

**INVESTIGATION INTO THE EFFECT OF SOLID SOLUTION CHEMISTRY ON LATTICE PARAMETERS
AND MICROSTRUCTURAL PROPERTIES OF BETA -TI ALLOYS.**

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A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfillment of the requirements for the degree of Master of Science in Engineering.

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DECLARATION

I declare that this dissertation is my own unaided work. It is being submitted for the degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other university.

.....

Rodwell BALOYI

..... Day of Year

Abstract

This research aimed at investigating the changes in lattice parameters with increase in solute concentration. A vacuum arc furnace with a tungsten electrode was used for alloying purposes. The alloys were then annealed at 1000°C for 28 hours followed by quenching in ice-water. Five Ti-Mn and five Ti-Fe alloys were prepared within their solid solution range. In addition, commercially pure titanium was doped with up to 2.7%O with the aim of evaluating the effect of this on lattice parameters. Optical microscopy was used to study microstructures and XRD was utilized for lattice parameter determination.

Lattice constants decrease with increase in solute concentration confirming the expected result since the solute elements are smaller than titanium. Grain size also decreased with increase in solute content. Hardness tests made confirmed an increase in hardness with solute concentration. This is caused by lattice straining as beta stabilizer concentration is increased.

Dedication

To Joyce and Christie. For understanding the long nights!

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CHAPTER ONE: INTRODUCTION

The use of titanium and its alloys in industry has rapidly grown over the past few decades. This is due to its relatively superior mechanical, chemical and heat resistant properties. Titanium has strength to weight ratio that is in between steel and aluminium and is also one of the most reactive metals in its pure form.

Development of titanium metal production technologies was initiated by the U.S Bureau of Mines in 1938 because of the metal's attractive properties and known abundance ^[1]. Production processes utilized since then include Kroll's magnesium reduction of titanium tetrachloride (TiCl_4), Hunter's sodium reduction of TiCl_4 van Arkle's and deBoer's decomposition of titanium tetraiodide, and electrowinning techniques. The Kroll process became the most utilized method for industrial production of pure titanium metal.

The most common industrial uses of titanium alloys are in the military and aerospace industries. After a drop in annual world production of titanium around 1957, growing production of jumbo airliners in the 1970s sparked a surge in titanium demand. The main production companies, e.g. Timet, DuPont, Cramet, Dow and Oremet (in the U.S) increased production in response to this new demand ^[1].

The most common ingot melting technologies currently being used are Vacuum Arc Re-melting (VAR), Induction Skull Melting (ISM), Electron Beam Melting (EBM) and Plasma Arc Melting (PAM). These technologies may be utilized for purifying the ingots as well as alloying purposes ^[7].

Titanium alloys may be classified into alpha, alpha-beta and beta depending on alloying elements. This research is mainly concerned with beta alloys. Over the past few years, beta titanium (β -Ti) alloys have continued on an increasing basis to be a very important class of materials. These alloys possess a combination of high strength, low density, good corrosion

resistance. They are heat treatable, deep hardenable and exhibit hot and cold processability ^[1, 2].

β -Ti alloys have experienced a continuing and growing role in the aerospace industry where historically the industry benefited from the unique combination of desirable properties and could support the cost of these high tech materials ^[2,3]. Their biocompatibility and corrosion resistance also earned them a commanding role in medical applications.

Recently, non-aerospace applications for β Ti alloys have led to design of lower cost alloys such as the β -Ti alloy LCB for automotive and other industrial applications ^[2]. Currently, key components fabricated from β -Ti alloys are found in many fields including aerospace, biomedical, sporting and consumer goods, gas/oil, and naval, amongst others. The two types of β stabilizers are known as eutectoid and isomorphous. The isomorphous stabilizers include Mo, V, Ta and Nb and the eutectoid stabilizers include Cr, Mn, Fe, Co, Ni and Cu ^[2].

β -Ti alloys have one greatest advantage over alpha alloys, their ability to be heat treated. This is because of the lowering of the alpha-beta transus thereby allowing beta phase to be easily retained at room temperature ^[2, 23]. This has a huge impact on mechanical properties of beta alloys since it gives materials engineers flexibility in materials design.

The purpose of this research was to make beta titanium alloys, characterize them, heat treat the alloys to get beta phase at room temperature followed by X-ray determination of the extent of the beta lattice distortion. The main aim being to trend changes in lattice parameters with amount of alloying in the solid solution range of titanium-manganese and titanium-iron alloys. Determination of hardness for the said alloys was an important part of this work. The aim for this was to use observed lattice distortions to explain hardness.

CHAPTER 2: LITERATURE REVIEW

This chapter highlights the history and the applications of titanium and its alloys. It also reviews XRD technology, microscopy and other technologies employed in titanium research.

2.1 Titanium and its uses

Titanium was discovered in 1790 and was named by the German chemist M.H. Klaproth after studying the physical and chemical properties of a lot of clay and rock minerals, amongst which there was the sample of mineral known today as rutile. Klaproth discovered that rutile was an oxide of an unknown metal, which he named Titanium after the Titans of Greek mythology ^[6].

This discovery spurred frantic research throughout the nineteenth century to produce titanium in its metallic form, but more often than not, there were failures, only nitrides and suboxides of titanium were made. An unintentional breakthrough occurred toward the end of the nineteenth century where 95% pure titanium was produced by M.A Hunter and associates at General Electric Company during the search for a new light bulb filament material ^[4].

In 1940 after relatively successful attempts by W.J Kroll's contemporaries, Kroll published an economical method of producing titanium from the reduction of titanium chloride with molten magnesium. This spurred the titanium exploitation ^[4, 6].

Titanium occurs naturally in three allotropic forms, rutile, anatase and brookite, and rutile being the most common. Titanium is the fourth widely distributed metal on the earth's crust, after, iron, aluminium and magnesium. It makes approximately 0.6% of the earth's crust ^[4]. It also belongs to an elite category of elements known as refractory metals. One of the more outstanding characteristics of these materials lies in the refractive abilities inherent in their oxides. Titanium is naturally platinum gray. By applying heat or electricity one may unleash its refractive properties by inducing various oxide thicknesses on the material surface. Titanium anodizing is best performed electrolytically. The resulting titanium oxide causes an optical

interference with a purity and vivacity much the same as witnessed in the luminescent colors of oil on water, peacocks feathers, or a rainbow ^[5].

Exploitable titanium concentrations are found all over the world where titanium is produced from, mineral sands, ilmenite and titanomagnetite rock deposits in the U.S.A, India, Scandanavia, Australia, South Africa and other countries. The industrial exploitation of titanium is fuelled by titanium's attractive mechanical and chemical (corrosion) properties ^[1].

Titanium and its alloys have long been attractive for advanced aerospace structural applications due to their high strength-to-weight ratio (with a density of about 60% that of steel or nickel-base superalloys) and excellent combination of ductility, fracture toughness and modulus (see *Table 2.1*). Its tensile strength (as an alloy) is comparable to lower-strength martensitic stainless steels but better than that of austenitic or ferritic stainless steels ^[6]. It has been termed as the *space age* material since more than 80% of titanium is used in the aerospace industry, although significant interest is growing in other industries such as the automotive industry. However, despite these attractive characteristics, the application of titanium and its alloys to large, highly loaded structures has been hindered due to problems associated with fabricating titanium into large structural shapes.

Forging has long been the preferred fabrication method because it yields excellent mechanical properties, but limitations in size and complexity have prevented designers from achieving the design flexibility desired for complex structures. The ability to use various casting technologies to make complex structural shapes is attractive to airframe designers because casting provides both structural complexity and near-net-shape capability. Moreover, the typical lead times for titanium castings (from casting to shipping) tend to be much shorter than for forgings ^[6, 7].

Table 2.1: Mechanical and Physical properties of titanium in comparison to other common engineering alloys ^[24].

MECHANICAL & PHYSICAL PROPERTIES

PROPERTY	Titanium Grade 2		90-10 Cu-Ni		70-30m Cu-Ni		316 Stainless	
	KSI	MPa	KSI	MPa	KSI	MPa	KSI	MPa
Tensile Strength (min)	50	345	40	275	52	360	75	515
Yield Strength (min)	40	275	15	105	18	125	35	240
Yield Strength (max)	65	450	--		--		--	
Elongation (min)	20%		30%		15%		30%	
Elastic Modulus (10^6 psi)	16		18		22		28	
Thermal Expansion Coeff. (Micro in/in $^{\circ}$ F)	4.8		9.5		9.0		8.9	
Thermal Conductivity (BTU/hr-ft 2 $^{\circ}$ F/in)	150		348		204		95	
Density (lbs/in 3)	0.163		0.323		0.323		0.286	

2.2 Crystal structure and alloy types

The atomic number of titanium is 22 and pure titanium melts at 1670 $^{\circ}$ C. The low density (4.51g/cm 3) accounts for its high strength to weight ratio. Titanium is a diallotropic element, alpha hcp (α) and beta bcc (β) phase stable below 880 $^{\circ}$ C and above 880 $^{\circ}$ C to melting temperature, respectively.

Titanium responds well to interstitial alloying with C, H, O, N and substitutional alloying by V, Sn, Zr etc. Oxygen is one of the prominent α stabilizer used in interstitial strengthening. Oxygen tends to reduce the ductility of titanium alloys, since high content of O in Ti promotes the formation of ordered α_2 phase which is highly brittle and suffers from ductile brittle transition temperature (DBTT) ^[8].

2.2.1 Effects of Alloying Elements on α - β Transformations.

Unalloyed titanium is allotropic. Its close-packed hexagonal structure (α phase) changes to a body-centered cubic, structure (β -phase) at 885°C (1625°F), and this structure persists at temperatures up to the melting point ^[9].

With respect to their effects on the allotropic transformation, alloying elements in titanium are classified as α stabilizers or β stabilizers. Alpha stabilizers, such as oxygen and aluminum, raise the α -to- β transformation temperature. Nitrogen and carbon are also α stabilizers, but these elements usually are not added intentionally during alloying. Beta stabilizers, such as manganese, chromium, iron, molybdenum, vanadium, and niobium, lower the α -to- β transformation temperature and, depending on the amount added, may result in the retention of some β phase at room temperature ^[9].

Depending upon the amount of stabilizers present in an alloy, the alloy will be a metastable or stable β -Ti alloy. The molybdenum equivalency ^[3] of the β stabilizer is used to assess the level of element necessary to prevent martensitic transformation upon quenching to room temperature. The molybdenum equivalency is the ratio of the level of a given stabilizer to the level of molybdenum required for the same degree of the β stability. In general, a molybdenum equivalency of $\approx 10\%$ is required to stabilize the β phase upon quenching ^[3].

Depending upon the thermomechanical treatment and alloying elements of metastable β Ti alloys, various phases and morphology result. The high temperature allotropic phase of titanium is retained upon quenching given the presence of sufficient levels of stabilizer elements and its crystal structure is bcc ^[3].

Silicides form at high temperatures when zirconium is present ^[10] as well as in the absence of zirconium such as in the case of beta-21S ^[2]. In general, at lower temperatures α phase forms followed by ω phase or β' . A study of the phase constitutions in binary titanium alloys was done which showed that for beta stabilizers, the lattice parameters varied linearly with concentration

of stabilizer ^[38]. Titanium-manganese and titanium-iron phase diagrams are used to highlight these phase transformations as shown in Fig. 2.1 and Fig. 2.2 below:

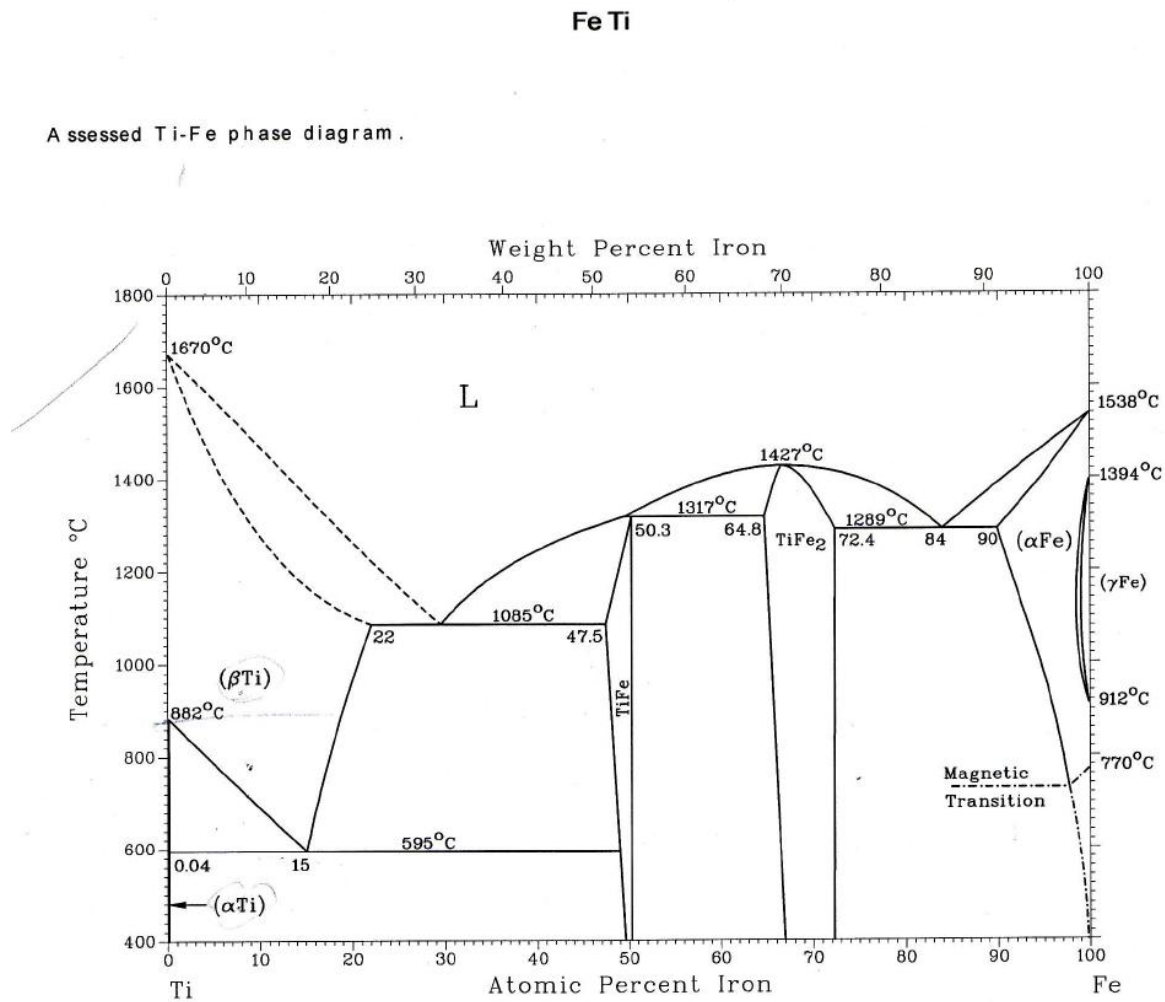


Fig. 2.1: Ti-Fe phase diagram showing an enlarged beta region due to iron stabilisation of the beta phase ^[48].

Mn Ti

Assessed Ti-Mn phase diagram.

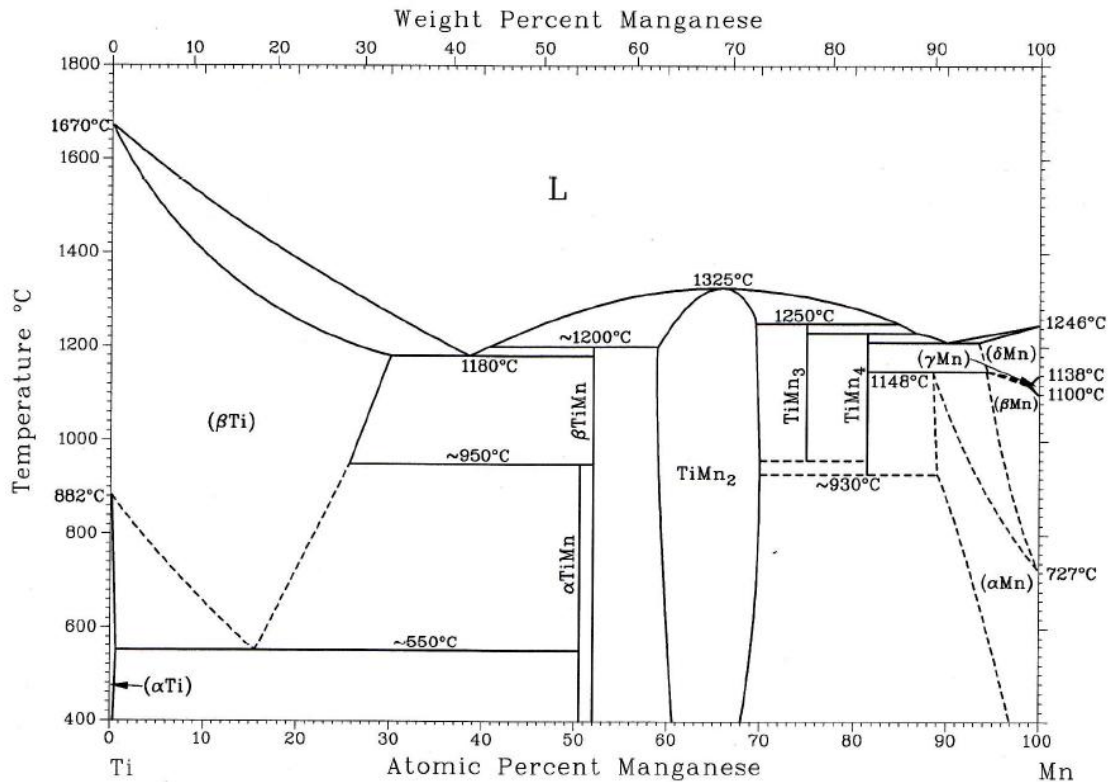


Fig. 2.2: Ti-Mn phase diagram showing an enlarged beta region due to manganese stabilisation of the beta phase ^[48].

Titanium alloys may be grouped into three main categories:

2.2.2 Alpha alloys

These are formed between alpha stabilising elements such as O, Al and N and pure titanium. Commercially pure titanium and alpha alloys of titanium are non-heat treatable and are generally very weldable.

They have:

- Low to medium strength
- Good notch toughness
- Reasonably good ductility
- Excellent mechanical properties at cryogenic temperatures

Pure titanium and alpha alloys possess the highest corrosion resistance.

More highly alloyed near-alpha alloys offer optimum high temperature creep strength and oxidation resistance ^[11].

2.2.3 Alpha Beta Titanium Alloys

Alpha Beta alloys are heat treatable and most are weldable.

Typical properties include:

- Strength levels are medium to high
- High temperature creep strength is not as good as most alpha alloys
- Cold forming may be limited but hot forming qualities are normally good
- Many alloys can be superplastically formed

The most commonly used alpha beta alloy is Ti6Al4V, developed in many variations of the basic formulation for the widest possible choice of key properties and for many widely differing applications ^[11].

2.2.4 Beta Titanium Alloys

Beta Ti alloys are the most versatile class of Ti alloys offering a wide range of processing and physical-chemical mechanical property combinations compared with any other class of Ti alloys.

Despite this wide range of attributes, there were very few applications of β alloys in the early 1990s, accounting for only 1% of the total Ti market. In the past, the majority of the development of β alloys has been driven by performance, and the high cost factor has slowed down the integration of β -Ti alloys. The usage of β -Ti alloys has increased significantly in the last 10 years due to the focused effort in reducing the formulation and processing costs. Currently, β -Ti alloys are widely used in aerospace, automotive, biomedical, and sporting applications ^[11].

Beta or near beta alloys are:

- Fully heat treatable
- Generally weldable
- Capable of high strengths
- Possess good creep resistance up to intermediate temperatures
- Excellent formability can be expected in the beta alloys in the solution treated condition

Beta-type alloys have good combinations of properties in sheet, as fasteners and are ideal for sporting applications. Some alloys offer uniform property levels through heavy sections.

Beta alloys tend to be used because of the relative formability of the bcc structure as compared to hcp alpha ^[12].

The higher alloy content of beta alloys increases the density of beta alloys typically by 7-10% compared to Ti6Al4V. Typical beta alloys include:

Ti3Al8V6Cr4Mo4Zr ASTM Grade 19	Ti10V2Fe3Al AMS 4983, 4984, 4987
Ti15Mo3Nb3Al2Si ASTM Grade 21	Ti15V3Cr3Sn3Al AMS 4914

It is only the metastable beta alloys which are heat treatable by solution treatment and ageing. Fully stable beta alloys can only be annealed ^[13].

2.3 Titanium and oxygen

Commercially pure titanium (approximately 99.6% Ti content) has virtually indistinguishable mechanical properties as high purity Titanium (greater than 99.8% Ti content). Oxygen is an α -stabilizer and has significant impact on the strength of the Ti-alloy. It has been shown that as the oxygen content increases, the ordered α_2 phase forms ^[8]. This phase impairs ductility and is affected by DBTT. Embrittlement of titanium by oxygen occurs below the maximum solubility of oxygen in titanium.

Although oxygen has a detrimental effect on the strength of titanium at high concentrations, addition of 0.1 wt% O in titanium has the same strength increase as addition of 2wt% Al and 4.5 wt% Zr and V. The strength rises by 7-10 kg/mm² ^[4]. This can have significant cost implications because oxygen is one of the most common elements on earth.

The effect of oxygen on the mechanical properties of commercially pure titanium is given in *Fig. 2.3*.

