10^{-7}$ Torr was considered unachievable up till the 1950s. The works of American scientist Nottingham (1948) and Alpert (1952) on the measurement of back-ground currents of ionization gauges allowed the range of measured pressures to get into the ultrahigh vacuum regime ($10^{-10}$ to $10^{-11}$Torr). This led to the invention of more pumps, the turbomolecular pump (Becker, 1958), the magnetic discharge pump (Jepsen and Holland, 1959), and the cryosorption pump (Lazarev and Fedorova, 1957). The diffusion oil-vapor pump was also improved. The development of non-polluting pumping devices opened new fields of applications in vacuum engineering.
3.3 Degrees of Vacuum

The dimensionless Knudsen criterion, \( Kn \), distinguishes vacuum into low, medium and high levels. The criterion is the ratio of the numbers of molecular collisions with one another to the collisions with the chamber walls. It is given by the formula:

\[
Kn = \frac{K_{av}}{K_m} = \frac{L}{d_{ef}}
\]

where \( K_{av} \) = average no. of collisions of one gas molecule with the chamber walls in unit time

\( K_m \) = frequency of molecular collision

L = mean free path length

d_{ef} = effective chamber size.

Low vacuum is a state of a gas where the mutual molecular collisions are more frequent than the collision of molecules with chamber walls. In this state, \( Kn \ll 1 \), \( Kn \) being usually taken less than \( 5 \times 10^{-3} \). The mean free path length of the gas molecules is far smaller than the chamber size and the gas flow occurs in a viscous mode. In medium vacuum, the frequency of mutual molecular collisions is equal to that of molecular collisions with the chamber walls, with \( L \cong d_{ef} \) and \( Kn \cong 1 \). The range of medium vacuum can be limited to \( 5 \times 10^{-3} < Kn < 1.5 \). Medium vacuum provides the best conditions for electric break down, glow and gas ionization. High vacuum is the state where the gas molecules collide with the chamber walls more frequently than with one another, with \( Kn > 1.5 \). Gas flow occurs in a molecular mode.

The change in temperature, for any degree of vacuum, separates the regions where the surface coverage of solids in vacuum, \( \theta \), will be low (\( \theta \ll 1 \)), medium (\( \theta \cong 1 \)), and high (\( \theta \gg 1 \)).

The range of high vacuum with low surface coverage is referred as ultrahigh vacuum, here \( Kn > \)
1.5 and $\theta < 5 \times 10^{-3}$. The number of adsorbed molecules in this region is small and the properties of pure surfaces can be characterized, which is important for various scientific and technological applications.

### 3.4 Measurement of Vacuum

The range of pressure used in vacuum engineering is very wide, i.e., atmospheric to $10^{-14}$ Torr. The measurement of pressure in this range cannot be provided by one device. In practice,

![Diagram of pressure range with different methods](image)

**Figure 3.1:** Working pressure of different vacuum gauges.
the pressure of rarefied gases is usually measured by various devices that are distinguished by their principle of operation and their accuracy. These devices are referred to as vacuum gauges or vacuum meters in vacuum engineering. Figure 3.1 shows the range of working pressures for these different vacuum gauges.

### 3.5 Mechanical Method of Vacuum Production

Figure 3.2 gives the working pressure range of different types of mechanical pumps. These pumps can be subdivided into displacement and molecular pumps. Displacement pumps

![Figure 3.2: Working pressure range of different mechanical vacuum pumps.](image-url)
operate by periodically changing the volume of the working chamber. The different construction variants of such pumps are of piston, liquid-ring and rotor types. Molecular pumps operate by imparting gas molecules an impulse from a rapidly moving solid, liquid or vapor surface. They are further divided into water-jet, ejectors, diffusion, molecular drag and turbomolecular pumps.

3.5.1 Displacement Pumping

Displacement pumping includes the following basic operation:

(i) Admittance of the gas by expanding the working chamber
(ii) Reduction of the volume of the working chamber and compression of the gas
(iii) Removal of the compressed gas from the working chamber to atmosphere or to a roughing pump.

The reciprocating/piston types of pump have lower efficiency than rotary pumps for a similar size pumping chamber. The reciprocating pumps can create $10^{-1}$ Torr for one stage and $10^{-2}$ Torr for two stage design with control acting valves. They are usually started at atmospheric pressure. Disadvantages of these pumps are the non-uniform pumping, and large friction losses. Rotary pumps have a limiting pressure dictated by the pressure of the working liquid vapor.

3.5.2 Molecular Pumping

In molecular pumping, the gas molecules are removed by a moving surface which drags along the molecules from the chamber. There are two types of molecular pumping. The first type is pumping through a channel, where one of the surface moves parallel to the channel axis. Gas
molecules collide with the moving surface and acquire addition impulse in the direction of the roughing pump. A difference in pressure is thus created. The maximum pumping speed achieved by this type of pumps is proportional to the speed of the surface. The second type, turbomolecular, uses the dependence of the conductance of an inclined channel which moves perpendicular to the gas flow. These pumps are used at high pressures stages in combination with other pumps having a mutually perpendicular movement of gas molecules and work surfaces, as well as for pumping gases with large molecular mass.

The designs of the turbomolecular pumps are classified by the orientation of the rotor shaft, i.e., horizontal or vertical and by the construction and shape of the body, i.e., cylindrical, conical, disc with radial flow, disc with axial flow or drum-type. The parameters of this pump are greatly affected by the design of the support bearings (lubricated rolling contact bearings, magnetic supports, or gas cushion).

### 3.5.3 Vapor Jet Pumping

During vapor jet pumping, molecules of the pumped gas pass through an inlet pipe and interact with the vapor jet in the direction of the roughing pump. The vapor jet mixture from the nozzle mixes with the pumped gas. The pumped gas and the working vapor are separated in a chamber by the condensation of the working vapor on the cooled surfaces, and the pumped gas leaving the pump through the outlet pipe. The condensed vapor passes to the boiler, where it is evaporated again. The process provides continuous pumping. The intensity of interaction of pumped gas and the vapor jet determines the degree of vacuum. At low vacuum, the molecules in the layer adjacent to the vapor jet entrain other gas layers due to internal friction. Such devices
are referred to as ejector pumps. At high vacuum, all the molecules of the pumped gas move by self-diffusion and directly interact with the moving vapor jet; pumps that use this principle are called diffusion pumps. As a vapor jet evolves into the high vacuum it expands due to the thermal velocities of its molecules. The best condition for trapping the pumped gas molecules are provided if the pressure in the vapor jet corresponds to medium vacuum. All the molecules of the pumped gas penetrate into the vapor jet at first collision.

Figure 3.3: Schematic of a diffusion pump.
The working liquids used in vapor jet pumps should meet the following requirements:

(i) Minimum vapor pressure at room temperature and maximum at the working temperature in the boiler

(ii) Resistance to decomposition on heating

(iii) Chemical stability in relation to pumped gases and to the structural materials of the pump

(iv) Minimum ability to dissolve gases and

(v) Low heat of vaporization.

Mercury, mineral oils, complex ethers of organic spirits and acids and silicon-organic compounds are used as working liquids for vapor jet pumps. Mercury is advantageous as it does not oxidize, has a homogenous structure, does not decompose at working temperatures and has a high vapor pressure at working temperatures. The drawbacks of mercury are its toxicity, chemical activity in relation to non-ferrous metals and high vapor pressure at room temperatures. Mineral oils have low vapor pressure \(10^{-8}\) Torr at room temperature, satisfactory thermal stability, but have low thermal oxidation resistance and form resin deposits on the internal parts of pumps. Polyphenyl ethers (PPE) have very low vapor pressure \(10^{-11}\) Torr at room temperature and a high thermal oxidation resistance. They are also a choice for the working fluid. Silicon-organic liquids have high thermal oxidation resistance and reasonably low vapor pressure \(10^{-7}\) Torr at room temperature. Hydrocarbon liquids have good oxidation stability and low vapor pressure.

Mineral oils are often used in pumps as they are inexpensive. Silicon-organic and hydrocarbon liquids are used for systems with frequent inlet to atmospheric air. Ether is only used in systems where ultra-high vacuum is desired, as it is expensive. Due to its toxicity,
mercury is used in vapor jet pumps only for pumping of mercury systems, for example, mercury rectifiers.

3.5.4 Traps for Vacuum Pumps

The limiting pressure of oil pumps is determined by the back flow of working liquid vapors from the pump to the pumped volume. The back flow is considerably reduced by installation of traps. The trap should meet the following requirements:

(i) Maximum protective action for the desired service life
(ii) Minimum resistance to the main flow of pumped gas
(iii) Capability of regeneration, reliability, simplicity, adaptability to various designs and convenience of operation.

The traps are subdivided into condensing, sorbing, and dissociating types based on their principle of operation. Condensing mechanical traps hinder the direct flow of working liquid vapor from the pump to the pumped volume. Vapor sorption in the oil trap occurs due to adsorption on the walls of capillary channels. Adsorption traps adsorb oil vapors by surface porous adsorbents, such as activated charcoal, zeolites, silicagels, etc. Constant temperature is maintained in traps by circulating water. Reducing trap temperatures additionally increases the protective action of traps, but somewhat reduces the specific conductance. In dissociating ion traps, the cylinder casing serves as the cathode for cold discharge and the anode, in the form of a rod, is arranged along the cylinder axis. The electrons emitted by the cathode ionize the residual gases. The positive ions bombard the surface casing destroying the surface oil films. This causes hydrogen
evolution and the polymerization of hydrocarbons to solid substances. These traps reduce the partial pressure of oil vapor by 10-100 times.

3.6 Physico-Chemical Methods of Vacuum Production

These type of pumps preclude pollution of the vacuum chamber with vapors of working liquids, used for lubrication and hermetic sealing in many mechanical pumps. The general operation principle of ion pumps is based on directed movement of previously charged gas molecules in an electrical field. The evaporation pumps works on the chemisorption phenomena. Physical adsorption and condensation are used to pump out gases by cryosorption pumps that are subdivided in to cryoadsorption and cryocondensation types. Because condensation heat is usually less than adsorption, condensation of the same amount of gas occurs at lower temperatures than adsorption. The advantage of condensation pumping compared to adsorption pumping is a higher pumping speed per unit of cooled surface area. The general operation principle of ion pumping combined with sorption is used in ion-sorption pumps.

3.7 Application of Vacuum Technology

(i) The use of vacuum began long before its properties were understood. Vacuum was used in water lifting and pneumatic mechanisms, by making use of its mechanical power. Water extractions and Magdeburg hemisphere were the first examples of this kind.

(ii) The property of vacuum to transmit electromagnetic radiation finds applications in heating, spectral diagnostics and temperature measurement in vacuum.
(iii) Vacuum finds use in vacuum clamps, pneumatic mechanisms and medical instruments.

(iv) The removal of oxygen by creating vacuum facilitates the processing of active metals and other materials. These conditions are favorable for the operation of high temperature heaters and cathodes.

(v) In vacuum, the rate of evaporation of materials increases substantially. This phenomenon is used for drying food products, wood and other commodities at room temperature. At a pressure 40 times lower than the atmospheric one, water boils at room temperature. Vacuum evaporation of materials is used for producing thin coatings.

(vi) The heat and sound insulating properties of vacuum are used in construction and for storage of heated or cooled materials.

(vii) Vacuum systems are used in chemistry for the study of pure substances, compositions, separation of mixtures and rates of chemical reactions.

(viii) In medicine, vacuum is used for the preservation of hormones, vaccines and vitamins as well as for the preparation of antibiotics, anatomic and bacteriological samples.

(ix) Scientific studies of physical processes, such as evaporation, condensation, surface phenomena, heat transfer, cryogenic experiments, nuclear and thermonuclear reactions are carried out in vacuum instruments. The acceleration of charged particles is done in vacuum.

(x) Modern instruments for materials characterization such as electron and ion microscopes and mass spectrometers include vacuum chambers.
The development of space investigation is much related to the simulation of space on earth. Mechanisms and devices can be tested in vacuum chambers hundreds cubic meters in volume that produces very low pressures and simulate direct solar radiation.

3.8 Vacuum Metallurgy

Vacuum technology is of considerable interest in metallurgy as most metallurgical processes involve heat and most metals react with atmospheric air when heated. Vacuum melting and remelting of metals eliminates detrimental dissolved gases and makes metals strong, ductile and tough. Vacuum metallurgy (VM) may be defined as “the making, shaping and treating of metals and alloys under pressure ranging from sub atmospheric to ultra-high vacuum and a study of their properties and applications”. The different vacuum metallurgical processes are classified as in Table 3.1.

<table>
<thead>
<tr>
<th>Liquid based process</th>
<th>Vapor based process</th>
<th>Solid based process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum degassing</td>
<td>Evaporation deposition</td>
<td>Vacuum degassing</td>
</tr>
<tr>
<td>Vacuum induction melting</td>
<td>Sputter deposition</td>
<td>Powder fabrication and consolidation</td>
</tr>
<tr>
<td>Vacuum arc melting</td>
<td>Vacuum induction melting</td>
<td>Vacuum electron beam cold hearth melting</td>
</tr>
</tbody>
</table>
Vacuum metallurgical processes have the following advantages:

(i) Cheapest way to achieve a desired result, e.g., special steel for high stress conditions

(ii) Successful method for processing materials like titanium, tantalum, germanium and zirconium

(iii) Produces a better product at a competitive price, e.g., vacuum brazing

(iv) Protects the metal from atmospheric attack during processing

(v) Dissolved gasses can be removed from molten metals at low pressure to give improved physical characteristics

(vi) Separation of constituents and contaminants of metals can be achieved by utilizing their differences in chemical and physical behavior at reduced pressure.

VM is used for the production of carbon-free iron electric motors, highly conducting copper, magnesium, calcium, tantalum, platinum, titanium, zirconium, beryllium, alloys and high quality steels. Vacuum sintering of tungsten and molybdenum powders is a basic technological process of powder metallurgy. Synthetic diamond, ruby and sapphire are grown in vacuum. High purity semiconductor and dielectric crystals are grown in vacuum. Diffusion vacuum welding produces joints of materials with different melting points, e.g., ceramics with metals, steel with aluminum etc. Electron beam vacuum welding ensures high quality of joints of materials whose properties are similar. In material science, the method of molecular beam vacuum epitaxy (MBVE) enables alloys of any compositions to be obtained. Ion implantation is a promising tool for the modification of surface properties of materials. Vacuum arc-melting is also used for processing high temperature alloys; for jet engines, high purity materials such as superalloys and aluminum billets for the manufacture of aluminum foil.
3.9 **Vacuum Arc Melting**

Vacuum arc-melting (VAM) was developed to process metals which are highly reactive with air and the refractory materials during processing. Hare, 1839, carried out chemical reactions using an electric arc in an evacuated enclosure. Siemens, 1878, built the forerunner of today’s electric steel furnace. Von Bolten, 1903, built the forerunner of the modern vacuum arc melting furnace consisting of an electric arc, a liquid cooled metallic platen or crucible to support the molten metal and a vacuum or inert gas enclosure. Kroll, 1939, introduced the water cooled copper mold to contain the liquid metal in his furnace for melting titanium under an inert atmosphere. Parke and Ham in 1946 reported the production of VAM molybdenum.

VAM gives uniform cleanliness, large sound ingots with low gas content and segregation and improved fatigue properties. The two main requirements of a metal for VAM are that it should form into suitable electrode and should have a low vapor pressure in the molten state. Metals that cannot be formed into electrodes can be melted by permanent electrode skull melting. The metal is either melted in a water cooled mould, where it solidifies, or in a crucible from which it is cast into a mould. Consumable electrodes are used with both the water cooled mould and crucible or skull melting method. The use of permanent electrodes is generally restricted to skull melting or small button melts.
3.9.1 Consumable Electrode Arc Melting Furnace

The most notable difference between the types of consumable electrode furnace is the type of electrode used. Simple furnaces use sintered rod which is fed through a vacuum seal during melting. The major disadvantage is its cost. The electrode should have a good surface finish, and each section has to be fixed to its predecessor and successor. Another

![Diagram of three main types of vacuum arc melting furnace](image.png)

Figure 3.4: Schematic diagram of the three main types of vacuum arc melting furnace, (a) consumable electrode arc melting furnace, (b) consumable electrode skull melting furnace, (c) permanent electrode skull melting furnace.
disadvantage is that alloy additions have to be shaken in the mold in powder form, and this is not reliable or economical. The advantage is its space; large ingots can be cast in small furnaces as it is not necessary to hold all the charge in the chamber before melting.

Another method is to fabricate the electrode by first pressing, then sintering sections, followed by welding of the different sections. This method is mechanically simple and hence the most reliable. The size of the ingot is limited to the volume of the electrode that can be stored in the furnace.

The third main method is used for fabrication of molybdenum. This involves pressing and sintering the powder into an electrode all inside the furnace. The main disadvantages of this method are its complexity and the comparatively small diameter of the electrode produced.

3.9.2 Consumable Electrode Skull Melting Furnace

The difficulty of forming, working and machining some of the refractory metals has led to the possibility of castings. This type is essentially similar to the consumable electrode arc melting furnace, but the material is melted into a water cooled crucible from which it is cast into a mold. The crucible is lined with a skull or a solid shell of the material being processed (Figure 3.3). The molten metal is contained in this skull. The arc is struck between the electrode and a plug of metal in the crucible and the power increased until sufficient metal has melted into the crucible. The arc is then stopped, the electrode is retracted and the melt is poured. This furnace is used to cast metals like titanium, zirconium and hafnium.
3.9.3 Permanent Electrode Skull Melting Furnace

Metals which cannot be easily formed into an electrode use this process. The metal can either be melted on a water cooled hearth and solidified, or melted in a crucible and subsequently cast. Melting on a shaped water cooled hearth allows only small quantities of metal to be melted - these are referred to as “button” melts. The hearth can be replaced by a water cooled mold such as in consumable electrode melting. The arc is struck between a metal plug at the bottom of the mold and the water cooled electrode. The charge is then fed into the mold where it melts and forms the ingot. In skull melting, the arc is struck between a metal plug at the bottom of the crucible and the water cooled electrode. The metal to be cast is fed into the arc and melted into the crucible. When a sufficient quantity of molten metal is obtained it is quickly cast into a mold. This method is useful for making castings of the reactive and refractory metals. The ingot size is limited to few pounds, compared to some tons for the consumable electrode process. These furnaces utilize an upper electrode made from refractory electrically conducting material, such as carbon, graphite or tungsten.

3.10 Vacuum Induction Melting

The vacuum induction melting process involves a normal type of furnace, operating at a low pressure, utilizing an ordinary refractory crucible. The melt is held in a crucible which is surrounded by the induction coil. This is supported in a water-cooled metal chamber. When the charge has been melted it can be cast either by bottom pouring or by tilting the crucible. The melt can be cast in vacuum into a standard type of ingot mold. Standard alloy compositions can be produced under greatly improved conditions. The major disadvantage of vacuum induction
melting is the use of the crucible - as at low pressures the reactions between the melt and the crucible proceeds much more quickly than at atmospheric pressure. This can lead to deleterious impurities in the melt. But it is advantageous for production of homogenous cast as the melt is stirred by induced currents. Induction melting is used in the ferrous and non-ferrous metal industries for a wide range of metals in quantities from a few grams to a few tons.
CHAPTER 4: COMMISSIONING OF AN ARC-MELTING AND VACUUM QUENCH FURNACE FACILITY

4.1 Introduction

The IVI Corporation Mark-14 general purpose metallurgical facility is a versatile research and development processing facility. This machine is capable of diverse metallurgical and coating processing. It has the unique ability of interchanging processing modules without changing many of the basic modules such as the vacuum chamber, vacuum pumping system, cabinet, console, supporting instruments, wiring, plumbing and power supplies.

4.2 Machine Components

The IVI Corporation Mark-14 controlled atmosphere arc-melting and vacuum quench furnace facility consists of the following main components:

4.2.1 Main Chamber

The 24 inch diameter and 39 inch long horizontally oriented stainless steel chamber (Figure 4.1), with full opening doors at each end, provides maximum accessibility to the processing area. The chamber is bolted on the main frame and has water jackets on front and rear doors as well as the sides, i.e., main chamber front and main chamber rear. It is water cooled during the arc melting and heat treatment process by the chilled water supply. The chamber is coupled to a 6 inch high speed pumping train to achieve excellent vacuum
Figure 4.1: IVI Corporation Mark-14 controlled atmosphere arc-melting and the vertical vacuum quench furnace facility.

levels (10^{-7} Torr). Additionally, the front and the rear door are provided with sight/blank ports for either sighting or insertion of new instruments into the vacuum chamber. Swing shields are also provided along the ports.
4.2.2 Control Console

The unit has a functionally attractive cabinet (Figure 4.2) insuring maximum visual and manual accessibility to controls for operation and routine maintenance of the system. The “Soft Start”\textsuperscript{TM} vacuum controller is for use on vacuum systems with electrically actuated valves. It provides automatic cycling of the system with complete safety against operator error or power supply to pumps.

Figure 4.2: Control console of IVI Corporation Mark-14 facility.
failure. These features provide maintenance of $10^{-4}$ Torr or lower vacuum in the high vacuum stack during mechanical to diffusion pump crossover. This feature virtually eliminates pumping fluid transfer into the processing chamber that occurs during conventional automatic vacuum controllers. The gauge controller has pressure reading dials and a digital ionization gauge controller. The ionization gauge controller gives precise readings of vacuum pressures from $10^{-4}$ to $10^{-8}$ Torr. At the bottom of the console is the power supply controller which controls and monitors the output of the furnace (vacuum quench furnace facility). The power supply is interlocked with the water supply for the heat treatment facilities.

4.3 Vacuum Production

IVI corporation Mark-14 facility uses a 6-inch diffusion pump backed by a mechanical pump to achieve high vacuum ($10^{-7}$ Torr). Figure 4.3 shows a schematic of the pumps layout with the pneumatic valves. The roughing pump is turned on first and it keeps on running during the entire process. The stages for creating vacuum are described below:

(i) Stage I: The first stage makes sure that the foreline pressure is at the required level. The foreline valve (FV) is opened and the foreline pressure is observed on TC 1 (on gauge controller, Figure 4.2) until the pressure is $5 \times 10^{-3}$ Torr. This is usually accomplished in less than 5 minutes.

(ii) Stage II: At a foreline pressure less than $5 \times 10^{-3}$ Torr, the diffusion/high-vacuum pump is turned on. This stage is to warm the high-vacuum pump oil. It takes about 45 minutes for the oil to warm up.
(iii) Stage III: The third stage is the roughing of the main chamber. After the diffusion pump oil has warmed up, the foreline valve is turned off and roughing valve is turned on. The roughing pump is now connected to the main chamber and the chamber pressure starts to drop. The roughing valve is left on till the chamber pressure is less than $5 \times 10^{-3}$ Torr (monitored on TC2- gauge controller, Figure 4.2).