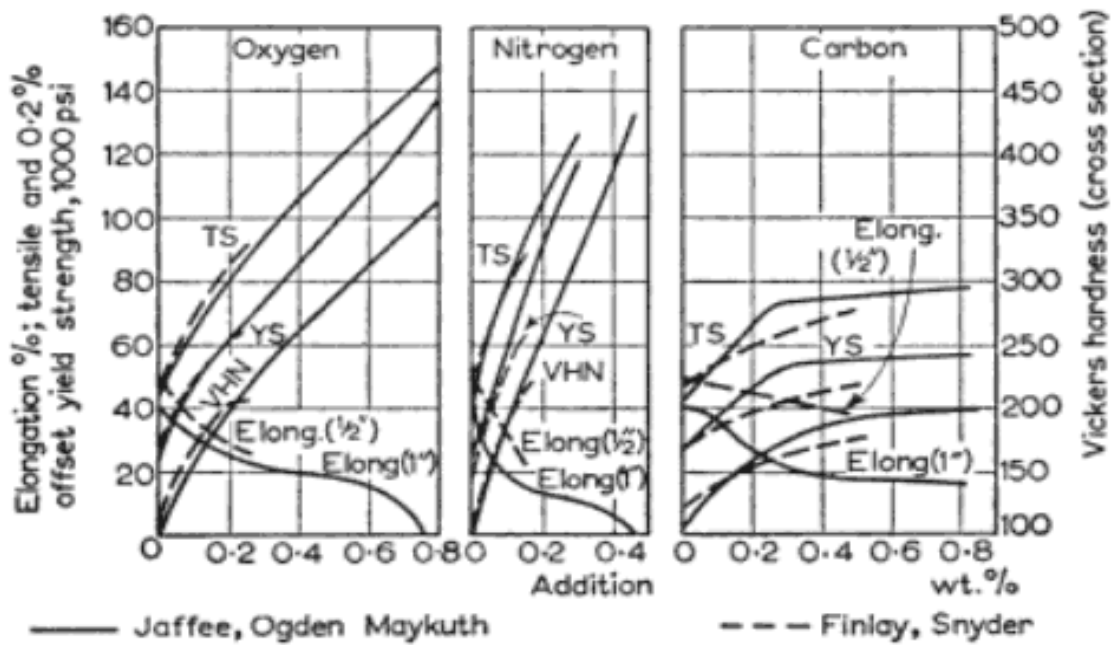


Figure 2.3: Effects of O, N and C on tensile and hardness properties of alpha Ti-alloys^[22]

It is clear that oxygen strengthens titanium and improves the mechanical properties. But, it also reduces its elasticity and ductility^[8].

There are various grades of titanium alloys alloyed with interstitial elements. A few of these grades have been tabulated in *Table 2.2*.

Table 2.2: Maximum interstitial content plus minimum mechanical properties of some titanium alloy grades ^[22]

	Max. Interstitial content allowed, wt%.				Max Tensile strength	Min yield strength	% elongation	Reduction in area%
Grade(a)	N	C	O	H	MPa	MPa	%	%
1	0.03	0.1	0.18	0.0125(b)	241	172	24	30
2	0.03	0.1	0.25	0.010 (b)	345	276	20	30
3	0.05	0.1	0.35	0.0125(b)	448	379	18	30
4	0.05	0.1	0.4	0.0125(b)	552	483	15	25

(a) Commercially pure alpha titanium bars and billets (ASTM B 348-781) (b) Bars only

2.4 Strengthening mechanisms

The ability of a metal to deform depends on the ability of dislocations to move. Restricting dislocation motion makes the material stronger ^[14]. Mechanisms of strengthening in single-phase metals include grain-size reduction, solid-solution alloying and strain hardening.

2.4.1 Grain size reduction

This mechanism works by restricting dislocation movement. Fig. 2.4 illustrates how this may be achieved by small grains with high-angle grain boundaries.

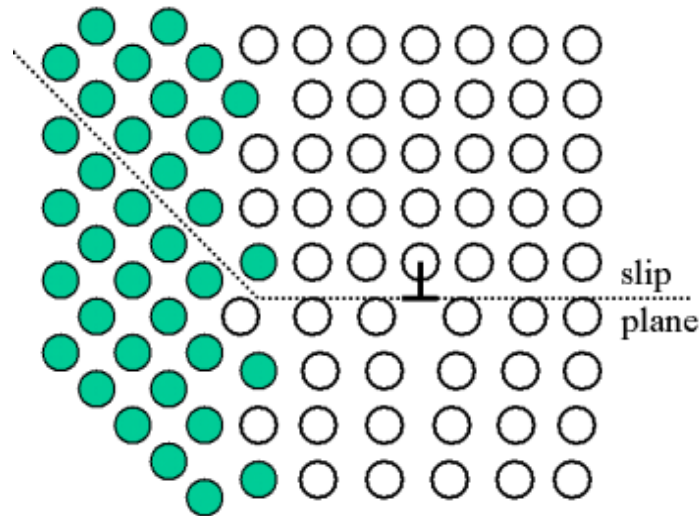


Fig. 2.4: Grain boundary barrier to dislocation motion: slip plane discontinues or change orientation ^[14] when it reaches the dislocation.

High-angle grain boundaries block slip and increase strength of the material. A stress concentration at end of a slip plane may trigger new dislocations in an adjacent grain. Generally, the finer the grains, the larger the area of grain boundaries that impedes dislocation motion. Grain-size reduction usually improves toughness as well. Usually, the yield strength varies with grain size d according to Hall-Petch equation:

$$\sigma_y = \sigma_0 + K_y/\sqrt{d}$$

where σ_0 and K_y are constants for a particular material, d is the average grain diameter.

Grain size d can be controlled by the rate of solidification, by plastic deformation and by appropriate heat treatment ^[14].

2.4.2 Solid solution strengthening

Alloys are usually stronger than pure metals of the solvent. Interstitial or substitutional impurities in a solution cause lattice strain. As a result, these impurities interact with dislocation strain fields and hinder dislocation motion. Impurities tend to diffuse and segregate around the

dislocation core to find atomic sites more suited to their radii. This reduces the overall strain energy and “anchor” the dislocation⁴³. Motion of the dislocation core away from the impurities moves it to a region of lattice where the atomic strains are greater (i.e. the dislocation strains are no longer compensated by the impurity atoms).

2.4.3 Strain Hardening

Ductile metals become stronger when they are deformed plastically at temperatures well below the melting point. The reason for strain hardening is the increase of dislocation density with plastic deformation. The average distance between dislocations decreases and dislocations start blocking the motion of each other.

The percent cold work (%CW) is often used to express the degree of plastic deformation:

$$\%CW = ((A_0 - A_d)/A_0) \times 100$$

Where A_0 is the original cross-section area, A_d is the area after deformation. %CW is just another measure of the degree of plastic deformation, in addition to strain^[14].

Alpha titanium alloys have properties that depend mainly on their composition. Interstitial and substitutional impurities can effect strengthening through pinning of dislocations to minimise slip. Interstitial alloying elements commonly used are oxygen, nitrogen and carbon while aluminium, tin and zirconium can be used as substitutional elements. Properties of alpha titanium alloys are also dependent, to some extent, on their processing history. This is because the history controls grain size and preferred orientation (texture)^[7]. Grain size and solid solution additions both restrict the operation of twinning and reduce the formability of the material.

By restricting grain growth, alloying elements such as Fe in CP Ti help in formation of fine grained structures. These in turn cause an increase in yield strength as described by the Hall-Petch relationship^[7].

Beta alloys can also be strengthened by heat treatment, in addition to processing history and composition. With enough beta stabilising elements, full beta structures may be realized after quenching to room temperature, without the martensitic transformation. Processing of beta alloys usually consists of a hot working operation followed by heat treatment. The heat treatment consists of an above beta transus solution treatment followed by quenching then aging. Solution treating above the beta-transus temperature yields coarse beta grains while solution treating below the beta transus temperature results in the precipitation of primary alpha ^[6]. Metastable beta titanium alloy is an attractive material in the applications of critical high-stress and corrosive service due to its excellent hot formability, deep hardenability and superior corrosion resistance ^[15]. Molybdenum equivalence (Mo.Eq.) is often considered to evaluate the overall beta stability for titanium alloy with various alloying element additions.

In order to retain 100% beta phase upon quenching from above the beta transus, the molybdenum equivalence should be greater than 10% ^[16]. The most important microstructural parameters that control the properties of β Ti alloys are prior β grain size, the primary and secondary α , including their volume fraction, morphology, size, and distribution, and the grain boundary α morphology and volume fraction ^[11].

2.5 Titanium applications

Titanium and its alloys are mainly used in high strength applications and highly corrosive environments.

2.5.1 Strength applications

The strength to weight ratio is higher than steel, hence in the aerospace industry where weight is an important design criteria, titanium and its alloys have found wide applications, from landing gears of jet aircraft and turbine blades in jet engines.

Materials of construction for secondary marine structures must exhibit an optimum combination of saltwater corrosion resistance, mechanical reliability, high strength-to-weight ratio, reliable fabricability and maintainability, and low life cycle cost. To minimize life cycle costs, design and materials selection must include engineering for reduced maintenance.

Titanium provides a unique combination of these features. Titanium exhibits ^[17]:

- Excellent corrosion resistance in all sea water environments
- Non-toxicity to people, aquatic life, or the surrounding environment
- Strength-to-weight ratio unmatched by any other common engineering metal
- Structural stiffness comparable to the best other common engineering metals
- Non-magnetic in all alloys and forms
- Simple and reliable forming, fabrication, and welding processes
- Reliable near net shape casting and forging processes
- Reliable commercial availability in sheet, plate, tube, pipe, and bar form
- Established industry standards worldwide.

2.5.2 Corrosion Applications

Titanium is well established for use in some of the most severe environments in many industries including the Chemical Process Industry (CPI), Energy (including Geothermal), Pulp & Paper, Desalination (in Multi-Stage Flash Desalination units), Refineries, and in the Utility Industry in Utility Steam Condensers. It is also playing a significant part in offshore rigs in Ballast Tanks, Fire-Main systems and general Service Water piping systems, linings for Flue Gas Desulfurization (FGD), among many others ^[18].

In the past decade there has been a significant increase in the usage of titanium for military applications including armor, protective linings, and especially in naval applications where seawater is the environment and where corrosion, erosion and maintenance are of primary concern. Within the context of seawater environments, applications for titanium include Heat Exchanger seawater cooling (both Shell & Tube and Plate/Frame); in service water lube Oil

Coolers and other general heat exchanger systems. It is also used, both shipboard and in land-based plants, in Hot Water Heater units as well as for Refrigeration, as Air Chillers and air-conditioning systems. Its products run the gamut from sheet for heat exchanger shells and baffles, plate for tube sheets and vessels, tubes for seawater cooling, pipe, fittings (elbows, tees, reducers, etc.), fasteners, flanges, pumps and valves for seawater service water input, fire protection systems and drainage^[18].

Titanium's ceramic-like outer protective oxide film (TiO_2) allows water velocities above 90 ft/sec (27 m/sec) and higher in the absence of suspended solids. Under sand-laden conditions, flow rates can be as high as 15-18 ft/sec (4.6 – 5.5 m/sec) without any erosion effects. This is in contrast to limitations put on some materials to as low as a range of from 7 to 12 ft/sec^[18] (2.1 to 3.7 m/sec) under ordinary (non silt/sand-laden) conditions.

The corrosion resistance of titanium and its alloys has made it replacement construction material where all construction materials would corrode and fail. However, titanium dissolves in concentrated strong acids such as hydrofluoric acid. Titanium is generally regarded as an exotic material due to the high cost of production, mainly incurred by the consumption of another expensive material, magnesium; in its production process.

In certain instances, the initial cost of titanium can be offset by its long service life in extremely corrosive environments.

2.5.3 Biomedical Applications

Titanium and its alloy grades started gaining widespread usage as implant materials in the early 1970s. Although commercially pure (C.P.) titanium offered better corrosion resistance and tissue tolerance than stainless steel, its comparatively lower strength and unfavorable wear properties restricted its usage to certain applications such as pacemaker cases, heart valve cages and reconstruction devices. The strength of C.P. titanium alloys can be further increased

through cold processing. The cold worked C.P. titanium alloy has been used for dental implant and maxillofacial applications.

More than 1000 tonnes (2.2 million pounds) of titanium devices of every description and function are implanted in patients worldwide every year. Requirements for joint replacement continue to grow as people live longer or damage themselves more in by hard sports play or jogging, or are seriously injured in road traffic and other accidents. For example, it is projected that approximately 272,000 total hip replacements will annually be performed by 2030. Additionally of the 152,000 total hip replacements performed in 2000 approximately, 12.8% involved revisions of previous hip replacements ^[19]. Light, strong and totally bio-compatible, titanium is one of few materials that naturally match the requirements for implantation in the human body. Medical grade titanium alloys have a significantly higher strength to weight ratio than competing stainless steels.

The range of available titanium alloys enables medical specialist designers to select materials and forms closely tailored to the needs of the application. The full range of alloys reaches from high ductility commercially pure titanium used where extreme formability is essential, to fully heat treatable alloys with strength above 1300 MPa, (190ksi). Shape–memory alloys based on titanium further extend the range of useful properties and applications.

A combination of forging or casting, machining and fabrication are the process routes used for medical products. Surface engineering frequently plays a significant role, extending the performance of titanium several times beyond its natural capability ^[20]. Titanium alloys are utilized in the following medical fields:

- Bone and Joint Replacement
- Dental Implants
- Maxillo and Cranio/facial treatments
- Cardiovascular devices
- External Prostheses
- Surgical Instruments ^[20].

2.5.4 Art and Decoration

Titanium has grown considerably in art and decoration since the early 80's ^[5]. It has become one of the choice materials for making jewelry and construction decorations. One good example is of the use of titanium on the Guggenheim Museum of Contemporary Art of Bilbao (Bilbo), located on the North Coast of Spain (Fig. 2.5).



Fig. 2.5: The Guggenheim Museum of Contemporary Art of Bilbao (Bilbo), located on the North Coast of Spain in the Basque region. Nicknamed "The Hole", this is a contemporary museum built of titanium and limestone ^[21].

2.6 Heat treatment of Titanium alloys

Heat treatment of titanium alloys is based on the phase transitions which take place during heating and cooling due to the occurrence of two allotropic forms of titanium. Alpha (α) titanium is stable up to 880°C after which there is an allotropic transformation to beta (β) titanium.

Through heat treatment one can produce desirable structure changes and consequently, changes of various properties. During slow continuous heating, when the transition $\alpha + \beta \rightarrow \beta$ takes place, instead of the expected structure refining, only a considerable coarsening is observed ^[4].

In general, grain refinement is the main goal of heat treatment since it ensures better mechanical properties. Owing to a small difference in the specific volumes of the α and β phases, the stresses produced during the transformation do not lead to grain refining even at high heating rates.

The high temperature of phase transitions and the tendency of the body-centered cubic β phase to polygonization rather than to recrystallization have an influence on the lack of grain refining during heating of titanium alloys ^[4].

With sufficient beta-stabilising elements, a metastable beta phase can be realized after quenching from above the α - β transus temperature to 25°C ^[12].

Titanium alloys are heat treated in order to:

- Reduce residual stresses developed during fabrication (stress relieving)
- Produce an optimum combination of ductility, machinability, and dimensional and structural stability (annealing)
- Increase strength (solution treating and aging)
- Optimize special properties such as fracture toughness, fatigue strength, and high-temperature creep strength ^[23].

2.7 Corrosion of Titanium

Titanium is one of the most corrosion resistant materials known to man. Like many other corrosion resistant materials, a tenacious oxide layer quickly forms on the surface of titanium alloys in corrosive environments. This layer (which consists basically of TiO_2) prevents or limits further attack on the metal itself ^[24].

Besides other important material features, the corrosion parameters and corrosion products are responsible for limiting the biocompatibility of metallic materials, and can produce undesirable reactions in implant-adjacent and/or more distant tissues. Titanium and some of its alloys are known as being the most biocompatible metallic materials due to their high strength, low modulus and high corrosion resistance in biological media ^[25]. Titanium often exceeds stainless steels in most corrosive environments and has outstanding corrosion resistance in the human body ^[6].

2.8 Titanium melting technologies

This section reviews the most common melting and casting techniques utilised for Titanium production. The technology is divided into MELTING and CASTING. Vacuum Arc Re-melting (VAR), Electron Beam Melting (EBM), Plasma Arc Melting (PAM) and Induction Skull Re-melting will be discussed under melting methods while Investment Casting, Vacuum-Die Casting (VDC) and Centrifugal Casting will be looked at under casting.

2.8.1 Vacuum Arc Re-melting (VAR)

This is currently the most common method of melting Ti and other reactive metals. Material is fed into a cold-wall metal crucible (usually Cu) as a consumable electrode (consumable arc-melting) or a tungsten electrode can be used to melt the charge (non-consumable arc melting) under a high vacuum (10^{-6} torr). The Cu crucible will be water-cooled and a solid skull forms between the molten metal and the crucible ^[12, 26, 27] as illustrated on one of the Consarc VAR furnaces in Fig. 2.6.

Melting rates as high as 1400Kg/hr with ingot diameters of 1280mm and 13.5t in weight can be realised. A liquid superheating of above 100°C is recommended for elimination of porosity. No ceramic inclusions are realised in this process since the crucible is pure copper. Alpha case formation due to oxygen pick-up is minimised by vacuum conditions. Improved stirring conditions ensure better alloy homogeneity. However, it is difficult to get high superheating

due to signal distortion in the Cu crucible; hence more energy than conventional ceramic crucible induction melting is needed.

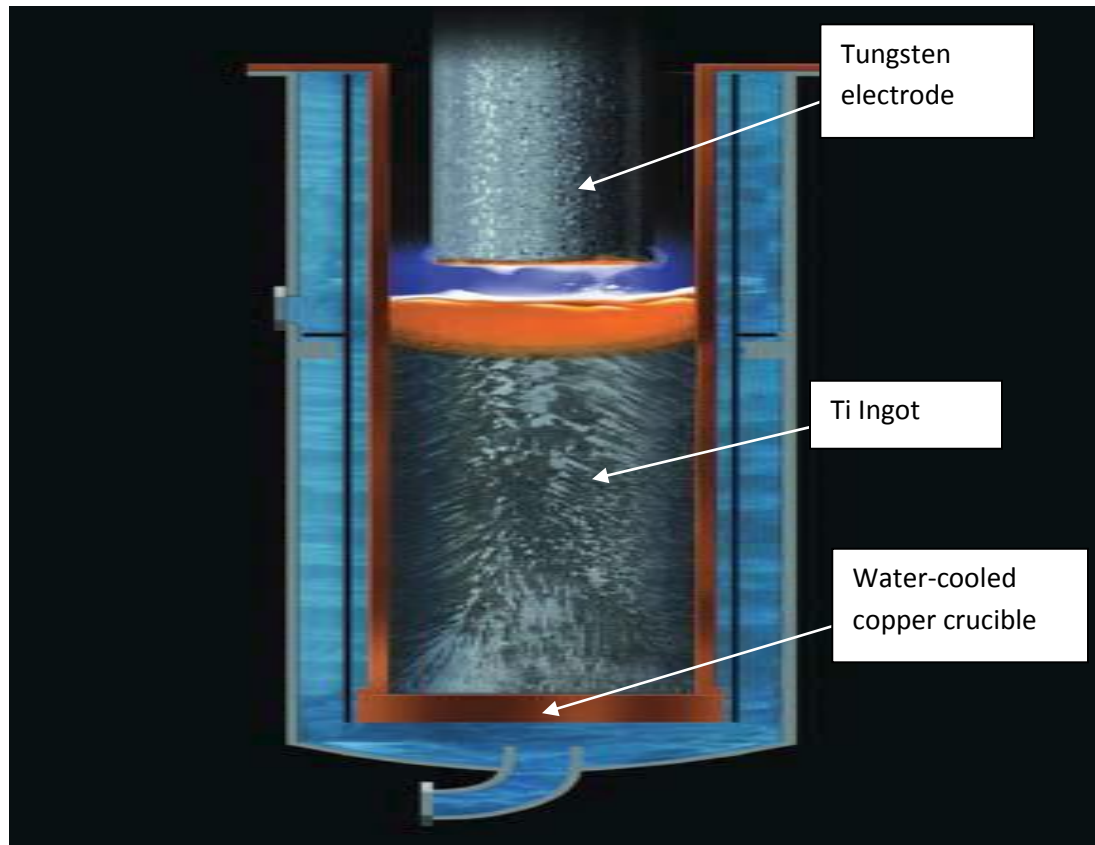


Fig. 2.6: Vacuum Arc Re-melting process schematic ^[30].

2.8.2 Electron Beam Melting (EBM)

This melting process is similar to VAR in terms of principles. In this method, a high energy electron beam is directed onto the charge, which is in a cold-wall crucible, melting it in very short periods. The molten Ti can then be used for other post casting processes such as casting and atomisation. All this occurs under high vacuum or inert atmosphere ^[12, 13, 26, 27].

This process is increasingly being used for melting pure titanium. However, its use with titanium alloys is limited by poor control of ingot composition which necessitates subsequent homogenization. This is caused by irregularities in feed chemistry, which can be adjusted

online, but also due to frequent freezing and re-melting of metal in the hearth as well as changes in throughput rate, which are difficult to control ^[28]. Fig. 2.7 shows the electron beam melting facility at Sandia National Laboratories.

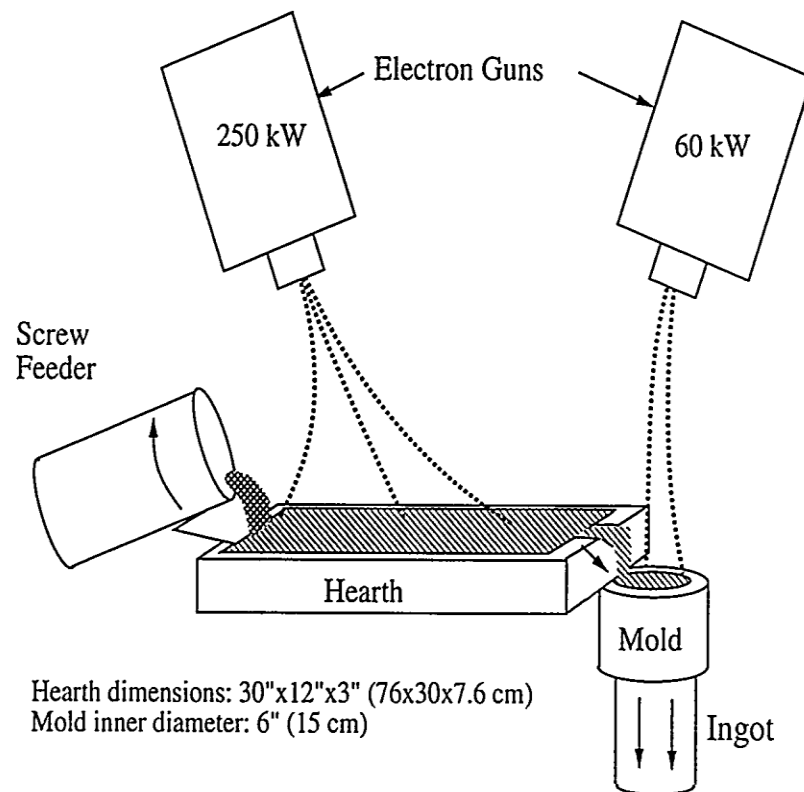


Fig. 2.7: Electron beam melting facility at Sandia National Laboratories ^[28].

2.8.3 Plasma Arc Melting (PAM)

Plasma Arc Melting (PAM) is similar to Electron Beam Melting (EBM) except that a high energy plasma torch is used to melt the charge. The process produces clean melts with high purity Ti as long as crucible contamination is minimised and the atmosphere is correctly maintained. A typical PAM process is illustrated in Fig. 2.8.

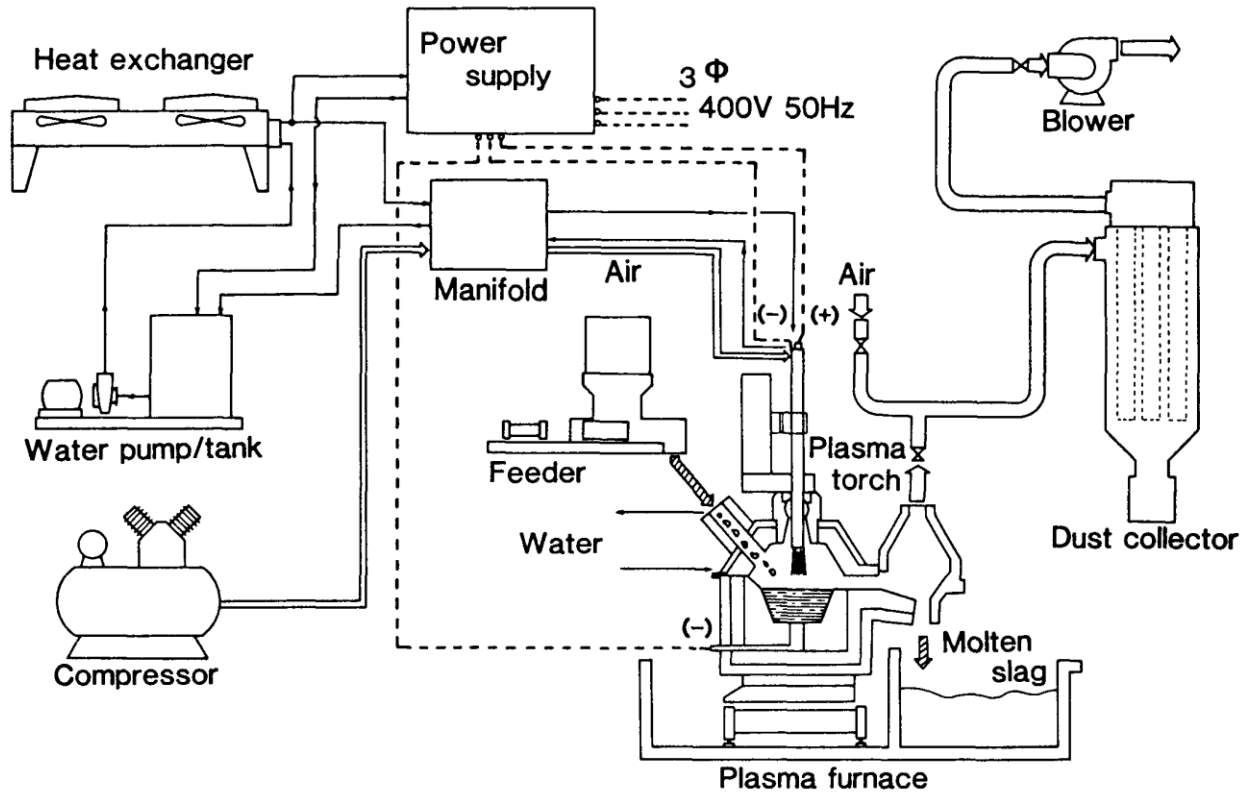


Fig. 2.8: Process flow diagram of Plasma arc melting ^[29].

2.8.4 Induction Skull Re-melting

This is a cold-wall induction method in which a charge of reactive metal in a water-cooled Cu segmented crucible under a non-reactive atmosphere is melted by induction heating with an induced alternating current.

Induction Skull Melting ISM is a method of melting metals in a segmented, water-cooled copper vessel while under vacuum or controlled atmosphere using an induction coil. This is done metal-to-metal, without a refractory lining. The copper crucible is made up of water-cooled segments or “fingers.” The magnetic field produced by the coil, in effect, passes through the crucible to induce heat in the metal charge causing it to melt. The field also intensely stirs the liquid metal pool in the pattern shown in the diagram. The stirring promotes a very

homogeneous melt pool and effectively distributes even higher density alloying elements evenly throughout the poured casting.

A thin layer of metal remains frozen against the bottom of the crucible forming a skull. The low velocity boundary layer in the liquid adjacent to the skull, together with the skull itself and the interface (joint) between the skull and the crucible all serve as thermal resistances, reducing the heat conducted from the hot liquid into the cold crucible ^[30]. An improved version of this technique, termed Inductoslag, uses slag as a self-healing coating for the crucible walls to prevent arcing and improve thermal insulation of the melt.

Cold-wall induction has been used for the production of small Ti ingots by 1990 (150mm diameter, 2m long). The use of ceramic materials for induction melting of Ti is restricted by the high reactivity of Ti with these materials. However, CaO, ZrO₂ or MgO have been seen to be relatively stable oxides with respect to TiO₂ thermodynamically, making them possible candidates.

In literature review so far, CaO has been reported to be the most stable although it has the disadvantage of easily hydrating. This problem can be solved by using methanol during mold/crucible preparation ^[30].

2.9 Casting Technologies

The actual casting of Ti can be done in a number of ways:

2.9.1 Investment Casting

Involves use of ceramic moulds prepared using ceramic materials and wax patterns; wax is then evaporated leaving the desired shape.

The lost-wax investment molding process, currently the principal technology for aerospace castings, was introduced in the mid-1960s and has come to be the predominant casting process for titanium (titanium is too reactive for conventional sand-casting methods). In the lost-wax process, a wax pattern of the part is produced by injection molding in hard dies. Once the wax pattern, sprues, runners, gates, and risers are joined, the wax pattern assembly is then

coated with a vendor-proprietary ceramic face coat. The primary characteristics of the face coats are low reactivity and the ability to withstand the thermal shock from contact with molten titanium. The more reactive the face coat, the thicker the reaction layer (known as alpha case) that will form on the metal surface. After the face coat, successive layers of ceramic stucco and slurries are applied until the mold has the required strength and rigidity for subsequent processing^[31].

Each ceramic layer is allowed to dry and cure under controlled temperature and humidity conditions. Once the ceramic mold build operations are completed, the wax pattern is melted out in a hydroclave. The ceramic mold is then fired to develop full strength against molten metal pressure during casting and combust any organic residues prior to casting^[26, 32].

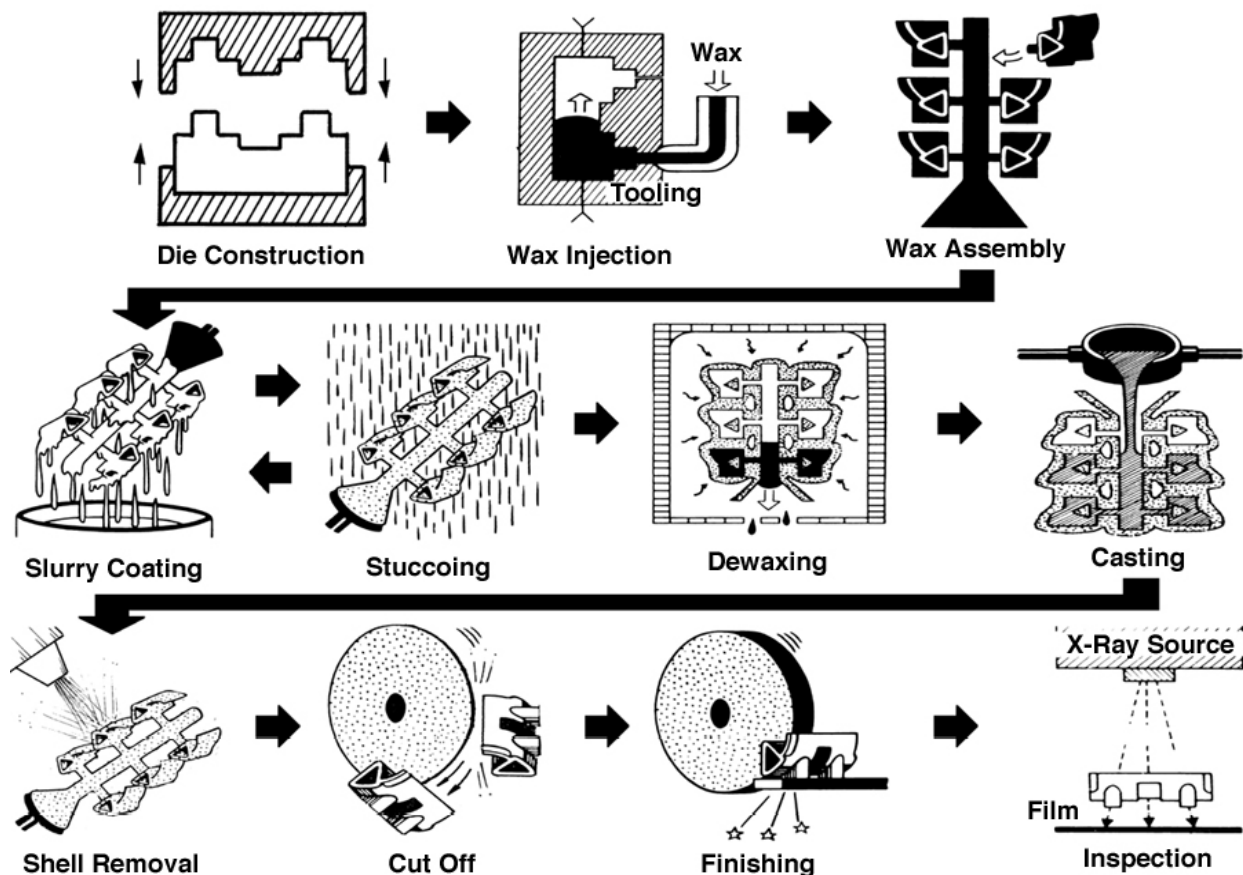


Fig. 2.9: Schematic of the Investment Casting Process^[33].

During the casting process, molten titanium is poured into the mold under vacuum and allowed to solidify. On extraction from the furnace and cooling, the casting is cleaned using fine alumina powder prior to chemical milling and other post-cast processes ^[26]. The ceramic shell material, sprues, gates, and risers are removed prior to hot-isostatic pressing (HIP) processing. The HIP process subjects the casting to elevated temperature and isostatic gas pressure, typically 900°C and 103 MPa pressure for 2 h for the Ti6Al4V alloy ^[34].

The intent of the HIP process is to eliminate internal void defects by collapse and diffusion bonding ^[35]. Casting, for Ti, is usually around mould temperatures of 800°C to reduce chilling effects. Common defects encountered in titanium castings are shown in Fig. 2.10 as well as ways to reduce their effects.

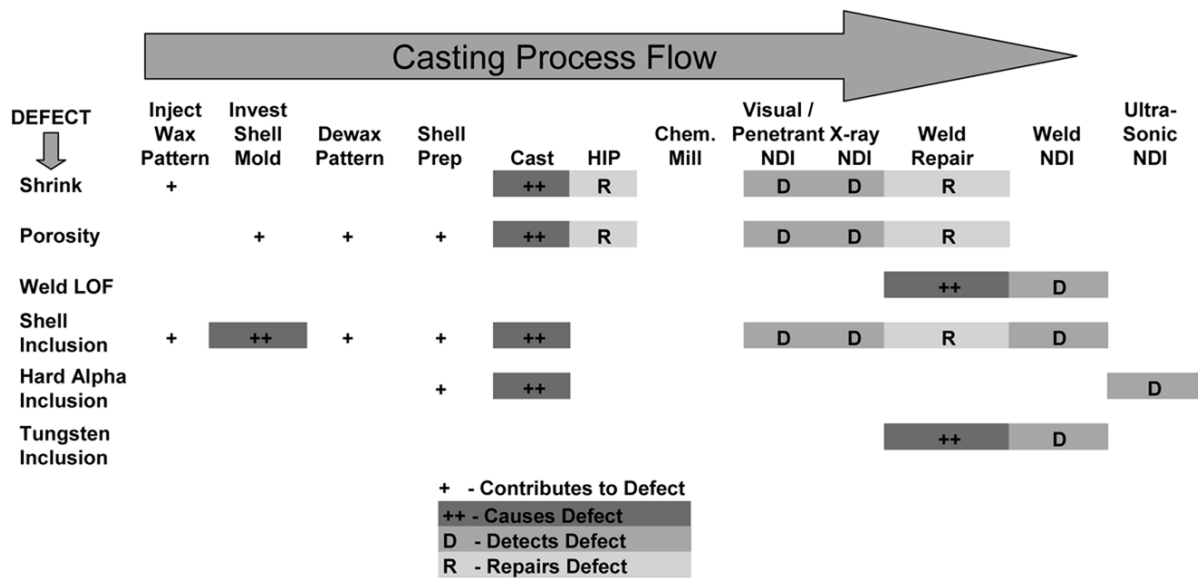


Fig. 2.10: Titanium casting defects versus process flow ^[31].

2.9.2 Vacuum Die Casting (VDC)

In VDC, the molten Ti is injected (at high pressure) into a set of reusable dies containing the desired component geometry under high vacuum as depicted in Fig. 2.11.

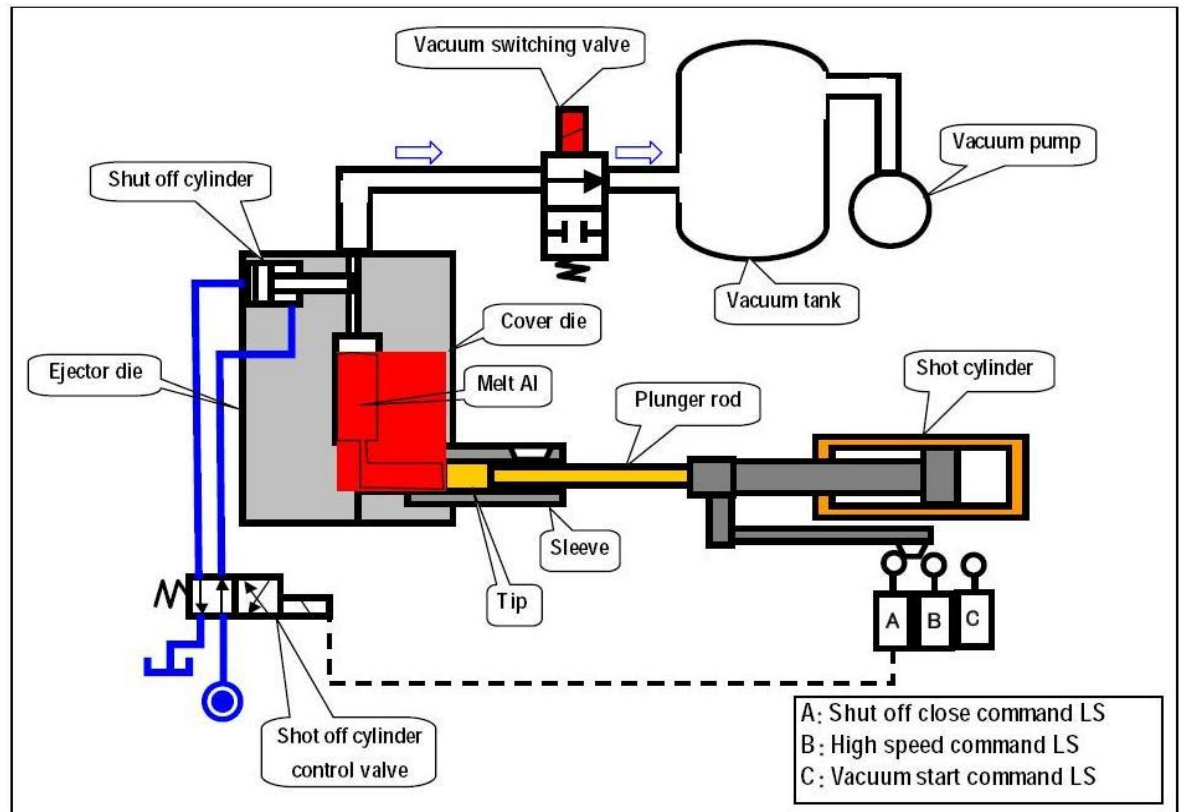


Fig. 2.11: Example of an early developed vacuum process ^[36].

Components made using this process are net-shape or near-net-shape requiring minimal post-cast processing. Compared to other processes, such as investment casting, VDC involves fewer steps, thus lowering costs.

2.9.3 Centrifugal casting

Centrifugal casting is similar to investment casting but for the rotating mould during casting. Mould speeds of up to 600rpm are common in this practice. Common Ti-Al alloys are being produced using this technology. Fig. 2.12 shows a schematic representation of the centrifugal casting machine.

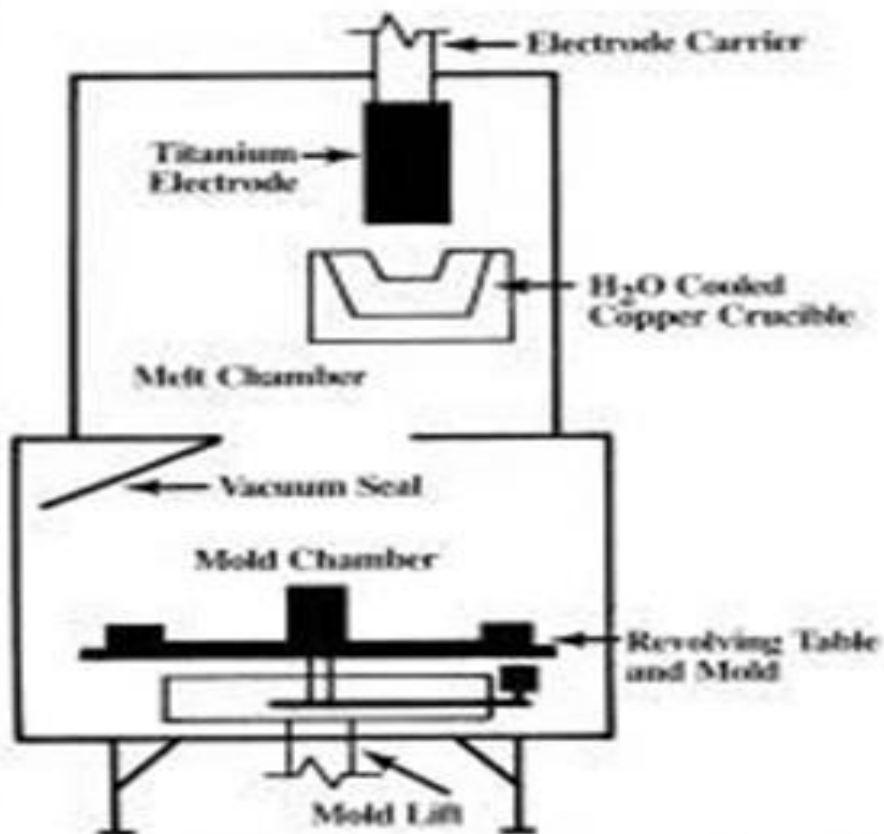


Fig. 2.12: Centrifugal Casting Schematic ^[37].

CHAPTER 3: EXPERIMENTAL PROCEDURE

This section describes the experimental procedures, raw materials, and equipment used in this research.

3.1 Raw Materials

The following raw materials were used:

- Commercially pure (CP) Titanium powder
- Commercially pure Manganese powder
- Commercially pure Iron powder
- Ultra High Purity (UHP) Argon gas
- Silica tubes
- Metallographic consumables

3.2 Equipment Used

The following equipment was used in carrying out the experimental work.

- **The Vacuum Arc Melter**

This is a vacuum chamber with two pumps for high vacuum applications: the rotary pump and the diffusion pump. Samples are placed on a water cooled copper base plate inside the vacuum chamber as shown in Fig. 3.1.

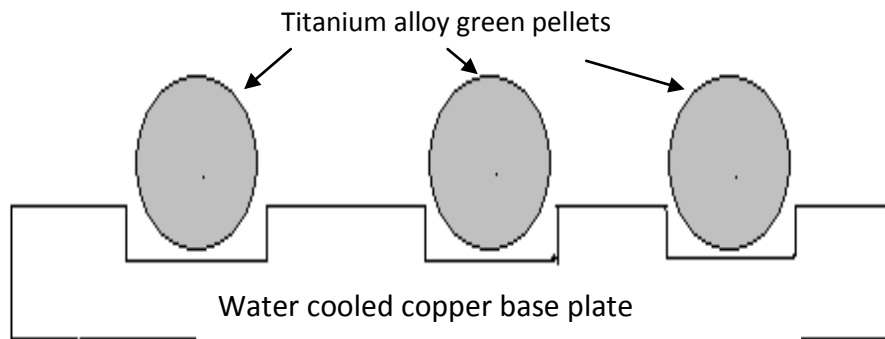


Fig. 3.1: Cross sectional schematic of the water cooled copper base plate inside the vacuum chamber onto which titanium alloys were melted

After 30 minutes of pumping with the rotary pump, the diffusion pump was switched on to evacuate up to 10^{-6} torr. This furnace is powered by Telwin's Linear 340 arc welding machine which can provide a current of up to 340A at 400V .

The chamber was backfilled with argon three times followed by arcing using a tungsten electrode. Fig. 3.2 shows the image of the vacuum arc melter.