(iv) Stage IV: The final stage is to attain high vacuum in the main chamber. At a chamber pressure less than $5 \times 10^{-3}$ Torr, the roughing valve is turned off. The foreline valve is turned on. The pressures on TC1 and TC2 are checked (less than $5 \times 10^{-3}$ Torr) again and

![Figure 4.3: Schematic of the pump and valve locations.](image-url)
the high-vacuum valve is turned on. This connects the main chamber to the diffusion pump and subsequently the chamber is pumped down to high vacuum. The pressure is then monitored on the digital ion gauge controller.

4.4 Arc-Melting Facility

The arc-melting facility is capable of melting metal powders and granules under controlled conditions. An inert environment at atmospheric pressure is created for melting. Ultra-high purity argon gas is generally used as the inert environment. The facility consists of a copper hearth and a water cooled electrode, with a tungsten tip. The hearth consists of a striker tip and button shaped pockets, resulting in button shaped solids after melting. Melts of desired shape can be achieved using a hearth with customized shaped pockets. Figure 4.4 shows the electrode and the copper hearth.

An arc is struck between the electrode tip and the striker tip. The arc is then moved gradually over the copper hearth to the pockets to melt the mixed powders. The flow of current is varied between 40 A and 250 A using the controls on the welder. The power consumed by the facility varies from 0.17 kW to 4.52 kW.

4.4.1 Machine Setup

The arc melting facility consists of the following components:
Non-consumable electrode: The non-consumable electrode is water cooled and has a tungsten tip. The tungsten tip screws into the electrode. The tip and the electrode have to be scrubbed with scotch-brite/sandpaper after every run for cleaning. This is to ensure long life of the components. The electrode can be maneuvered using the handle provided outside the main chamber to reach all the four pockets. The gap between the electrode and the hearth can be varied by pushing/pulling the handle.
(ii) Hearth: The water cooled hearth is made of copper. The hearth consists of four button shaped pockets. The hearth is also scrubbed after every run for cleaning.

(iii) Welder: The welder uses the GTAW (gas tungsten arc welding) mode to strike an arc. The maximum current rating of the welder is 300 A. The power is supplied via water cooled cables. These cables are continuously water cooled and hence named so. The conductor inside the cable is made of electrolytic refined tough pitch copper and has a diameter ranging from 0.5 to 1.8 mm, according to the application [37]. These cables are generally used for power supply in arc-melting furnaces and ladle furnaces in iron and steel plants, foundries, coking plants and steel melting shops [38].

4.4.2 Operating Procedure for Arc-Melting

(i) Load all desired pockets (cavities) with the material to be processed.

(ii) Ensure that the non-consumable electrode located on the top of the chamber reaches all the cavities.

(iii) Ensure that the power lead from the negative terminal of the welder is connected to the non-consumable electrode and positive lead is connected to the hearth.

(iv) Close the chamber doors and lock.

(v) Ensure that the oil level in the mechanical pump is between the maximum and the minimum levels.

(vi) Connect the air duct from the mechanical pump outlet to the fume hood.
(vii) Turn on the fume hood.
(viii) Turn on the compressed air supply to the facility.
(ix) Turn on the ultra-high purity argon supply to the main chamber.
(x) Turn on the power supply to the water pump.
(xi) Turn on the inlet and outlet of the chilled water supply.
(xii) Turn on the cooling water valves for diffusion pump and pump nozzle, at the rear of the facility.
(xiii) Switch on the water pump.
(xiv) Turn on the power supply to the facility.
(xv) Reset the soft start vacuum controller (red colored push button).
(xvi) Select the mode of operation, i.e., manual interlock mode.
(xvii) Turn on the ion gauge controller.
(xviii) Turn on the mechanical/roughing pump.
(xix) Open the foreline valve.
(xx) Observe the vacuum gauge monitoring the foreline pressure (TC 1) on the ion gauge controller.
(xxi) At foreline pressure of 0.050 Torr, switch on the diffusion/high vacuum pump.
(xxii) Diffusion pump takes nearly 45 minutes to warm up.
(xxiii) After the diffusion pump has warmed up, switch off the foreline valve.
(xxiv) Make sure that the vent valve is closed, then open chamber rough valve.
(xxv) Bleed argon line (approximately 10 seconds) and set the argon regulator between 3 to 5 psi.
(xxvi) Observe the vacuum gauge monitoring the chamber pressure (TC 2) on the ion gauge controller. Diffusion pump turns on and off during this process.

(xxvii) At chamber pressure of 0.050 Torr, close the rough valve.

(xxviii) After 6-10 seconds open the foreline valve.

(xxix) At foreline pressure of 0.050 Torr, open the high vacuum valve.

(xxx) The ionization gauge can be turned in interval of 30 minutes to observe the chamber pressure. The operating range of the gauge is from $10^{-4}$ Torr to $10^{-8}$ Torr.

(xxxi) At a pressure of $\sim 10^{-7}$ Torr, ensure that the ion gauge filament is turned off and then switch off the high vacuum valve and the diffusion pump.

(xxxii) Backfill the main chamber with high purity argon up to atmosphere.

(xxxiii) Turn on the cooling water to the following:

a. Non-consumable electrode

b. Hearth

c. Front door

d. Main chamber front

e. Main chamber rear

f. Rear door

(xxxiv) Setup the welder

a. Output pot: 0

b. Inductance pot: 5

c. Output terminal switch: On

d. Meter switch: A (ampere)
e. Remote/local switch: Local (right)
f. Welding mode switch: GTAW

(xxxv) Ensure that the output adjust pot on the front of the welder is set to zero and then turn on the welder using the circuit breaker on the back of the welder.

(xxxvi) Turn up the output to approximately 3.

(xxxvii) Strike an arc from the non-consumable electrode to the striker on the hearth.

(xxxviii) Move the arc from the tip of the non-consumable electrode to the pocket and melt the material in the pockets, turn up the output pot to increase the power if required. Maximum power from the welder is 300 A.

(xxxix) To shut down, turn the welder output pot to zero. This will cause the arc to go out.

(xl) **Important – Turn off the circuit breaker on the rear panel of the arc melting power supply.**

(xli) Allow the melted metal to cool.

(xlii) Shut off the argon gas.

(xliii) Turn off the foreline valve.

(xliv) Turn off the roughing pump.

(xlv) Vent the chamber.

(xlvi) Turn off the ion gauge controller.

(xlvii) Turn the mode of operation to off.

(xlviii) Remove the processed metal from the cavities.

(xlix) Shut off compressed air supply.

(l) Switch off the water pump.
(li) Turn off the cooling water valves at the rear of the facility.

(lii) Turn off inlet and outlet of the chilled water supply.

(liii) Switch off the power supply to the facility, water pump and fume hood.

(liv) Remove the air duct.

4.5 Vertical Vacuum Quench Furnace Facility

Figure 4.5: IVI Corporation Mark-14 vertical vacuum quench furnace facility.
The IVI Corporation Mark-14 vertical vacuum quench furnace facility is rated for heat treatments up to 1200 °C in an extremely clean environment (Figure 4.5). The environment can be a high vacuum or an inert atmosphere. This accessory offers the advantage of directly quenching the heated materials, under vacuum, to achieve specific superior material properties. This accessory is assembled inside the main chamber, after disassembling the arc melting facility.

### 4.5.1 Machine Setup

The main components of the vertical vacuum quench furnace are given below:

(i) Heating element: The heating element is clamped to the feed-through rod. Two heating elements of molybdenum with a maximum temperature rating of 1000 °C and 1200 °C are available for heat treatments.

(ii) Power feed-through and insulating flanges: The left and right power feed-through rods supply power to the heating element. The power is supplied by water cooled cables.

(iii) Alignment bar: The bar is in the shape of a rectangular plate. The bar extends from the outer edge of one feed-through, when mounted, to the outer edge of the other. It helps to correctly align the feed-through rods and keep the heating element in the correct position to avoid excessive mechanical and thermal stresses.

(iv) Jail assembly: This assembly shields the heat from the heating element to the inner surface of the main chamber. The jail assembly consists of a cylindrical chamber with a plate covering the open top and a circular opening at the bottom. The opening provides a path for the materials to be treated to enter into the heat zone.
(v) Work lowering device: The materials to be treated are attached to this device. This device is used for placing the materials upward in the heat zone or downwards into the quench reservoir.

(vi) Quench reservoir: This reservoir is placed directly underneath the heating element and the top is covered with the top plate. The reservoir, in the shape of a cylinder (outer diameter: 60 mm, inner diameter: 53 mm, height: 240 mm), is placed whenever quenching is required.

4.5.2 Operating Procedure for Solutionizing

(i) Load work sample onto the work-lowering device, and retract into the furnace hot zone.

(ii) Ensure that there is no contact between the facility parts, i.e., jail assembly, thermocouple, work lowering device and heating element.

(iii) Close the chamber doors and lock.

(iv) Ensure that the oil level in the mechanical pump is between the maximum and the minimum levels.

(v) Connect the air duct from the mechanical pump outlet to the fume hood.

(vi) Turn on the fume hood.

(vii) Turn on the compressed air supply to the facility.

(viii) Turn on the ultra high purity argon supply to the main chamber.

(ix) Turn on the power supply to the water pump.

(x) Turn on the inlet and outlet of the chilled water supply.
(xi) Turn on the cooling water valves for diffusion pump and pump nozzle, at the rear of the facility.

(xii) Switch on the water pump.

(xiii) Turn on the power supply to the facility.

(xiv) Reset the soft start vacuum controller.

(xv) Select the mode of operation, i.e., manual interlock mode.

(xvi) Turn on the ion gauge controller.

(xvii) Turn on the mechanical/roughing pump.

(xviii) Open the foreline valve.

(xix) Observe the vacuum gauge monitoring the foreline pressure (TC 1) on the ion gauge controller.

(xx) At foreline pressure of 0.050 Torr, switch on the diffusion/high vacuum pump.

(xxi) Diffusion pump takes nearly one hour to warm up.

(xxii) After the diffusion pump has warmed up, switch off the foreline valve.

(xxiii) Ensure that the vent valve is closed, then open chamber rough valve.

(xxiv) Bleed argon line (approximately 10 seconds) and set the argon regulator between 3 to 5 psi.

(xxv) Observe the vacuum gauge monitoring the chamber pressure (TC 2) on the ion gauge controller.

(xxvi) At chamber pressure of 0.050 Torr, close the rough valve.

(xxvii) After 6-10 seconds open the foreline valve.

(xxviii) At foreline pressure of 0.050 Torr, open the high vacuum valve.
(xxix) The ionization gauge can be turned in interval of 30 minutes to observe the pressure in the main chamber. The operating range of the gauge is from $10 \times 10^{-4}$ Torr to $10 \times 10^{-8}$ Torr.

(xxx) At a pressure of $\sim 10^{-7}$ Torr, turn on the water supply to the following:

a. Quench shaft
b. Furnace
c. Front door
d. Main chamber front
e. Main chamber rear
f. Rear door

(xxxi) Turn on the furnace power supply in manual mode.

(xxxii) Press the start button on the furnace power supply.

(xxxiii) Supply power to achieve temperature in 200 °C increments, allowing adequate time for equilibrium.

(xxxiv) Heat at the order of 1 °C every 2-3 seconds. This ensures long life of the heating element.

(xxxv) Furnace may be operated with an inert argon atmosphere up to atmospheric pressure. This will require additional power.

(xxxvi) After the solutionizing treatment, return all controls to zero.