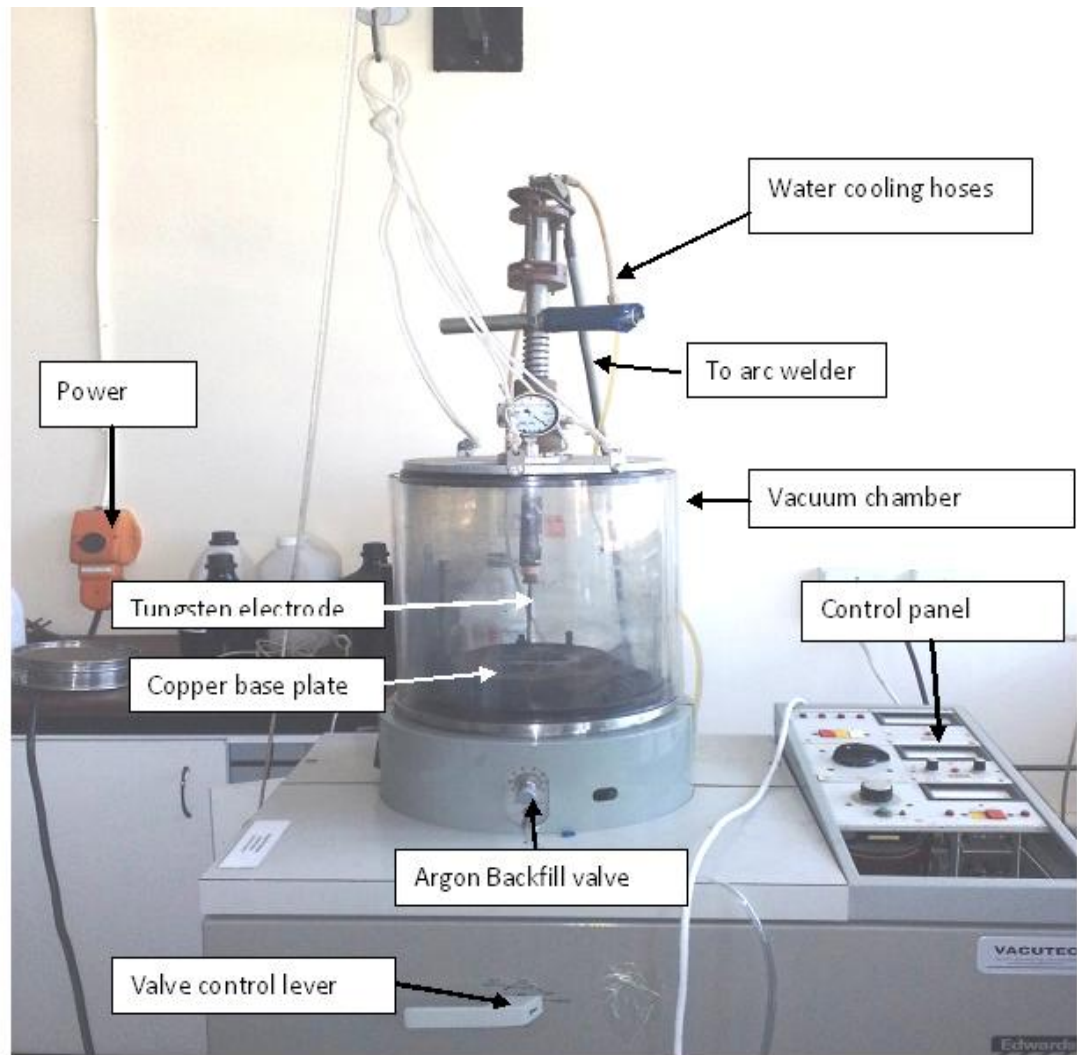


Fig. 3.2 The Vacutec vacuum arc melter used for alloy production in this study.

- **Vacuum Manifold**

The manifold was designed specifically for this work. It was designed for use during the encapsulation of melted titanium alloy buttons in silica tubes to maintain purity during the homogenising annealing treatment of these alloys. It is a simple machine with two valves for controlling the argon gas pressure and the vacuum pump as shown on Fig. 3.3

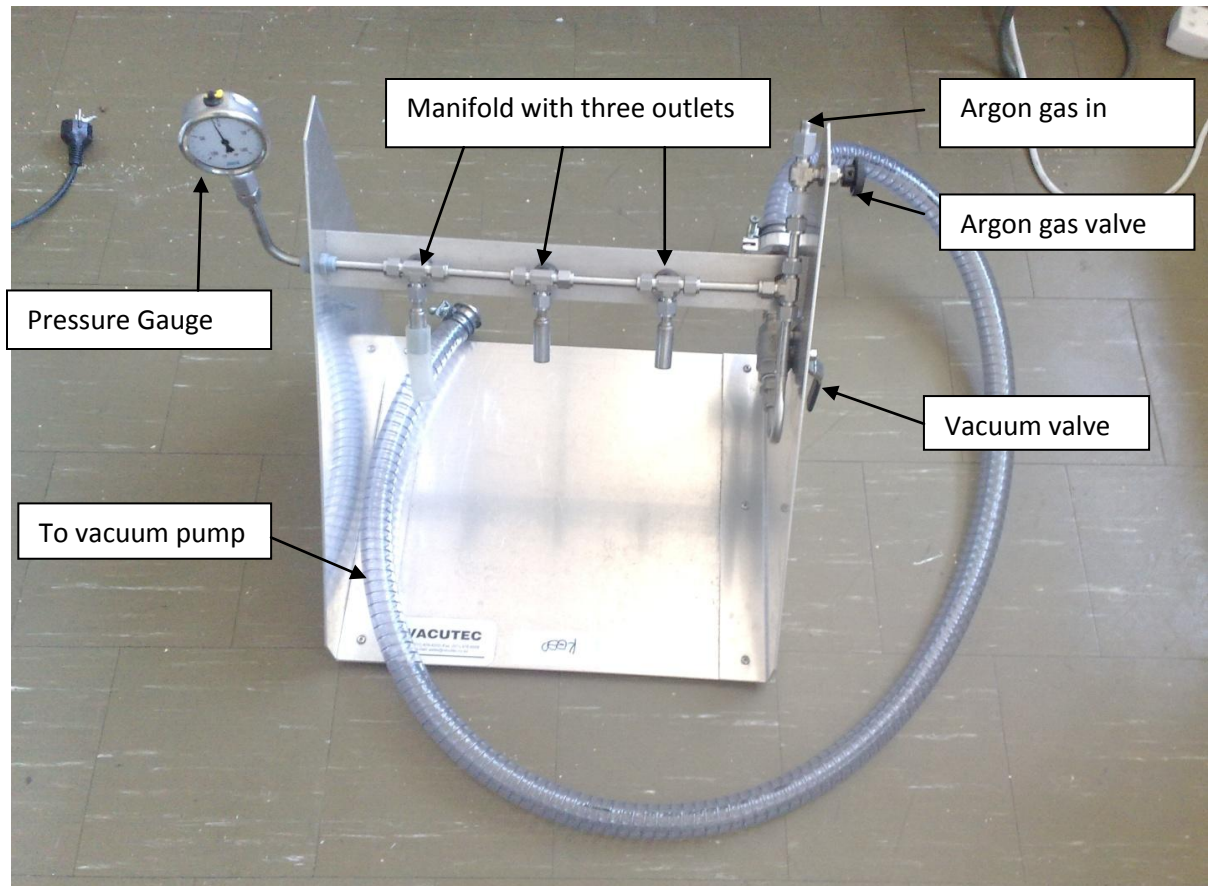


Fig. 3.3: The Vacutec vacuum manifold used for encapsulation of titanium alloys in silica tubes.

The manifold is coupled to the same rotary pump used in the vacuum arc melter to achieve a vacuum of 10^{-3} in the silica glass tubes. The silica tubes, after inserting the buttons, were evacuated then backfilled with argon. This procedure was repeated for 3 times before the tubes were sealed using a gas torch.

- **Muffle Furnace**

A 1600°C muffle furnace was used for annealing of titanium alloys inside the silica glass ampoules. The ramp rate was 10°C/min and holding time of 28 hours at 1000°C was used.

- **X-Ray diffraction (XRD)**

The phase compositions of the titanium alloys were determined by X-ray diffraction techniques utilising a Phillips PW1710 with a PW1830 diffractometer. A monochromatic Cu-K α radiation at 40kV and 20mA was used over a 2θ angle from 20 to 80°. A step scan time of 1 seconds and a step size of 0.02° 2θ was applied. Patterns were collected and phase identification was done using DIFFRAC^{PLUS} EVA software containing the ICDD (International Centre for Diffraction Data).

Lattice parameters were calculated using the DIFFRAC^{PLUS} EVA software. This software utilises the pattern shifts caused by alloying in beta titanium. It calculates the parameters automatically when the measured pattern is superimposed onto the database pattern.

- **Scanning Electron Microscope (SEM)**

A Phillips XL-30 SEM ESEM-FEG scanning electron microscope equipped with a field emission gun operating between 8-20kV was used to assess accuracy of melted titanium alloy buttons. The samples were put on a sample holder and mounted on the stage of the microscope. Secondary electrons were used to capture images at voltage of 10kV and a magnification range of 150x-20000x at various spots. Element analysis was done using energy dispersive spectrometer (EDS) analyser.

- **Micro Hardness Tester**

A Vickers micro hardness tester was used for all hardness measurements. This essentially consists of a diamond indenter in the form of a pyramid with a square and an angle of 136° between opposite faces. A load of 500g was applied and readings were automatically displayed on the screen after the machine calculates the size of the indentation. Three indentations were performed per sample.

- **Optical microscope**

An Axiotech optical microscope coupled to a ZEISS Axiocam MRc was used for viewing of micrographs of the titanium alloys after quenching. This microscope has a live feed camera coupled to a computer which enables image capturing and grain size measurements.

- **Automatic sample mounting machine**

A Struers Cito Press-10 automatic mounting machine was utilised for samples which were to undergo metallographic analysis.

- **Automatic sample cutting machine**

A Struers Secotom-10 automatic cutting machine was used to cut samples for flat surfaces and to get the number of samples needed for the various analyses to be carried out. A diamond cutting disc was used with a cutting speed of 3000rpms and a feed speed of 0.05mm/s.

- **Tube furnace**

Lenton's Elite (TSH17/75/150) tube furnace was utilised for annealing of oxygen samples and the pure titanium sample. This is a horizontal type furnace which operates to a maximum of 1600°C. It consists of heating elements on the side walls and a platinum-rhodium thermocouple positioned in the heating chamber. The furnace also has a mullite tube of length 1.2m and an inner diameter of 0.74m. The furnace is surrounded by a refractory board for insulation and has a panel for programming temperatures, ramp rates and time. A ramp rate of 10°C/min was used in the experiments. An argon atmosphere was also maintained in the Ti-O annealing runs.

- **Sample polishing**

A Leco Spectrum system 2000 automatic polishing machine was used for metallographic preparation. Grinding was performed using silicon carbide paper. Polishing was done using diamond paste (9µm, 6µm, 3µm, 1µm and OPS) on Struers MD Largo, MD Dac, MD Nap and MD Chem polishing cloths. The head speed was set at 200rpms while the wheel speed was at 150rpms. An individual load of 45N was used during grinding and 35N during polishing.

3.3 Alloying

Commercially pure titanium powder (CPTi) of 99.95wt% purity was used to make binary alloys of Ti and Fe as well as Ti and Mn. The Table below shows specification of powders used.

Table 3.1: Materials used with their respective suppliers and purity levels.

	Purity (wt. %)	Particle size	Supplier
CP Ti	99.95	25micron	Industrial Analytical
Fe	99.98	25micron	Industrial Analytical
Mn	99.99	50micron	Industrial analytical
Silica tubes		16mm OD	Glasstech
UHP Argon	99.95	-	Afrox

3.3.1 Compaction

5g powder mixtures of Ti and the two alloying elements were prepared using an electronic mass balance and mortar and pestle. Ten alloys were made namely Ti2wt%Fe, Ti2wt%Mn, Ti4wt%Fe, Ti4wt%Mn, Ti6wt%Fe, Ti6wt%Mn, Ti8wt%Fe, Ti10wt%Fe and Ti10wt%Mn. After mixing, the powders were compacted at 100MPa using a hydraulic pressing machine. This step was necessary to avoid loss of fine powder in the vacuum chamber. The resulting green pellet had an outside diameter (OD) of 18mm and a height of 10mm as shown in Fig. 3.4.

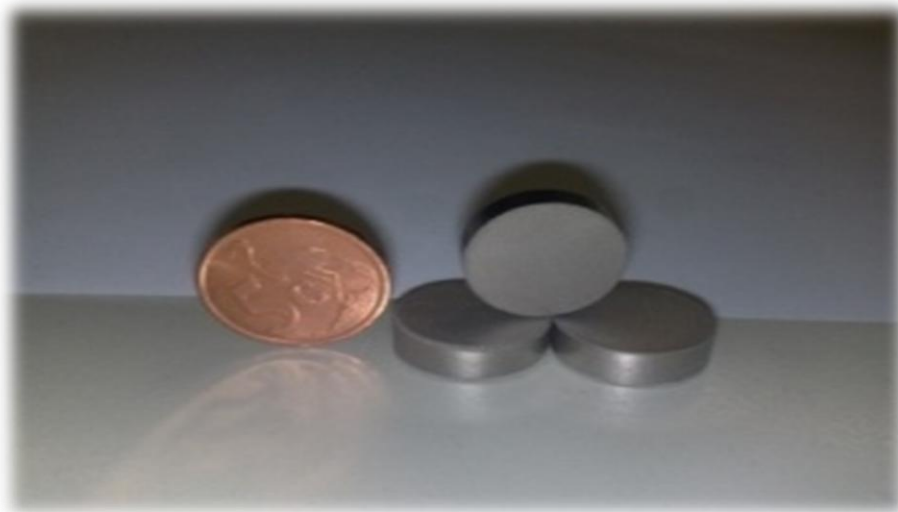


Fig. 3.4: “Green” pellets after compressing at 100MPa in a mechanical die. Dimensions are 18mm OD and 10mm height.

Oxygen containing titanium samples

The following procedure was used for doping titanium with oxygen. 5g samples of commercially pure titanium were carefully weighed using a highly sensitive electronic balance. The samples were then placed in a muffle furnace in an air atmosphere. The furnace was ramped up to 400°C for 2, 4 and 6 hours accompanied by weighing of the samples after every experiment to determine any changes in mass. Table 3.2 shows the details.

Table 3.1: Ti samples and oxygen content

	Sample 1	Sample 2	Sample 3	Sample 4 (CP Ti)
Dwell Time (hr)	2	3	6	n/a
Temp (°C)	400	400	400	n/a
% O	0.48	0.75	2.73	Unknown

3.3.2 Melting

After compaction, green pellets were loaded into a vacuum arc melting furnace. The vacuum chamber was then evacuated to a vacuum of 10^{-6} torr.

After attaining this vacuum UHP argon was allowed into the chamber up to 1 atm and then pumping was done to 10^{-6} torr again. This was repeated 3 times to ensure an inert atmosphere. When flushing with argon was finished, backfilling of the vacuum chamber with UHP argon was done to a pressure of 0.25 atm. Arcing was then done under this atmosphere, melting 5 samples at a time in approximately 10 seconds per sample.

The samples were triple-melted, to reduce segregation effects and porosity. After waiting for a few minutes, air was then admitted into the vacuum chamber and the chamber was opened to retrieve the samples. Samples were cold to the touch due to the water cooled copper base plate on which they were being melted.

The oxygen containing Titanium samples were then melted under the same conditions. A reference pure titanium sample was also melted.

3.4 Density measurements

The density of melted alloys was determined by the standard Archimedes' method which consisted of the following steps;

- i) The dry weight of the samples (m_d) was determined using a balance. (Used for all weight measurements).
- ii) Sample was boiled in distilled water for 3 hours.
- iii) The suspended weight of the sample (m_s) was determined.
- iv) The surface moisture was removed by a light wipe with a paper towel to remove excess water from the surface and the wet weight (m_w) determined.
- v) The procedure (steps (i) to (iv)) was repeated to check consistency in weighing.

The density (ρ_s) was determined using the following equation:

$$\rho_s = \frac{m_d \rho_{water}}{(m_s - m_w)}$$

Where, m_s = suspended mass

m_w = water saturated mass

m_d = dry mass

3.5 Vacuum encapsulation

Silica tubes were used to encapsulate the melted buttons under a partial UHP argon atmosphere. The quartz glass sealing was done as shown in Fig. 3.5.

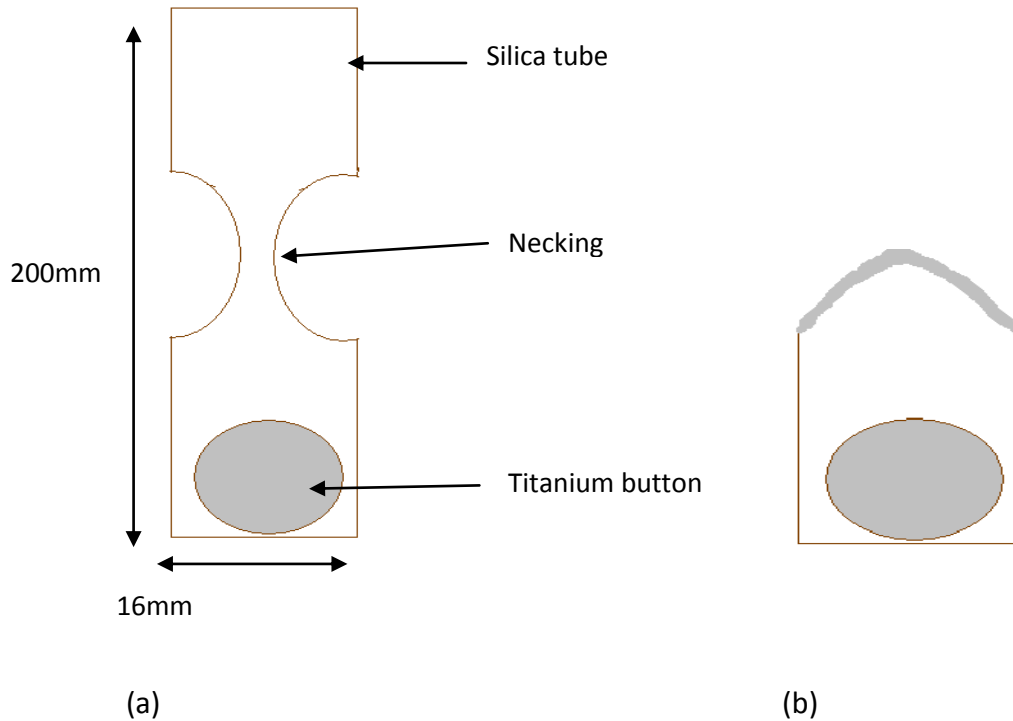


Fig. 3.5: Schematic of a silica tube (1mm thick) with a titanium alloy button inside: a) after necking the mid-section and b) after sealing the button under partial argon atmosphere.

A specially designed manifold (Fig. 3.3) was then used to evacuate the 'necked' tubes with their buttons inside as described in section 3.2.

One cycle involved evacuating to a vacuum of 10^{-3} torr, backfilling with UHP argon to a pressure of 1.2atm and then evacuating again to 10^{-3} torr. This was repeated three times to ensure an inert atmosphere. After this, a partial argon atmosphere of 0.23atm was left in the tube before using a gas torch to seal off the button in this atmosphere. This procedure was repeated for all 11 samples, including the reference pure titanium sample.

For oxygen containing titanium samples, the tube furnace was used. Samples were placed in the tube furnace without being encapsulated in silica. This was because there was no need for quenching with these samples hence they could be furnace cooled in an inert atmosphere.

3.6 Annealing

The encapsulated melted samples were annealed in a muffle furnace at 1000°C for 28 hours to homogenise the microstructure. Fig.3.6 shows the annealing cycle followed in this procedure. The temperature was chosen to ensure that the silica tubes survive for such long periods in the furnace.

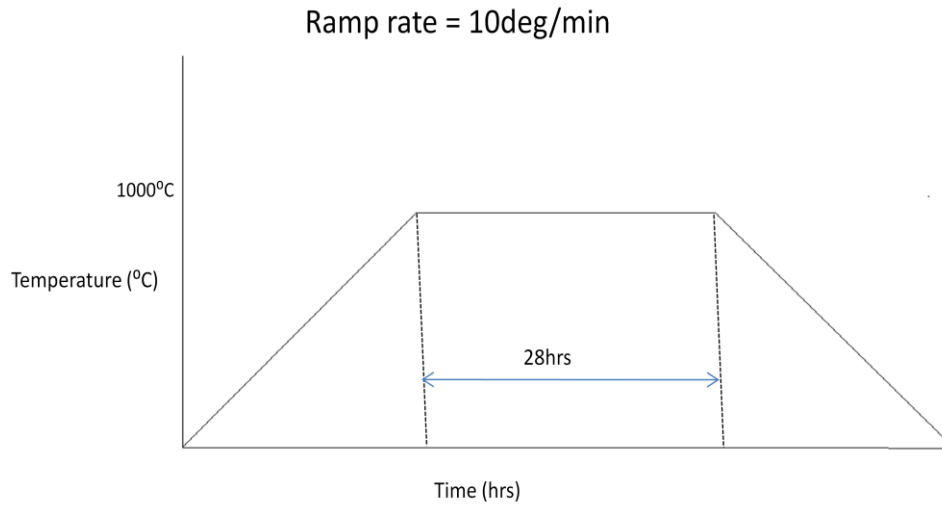


Fig. 3.6: Annealing temperature profile for titanium alloys.

Oxygen containing titanium samples

Annealing of the oxygen containing titanium samples was done in a tube furnace as described before. After holding for 10 hours at temperature, the samples were cooled down at a rate of 10°C per minute in a flowing argon atmosphere at 10l/min.

3.7 Quenching

After the annealing cycle, the encapsulated samples were taken out of the furnace one at a time and promptly smashed open using a hammer, dropping them red-hot into a cold water bath. The oxygen samples, however, were not water quenched as the other alloys. They were furnace cooled while still inside their protective silica tubes.

3.8 Sample preparation

The quenched buttons were cut into three sections using the Secotom-10 automatic cutting machine. The middle section, which was flat and thin, was sent for XRD analysis. The other two sections were mounted for SEM and Optical Microscopy analyses.

Mounting was performed using a Struers automatic sample mounting machine as mentioned in section 3.2. Metallographic sample preparation then followed by grinding the samples through 220 to 1200 grit silicon carbide paper. Polishing steps of 9 μ , 3 μ then OPS diamond paste were done using a Leco automatic polishing machine at a wheel speed of 150rpms and head speed of 200rpms. Samples were placed in an ultrasonic bath between polishing steps for two minutes.

3.9 Etching

Etching was performed using Kroll's reagent. The reagent was poured into a beaker then freshly polished and cleaned samples were dipped into the chemical. In order to be able to compare the behaviour of the different alloys, a constant concentration of Kroll's reagent was used (2%Hydrogen peroxide was added to the reagent). An etching period of one second was initially applied to all samples. In this case, only lower concentration alloys were etched. Therefore etching times were adjusted according to the needs of the alloy.

CHAPTER 4: EXPERIMENTAL RESULTS

This chapter presents the findings of this work. These include characterisation of alloys made from the Arc Melter, structure determination results on annealed samples and lattice size calculations made from X-ray data.

4.1 Alloying Experiments

A deliberate choice of alloys was made to remain in the solid solution range where there is formation of mostly beta phase on quenching. Commercially pure Titanium powder was intimately mixed with an appropriate amount of the doping elements as described in the preceding section. A pellet was made out of this mixture which was then melted in the Arc Melter. The alloys obtained were analysed using scanning electron microscopy (SEM) and optical microscopy (OM) to determine homogeneity. Table 4.1 shows the measured densities of manufactured alloys as compared to that of pure titanium.

Table 4.1: Density of alloys made.

Alloy	CP-Ti	Ti2Mn	Ti4Mn	Ti6Mn	Ti8Mn	Ti10Mn	Ti2Fe	Ti4Fe	Ti6Fe	Ti8Fe	Ti10Fe
Density (g/cm ³)	4.51	4.51 ± 0.02	4.52 ± 0.02	4.54 ± 0.01	4.59 ± 0.02	4.65 ± 0.01	4.50 ± 0.01	4.55 ± 0.01	4.61 ± 0.01	4.67 ± 0.02	4.76 ± 0.03

4.1.1 SEM Analysis

Alloy composition was confirmed using a scanning electron microscope coupled to an energy dispersive spectrometer (EDS). The results are shown in Fig. 4.1 and Table 4.2. LECO oxygen analysis (Table 4.3) on the melted CP Titanium confirmed minimal unintentional oxygen contamination.

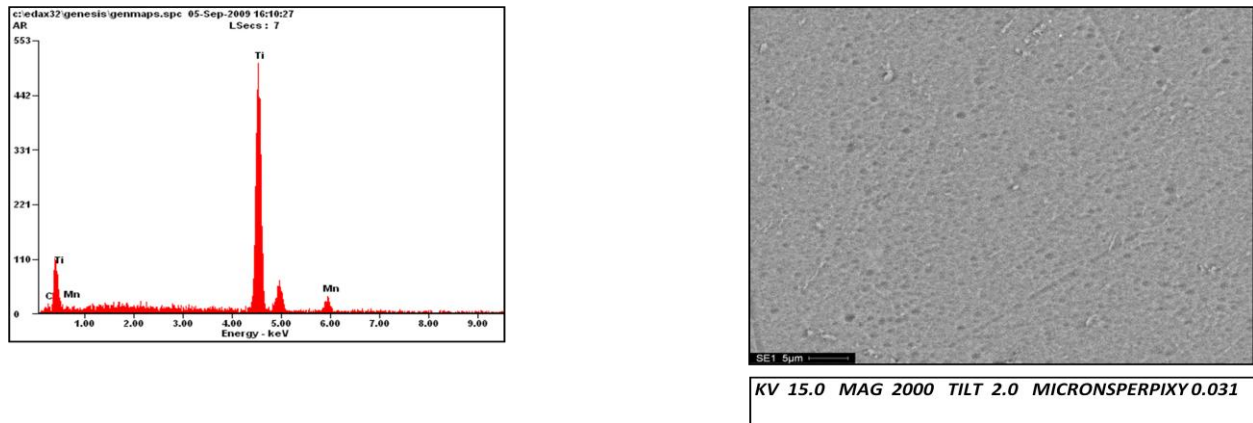


Fig. 4.1 SEM image for the Ti-10%Mn alloy with EDS elemental analysis (Table 4.2).

Table 4.2: There is confirmation of minimal loss of doping elements during melting (Mn averaged 9.66Wt% compared to the weighed 10wt %). A number of spot analyses were performed.

Measured Composition			Standard Composition		
Element	Wt%	At%	Element	Wt%	At%
TiK	90.3 ± 0.5	92.1 ± 0.5	Ti	90.0	91.2
MnK	9.7 ± 0.5	7.9 ± 0.5	Mn	10.0	8.8

Table 4.3: LECO oxygen analysis on intentionally oxygen doped samples and pure titanium

Sample	Ti-0.48%O	Ti-0.75%O	Ti2.73%O	CP Ti
Oxygen content (wt%)	0.48	0.75	2.73	0.01

4.2 XRD Analysis

Flat, thin samples (average of 3mm thickness) were used for XRD study. Results obtained are as detailed in this section.

4.2.1 XRD analysis of Ti-Fe alloys

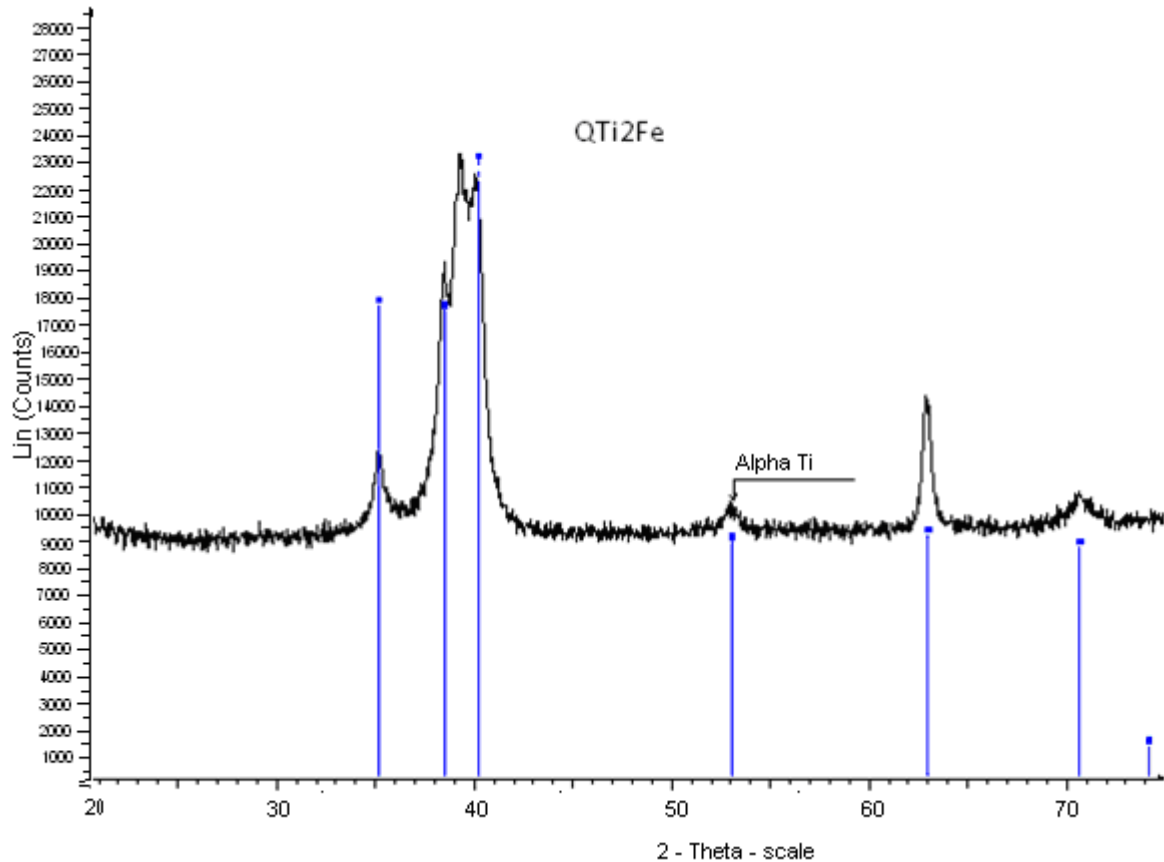


Fig. 4.2: XRD Diffractogram of Ti 2% Fe showing no signs of beta retention after quenching from 1000°C.

At 2%Fe, no beta phase is observed after quenching (Fig. 4.2). The only difference with the 2%Mn spectrum is the distorted shape which could be noise or surface imperfections encountered during running of the XRD machine. This shows that iron can not stabilise the beta phase at 2%.

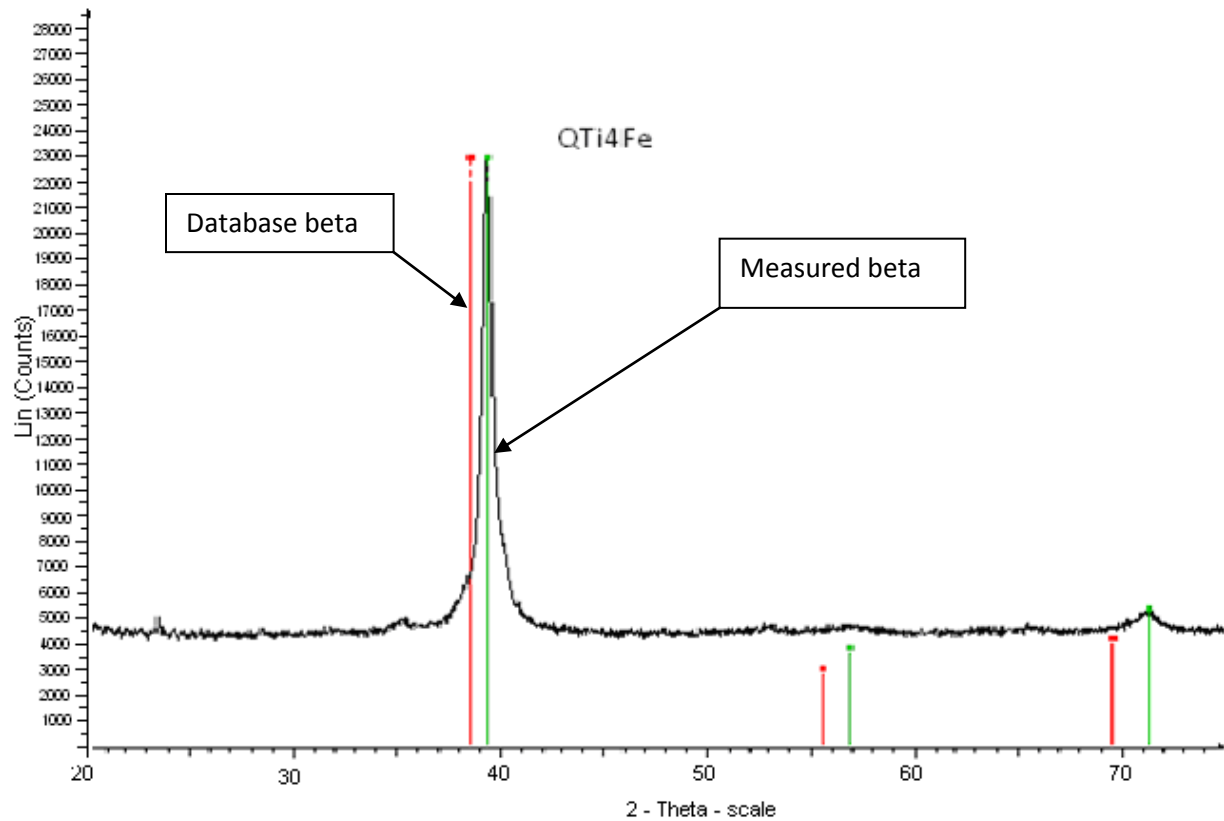


Fig. 4.3: XRD Diffractogram of Ti 4% Fe showing mostly beta Ti-phase after quenching from 1000°C .

In Fig. 4.3, the red pattern shows the expected peak position for pure titanium beta phase. The green pattern represents the shift caused by alloying. A small amount of α -Ti is still encountered as shown in Fig. 4.4.

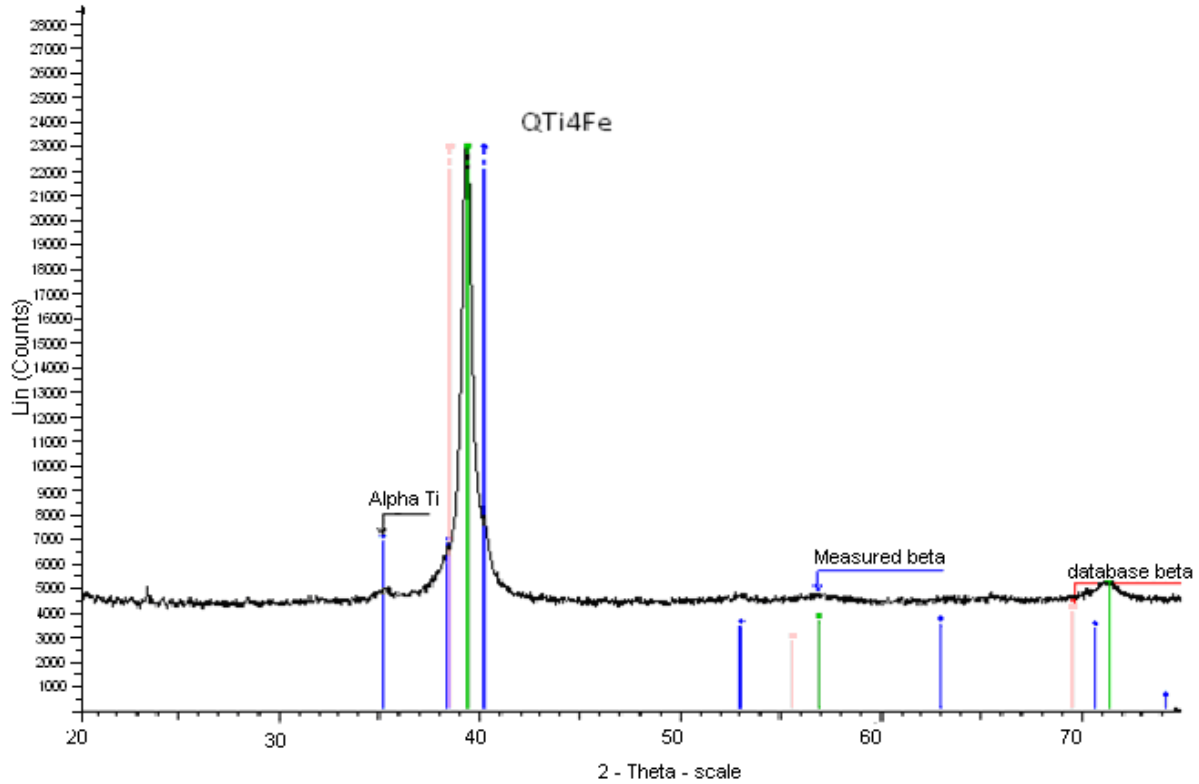


Fig. 4.4: XRD Diffractogram of Ti 4% Fe showing a little alpha Ti-phase (the blue pattern) after quenching from 1000°C.

The 4%Fe (Fig. 4.3 and 4.4) alloy shows a remarkable difference to the 4%Mn one. The diffractogram shows a predominantly beta phase with low intensity alpha peaks still visible (shown by the blue lines). This confirms that Fe does not fully stabilise the beta phase at 4wt%.

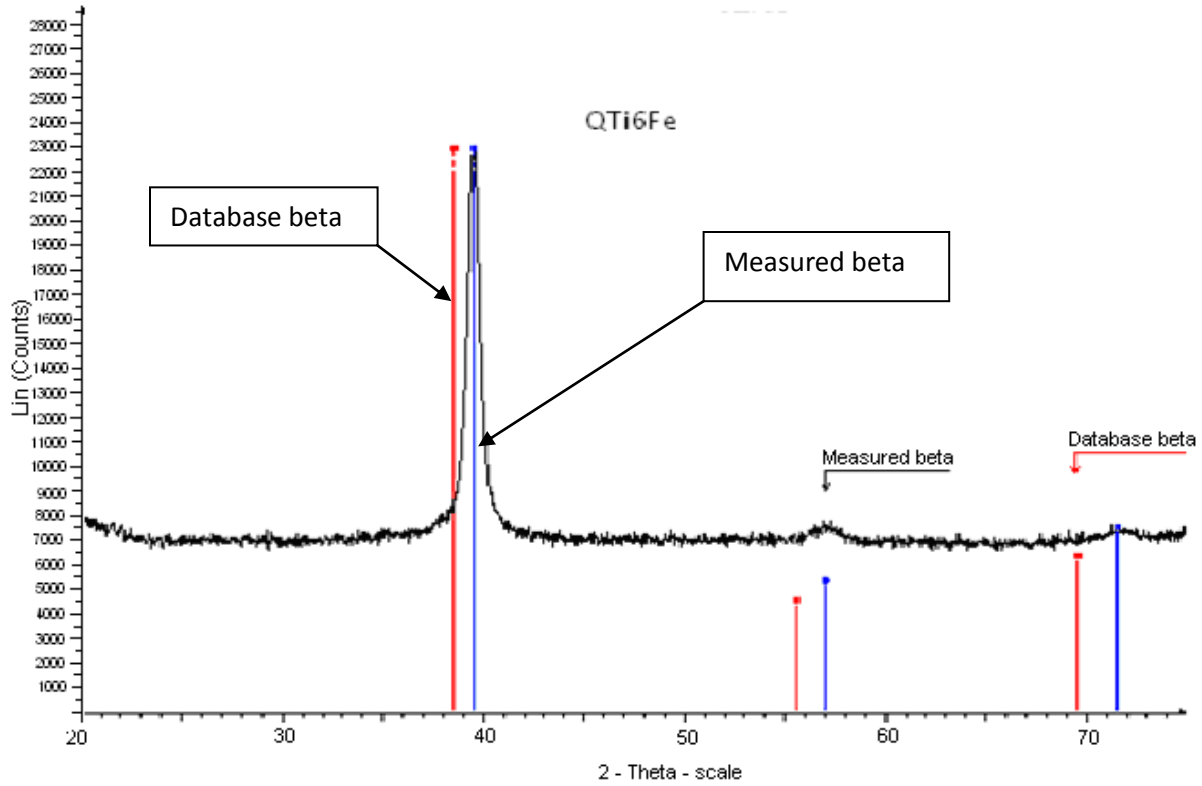


Fig. 4.5: XRD Diffractogram of Ti 6% Fe showing no alpha Ti-phase after quenching from 1000°C. A full beta structure has been retained.

At 6wt%Fe beta stabilisation is fully realised. No evidence of residual alpha phase is observed from the diffractogram of Ti6wt%Fe as depicted in Fig. 4.5. Lattice parameter measurements confirmed that they had indeed increased as compared to the normal pure beta phase in the database as detailed in Table 4.4.

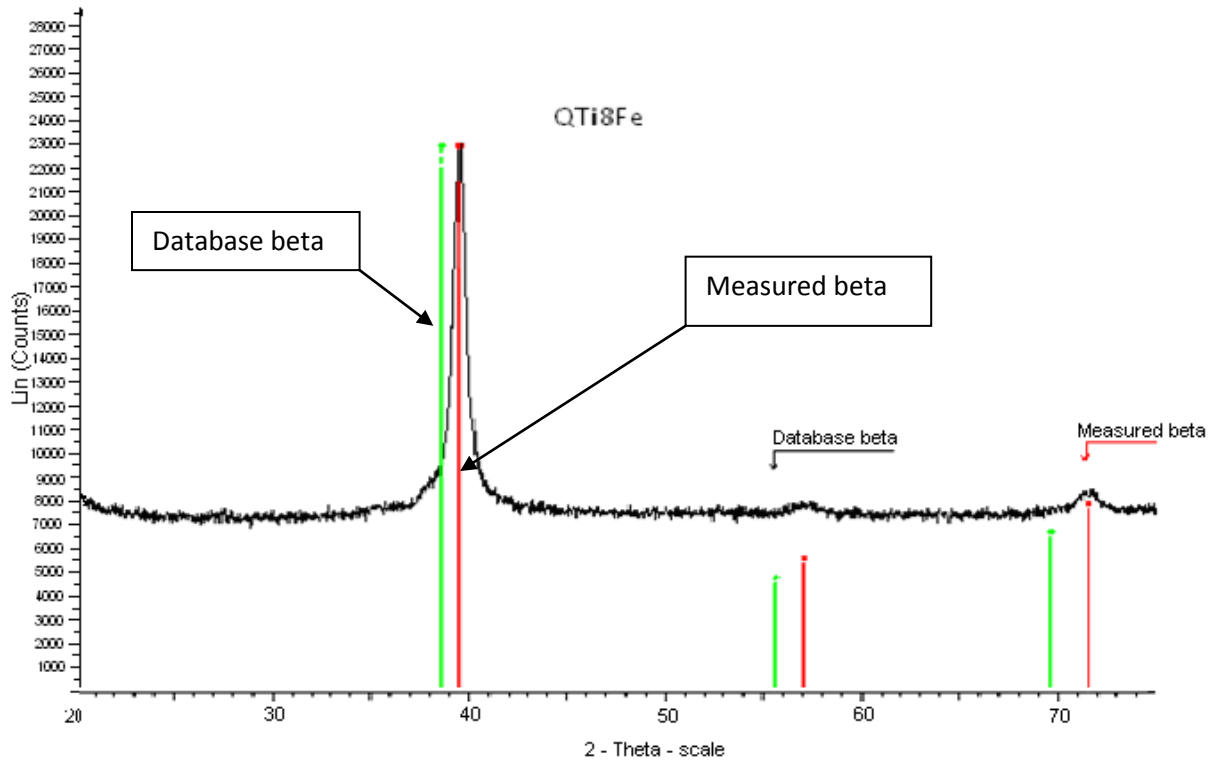


Fig. 4.6: XRD Diffractogram of Ti 8% Fe showing no alpha nucleation after quenching from 1000°C. A full beta structure has been retained.

Increases in the Fe content within the solid solution range results in better beta phase stabilisation and increased lattice parameter values. Fig. 4.6 shows a full beta structure obtained after quenching with 8wt%Fe doping of titanium.