(xxxvii) Turn off the furnace power supply.

(xxxviii) When the temperature of the work falls below 100 °C, close the high vacuum valve.

(xxxix) Turn off the diffusion pump.
(xl) After the diffusion pump has cooled (nearly 90 minutes), turn off the foreline valve.

(xli) Turn off the roughing pump.

(xlii) Vent the chamber.

(xliii) Turn off the ion gauge controller.

(xliv) Turn the mode of operation to off.

(xlv) Shut off compressed air and argon supply.

(xlvi) Switch off the water pump.

(xlvii) Turn off the cooling water valves at the rear of the facility.

(xlviii) Turn off inlet and outlet of the chilled water supply.

(xlix) Switch off the power supply to the facility, water pump and fume hood.

(l) Remove the air duct.

4.5.3 Operating Procedure for Quenching

(i) Fix the attachment on the button flipper, to remove the quench reservoir top plate for quenching.

(ii) Load the sample onto the work-lowering device, and retract into the furnace hot zone.

(iii) Fill the quench reservoir with vacuum quench oil and place in the main chamber.

(iv) Place the top plate on the quench reservoir.

(v) Ensure that the top plate of the quench reservoir can be removed with the attachment on the button flipper.

(vi) Perform steps (ii) to (xxxiv) of Section 4.3.2 and then perform the following.

(vii) Return all furnace power supply controls to zero.
(viii) Turn off the furnace power supply.

(ix) Quickly turn off the diffusion pump and high vacuum valve.

(x) Simultaneously topple the top plate from the reservoir and lower the sample into the reservoir using the work lowering device.

(xi) After the diffusion pump has cooled (nearly 90 minutes), turn off the foreline valve.

(xii) Turn off the roughing pump.

(xiii) Vent the chamber.

(xiv) Turn off the ion gauge controller.

(xv) Turn the mode of operation to off.

(xvi) Shut off compressed air and argon supply.

(xvii) Switch off the water pump.

(xviii) Turn off the cooling water valves at the rear of the facility.

(xix) Turn off inlet and outlet of the chilled water supply.

(xx) Switch off the power supply to the facility, water pump and fume hood.

(xxi) Remove the air duct.
CHAPTER 5: FABRICATION OF Ni-Ti-Fe SHAPE MEMORY ALLOYS

5.1 Introduction

The chapter describes the fabrication of Ni-Ti-Fe shape memory alloys (SMAs) from the initial state of elemental powders to the melted alloys and their subsequent thermo-mechanical treatment. The controlled atmosphere arc-melting and vertical vacuum quench furnace facility were utilized for the alloy fabrication. The process of fabricating these alloys has incorporated many improvements. These improvements are discussed in chapter 7.

5.2 Powder Mixing

Table 5.1: List of powders and their purities.

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Name</th>
<th>Mesh size</th>
<th>Chemical purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Titanium powder</td>
<td>-60 +100</td>
<td>99.500 %</td>
</tr>
<tr>
<td>2</td>
<td>Titanium powder, dehydrided</td>
<td>-325</td>
<td>99.900 %</td>
</tr>
<tr>
<td>3</td>
<td>Nickel powder</td>
<td>-100 +200</td>
<td>99.900 %</td>
</tr>
<tr>
<td>4</td>
<td>Nickel powder Puratronic*</td>
<td>-120</td>
<td>99.996 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C typically &lt;0.05</td>
</tr>
<tr>
<td>5</td>
<td>Nickel powder, low carbon,</td>
<td>--</td>
<td>99.999 %</td>
</tr>
<tr>
<td></td>
<td>Puratronic*</td>
<td></td>
<td>C &lt;100 ppm</td>
</tr>
<tr>
<td>6</td>
<td>Iron powder, reduced</td>
<td>-325</td>
<td>98.000 %</td>
</tr>
<tr>
<td>7</td>
<td>Iron powder Puratronic*</td>
<td>-22</td>
<td>99.998 %</td>
</tr>
</tbody>
</table>

* Alfa Aesar designation for high purity base metals and salts (minimum purity 99.99 %, many exceed 99.999 %)
Nickel, titanium and iron powders were selected over their respective slugs, as the powders could be easily mixed to form a homogenous mixture. Table 5.1 lists the powders used for the preparation of the twenty Ni-Ti-Fe SMAs. The powders were weighed on an Acculab, VI-I mg, balance (readability = 0.001 gm) in, ultra-high pure argon atmosphere, basic glove box and ultimately contained inside a vial along with four 440C stainless steel balls (0.5 inch diameter). The vial was clamped in the 8000M Mixer-Mill and mixed for 20 minutes. The alloys 1-7, Table 5.2, were mixed using the Mixer-Mill.

A laboratory rotary mill was setup later, to mix the powders. Alloys 8-17 and alloys 19-21, Table 5.2 were mixed using the rotary mill. Figure 5.1 shows the mill, which consists of an AC motor with a variable speed control. A rectangular plate is fixed to the end of

![Figure 5.1](image) Laboratory rotary mill (a) with the low density polyethylene (LDPE) wide mouth bottle (b) attached. The mill uses an alternating current (AC) motor.
the rotating shaft. After weighing, the powders were contained in a low density polyethylene (LDPE) wide mouth bottle. The LDPE bottles were then fixed to the rectangular plate using a tape. The mixing was done at 50 rpm for 24 hours.

Twenty compositions of Ni-Ti-Fe were mixed. Table 5.2 lists these compositions with their elemental purity.

Table 5.2: Fabricated Ni-Ti-Fe shape memory alloys with their constituent purity.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Purity of powders</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>2</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>3</td>
<td>Ni$<em>{48.2}$ Ti$</em>{50}$ Fe$_{1.8}$</td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>4</td>
<td>Ni$<em>{48.2}$ Ti$</em>{50}$ Fe$_{1.8}$ (cold rolled)</td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>5</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>6</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>7</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>8</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>9</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>Dehydrided 99.900%</td>
<td>99.998%</td>
</tr>
<tr>
<td>10</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>Dehydrided 99.900%</td>
<td>99.998%</td>
</tr>
<tr>
<td>11</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>Dehydrided 99.900%</td>
<td>99.998%</td>
</tr>
<tr>
<td>12</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>Dehydrided 99.900%</td>
<td>99.998%</td>
</tr>
<tr>
<td>13</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>Dehydrided 99.900%</td>
<td>99.998%</td>
</tr>
<tr>
<td>14</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>Dehydrided 99.900%</td>
<td>99.998%</td>
</tr>
<tr>
<td>15</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>Dehydrided 99.900%</td>
<td>99.998%</td>
</tr>
<tr>
<td>16</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>Dehydrided 99.900%</td>
<td>99.998%</td>
</tr>
<tr>
<td>17</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>Dehydrided 99.900%</td>
<td>99.998%</td>
</tr>
<tr>
<td>18</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>Dehydrided 99.900%</td>
<td>99.998%</td>
</tr>
<tr>
<td>19</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>Dehydrided 99.900%</td>
<td>99.998%</td>
</tr>
<tr>
<td>20</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>Dehydrided 99.900%</td>
<td>99.998%</td>
</tr>
<tr>
<td>21</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>99.900%</td>
<td>Dehydrided 99.900%</td>
<td>99.998%</td>
</tr>
</tbody>
</table>
5.3 Arc-Melting

The mixed powders were then melted into solid buttons utilizing the IVI Corporation Mark-14 controlled atmosphere arc-melting facility. The mixed powders and titanium slugs
(diameter 3.175 mm; length 6.35 mm; 99.98% purity) were placed in the different pockets. The furnace operation procedure, see Section 4.4.2, was followed to obtain a high vacuum ($10^{-7}$ Torr). The vacuum system was then disconnected from the main chamber and the main chamber backfilled with ultra-high purity argon. At near atmospheric pressure the welder was switched on, following which an arc was struck between the tungsten electrode and the striker tip. The titanium slugs were arc-melted first, in order for any remnant oxygen to react with it. The arc was then gradually moved over the hearth to the pocket containing mixed powders. During the initials attempts a large quantity of powder particles were lost as they flew when the arc struck them. A probable cause of this loss was the striking force of the arc. The later attempts involved compaction of the powders, using a hammer, before running the arc melting facility. Also the top layer of the compacted powders was melted first with small supply of current, varying from 40 A to 60 A. Then the current was gradually increased to melt the whole chunk. The maximum current drawn was 200 A. The welder was turned off and the button flipper accessory was used to flip buttons after the molten Ni-Ti-Fe (Figure 5.2) had solidified. The buttons were re-melted five times. The maximum power consumed by the furnace during melting was 2.595 kW. Time taken for melting varied from 30 seconds to 60 seconds. The buttons melted weighed in the range of 0.01 kg to 0.025 kg. The whole process from creating vacuum, arc-melting and complete shutdown of the arc-melting facility took nearly six hours.
5.4 **Thermo-Mechanical Processing**

5.4.1 **Button Cutting**

The Ni-Ti-Fe buttons were cut by electro-discharge machine wire cutting (EDM-WC) and by Isomet® low speed saw, into strips.

(i) **Electro-discharge machine wire cutting (EDM-WC):** EDM-WC is a thermal mass-reducing process where a continuously moving wire removes the material by means of rapid controlled and repetitive spark discharges. A dielectric fluid is used to flush the removed particles and regulate the discharge. The fluid also keeps the wire and work piece cool. The wire and work piece should be electrically conductive. EDM-WC of Ni-Ti-Fe SMAs was outsourced to a vendor. Strips with thicknesses of 0.37 mm were cut.

(ii) **Isomet® low speed saw:** The cutting was done in the laboratory and at the Material Characterization Facility, University of Central Florida. Diamond wafer blade with Isocut® fluid as the cutting fluid was used for cutting. The blade was periodically cleaned using a dressing stone after 3-5 cuts, to remove the particles clinging on the blade. The cutting speed was varied from 20 to 30 rpm.
5.4.2 Cold Rolling

A cold rolling mill was re-commissioned in the laboratory, Figure 5.3. Strip of Ni-Ti-Fe SMAs was successfully cold rolled. The strip with an initial thickness of 0.37 mm was passed five times through the rolls giving a final thickness of 0.26 mm. For calculation see Section 7.7.
5.4.3 Heat Treating

The heat treatment of the samples was done in the IVI corporation Mark-14 vertical vacuum quench furnace facility. The Ni-Ti-Fe buttons/strips were placed in the sample attachment setup (described in Section 7.1.1) and connected to the work lowering device. The operation procedure, see Section 4.5.2 and Section 4.5.3, was followed for heat treating. Vacuum of the order of $10^{-7}$ Torr was created and subsequently the power to the heating element was started. Heating of the order of 1 °C every 5-10 second (recommended 2-3 seconds) was followed. After reaching the desired temperature and completing the required duration of heat treatment, the power supply to the heating element was turned off. The different heat treatments carried out on the Ni-Ti-Fe buttons/strips are given in Table 5.3.

Table 5.3: Different heat treatments on Ni-Ti-Fe shape memory alloys.