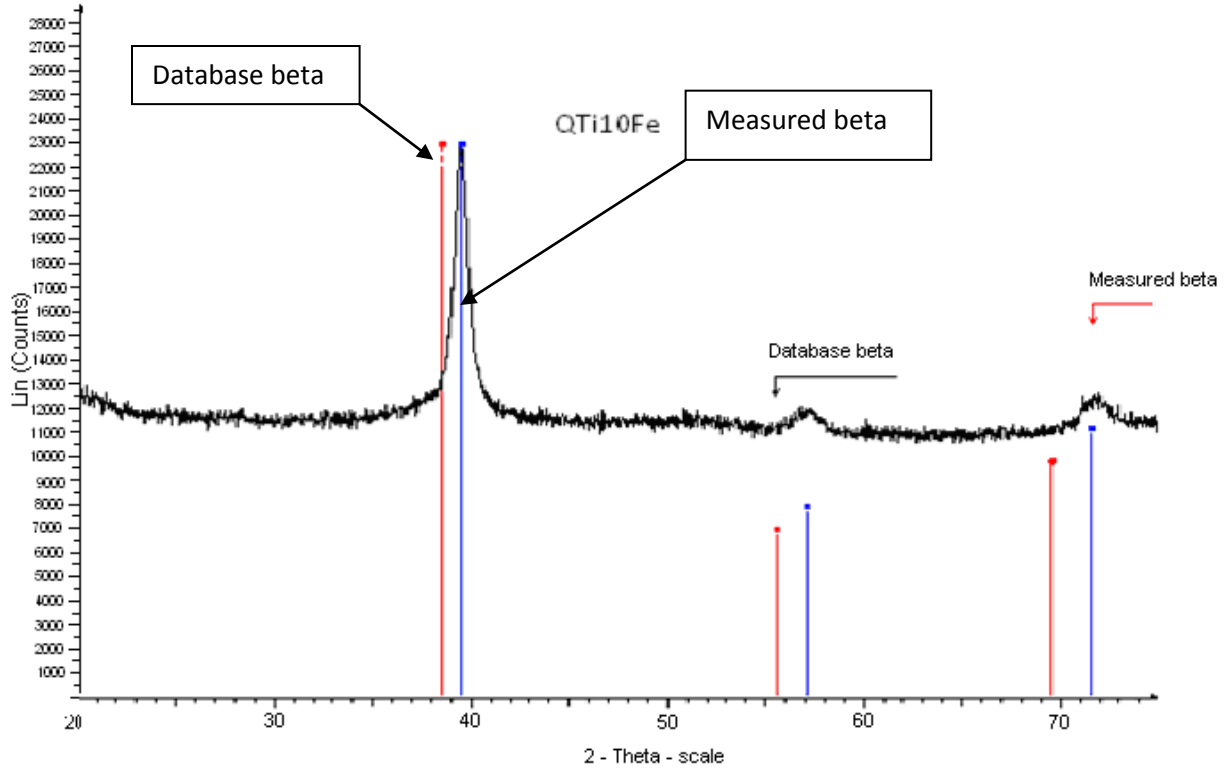


Fig. 4.7: XRD spectra of Ti 10% Fe showing no alpha nucleation after quenching from 1000°C. A full beta structure has been retained.

Fig. 4.7 shows a full beta structure was obtained on quenching the 10wt%Fe. Lattice measurements using the described method showed an increase in beta phase lattice parameters of this alloy as shown in Table 4.4.

4.2.2 XRD analysis of Ti-Mn Alloys

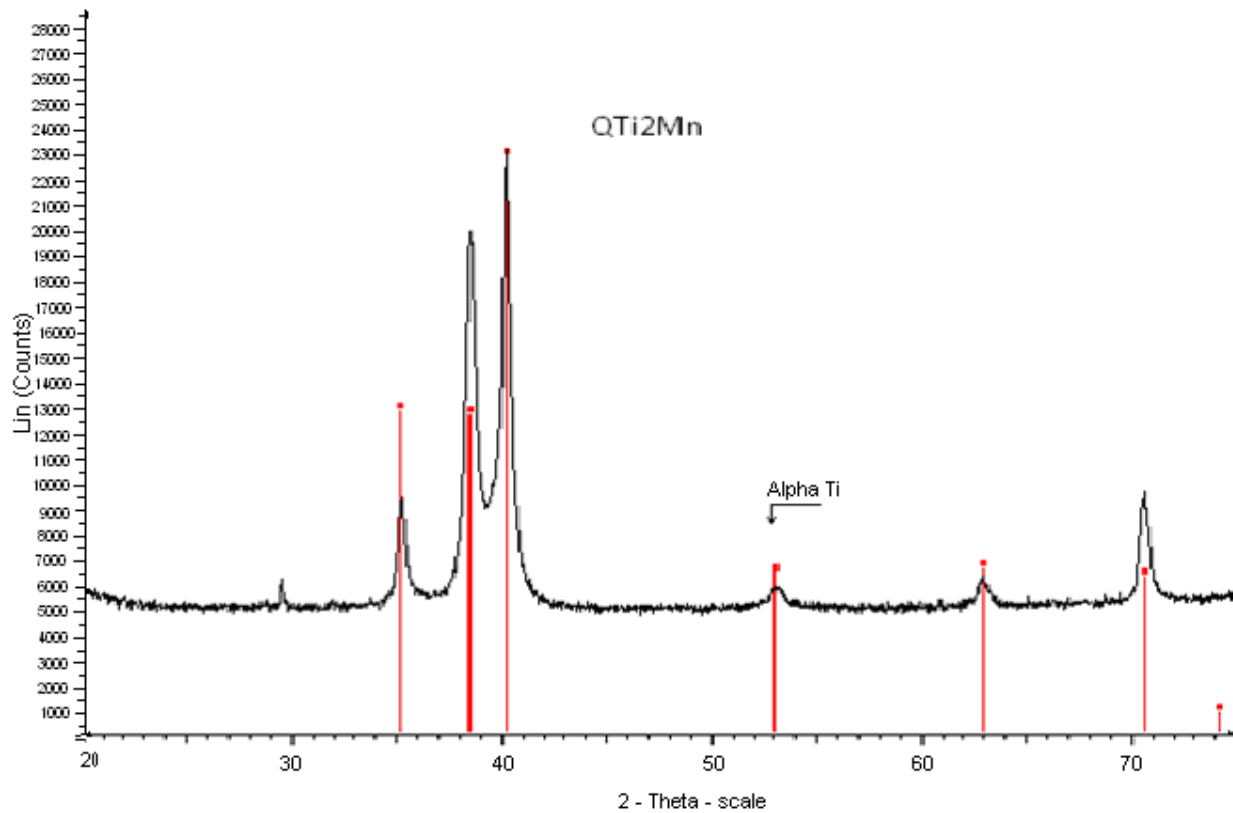


Fig. 4.8: XRD Diffractogram of Ti 2% Mn showing only alpha phase after quenching from 1000°C. No beta structure has been retained.

XRD analysis of the 2%Mn (Fig. 4.8) alloy shows virtually no presence of the beta titanium phase. It is predominantly alpha phase. This result is clear evidence that manganese does not stabilise the beta phase in such low quantities. In fact, alpha phase is obtained after quenching from a full beta structure. Lattice measurements of this phase was not done since the scope of the project is on the beta phase.

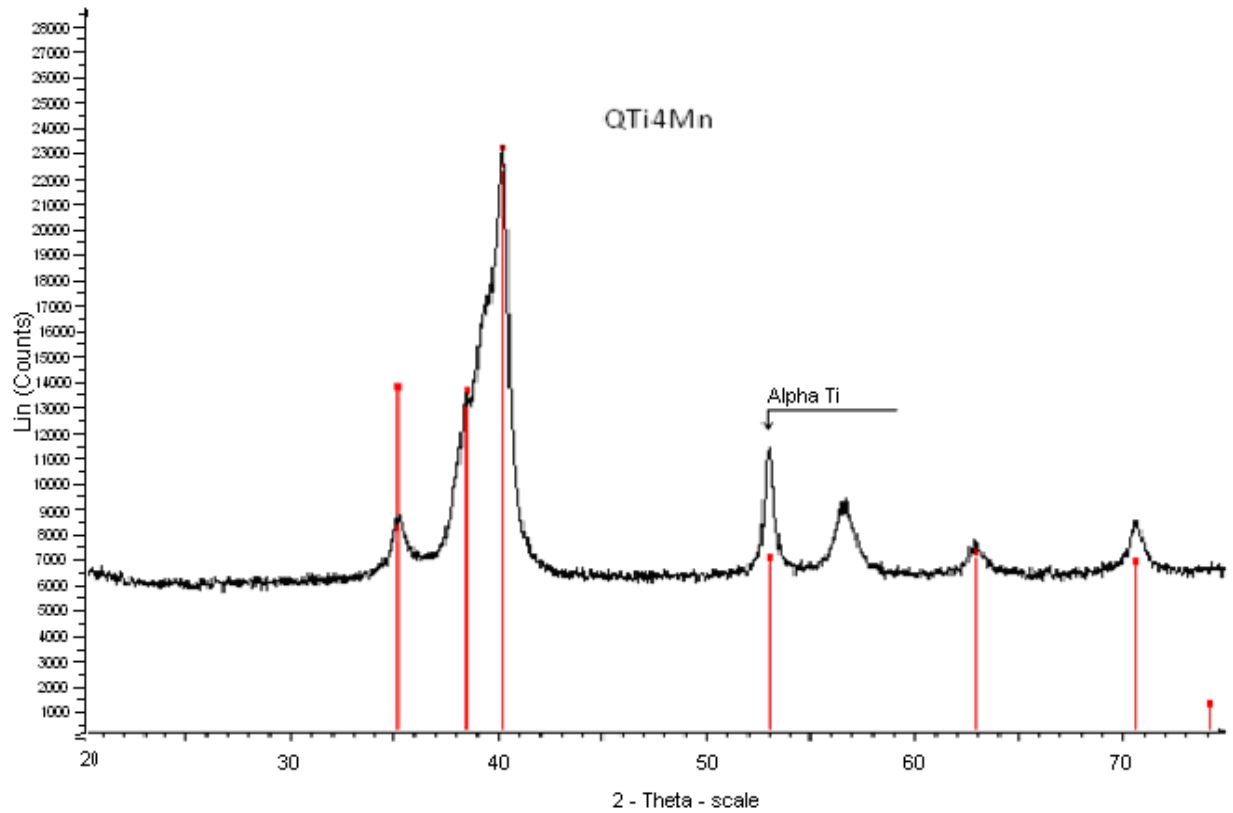


Fig. 4.9: XRD Diffractogram of Ti 4% Mn showing mostly alpha Ti-phase after quenching from 1000°C.

The 4%Mn (Fig. 4.9) alloy analysis basically shows the same observation. However, there is an unidentified peak at position 57°. This peak corresponds to the beta phase but the relative intensity of the peak does not tally with the expected pattern for beta titanium in the database. Repeated measurement still brought up the same trace with that un-identified peak.

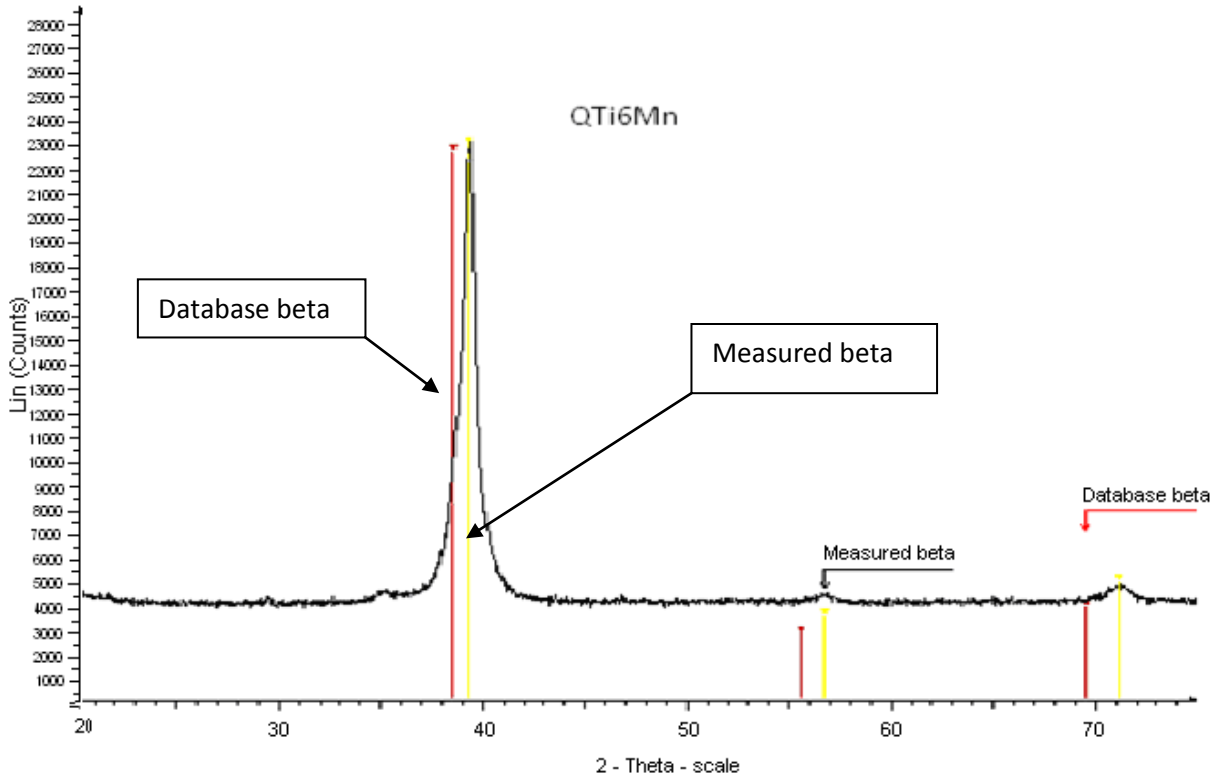


Fig. 4.10: XRD Diffractogram of Ti 6% Mn showing mostly beta Ti-phase after quenching from 1000°C.

At 6wt%Mn, a predominantly beta titanium phase is realised as shown in Fig.4.10. Lattice measurements (Table 4.4) confirmed an increase in lattice constants in this alloy as compared to the pure beta in the database.

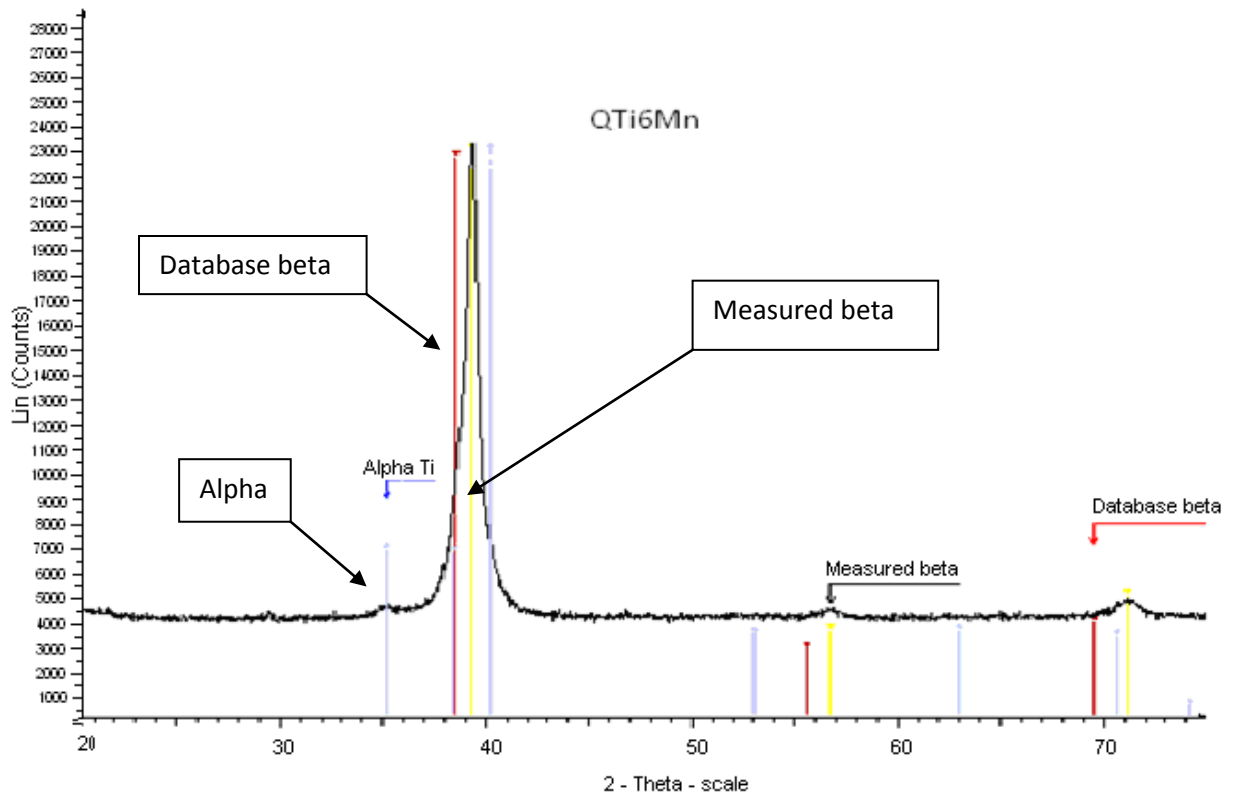


Fig. 4.11: XRD Diffractogram of Ti 6% Mn showing a small amount of alpha Ti-phase (violet pattern) after quenching from 1000°C.

As shown in Fig.4.10, a predominantly beta structure is obtained when a Ti6wt%Mn alloy is quenched. However, low intensity alpha peaks are still visible for this alloy as shown in Fig. 4.11. This shows that Mn does not fully stabilise beta titanium phase at 6wt%. In comparison, the 6wt%Fe alloy showed a full beta structure.

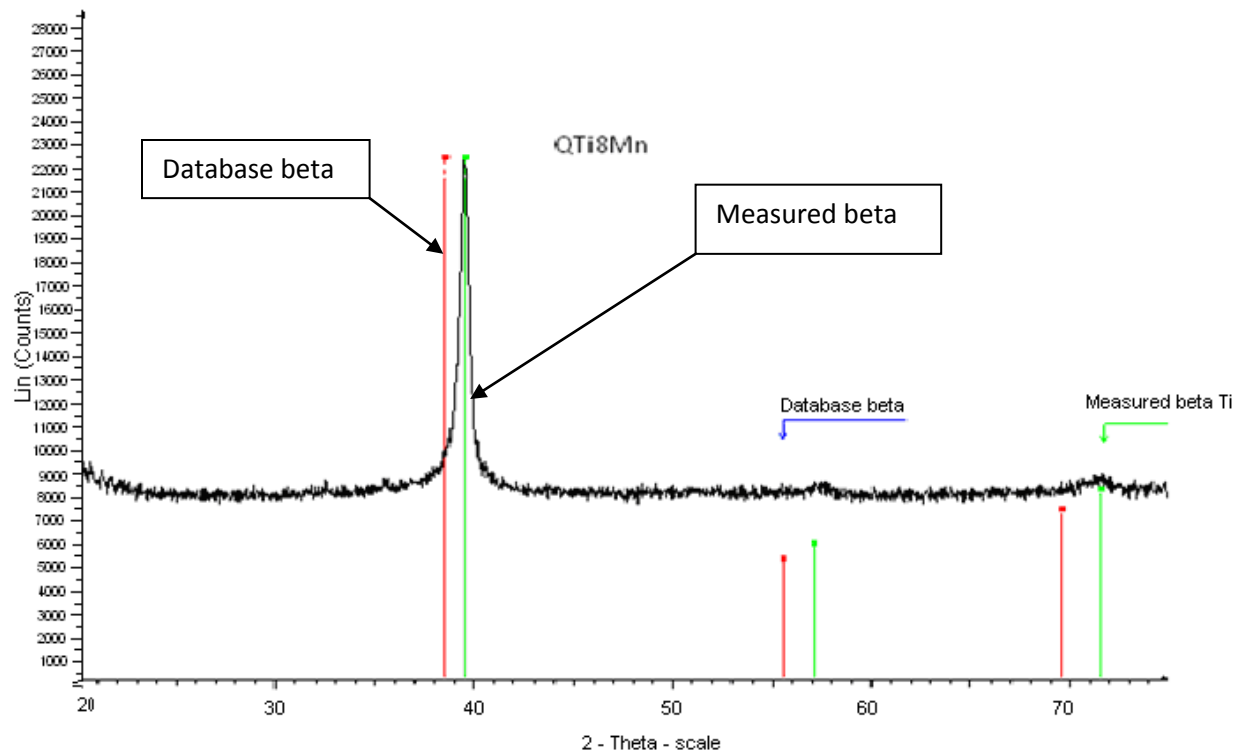


Fig. 4.12: XRD Diffractogram of Ti 8% Mn showing no alpha retention after quenching from 1000°C. A full beta structure has been retained.

At 8%Mn, a full beta structure is observed (Fig. 4.12) with no alpha phase nucleation after quenching from a full beta temperature of 1000°C. Lattice measurements of this structure showed an increase in the beta lattice parameter as compared to the pure beta phase parameters in the database.

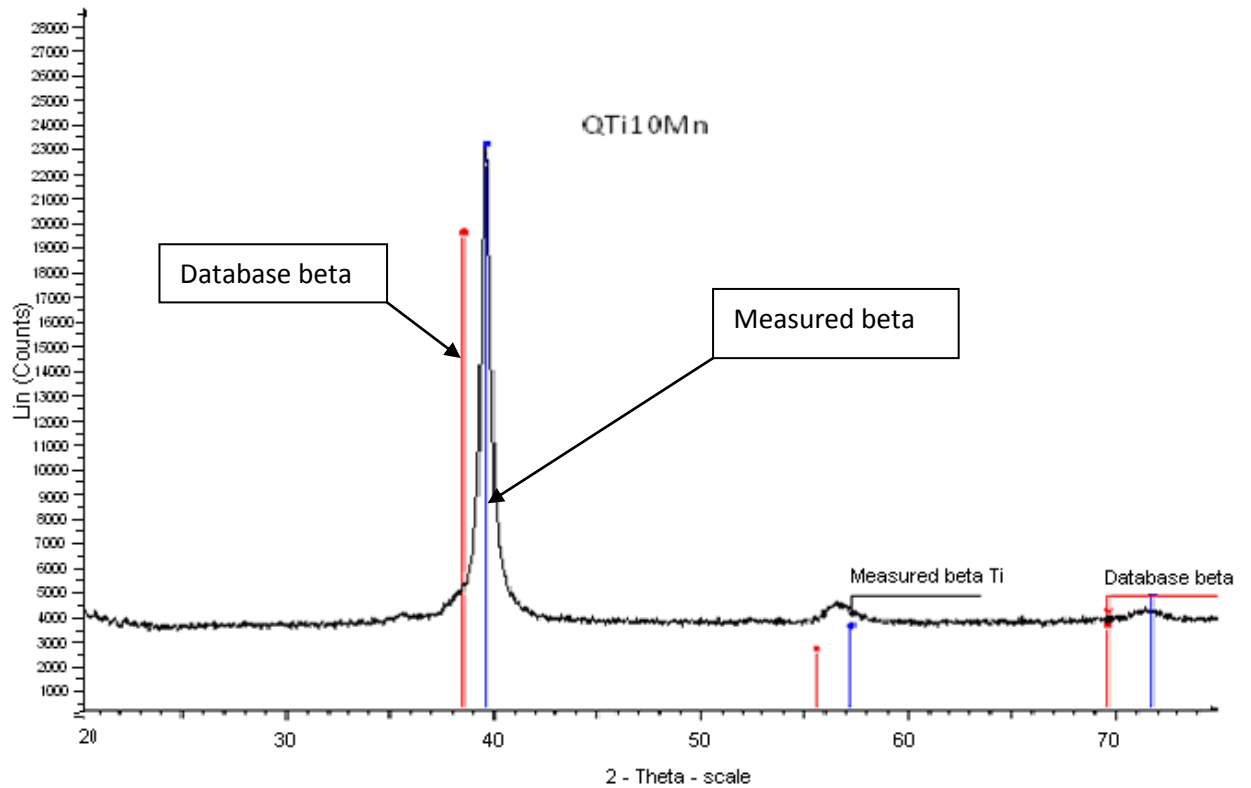


Fig. 4.13: XRD Diffractogram of Ti 10% Mn showing no alpha retention after quenching from 1000°C. A full beta structure has been retained.

At 10wt%Mn a full beta phase was also observed confirming beta stabilisation capacity of manganese at higher solid solution range concentrations. Fig. 4.13 shows the measured diffractogram as compared to the database one (pure beta).

Lattice constants for these alloys were determined using DIFFRAC^{PLUS} EVA software ^[49]. This software compares the measured beta-Ti XRD trace to the one existing in the database. By superimposing the two (since there will be a shift due to doping elements), the new lattice constants can be evaluated. Three XRD scans were performed per sample and the average values were used in Table 4.4.

Table 4.4: Calculated Lattice constants for Ti-Mn and Ti-Fe alloys

Alloy	Ti2Fe	Ti4Fe	Ti6Fe	Ti8Fe	Ti10Fe	Ti2Mn	Ti4Mn	Ti6Mn	Ti8Mn	Ti10Mn
a (ref = 3.3065)	Alpha phase	3.2354 ± 0.0005	3.2285 ± 0.0005	3.2210 ± 0.001	3.2190 ± 0.0005	Alpha phase	Alpha phase	3.2436 ± 0.0005	3.2250 ± 0.001	3.2181 ± 0.0005
% Contraction	n/a	2.15	2.36	2.27	2.46	n/a	n/a	1.90	2.46	2.67

4.2.3 Oxygen containing Titanium alloys

The XRD patterns of the samples were analyzed using the control sample as a reference. It was observed that the changes in peak positions were small in all samples tested. The maximum distortion (changes in lattice parameters) was achieved with sample 3 which contained 2.73wt% oxygen (Fig.4.15). The 0.48wt%O sample did not show any shift from the CP titanium pattern as shown in Fig.4.14.

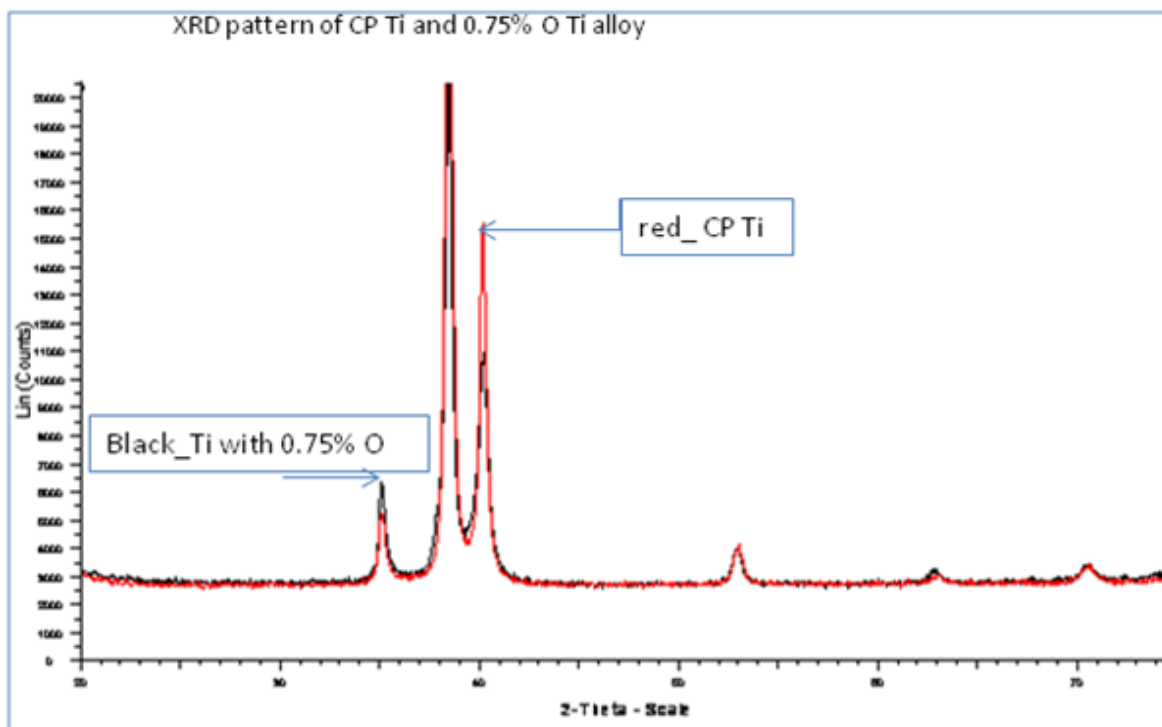


Fig. 4.14: Superimposed CP Ti and 0.75%O Ti-O alloy XRD patterns.

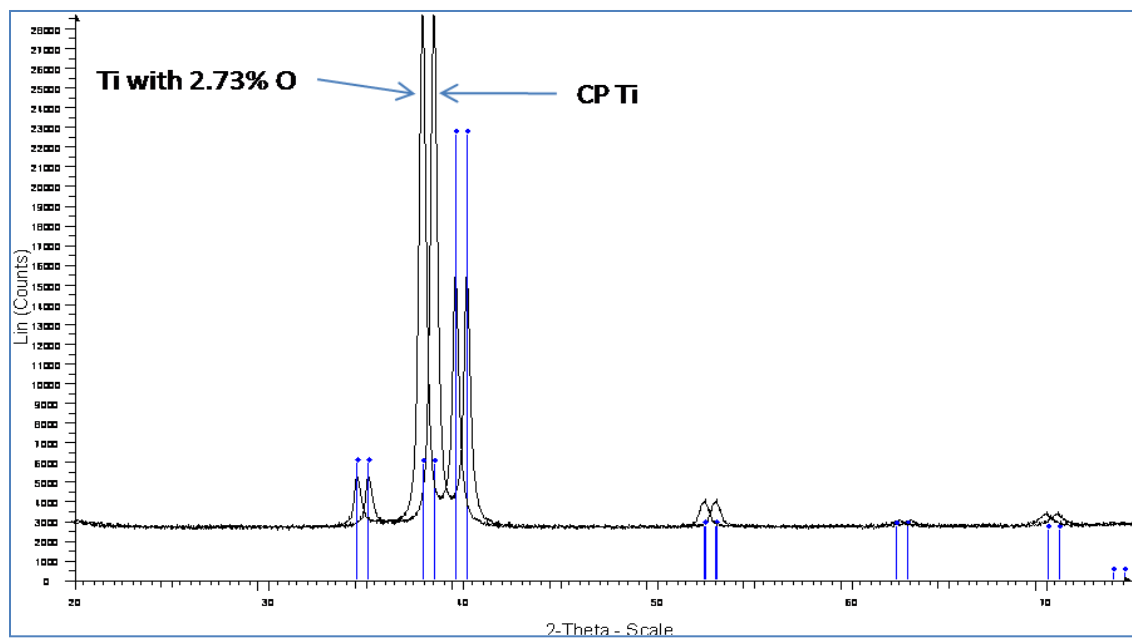


Fig. 4.15: XRD pattern showing Ti with 2.73wt% O shifting to the left as compared to CP Ti.

There was more pronounced shift to the left for 2.73% O titanium alloy. Distortion in the c parameter as compared to the a parameter is shown in Table 4.5.

Table 4.5: Variation of lattice parameters with oxygen content.

	Ti-0.48%O	Ti-0.75%O	Ti-2.73%O	CP Ti
a (Å)	2.9503 ± 0.001	2.9504 ± 0.002	2.9504 ± 0.001	2.9526 ± 0.0005
a distortion (%)	0.078	0.074	0.075	0
c (Å)	4.6828 ± 0.001	4.6833 ± 0.003	4.7241 ± 0.001	4.678 ± 0.005
c distortion (%)	0.103	0.113	0.984	0
c/a	1.5872	1.5873	1.6012	1.5844
% O content	0.48	0.75	2.73	0.01

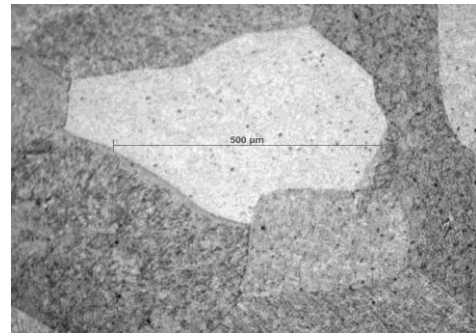
4.3 Optical Microscopy

This was performed as described before for each of the titanium alloys after annealing. Optical microscopy was undertaken immediately after etching the samples in Kroll's reagent.

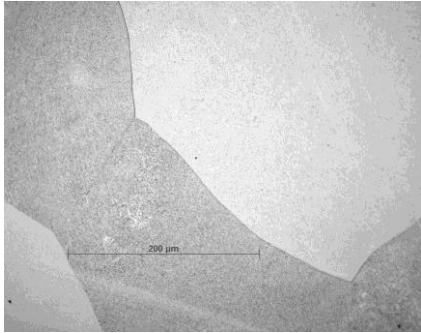
4.3.1 Ti-Mn alloys



a)



b)



c)

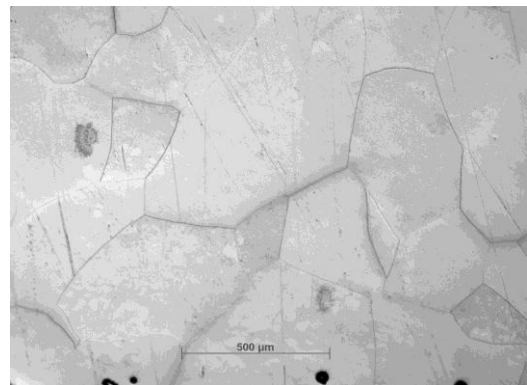


d)

Fig. 4.16: Optical Micrographs of quenched and etched **a)** Ti 2%Mn, **b)** Ti-4%Mn, **c)** Ti-6%Mn, **d)** Ti-8%Mn showing grain refinement with increase in manganese composition.



a)



b)

Fig. 4.17: Optical Micrographs of quenched and etched **a)** Ti 10%Mn, **b)** Ti 8%Mn showing grain refinement with increase in manganese composition as well as uneven surface erosion for the 8%Mn alloy.

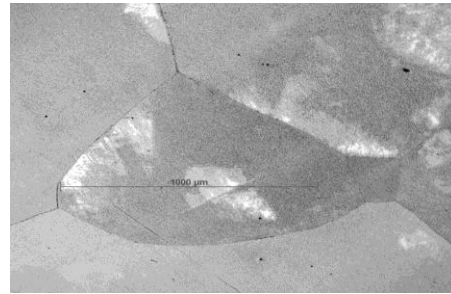
The 2%Mn (Fig. 4.16 (a)) alloy could hardly be properly etched. The sample was over-etched even after less than a second in Kroll's reagent (with 2%Hydrogen peroxide). However, when more hydrogen peroxide was added, better etching was achieved at 10%Hydrogen peroxide. This is evidence for weak corrosion resistance of this alloy. On the other hand, massive grain growth of columnar grains was observed with grains as much as 1mm being encountered in the microstructure. For the 4%Mn (Fig. 4.16 (b)) alloy, over-etching could be observed for times higher than 8 seconds in Kroll's reagent. Grain growth is also a distinct feature of this alloy although these grains are of the order of 0.5mm. The grains are also columnar.

The 6%Mn, 8%Mn and 10%Mn (Fig. 4.16 (c-d) and Fig. 4.17 (a)) alloy exhibits even smaller grains compared to the alloys discussed so far.

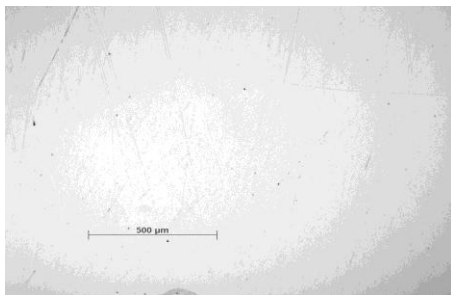
4.3.2 Ti-Fe Alloys



(a)



(b)



(c)



(d)

Fig. 4.18: Optical Micrographs of **a)** Ti 2%Fe, **b)** Ti 4%Fe **c)** Ti 6%Fe, **d)** Ti 8%Fe after annealing for 28 hrs at 1000°C followed by water quenching and etching.

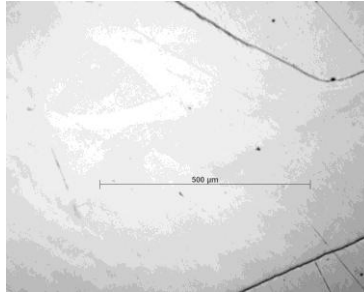


Fig. 4.19: Optical Micrograph of Ti 10%Fe after annealing for 28 hrs at 1000°C followed by water quenching and etching.

The micrographs show evidence of corrosion resistance from 6%Fe (Fig. 4.18 (c-d)) since there is little attack on the grains in pure reagent (Kroll) therefore no discernible microstructure was obtained. The 2%Fe and 4%Fe (Fig. 4.18 (a-b)) alloy was not so much different from the 2%Mn alloy. Over-etching was also a problem with this alloy until a more dilute reagent (10%Hydrogen peroxide) was used. There is massive grain growth of columnar grains (average of 2mm) due to the homogenisation treatment that the alloys were subjected to. Table 4.6 details measured grain sizes with increase in beta solute concentration.

Table 4.6: Variation of grain size with alloying content in investigated alloys

Alloy	Ti2Mn	Ti2Fe	Ti4Mn	Ti4Fe	Ti6Mn	Ti6Fe	Ti8Mn	Ti8Fe	Ti10Mn	Ti10Fe
Average grain size (mm)	1.0	2.0	0.5	1.0	0.4	n/a	0.3	n/a	0.2	n/a

4.3.3 Oxygen containing Titanium alloys

The observed micrographs show no perceptible differences to the control sample (C.P titanium).

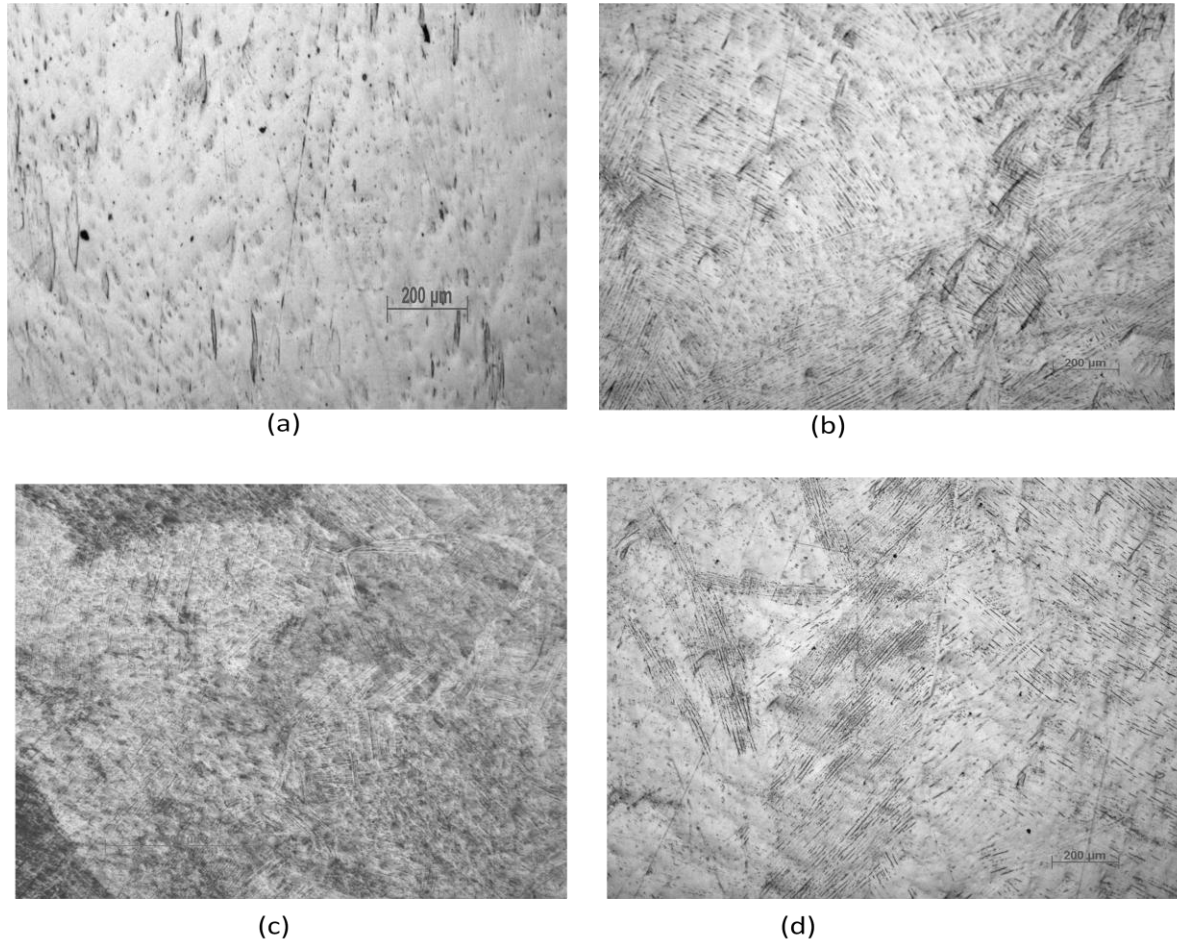


Fig. 4.20: Optical Micrographs of (a) un-etched C.P Ti, (b) etched 0.48%O Ti-O alloy (c) etched 0.15% O Ti-O alloy (d) etched 2.73% O titanium alloy.

Fig. 4.20 (b-d) is similar to un-etched C.P titanium micrograph (Fig. 4.20a) and no perceptible differences were observed. Fine lamellar structure was observed on all the samples.

4.4 Hardness Tests

Micro hardness test was done using a micro hardness tester with a pyramid diamond indenter at a load of 500g. The hardness values are given in Table 4.7.

Table 4.7: Hardness tests results for titanium alloys.

Alloy	Ti2Mn	Ti2Fe	Ti4Mn	Ti4Fe	Ti6Mn	Ti6Fe	Ti8Mn	Ti8Fe	Ti10Mn	Ti10Fe	CP Ti
Hardness (HV) at 500g	300 ± 5	285 ± 5	315 ± 6	320 ± 7	345 ± 3	435 ± 5	375 ± 5	459 ± 7	380 ± 3	360 ± 4	259 ± 1

Oxygen containing Titanium alloys

It has been noted that although micro-structural differences are very low, the hardness values are quite significantly increased by oxygen alloying as shown in Table 4.8.

Table 4.8: Impact of oxygen on hardness

Ti Alloy	Ti-0.48%O	Ti-0.75%O	Ti2.73%O	CP Ti
Hardness(HV)	268 ± 2	294 ± 1	306.8 ± 3	259 ± 1

CHAPTER 5: DISCUSSION OF RESULTS

This section details discussion of the results obtained in this study. These results include optical microscopy, XRD analysis, Scanning electron microscopy, hardness tests and oxygen content tests.

5.1 Microstructure of the investigated Ti-alloys

The large grains generally observed were due to the homogenising annealing treatment which the alloys were subjected to for 28 hours. The huge columnar grains encountered at lower solute concentrations could be evidence of the hexagonal (α) phase of titanium as confirmed by XRD analysis showing only α phase at lower concentrations of beta stabiliser.

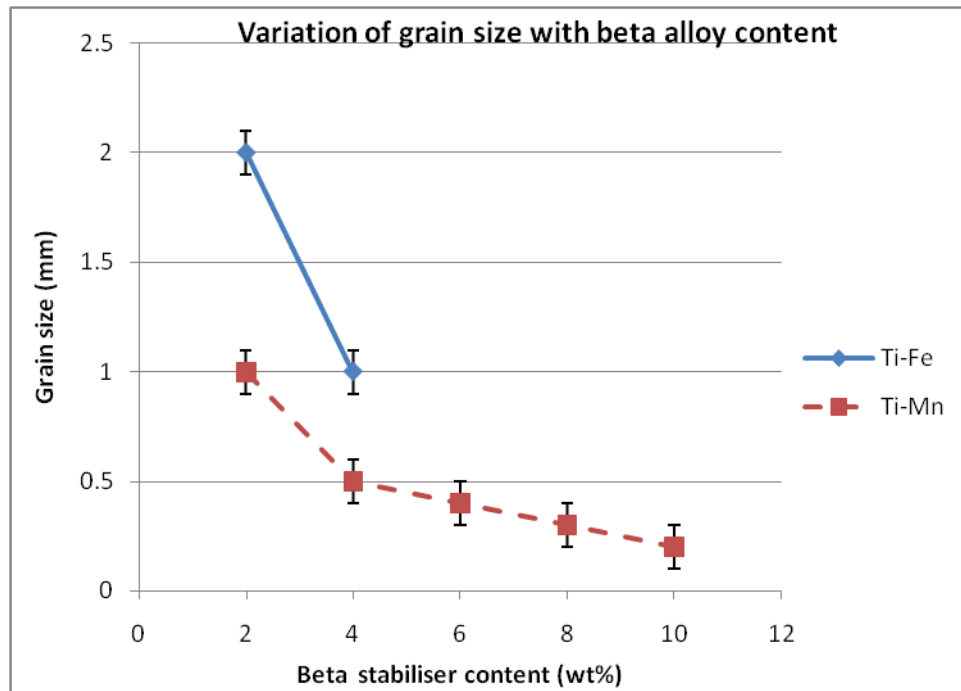


Fig. 5.1: Variation of grain size with beta alloy content.