<table>
<thead>
<tr>
<th>Heat treatment designation</th>
<th>Ni-Ti-Fe sample</th>
<th>Temperature (°C)</th>
<th>Duration (minutes)</th>
<th>Type of cooling to room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ht 1</td>
<td>Strip</td>
<td>900</td>
<td>10</td>
<td>Vacuum oil quench</td>
</tr>
<tr>
<td>Ht 2</td>
<td>Strip</td>
<td>700</td>
<td>60</td>
<td>Vacuum cooled</td>
</tr>
<tr>
<td>Ht 3</td>
<td>Strip</td>
<td>700</td>
<td>30</td>
<td>Vacuum cooled</td>
</tr>
<tr>
<td>Ht 4</td>
<td>Strip</td>
<td>700</td>
<td>60</td>
<td>Vacuum with argon backfilling</td>
</tr>
<tr>
<td>Ht 5</td>
<td>Strip</td>
<td>700</td>
<td>60</td>
<td>Vacuum cooled</td>
</tr>
<tr>
<td>Ht 6</td>
<td>Strip</td>
<td>700</td>
<td>60</td>
<td>Vacuum muffle furnace cooled</td>
</tr>
<tr>
<td>Ht 7</td>
<td>Strip</td>
<td>850</td>
<td>30</td>
<td>Vacuum slow cooled</td>
</tr>
<tr>
<td>Ht 8</td>
<td>Strip</td>
<td>850</td>
<td>30</td>
<td>Vacuum oil quench</td>
</tr>
<tr>
<td>Ht 9</td>
<td>Button</td>
<td>850</td>
<td>30</td>
<td>Vacuum cooled</td>
</tr>
</tbody>
</table>
CHAPTER 6: RESULTS

6.1 Commissioning of an Arc-Melting Facility

The IVI Corporation Mark-14 controlled atmosphere arc-melting facility has been successfully commissioned. The facility creates high vacuum of the order $10^{-7}$ Torr and melts highly reactive materials like titanium in a controlled atmosphere. The arc-melting of materials was done under an inert environment, ultra-high purity argon. This protects materials from reacting with the atmospheric components, mainly oxygen. Twenty compositions of Ni-Ti-Fe shape memory alloys (SMAs) were successfully melted from mixed powders into a button shaped solid using the facility.

6.2 Commissioning of a Vertical Vacuum Quench Furnace Facility

The IVI Corporation Mark-14 controlled atmosphere vertical vacuum quench furnace facility has been successfully commissioned. The quench setup has been modified to suit the research needs of this project. The facility heat treats materials under vacuum ($10^{-7}$ Torr) up to 977 °C. The high vacuum shields the material from oxidation at high temperatures. This gives superior properties to the materials. Each of the twenty compositions was subjected to different heat treatments. A total of nine different heat treatments were performed on Ni-Ti-Fe strips/buttons using the facility.
Figure 6.1: Ni-Ti-Fe shape memory alloys processing methodology.
6.3 **Process Methodology for Fabrication of Ni-Ti-Fe SMAs**

Figure 6.1 shows the fabrication process for Ni-Ti-Fe SMAs. Powders of nickel, titanium and iron, Figure 6.1 (a), were mixed to form a Ni-Ti-Fe powder, Figure 6.1 (b). The mixed powders were then arc-melted, Figure 6.1 (c), to form into a button shaped solid, Figure 6.1 (d). The buttons were then cut into strips, Figure 6.1 (e), either by electro-discharge machine wire cutting or by low speed saw cutting. They were subjected to combinations of thermo-mechanical processing steps, i.e., cold rolling, Figure 6.1 (f) and heat treatment, Figure 6.1 (g). A process methodology for fabricating Ni-Ti-Fe SMAs is established for future research on these materials.

6.4 **Shape Memory Effect in Ni-Ti-Fe Strips**

Strips of Ni-Ti-Fe SMAs were checked for the shape memory effect in a constrained recovery experiment. The experiment consisted of a clamp, Figure 6.2 (a), fixed to one end of the strip while the other end was fixed to a copper fixture, Figure 6.2 (b). The setup was immersed in liquid nitrogen (-196 °C) and subsequently deformed, by bending, Figure 6.2 (a). As the strip gained heat from the atmosphere it recovered its parent shape, Figure 6.2 (b). This demonstrated shape memory effect in Ni-Ti-Fe alloys.
Figure 6.2: Demonstration of shape memory effect in a strip of Ni$_{47.5}$Ti$_{50}$Fe$_{2.5}$, following no heat treatment, at cryogenic state (a) and ambient state (b).

6.5 **Dilatometry Results**

A dilatometry setup (Figure 6.3) was designed for the characterization of the transformation temperatures of Ni-Ti-Fe SMAs. The design was based on the principle of strain recovery by shape memory alloys with the transformation temperatures. The setup consisted of a linear displacement measuring digital gauge, for recording the deflection. A digital temperature gauge was used to measure the temperature. The gauge was in contact with the strip. The oxygen free copper fixture provided a path for thermal energy to transfer from the liquid nitrogen bath to the Ni-Ti-Fe strip. One end of the strip was fixed to the copper fixture, placed in a liquid nitrogen bath. A load was applied to the other end of the strip (Figure 6.3). As the bath was filled with
liquid nitrogen, the temperature of the strip decreased. The strip deflected, downwards, under the load. A change in the reading from the linear displacement measuring digital gauge was observed, which corresponded to a phase transformation. The setup provided uniform cooling up to -150 °C. However the cooling was irregular from -150 °C to -196 °C. The strip was heated by

Figure 6.3: Dilatometer setup.
natural convection. Occasionally hot water was used for heating. The strip started to return to its parent shape, upon heating. The temperature and deflection of the strip were continuously recorded. This data was plotted as graphs.

The graphs from the different as-fabricated and heat treated Ni-Ti-Fe SMAs are presented.
Figure 6.4: Deflection (mm) versus temperature (°C) response of Ni$_{48.4}$Ti$_{50}$Fe$_{1.6}$ strip heat treated at 700 °C for 60 minutes followed by vacuum cooling to room temperature.
Figure 6.5: Deflection (mm) versus temperature (°C) response of as-fabricated Ni$_{48.4}$Ti$_{50}$Fe$_{1.6}$ strip.
Figure 6.6: Deflection (mm) versus temperature (°C) response of Ni$_{48.4}$Ti$_{50}$Fe$_{1.6}$ strip heat treated at 850 °C for 30 minutes followed by vacuum cooling to room temperature.
Figure 6.7: Deflection (mm) versus temperature (°C) response of as-fabricated Ni$_{47.5}$Ti$_{50}$Fe$_{2.5}$ strip.
Figure 6.8: Deflection (mm) versus temperature (°C) response of Ni$_{47.5}$Ti$_{50}$Fe$_{2.5}$ strip heat treated at 850 °C for 30 minutes followed by vacuum slow cooling to room temperature.
Figure 6.9: Deflection (mm) versus temperature (°C) response of as-fabricated Ni$_{47.3}$Ti$_{50.2}$Fe$_{2.5}$ strip.
Figure 6.10: Deflection (mm) versus temperature (°C) response of Ni$_{47.3}$Ti$_{50.2}$Fe$_{2.5}$ strip heat treated at 850 °C for 30 minutes followed by vacuum cooling to room temperature.
Figure 6.11: Deflection (mm) versus temperature (°C) response of as-fabricated Ni$_{47.7}$Ti$_{49.8}$Fe$_{2.5}$ strip.
Figure 6.12: Deflection (mm) versus temperature (°C) response of as-fabricated $\text{Ni}_{47}\text{Ti}_{50}\text{Fe}_3$ strip.
Figure 6.13: Deflection (mm) versus temperature (°C) response of as-fabricated Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ strip.
Figure 6.14: Deflection (mm) versus temperature (°C) response of as-fabricated Ni$_{45}$Ti$_{50}$Fe$_5$ strip.
The results from Figure 6.4 to Figure 6.14 are consolidated in Table 6.1.
Table 6.1 Dilatometry data.

<table>
<thead>
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<th>Alloy</th>
<th>Composition</th>
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<th>Cooling (°C)</th>
<th>Heating (°C)</th>
<th>Transf. Hyst.</th>
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<td>M to R Phase</td>
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<td>Ht9</td>
<td>- - -</td>
<td>transformation very low, hence peaks not detected</td>
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</table>

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6.6 Differential Scanning Calorimetry Results

Certain combinations of compositions and thermal treatment were characterized with differential scanning calorimetry (DSC). Two types of DSC experiments were performed -

(i) Cyclic DSC measurements using the Mechanical Cooling Accessory (MCA) that allows controlled cooling. The temperature cycles consisted of four segments:

- Equilibration at 70 °C
- Temperature ramp from 70 °C to -70 °C
- Equilibration at -70 °C and
- Temperature ramp from -70 °C to 70 °C.

(ii) Standard DSC measurements that allow determination of low temperature transformations. The temperature program consisted of two segments:

- Equilibration at -150 °C (cooling with liquid nitrogen)
- Temperature ramp from -150 °C to 150 °C

The differential scanning calorimetry results for as-fabricated and heat treated Ni-Ti-Fe SMAs are presented.
Figure 6.15: Differential scanning calorimeter curve of Ni$_{48.4}$Ti$_{50}$Fe$_{1.6}$ heat treated at 700 °C for 60 minutes followed by vacuum cooling to room temperature. The differential scanning calorimeter cycle was from -150 °C to 150 °C and from 150 °C to -150 °C at 10 °C per minute.
Figure 6.16: Differential scanning calorimeter curve of as-fabricated Ni$_{48.4}$Ti$_{50}$Fe$_{1.6}$ alloy. The differential scanning calorimeter cycle was from -150 °C to 30 °C and from 30 °C to -150 °C at 20 °C per minute.
Figure 6.17: Differential scanning calorimeter curve of Ni$_{48.4}$Ti$_{50}$Fe$_{1.6}$ heat treated at 850 °C for 30 minutes followed by vacuum cooling to room temperature. The differential scanning calorimeter cycle was from -150 °C to 30 °C and from 30 °C to -150 °C at 20 °C per minute.
Figure 6.18: Differential scanning calorimeter curve of as-fabricated Ni$_{48.4}$Ti$_{50}$Fe$_{1.6}$ alloy. The differential scanning calorimeter cycle was from -150 °C to 30 °C and from 30 °C to -150 °C at 20 °C per minute.
Figure 6.19: Differential scanning calorimeter curve of Ni$_{47.5}$Ti$_{50}$Fe$_{2.5}$ heat treated at 850 °C for 30 minutes followed by vacuum slow cooling to room temperature. The differential scanning calorimeter cycle was from -150 °C to 150 °C and from 150 °C to -150 °C at 10 °C per minute.
Figure 6.20: Differential scanning calorimeter curve of Ni$_{47.5}$Ti$_{50}$Fe$_{2.5}$ heat treated at 850 °C for 30 minutes followed by vacuum slow cooling to room temperature. The differential scanning calorimeter cycle was from 70 °C to -70 °C and from -70 °C to 70 °C using mechanical cooling accessory at 10 °C per minute.
Figure 6.21: Differential scanning calorimeter curve of as-fabricated Ni_{47.3}Ti_{50.2}Fe_{2.5} alloy. The differential scanning calorimeter cycle was from 70 °C to -70 °C and from -70 °C to 70 °C using mechanical cooling accessory at 10 °C per minute.
Figure 6.22: Differential scanning calorimeter curve of as-fabricated Ni\textsubscript{47.7}Ti\textsubscript{49.8}Fe\textsubscript{2.5} alloy. The differential scanning calorimeter cycle was from 70 °C to -70 °C and from -70 °C to 70 °C using mechanical cooling accessory at 10 °C per minute.
Figure 6.23: Differential scanning calorimeter curve of as-fabricated Ni$_{47}$Ti$_{50}$Fe$_3$ alloy. The differential scanning calorimeter cycle was from -150 °C to 30 °C and from 30 °C to -150 °C at 20 °C per minute.
Figure 6.24: Differential scanning calorimeter curve of Ni_{46.8}Ti_{50}Fe_{3.2} heat treated at 850 °C for 30 minutes followed by vacuum cooling to room temperature. The differential scanning calorimeter cycle was from -150 °C to 30 °C and from 30 °C to -150 °C at 20 °C per minute.
Figure 6.25: Differential scanning calorimeter curve of Ni<sub>46.8</sub>Ti<sub>50</sub>Fe<sub>3.2</sub> button heat treated at 850 °C for 30 minutes followed by vacuum cooling to room temperature. The differential scanning calorimeter cycle was from -150 °C to 70 °C at 10 °C per minute.
Figure 6.26: Differential scanning calorimeter curve of as-fabricated Ni$_{45}$Ti$_{50}$Fe$_5$ alloy. The differential scanning calorimeter cycle was from -150 °C to 70 °C at 10 °C per minute.
Figure 6.27: Differential scanning calorimeter curve of Ni$_{45}$Ti$_{50}$Fe$_5$ button heat treated at 850 °C for 30 minutes followed by vacuum cooling to room temperature. The differential scanning calorimeter cycle was from -150 °C to 70 °C at 10 °C per minute.
The results from Figure 6.15 to Figure 6.27 are consolidated in Table 6.2.
Table 6.2: Differential scanning calorimetry data.