The grain size obtained after solidification is determined by competition between the nucleation and growth rates. Iron and manganese additions are likely to enhance the nucleation rate by providing additional driving force and/or slowing the growth rate by

influencing the liquid/solid interfacial characteristics ^[42]. Although more fundamental calculations and/or instrumented experiments are necessary to ascertain the exact grain refinement mechanism via iron and manganese additions, previous studies have established that grain refinement occurs through solute mechanisms ^[41-43]. This occurs during solidification when the solute is rejected from the nucleating primary beta phase into the liquid phase thereby causing solute partitioning into the liquid ahead of the advancing solidification front. This causes variation in the liquidus temperature resulting in a higher Constitutional Supercooling (CS). CS then causes instability at the liquid/solid interface providing additional driving force for the nucleation of more fine beta grains ahead of the solid/liquid interface ^[42]. However, solute mechanisms may not explain the observed behavior in this study because of the annealing treatment that the alloys were subjected to after solidification.

The proposed mechanism from this study is that lattice straining interferes with beta phase nucleation as we cross the transus line back into the full beta region. This interference creates more nucleation sites during the transition hence resulting in a finer grain structure. Since manganese and iron have been seen to cause increased lattice straining with increase in their respective concentrations, it is therefore possible that the greater lattice straining has a more pronounced effect on beta phase nucleation thus restricting grain size with increasing concentration of alloying elements.

Manganese seems to have greater solid solution effect on microstructure than iron as illustrated in Fig. 5.1 where it caused smaller grain size as compared to iron. This is expected to be the case for mechanical strength since grain size is generally inversely proportional to yield strength in crystalline solids ^[11]. There is a very small difference in atomic radii of manganese and iron which may not explain the difference in grain size i.e. 127pm and 126pm respectively, while that of titanium is 140pm ^[7].

The optical micrographs are in agreement with XRD findings showing beta phase retention at higher beta solute concentration (i.e. 5.3 at. %Mn and 3.5 at. %Fe) within the solid solution range. This is in agreement with the other researchers ^[38, 43]. Iron alloys are seen to cause

smaller unit cells and beta stabilisation at around 5 at.% according to A.V. Dobromyslov, *et al* [38]. Iron is smaller than manganese and is therefore expected to effect greater lattice distortion as compared to the slightly larger manganese atom.

In substitutional solid solutions, the unit cell parameters are distorted by the inclusion of foreign elements in the lattice or other processes that can strain the lattice like cold and hot working. In this case, substitutional elements are causing distortion to the cell parameters because of size differences with the host element [6, 7].

Since manganese and iron are smaller than titanium in terms of size, this has an effect of reducing the size of the unit cell even further with increase in concentration as more substitutional sites are occupied in the bcc unit cell.

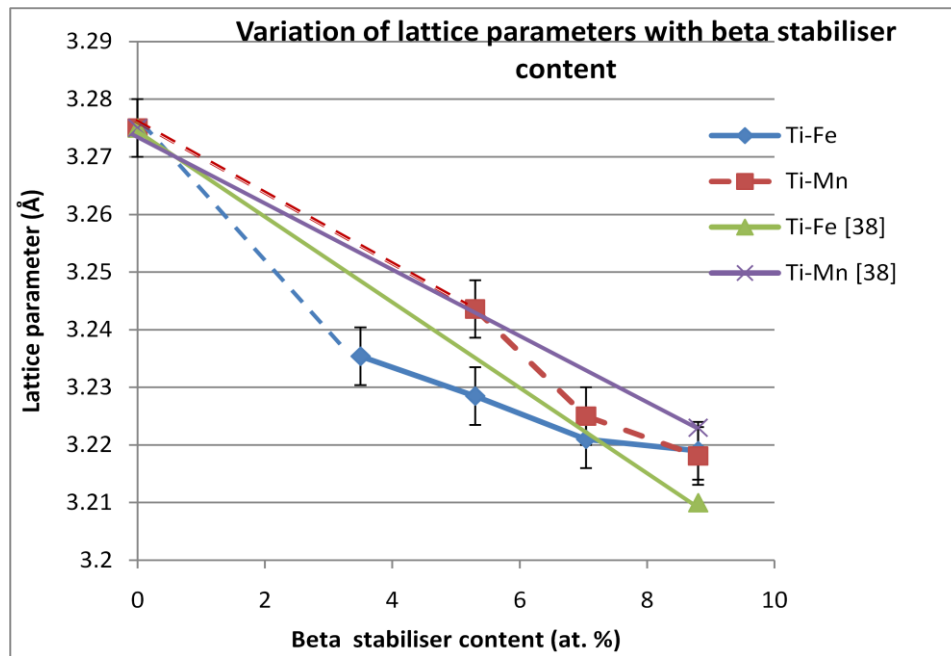


Fig 5.2: Variation of lattice parameter with content of beta alloying element. Values obtained from literature are included in the graph for comparison.

The lattice parameter of pure beta titanium has been measured by other researchers over the temperature range 900°C to 1100°C; this led to values of $a = 3.3174 \text{ Å}$ at 1067°C while the coefficient of expansion was equal to about $12 \times 10^{-6} \text{ °C}^{-1}$ according to literature [39]. The referenced work [38] recorded a value of 3.275 Å at 0°C as shown in Fig. 5.2. Using the thermal

expansion coefficient, a simple calculation of the expected beta lattice parameter at room temperature yielded a value of 3.2759 Å. An assumption had to be made that the expansion coefficient is constant over the considered temperature range.

Oxygen containing titanium samples

Oxygen causes the c direction to stretch as it occupies the interstitial sites in the HCP lattice of titanium. There is more pronounced distortion on the c parameter than the a parameter. This could be attributed to the packing efficiency of the sites along the c axes which is less packed than the a as shown in Fig. 5.5. Thus, oxygen preferentially diffuses on to the less packed sites since they have more interstitial sites and thenceforth the more marked dilation of the c parameter than the a parameter.

The axial ratio or c/a ratio increases with oxygen concentration as shown in Fig. 5.3.

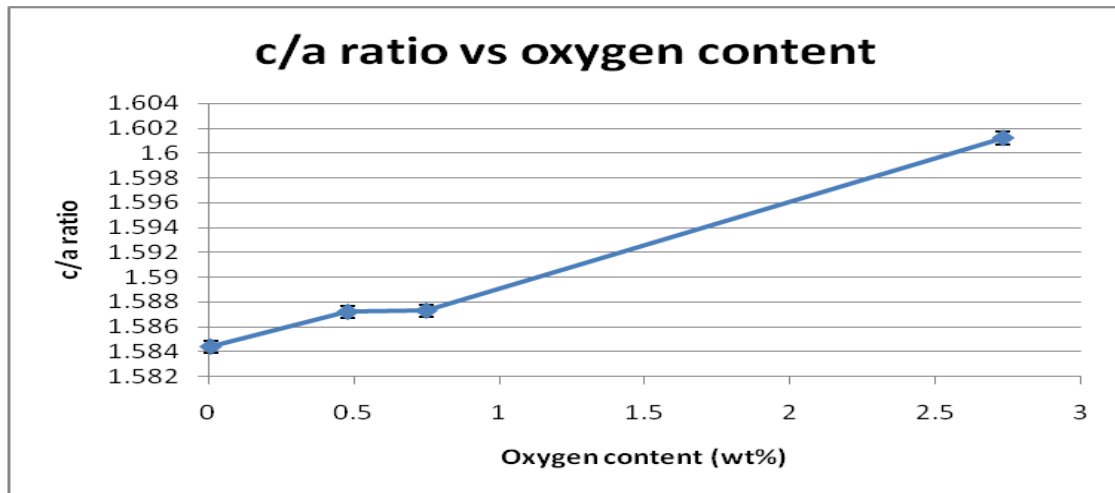


Fig. 5.3: Effect of oxygen on the axial ratio of α -titanium

As oxygen content increases in titanium, the axial ratio increases. This is due to the general increase in the c lattice parameter with increase in oxygen concentration as shown in Table 4.5.

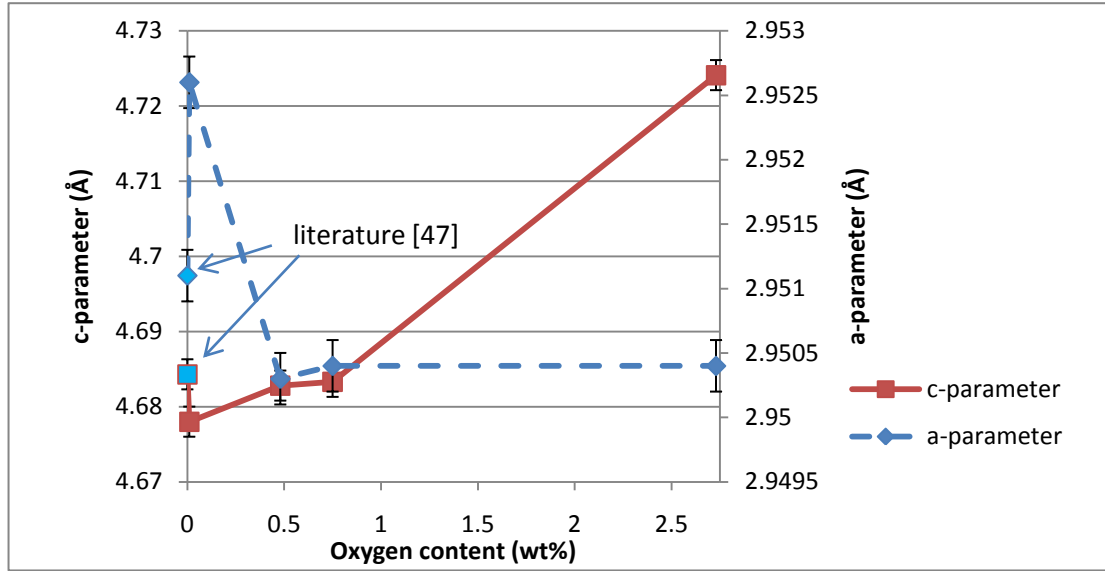


Fig. 5.4: Effect of oxygen on the *a* and *c* lattice parameters α -titanium.

The *c* direction shows a general increase as expected if oxygen is mostly occupying interstices in this direction than in the *a* direction (Fig. 5.4). R. M Wood has reported the *a* and *c* parameters of pure titanium to be: $a_0 = 2.95111 \text{ Å} \pm 6 \times 10^{-5}$ and $c_0 = 4.68433 \text{ Å} \pm 10 \times 10^{-5}$ [47]. However, the measured lattice constants for pure titanium which followed the melting route in this study were slightly larger i.e. $a = 2.9526 \text{ Å}$ and $c = 4.678 \text{ Å}$.

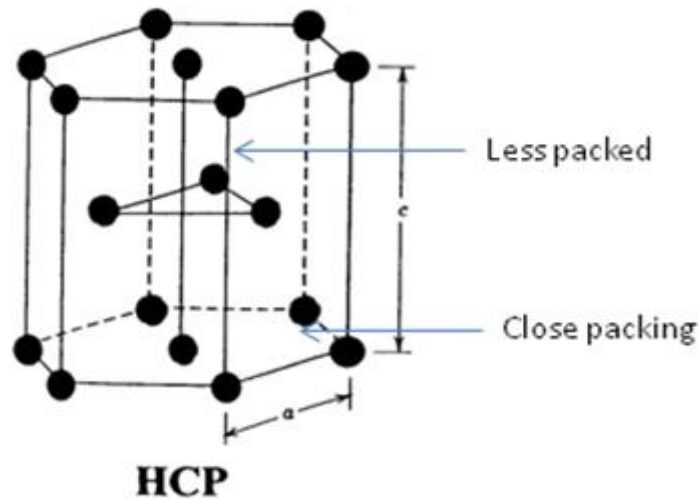


Fig. 5.5: HCP unit cell, showing atomic packing ^[46].

Leco results confirm that the arc furnace and the subsequent heat treatment processes managed to keep the titanium alloys free from appreciable oxygen contamination. The concentration measured was 0.01 wt. %.

5.2 Hardness

The general trend of an increase in hardness (Fig. 5.6) for these alloys can be explained by solid solution strengthening mechanisms ^[44, 45]. When the titanium lattice is distorted by substitutional solid solution additions, it becomes strained or there is an increase in internal energy of the system due to lattice straining caused by an increase in amount of the doping element which results in localized straining on substitutional sites. This is manifested on the macroscopic level by a change in mechanical properties. Yield strength is expected to improve. One of the mechanical properties which are expected to increase with solute concentration is hardness. A similar trend was recorded by F. Zhang *et al* ^[44] for titanium manganese alloys although the alloys were mechanically alloyed and then sintered.

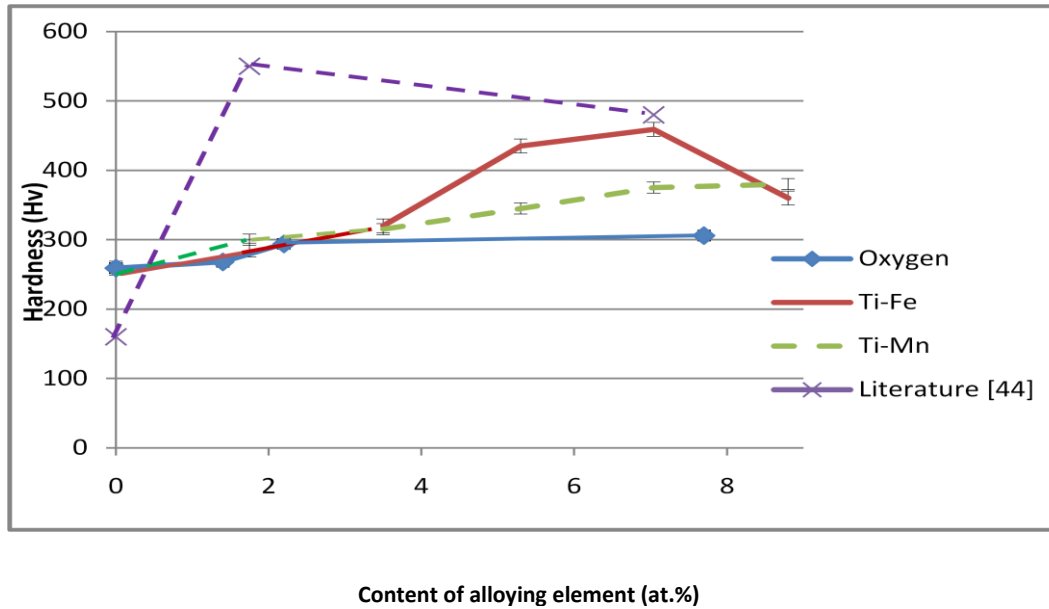


Fig 5.6: Variation of hardness as a function of content of the alloying element.

Table 5.1 also shows that alloying with increasing amount beta stabilising elements increases hardness of titanium alloys. An interesting note is that the hardest alloys from the table contain iron in small quantities i.e 2.5 wt. %Fe for SP700 and 2 wt. % for Ti-10-2-3. Titanium-iron binary alloys were also seen to be harder than titanium-manganese alloys in this study.

Table 5.1: Hardness values of some common metastable beta-titanium alloys ^[6, 40].

Alloy	Chemical composition	Hardness (Hv)
SP700	Ti-4.5Al-2.5Fe-2Mo-3V	300-500
Ti-15-3	Ti-15V-3Sn-3Cr-3Al	300-450
Ti-15-5-3	Ti-15Mo-5Zr-3Al	340
Ti-10-2-3	Ti-10V-2Fe-3Al	300-470
Beta C	Ti-3Al-8V-6Cr-4Mo-4Zr	300-450

Oxygen containing titanium alloys

The hardness of titanium increases with oxygen content. Also, as the oxygen amount increases in the alloy, the degree of lattice distortion also increases (Fig. 5.6). The hardness increase can be correlated to the a and c lattice parameters. As discussed, the changes in these parameters highlight lattice straining and hence hardening. However, it must also be said that relatively small increases in oxygen content causes larger changes in hardness than similar changes in beta stabilizer content.

5.3 Beta phase stabilization

Fig. 5.7 shows a Ti-Fe equilibrium phase diagram. The red line shows the holding temperature which was used for this study. The choice of temperature was made to ensure a complete beta structure at temperature after 28 hours. Using this diagram to explain observed data, it may be noted that the 10wt%Fe alloy is much deeper into the beta phase range at 1000°C whereas the 2wt%Fe alloy is closer to the alpha/beta transition temperature. This could be responsible for the ease with which beta phase is stabilized at higher stabilizer concentrations.

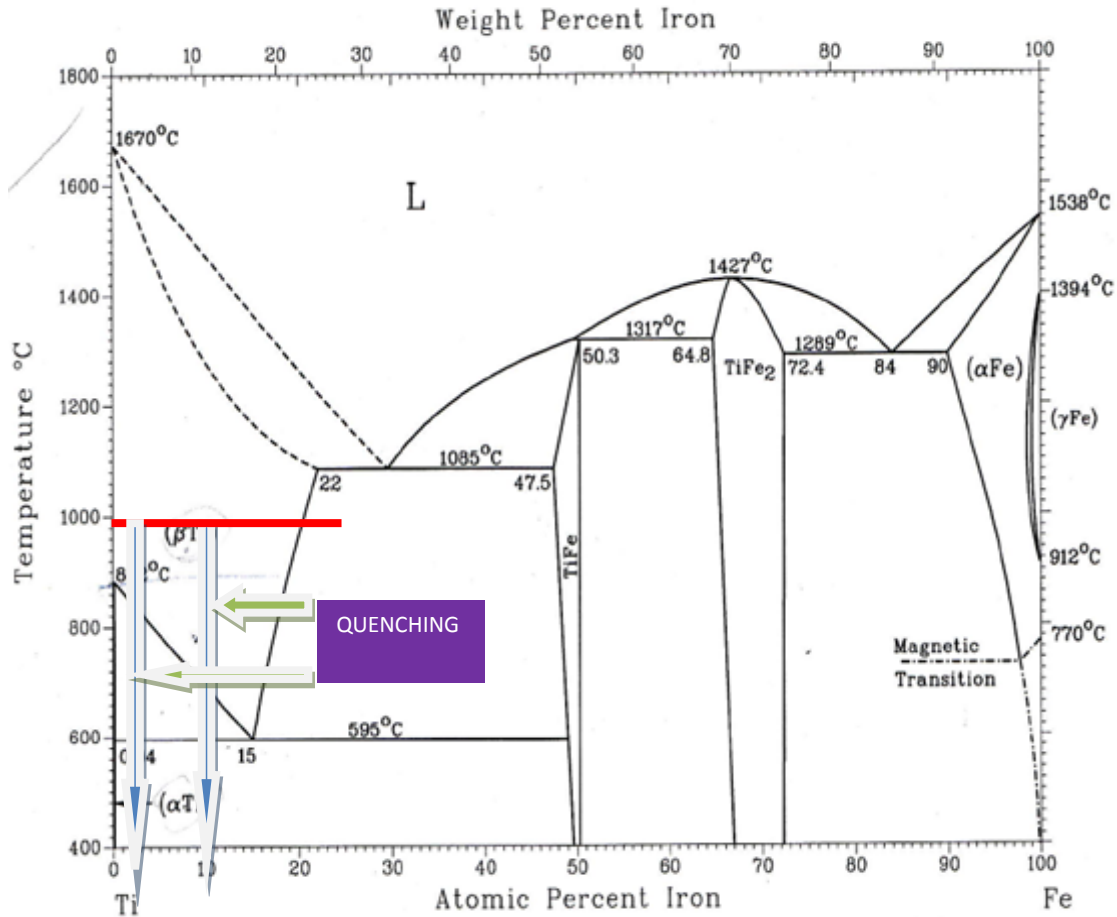


Fig. 5.7: Ti-Fe equilibrium phase diagram showing the quenching route followed ^[48].

From literature, it was found that beta stabilization occurs at around 5 at. %Fe and 6 at. %Mn as shown in Table 5.2 ^[38]. The referenced work followed a similar alloy production route to the one conducted in this study. Their alloys were melted in a tungsten arc furnace and then annealed at 1000°C (for 3 hours) followed by iced-water quenching. This confirms that iron can stabilize the beta phase at lower concentrations than manganese under these conditions. This investigation, however, has established that beta stabilization can be achieved at 3.5 at. %Fe and 5.3 at. %Mn although there is evidence of a small amount of alpha at these concentrations as discussed before.

Table 5.2: Minimum concentration of the alloying element necessary for the complete stabilization of the β -Phase in Binary Titanium Alloys with d-Metals of 4–6 Periods, after quenching from 1000°C (at. %) ^[38]. * stabilization concentrations established in this research.

Alloy	Min. Conc. (at.%)	Alloy	Min. Conc. (at.%)	Alloy	Min. Conc. (at.%)	Alloy	Min. Conc. (at.%)
Ti-V	15	Ti-W	10	Ti-Ru	33	Ti-Ni	9
Ti-Nb	23	Ti-Mn	6 [5.3]*	Ti-Os	3	Ti-Pd	11
Ti-Ta	35	Ti-Tc	?	Ti-Co	7	Ti-Pt	7
Ti-Cr	7	Ti-Re	5	Ti-Rh	4	Ti-Cu	11
Ti-Mo	5	Ti-Fe	5 [3.5]*	Ti-Ir	3	Ti-Au	?

The same researchers also analysed dependence of beta lattice parameter with increase in alloying element and a similar trend was established on a wider alloying range than investigated in this work. Fig 5.2 shows that iron causes larger lattice changes at 5.3 at. % than manganese.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

There is a general decrease in lattice constants for the beta-titanium phase as solute concentration is increased for Ti-Mn and Ti-Fe alloys. This is true for the solid solution range studied in this project. In comparison, Iron is a better beta phase stabiliser than manganese. This is evident since iron stabilises beta phase at lower concentrations than manganese.

An increase in solute concentration is generally accompanied by reduction in average grain size for the studied alloys. However, Ti-Fe alloys results in smaller grain sizes as compared to Ti-Mn alloys. In terms of lattice straining, iron causes greater lattice distortions than manganese at the same concentrations. A relatively small increase in oxygen content causes larger changes in hardness than similar changes in beta stabilizer content.

Hardness of the studied alloys increases with increasing amount of doping elements. Oxygen contamination is also seen to harden commercially pure titanium. The 6%Fe, 8%Fe and 10%Fe alloys exhibit superior resistance to chemical attack by Kroll's reagent than Ti-Mn alloys.

6.2 Recommendations

1. Testing of other mechanical properties (other than hardness) of these alloys needs to be done in order to get a more complete picture of how the reported microscopic changes affect beta Ti-Mn and Ti-Fe alloys.
2. Further work needs to be done on corrosion characteristics of the alloys, particularly Ti-Fe alloys.

3. More alloys in the solid solution range may also be made to get more data so that trends become clearer.

4. Ternary and multi-component alloys may also be designed and investigated similarly in order to understand the combined effect of solute elements on microstructure and mechanical properties.

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