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<th>DSC</th>
<th>Heating (°C)</th>
<th>Hyst. in R phase</th>
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<td>R to M Phase</td>
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<td>R to A Phase</td>
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<td></td>
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<td>F</td>
<td>Range</td>
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<td>-</td>
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<td>Ht 2</td>
<td>34.16</td>
<td>13.6</td>
<td>20.49</td>
<td>-26.32</td>
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| 3     | Ni<sub>48.2</sub> Ti<sub>50</sub> Fe<sub>1.8</sub> (cold rolled) | Ht 2 | strip brittle -no Shape Memory effect (oxidation of strip)
| 4     | Ni<sub>47.8</sub> Ti<sub>50</sub> Fe<sub>2.2</sub> | Ht 3 | strip brittle -no shape memory effect (oxidation of strip)
| 5     | Ni<sub>47.4</sub> Ti<sub>50</sub> Fe<sub>2.2</sub> | Ht 2 | strip brittle -no shape memory effect (oxidation of strip)
| 6     | Ni<sub>47.4</sub> Ti<sub>50</sub> Fe<sub>2.2</sub> | Ht 4 | strip brittle -no shape memory effect (oxidation of strip)
| 7     | Ni<sub>47.4</sub> Ti<sub>50</sub> Fe<sub>2.2</sub> | Ht 5 | strip brittle -no shape memory effect (oxidation of strip)
| 8     | Ni<sub>47.4</sub> Ti<sub>50</sub> Fe<sub>2.2</sub> | Ht 6 | strip brittle -no shape memory effect (oxidation of strip)
| 9     | Ni<sub>48.4</sub> Ti<sub>50</sub> Fe<sub>1.6</sub> | Ht 7 | 20.88 | 6.67 | 14.21 | - | - | - | - | - | - | 6.62 | 24.89 | 18.27 | 2.41 |
| 10    | Ni<sub>48.4</sub> Ti<sub>50</sub> Fe<sub>1.6</sub> | Ht 8 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 11    | Ni<sub>47.3</sub> Ti<sub>50</sub> Fe<sub>2.5</sub> | Ht 9 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 12    | Ni<sub>47.3</sub> Ti<sub>50</sub> Fe<sub>2.5</sub> | Ht 10 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 13    | Ni<sub>46.5</sub> Ti<sub>50</sub> Fe<sub>1.8</sub> (Special Metals) | Ht 11 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 14    | Ni<sub>46.5</sub> Ti<sub>50</sub> Fe<sub>1.8</sub> (Special Metals) | Ht 12 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 15    | Ni<sub>46.5</sub> Ti<sub>50</sub> Fe<sub>1.8</sub> (Special Metals) | Ht 13 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 16    | Ni<sub>46.5</sub> Ti<sub>50</sub> Fe<sub>1.8</sub> (Special Metals) | Ht 14 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 17    | Ni<sub>46.5</sub> Ti<sub>50</sub> Fe<sub>1.8</sub> (Special Metals) | Ht 15 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 18    | Ni<sub>46.5</sub> Ti<sub>50</sub> Fe<sub>1.8</sub> (Special Metals) | Ht 16 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 19    | Ni<sub>46.5</sub> Ti<sub>50</sub> Fe<sub>1.8</sub> (Special Metals) | Ht 17 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 20    | Ni<sub>46.5</sub> Ti<sub>50</sub> Fe<sub>1.8</sub> (Special Metals) | Ht 18 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 21    | Ni<sub>46.5</sub> Ti<sub>50</sub> Fe<sub>1.8</sub> (Special Metals) | Ht 19 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |

transformation very low, hence peaks not detected
Ht 1 - Strip at 900 °C, 10 minute and vacuum oil quenched
Ht 2 - Strip at 700 °C, 60 minute and vacuum cooled
Ht 3 - Strip at 700 °C, 30 minute and vacuum cooled
Ht 4 - Strip at 700 °C, 60 minute and cooled with argon backfilling
Ht 5 - Strip at 800 °C, 60 minute and vacuum cooled
Ht 6 - Strip at 700 °C, 60 minute and muffle furnace cooled
Ht 7 - Strip at 850 °C, 30 minute and vacuum cooled
Ht 8 - Strip at 850 °C, 30 minute and vacuum slow cooled
Ht 9 - Button at 850 °C, 30 minute, vacuum cooled and low speed saw cut
CHAPTER 7: ANALYSIS AND DISCUSSION

7.1 Vertical Vacuum Quench Furnace Facility Modification

During the commissioning of the vacuum quench furnace facility, certain problems were encountered. These problems and the measures taken to overcome them are as follows:

7.1.1 Sample Attachment Setup

Figure 7.1: The sample attachment setup.
The heat treatment of the Ni-Ti-Fe SMAs required a unique way to attach the strips/buttons to the work lowering device. The objective was to prevent Ni-Ti-Fe coming in contact with any other metal. This is because of the possibility of forming a eutectic. The attachment consisted of a 19 gauge, AISI 300 series stainless steel wire inserted in ‘Nextel 312’ ceramic fiber sleeve suspended from the work lowering device (Figure 7.1). The samples were attached to this wire. To further reduce the chances of titanium in Ni-Ti-Fe reacting with any remnant oxygen in the chamber, a titanium getter (purity: 99.4 % metal basis) was introduced in the attachment (Figure 7.1). The titanium getter was in the form of thin foils.

7.1.2 Vaporization of Vacuum Quench Oil

Prior to heat treating Ni-Ti-Fe SMAs, a mock operation of the vacuum quench furnace was scheduled to anneal a NiTi sample at 900 °C for 10 minutes followed by quenching in vacuum quench oil to room temperature. The procedure for quenching, see Section 4.5.3, was followed. At 700 °C, an increase in the chamber pressure was observed. Oil droplets were seen on the inside chamber walls, as seen through the sight glass. This indicated evaporation of the vacuum quench oil. The system was immediately shutdown. Upon inspection, a large quantity of oil was found inside the chamber and the quench reservoir was extremely hot. The following attempts were made to overcome this problem:

(i) Argon backfill: After attaining a high vacuum, the chamber was backfilled with high purity argon up to atmosphere. The power supply unit was then turned on. Shortly thereafter, a dense mist of vaporized oil was seen in the chamber through the sight port.
Inspection of the furnace showed oil on the inside chamber walls and the quench reservoir was hot. This attempt was unsuccessful.

(ii) Heat shield: The gap between the jail assembly (covering the heating element) and the quench reservoir was 4.0 mm; an appreciable amount of heat was being transferred to the quench reservoir. Also the quench reservoir was hot, as the chamber doors were opened. Semicircular foils of stainless steel were used to create a heat shield between the jail assembly and the quench reservoir. The heat shield consisted of two circular sheets folded into two semicircular foils which covered the circular hole in the bottom of the jail assembly. The shields were designed in a manner where they could easily separate when the sample was lowered into the quench reservoir by the work lowering device. This setup delayed the vaporization of the oil but oil droplets were still seen on the chamber walls at 770 °C.

(iii) New quench reservoir: To create substantial distance between the jail assembly and the quench reservoir, a new reservoir was selected. The new reservoir had a wider base and a shorter height (diameter: 160 mm, height: 150 mm) than the original quench reservoir (diameter: 60 mm, height: 240 mm). The new reservoir was kept in a container, in order to contain the spilled vacuum quench oil (Figure 7.2). The furnace was operated with the new reservoir container. Bubbles of the vacuum quench oil were seen vaporizing at 630 °C.

(iv) New quench reservoir-modified: The vacuum quench oil in the reservoir had to be isolated from the low pressure chamber environment. Two solutions were proposed, the
first was to cover the mouth of the new reservoir with aluminum foil. The issue here was the compatibility of the aluminum foil during the heat treatment process. The second solution was to use a lightweight plate to cover the new reservoir. Both cases required a mechanism to either tear the aluminum foil or to move the top plate to quench the samples. A lightweight rod was attached to the shaft of the button flipper accessory. Using the knob of the button flipper accessory, the rod could be maneuvered to either tear the Al foil or lift the top plate. The two methods were tested and the latter

![Figure 7.2: The modified vertical vacuum quench furnace facility.](image)
one was chosen because of its simplicity. This setup was successful and did not result in the vaporization of quench oil.

7.1.3 Maximum Temperature

The maximum temperature attained during the initial runs was only 770 °C compared to 1000 °C specified by the manufacturer. Upon the manufacturer’s suggestion, the transformer was stepped up, from X1-X2 to X1-X3 taps, and a maximum temperature of 904 °C was attained. A new heating element, rated at 1200 °C was purchased from the manufacturer. The silicon controlled rectifier and the power supply unit were shipped to the manufacturer to make them compatible with the 1200 °C rated heating element. The new element could only go up to 760 °C and then the fuse failed. The transformer taps were changed from X1-X3 to X1-X2. A maximum temperature of 822 °C was attained and the fuse failed again. The manufacturer recommended replacing the 10 A fuse with a 15 A fuse. This took the maximum temperature to 968 °C. The manufacturer recommended a 20 A fuse for higher temperatures. A maximum temperature of 977 °C was attained with the 20 A fuse. The condition of the jail assembly should be checked before changing the fuse to 20 A as there is a possibility of the jail assembly cracking at higher temperatures.

7.2 Effect of Fe Addition in NiTi

The effect of Fe addition, in place of Ni in NiTi, on the transformation temperatures are:
(i) R-phase: The R-phase was observed in the heating as well as the cooling curves of Ni-Ti-Fe SMAs, Figure 7.3. This phase transformation is characterized by hysteresis ranging from 2.41 °C to 10.61 °C. It was observed that heat treatment did not have a systematic effect on the hysteresis.

Figure 7.3: Differential scanning calorimeter curve for Ni$_{48.4}$Ti$_{50}$Fe$_{1.6}$ heat treated at 850 °C for 30 minutes followed by vacuum cooling to room temperature.
(ii) Martensite phase: The effect of iron addition to the martensite phase is depicted in Figure 7.4, Figure 7.5 and Figure 7.6. The figures show the suppression of the martensite phase transformation with the addition of iron.

Figure 7.4: Differential scanning calorimetry curves for Ni$_{48.4}$Ti$_{50}$Fe$_{1.6}$ heat treated at 850 °C for 30 minutes followed by vacuum cooling to room temperature. The addition of 1.6 at.\% Fe in place of Ni in NiTi shifts the start of martensite phase to -94.98 °C. Also seen is the R-phase transformation.
Figure 7.5: Differential scanning calorimetry curves for Ni$_{46.8}$Ti$_{50}$Fe$_{3.2}$ heat treatment at 850 °C for 30 minutes followed by vacuum cooling to room temperature. The addition of 3.2 at.% Fe in place of Ni in NiTi has suppressed the start of martensite so low that it cannot be detected using liquid nitrogen as the cooling medium. Only the R-phase transformation is seen.
Figure 7.6: Differential scanning calorimetry curves for Ni$_{45}$Ti$_{50}$Fe$_5$ heat treated at 850 °C for 30 minutes followed by vacuum cooling to room temperature. The addition of 5 at.% Fe in place of Ni in NiTi has suppressed the start of martensite so low that it cannot be detected using liquid nitrogen as the cooling medium. The R-phase transformation could not be detected.

(iii) R-phase to martensite transformation: Based on the results from Table 6.2, i.e., data from dilatometry curves of Figure 6.5, Figure 6.7, Figure 6.12, Figure 6.13 and Figure 6.14 a plot of at.% Fe versus the start and finish of the R-phase to martensite transformation is shown in Figure 7.7. The start of the transformation has a gradient
of 9.25 °C/at.% Fe whereas the finish has a gradient of 17.89 °C/at.% Fe. This suggests that the finish of the R-phase to martensite transformation is suppressed more than the start of the transformation with Fe addition in NiTi.

Figure 7.7: Effect of Fe addition in NiTi on the R-phase to martensite transformation.
(iv) Austenite transformation: It was observed that the austenite phase transformation remains in the region of -25 °C to 25 °C for the samples melted and no systematic effect was seen.

7.3 Effect of Heat Treatment in Ni-Ti-Fe

Figure 7.8 and Figure 7.9 shows the effect of heat treatment on Ni$_{48.4}$Ti$_{50}$Fe$_{1.6}$ and Ni$_{47.5}$Ti$_{50}$Fe$_{2.5}$ alloys respectively. Heat treatment gives sharper peaks in the transformation with no systematic shift in transformation temperatures for the composition investigated.
Figure 7.8: Figure (a) shows the differential scanning calorimetry curve for Ni$_{48.4}$Ti$_{50}$Fe$_{1.6}$ alloy without any heat treatment and (b) shows the curve for Ni$_{48.4}$Ti$_{50}$Fe$_{1.6}$ after heat treating at 850 °C for 30 minutes followed by vacuum cooling to room temperature.
Figure 7.9: Figure (a) shows the differential scanning calorimetry curve for Ni$_{47.3}$Ti$_{50.2}$Fe$_{2.5}$ alloy without any heat treatment and (b) shows the curve for Ni$_{47.5}$Ti$_{50}$Fe$_{2.5}$ after heat treating at 850 °C for 30 minutes followed by vacuum slow cooling to room temperature.
7.4 Effect of Ni/Ti Ratio in Ni-Ti-Fe

Based on the results from Figure 6.17, Figure 6.18 and Figure 6.19, the differential scanning calorimetry data is re-plotted in Figure 7.10. The curves for $\text{Ni}_{47.3}\text{Ti}_{50.2}\text{Fe}_{2.5}$ with no heat treatment, $\text{Ni}_{47.5}\text{Ti}_{50}\text{Fe}_{2.5}$ heat treated at 850 °C for 30 minutes followed by vacuum slow cooling to room temperature and $\text{Ni}_{47.7}\text{Ti}_{49.8}\text{Fe}_{2.5}$ with no heat treatment are shown in Figure 7.10. The Ni/Ti ratio in the above alloys was varied keeping the same Fe content. The ratio was varied by ±0.01 to the ratio of 0.95 in $\text{Ni}_{47.5}\text{Ti}_{50}\text{Fe}_{2.5}$. This variation gave a Ni-rich and a Ni-poor Ni-Ti-Fe alloy. The curves in Figure 7.10 are arranged with increasing Ni/Ti ratio, i.e., (a) to (c). The figure indicates suppression of the R-phase with the increase in the Ni/Ti ratio. The compositions investigated are comparable as no systematic shift in the transformation temperatures with heat treatment was observed. Table 7.1 lists the peak temperatures for these R-phase transformations.

Table 7.1: R-phase transformation peak temperatures with increasing Ni/Ti ratio and same Fe content.

<table>
<thead>
<tr>
<th>Ni/Ti ratio</th>
<th>R-phase to austenite transformation peak temperature(°C)</th>
<th>Austenite to R-phase transformation peak temperature(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ni}<em>{47.3}\text{Ti}</em>{50.2}\text{Fe}_{2.5}$</td>
<td>0.94</td>
<td>15.69</td>
</tr>
<tr>
<td>$\text{Ni}<em>{47.5}\text{Ti}</em>{50}\text{Fe}_{2.5}$ (Ht 8)</td>
<td>0.95</td>
<td>-19.44</td>
</tr>
<tr>
<td>$\text{Ni}<em>{47.7}\text{Ti}</em>{49.8}\text{Fe}_{2.5}$</td>
<td>0.96</td>
<td>-34.22</td>
</tr>
</tbody>
</table>

Ht 8 - Heat treated at 850 °C for 30 minutes followed by vacuum slow cooling to room temperature
Figure 7.10: Differential scanning calorimetry curves for (a) Ni$_{47.3}$Ti$_{50.2}$Fe$_{2.5}$ with no heat treatment, (b) Ni$_{47.5}$Ti$_{50}$Fe$_{2.5}$ heat treated at 850 °C for 30 minutes followed by vacuum slow cooling to room temperature and (c) Ni$_{47.7}$Ti$_{49.8}$Fe$_{2.5}$ with no heat treatment
### 7.5 Effect of Impurities in Ni-Ti-Fe

Table 7.2: Fabricated Ni-Ti-Fe shape memory alloys with their constituent purity.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Heat treatment</th>
<th>Purity of powders</th>
<th>Ni</th>
<th>Ti</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>Ht1</td>
<td></td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>2</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>Ht 2</td>
<td></td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>3</td>
<td>Ni$<em>{48.2}$ Ti$</em>{50}$ Fe$_{1.8}$</td>
<td>Ht 2</td>
<td></td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>4</td>
<td>Ni$<em>{48.2}$ Ti$</em>{50}$ Fe$_{1.8}$ (cold rolled)</td>
<td>Ht 3</td>
<td></td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>5</td>
<td>Ni$<em>{47.8}$ Ti$</em>{50}$ Fe$_{2.2}$</td>
<td>Ht 2</td>
<td></td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>6</td>
<td>Ni$<em>{47.8}$ Ti$</em>{50}$ Fe$_{2.2}$</td>
<td>Ht 4</td>
<td></td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>7</td>
<td>Ni$<em>{47.8}$ Ti$</em>{50}$ Fe$_{2.2}$</td>
<td>Ht 5</td>
<td></td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>8</td>
<td>Ni$<em>{47.8}$ Ti$</em>{50}$ Fe$_{2.2}$</td>
<td>Ht 6</td>
<td></td>
<td>99.900%</td>
<td>99.500%</td>
<td>98.000%</td>
</tr>
<tr>
<td>9</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>--</td>
<td></td>
<td>99.999%</td>
<td>Dehydrided</td>
<td>99.998%</td>
</tr>
<tr>
<td>10</td>
<td>Ni$<em>{48.4}$ Ti$</em>{50}$ Fe$_{1.6}$</td>
<td>Ht 7</td>
<td></td>
<td>99.999%</td>
<td>Dehydrided</td>
<td>99.998%</td>
</tr>
<tr>
<td>11</td>
<td>Ni$<em>{47.5}$ Ti$</em>{50}$ Fe$_{2.5}$</td>
<td>--</td>
<td></td>
<td>99.999%</td>
<td>Dehydrided</td>
<td>99.998%</td>
</tr>
<tr>
<td>12</td>
<td>Ni$<em>{47.5}$ Ti$</em>{50}$ Fe$_{2.5}$</td>
<td>Ht 8</td>
<td></td>
<td>99.999%</td>
<td>Dehydrided</td>
<td>99.998%</td>
</tr>
<tr>
<td>13</td>
<td>Ni$<em>{47.3}$ Ti$</em>{50.2}$ Fe$_{2.5}$</td>
<td>--</td>
<td></td>
<td>99.999%</td>
<td>Dehydrided</td>
<td>99.998%</td>
</tr>
<tr>
<td>14</td>
<td>Ni$<em>{47.3}$ Ti$</em>{50.2}$ Fe$_{2.5}$</td>
<td>Ht 7</td>
<td></td>
<td>99.999%</td>
<td>Dehydrided</td>
<td>99.998%</td>
</tr>
<tr>
<td>15</td>
<td>Ni$<em>{47.7}$ Ti$</em>{49.8}$ Fe$_{2.5}$</td>
<td>--</td>
<td></td>
<td>99.999%</td>
<td>Dehydrided</td>
<td>99.998%</td>
</tr>
<tr>
<td>16</td>
<td>Ni$<em>{47}$ Ti$</em>{50}$ Fe$_{3}$</td>
<td>--</td>
<td></td>
<td>99.999%</td>
<td>Dehydrided</td>
<td>99.998%</td>
</tr>
<tr>
<td>17</td>
<td>Ni$<em>{46.8}$ Ti$</em>{50}$ Fe$_{2.2}$</td>
<td>--</td>
<td></td>
<td>99.996%</td>
<td>Dehydrided</td>
<td>99.998%</td>
</tr>
<tr>
<td>18</td>
<td>Ni$<em>{46.8}$ Ti$</em>{50}$ Fe$_{2.2}$ (Special Metals)</td>
<td>Ht 7</td>
<td></td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>19</td>
<td>Ni$<em>{46.5}$ Ti$</em>{50}$ Fe$_{2.2}$</td>
<td>Ht 9</td>
<td></td>
<td>99.999%</td>
<td>Dehydrided</td>
<td>99.998%</td>
</tr>
<tr>
<td>20</td>
<td>Ni$<em>{45}$ Ti$</em>{50}$ Fe$_{3}$</td>
<td>--</td>
<td></td>
<td>99.999%</td>
<td>Dehydrided</td>
<td>99.998%</td>
</tr>
<tr>
<td>21</td>
<td>Ni$<em>{45}$ Ti$</em>{50}$ Fe$_{3}$</td>
<td>Ht 9</td>
<td></td>
<td>99.999%</td>
<td>Dehydrided</td>
<td>99.998%</td>
</tr>
</tbody>
</table>
Ht 1 - Strip at 900 °C, 10 minute and vacuum oil quenched
Ht 2 - Strip at 700 °C, 60 minute and vacuum cooled
Ht 3 - Strip at 700 °C, 30 minute and vacuum cooled
Ht 4 - Strip at 700 °C, 60 minute and cooled with argon backfilling
Ht 5 - Strip at 800 °C, 60 minute and vacuum cooled
Ht 6 - Strip at 700 °C, 60 minute muffle furnace cooled
Ht 7 - Strip at 850 °C, 30 minute and vacuum cooled
Ht 8 - Strip at 850 °C, 30 minute and vacuum slow cooled
Ht 9 - Button at 850 °C, 30 minute vacuum cooled and low speed saw cut

The alloys 1-8 were fabricated from the elemental powders, of purities shown in Table 7.2. The Table indicates that the powders were not of the highest grade. Among these alloy 2 demonstrated the shape memory effect. The failure of the remaining alloys is attributed to

Figure 7.11: Differential scanning calorimetry curve for Ni_{48.4}Ti_{50}Fe_{1.6} heat treated at 700 °C for 60 minutes followed by vacuum cooling to room temperature.
the impurities in the elemental powders. Figure 7.11 shows the differential scanning calorimetry curve of alloy 2 which has many small peaks corresponding to the impurities present in the sample. The remaining alloys, i.e., alloy 9 to alloy 21, were fabricated from the highest purity of commercially available powders, Table 7.2. An alloy 18 was commercially fabricated from a vendor. These alloys successfully demonstrated the shape memory effect.

7.6 **Stress Recovery with Shape Memory Effect in Ni-Ti-Fe**

The constraint recovery experiment, Figure 6.2, demonstrated that the Ni-Ti-Fe strip recovered its shape against a stress upon heating, after being deformed in the low temperature phase. The constraint recovery experiment was essentially a cantilever beam setup, Figure 7.12. The bending stress calculations for the strip simulating the setup are presented.

![Figure 7.12](image)

**Figure 7.12:** The constraint recovery experiment setup (a) and a schematic of the cantilever beam under load $P$ for bending stress calculations (b).
Dimensions of strip: \( l = 21.41 \text{ mm} \)

\[ w = 8.62 \text{ mm} \]

\[ h = 0.25 \text{ mm} \]

Distance: \( d = 12.04 + (26.91/2) \text{ mm} \)

\[ = 16.01 \text{ mm} \]

Load on Clamp: \( P = (16.01 \times 10^{-3}) \times 9.81 \text{ N} \)

\[ = 0.157 \text{ N} \]

Moment of Inertia: \( I = (1/12) bh^3 \text{ m}^4 \)

\[ = (1/12) \times (8.62 \times 10^{-3}) \times (0.25 \times 10^{-3})^3 \text{ m}^4 \]

\[ = 1.122 \times 10^{-4} \text{ m}^4 \]

Moment: \( M = P \ d \text{ Nm} \)

\[ = 0.157 \times 25.495 \times 10^{-3} \text{ Nm} \]

\[ = 4.002 \times 10^{-3} \text{ Nm} \]

\[ y = h/2 \text{ m} \]

\[ = (0.251 \times 10^{-3}) / 2 \text{ m} \]

\[ = 0.125 \times 10^{-3} \text{ m} \]

Bending stress: \( \sigma_b = (M \times y)/I \text{ N/m}^2 \)

\[ = [(4.002 \times 10^{-3}) \times (0.125 \times 10^{-3})] / 1.22 \times 10^{-4} \text{ N/m}^2 \]

\[ = 0.44595 \times 10^8 \text{ N/m}^2 \]

\[ = 44.595 \text{ MPa} \]
A deformed strip (bended, Figure 6.2) in the low temperature phase generated stress greater than 44.595 MPa while recovering to the parent shape, i.e., going from the low temperature phase to the austenite phase.

Another important observation is the ratio of the weight of the clamp to the strip.

\[
\text{Ratio} = \frac{16.01}{0.238} = 67.27
\]

A strip of Ni\textsubscript{47.5}Ti\textsubscript{50}Fe\textsubscript{2.5} with no heat treatment lifted a weight 67 times its own weight.

### 7.7 Workability of Ni-Ti-Fe

A cold rolling mill was re-commissioned. A strip of Ni-Ti-Fe alloy was prepared by electro-discharge machine wire cutting and was subsequently cold rolled. The material was successfully rolled and the calculations for the percentage reduction in thickness are presented below.

Number of passes = 5

Initial thickness of strip = 0.37 mm

Final thickness of strip = 0.26 mm

Hence, reduction in thickness = (Initial thickness – final thickness) / Initial thickness

\[
= \frac{(0.37-0.26)}{0.37}
\]

\[
= 0.2972
\]
There is 29.7% reduction in thickness of the Ni-Ti-Fe strip after cold rolling. There were no cracks observed after rolling, Figure 7.13. This demonstrates the workability of the Ni-Ti-Fe alloys.

Figure 7.13: Cold rolled Ni-Ti-Fe strip.
7.8  

**Necessity for Liquid Helium Dilatometer**

Although the boiling temperature of liquid nitrogen is -196 °C, the cooling becomes uncontrollable in the laboratory dilatometry setup. The same is true for the DSC instrument. Liquid nitrogen restricts the ability to detect transformation temperatures below -150 °C. The transformation occurring below this temperature cannot be detected. This is seen in Figure 7.14. Liquid helium, with boiling temperature of -269 °C, could further enhance the ability to detect transformation temperature further below -150 °C. A liquid helium dilatometer is being commissioned.
Figure 7.14: Differential scanning calorimetry curve for Ni$_{45}$Ti$_{50}$Fe$_5$ strip heat treated at 850 °C for 30 minutes followed by vacuum cooling to room temperature.
CHAPTER 8: CONCLUSION AND FUTURE RESEARCH

8.1 Conclusion

Shape memory alloys (SMAs) when deformed, in the lower temperature phase, produce strains as high as 8%. Heating the deformed alloy results in a phase transformation associated with the recovery of all the accumulated strain. The strain recovery can occur against large forces, resulting in their use as actuators. SMAs with sub-ambient operating temperatures have tremendous potential for applications in cryogenic switches, seals, valves, fluid line repair and self healing gaskets for space related technologies. This project has successfully fabricated different compositions of cryogenic Ni-Ti-Fe alloys, demonstrated the shape memory effect at liquid nitrogen temperatures and characterized the alloys with differential scanning calorimetry and dilatometry.

A controlled atmosphere arc-melting facility and vertical vacuum quench furnace facility were commissioned for the fabrication of Ni-Ti-Fe alloys. The standard operating procedures for arc-melting and heat treating have been documented. The facility creates high vacuum in the order of $10^{-7}$ Torr. Modifications were made to the vertical vacuum quench furnace facility to meet specific requirements for heat treating these alloys. These included a sample attachment setup for the strips/buttons of Ni-Ti-Fe alloys and a new quench reservoir-modified for quenching. The reservoir-modified avoids vaporization of the vacuum quench oil.

Nickel, titanium and iron powders were mixed in varying compositions using a ball mill and a rotary setup. These powders were then melted using the arc-melting facility into small buttons, weighing 0.010 kg to 0.025 kg. The buttons were subsequently thermo-mechanically processed. The buttons were cut using electro-discharge machine wire cutting and low speed saw
cutting into strips. The strips were cold rolled resulting in a 29.7% reduction in thickness. The cold rolled strip had no cracks which demonstrated the workability of Ni-Ti-Fe alloys. The alloys were then heat treated using the vertical vacuum quench furnace facility. Nine different heat treatments were performed on the alloys with the temperature and duration of treatment varying from 700 °C to 900 °C and 10 to 60 minutes respectively. Different methods of cooling to room temperature were employed, i.e., muffle furnace cooling, slow vacuum cooling, vacuum cooling, cooling with ultra high purity argon backfilling and vacuum oil quenching. The strips were then checked for the shape memory effect by submerging them in liquid nitrogen (-196 °C) and subsequently deforming it, i.e., by bending the strip. A majority of the strips became soft/mushy when immersed, indicating a phase transformation, and were easily deformed. Some strips cracked when deformed and were found to be brittle. Seven combinations of compositions and heat treatment of Ni-Ti-Fe alloys did not demonstrate the shape memory effect as they were fabricated from powders with purity varying from 98.0% to 99.9%. The remaining twelve combinations were fabricated from powders with purity varying from 99.9% to 99.999% and demonstrated the shape memory effect. The transformation characteristics of Ni-Ti-Fe strips were characterized using a differential scanning calorimeter and a dilatometer setup. The dilatometry setup was based on the principle of strain recovery in a strip after being deformed under an applied load. The setup used liquid nitrogen as the cooling medium and the heating was done with natural convection. The temperature versus deflection response of eleven combinations of compositions and heat treatment were plotted using the setup. Eleven combinations of Ni-Ti-Fe SMAs were characterized using a differential scanning calorimeter.

The alloys Ni$_{47.5}$Ti$_{50}$Fe$_{2.5}$ and Ni$_{48.4}$Ti$_{50}$Fe$_{1.6}$ after being heat treated at 850 °C for 30 minutes followed vacuum cooling to room temperature showed sharp peaks, with no systematic
shifts in transformation temperatures. The variation of nickel content in Ni\textsubscript{47.5}Ti\textsubscript{50}Fe\textsubscript{2.5}, i.e., 0.2 at.\% increase and decrease to give Ni\textsubscript{47.7}Ti\textsubscript{49.8}Fe\textsubscript{2.5} and Ni\textsubscript{47.3}Ti\textsubscript{50.2}Fe\textsubscript{2.5} respectively, showed an interesting result. It indicated that an increase in the nickel content in place of titanium, with the same iron content, further suppressed the R-phase. The two techniques used to characterize Ni-Ti-Fe alloys showed that the addition of Fe in place of Ni in NiTi alloys, suppressed the martensite phase, introduced R-phase in the cooling as well the heating curves, decreased the start and finish temperatures of the R-phase transformation, austenite transformation remained in the region of -25 °C to 25 °C. The decrease in the finish temperature of the R-phase was greater than the decrease in the start temperatures. A constrained recovery experiment was conducted on a Ni-Ti-Fe strip. The experiment used the strip in a cantilever type of setup, where one end was clamped to a copper fixture and the other end a load was applied. The strip was immersed in liquid nitrogen and subsequently bended. As the strip gained heat from the atmosphere, it started to recover its shape and lift the attached load. The Ni-Ti-Fe strip demonstrated its use as an actuator material by successfully lifting the attached load, 67 times its weight and generating stresses of over 40 MPa while returning to its original position.

8.2 Future Research and Applications

(i) Cryogenic shape memory actuator materials (Ni-Ti-Fe) development: This project has setup a processing methodology for the development of cryogenic shape memory actuator materials. The Ni-Ti-Fe alloy system has tremendous potential for applications in seals, valves, fluid line repair and self healing gaskets for space related technologies. Also the system has the potential to meet NASA’s requirement of a suitable materials for
thermal management at cryogenic temperatures. Ni-Ti-Fe alloys have to be further researched considering the need for the above requirements. The areas of focus are the effect of heat treating at different temperatures, effect of cold rolling on the hysteresis and the different characteristics associated with the transformations.

(ii) Application of R-phase transformation: The fabricated Ni-Ti-Fe shape memory alloys (SMAs) have shown the presence of R-phase in the heating as well as the cooling curves. The transformation is associated with a hysteresis ranging from 2.41 °C to 10.61 °C. The transformation has potential application in cryogenic actuators.

(iii) Cryogenic thermal conduction switch testing: Krishnan [7] designed an SMA based cryogenic thermal conduction switch. The switch demonstrated actuation with commercially available NiTi SMAs. The next generation of this switch is being tested using strips from fabricated Ni-Ti-Fe compositions. The ultimate goal of the switch is to operate between dewars of liquid methane and liquid oxygen in a common bulkhead arrangement. A suitable composition of Ni-Ti-Fe alloys and appropriate thermo-mechanical processing techniques has to be researched to achieve actuation between the two dewars.

(iv) Mechanical characterization using nanoindentation: Instrumented nanoindentation is a convenient tool for mechanical characterization of small sample volumes. It can be used to test materials not immediately available in bulk quantities. The fabricated Ni-Ti-Fe alloys being of small volumes can be mechanically characterized with the help of nanoindentation.
REFERENCES


