LASER DEPOSITION, HEAT-TREATMENT, AND CHARACTERIZATION

OF THE BINARY Ti-xMn SYSTEM

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The present research seeks to characterization of an additively manufactured and heat-treated Ti-xMn gradient alloy, a binary system that has largely been unexplored. In order to rapidly assess this binary system, compositionally graded Ti-xMn (0<x<15 wt%) specimens were fabricated using the LENS (Laser Engineered Net Shaping) and were subsequently heat-treated and characterized using a wide range of techniques. Microstructural changes with respect to the change in thermal treatments, hardness and chemical composition were observed and will be presented. These include assessments of both continuous cooling, leading to observations of both equilibrium and metastable phases, including the titanium martensites, and to direct aging studies looking for composition regimes that produce highly refined alpha precipitates – a subject of great interest given recent understandings of non-classical nucleation and growth mechanisms. The samples were characterized using SEM, EDS, TEM, and XRD and the properties probed using a Vickers Microhardness tester.
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INTRODUCTION

Titanium alloys, as with most non-ferrous structural engineering alloys, exhibit an attractive balance of mechanical properties that are governed by their compositions and microstructures. Many industrially used alloys owe their evolution to research that stems back to the 1950s, including the workhorse alloy Ti-6Al-4V. However, there remains a significant knowledge gap with respect to some potentially interesting binary systems (e.g., Ti-Mn).

For example, the alloying addition Mn is rather interesting as it exhibits a complex crystal structure with 58 atoms in a super cell its elemental form, yet stabilizes the beta phase. This binary system, though explored initially in the 1950s, has largely been neglected owing to processing difficulties including liquid phase separation, which rendered mechanical properties rather inhomogeneous. Thus, even though this alloy's research began in the early 1950s, there is not a sufficient body of research on the microstructural stability and mechanical response when subjected to different thermal treatments. In order to rapidly assess this often-neglected binary system, compositionally graded Ti-xMn specimens were fabricated using LENS (Laser Engineered Net Shaping), subsequently heat-treated and characterized using a wide range of techniques.

Following the LENS™ deposition of the Ti-xMn(0<x<15wt%) gradient sample, solutionizing and lower temperature age hardening treatments were performed at different temperatures in an inert argon atmosphere to observe microstructural features present with respect to the change in chemical composition and hardness. Scanning Electron microscopy (SEM), SEM with Energy Dispersive Spectroscopy (EDS), and Vickers hardness testing were primarily employed to characterize the samples. Microstructural changes with respect to the
change in thermal treatments, hardness and chemical composition were observed and explained. A corresponding trend in the hardness values was observed from the plots of Vickers hardness calculations. Virtual calculations were performed using Vegards law to understand the change in the lattice constant of the Ti-Mn alloy with change in the composition of the wt% Mn. X-ray diffraction (XRD) and transmission electron microscopy (TEM) experiments were also conducted to calculate the change in lattice constant Ti-Mn alloy. TEM studies report the presence of omega phase in the solutionized and water quenched sample. Initial assessments were performed to determine whether a new mechanism to alpha precipitation, namely the pseudospinodal [1], may occur in the Ti-Mn system.
2.1 Crystal Structure of Titanium

Titanium exhibits allotropic forms. At low temperature, it has a hexagonal close packed (HCP) structure denoted with alpha (α). At 882°C, pure Ti undergoes an allotropic transformation to body centered cubic (BCC) crystal structure called beta (β). The beta phase in pure titanium is stable up to the melting point i.e., 1668°C. [2]. The crystal structure of both BCC and HCP with the close packed planes and directions are shown schematically in Fig 1 [2]. Atoms in the bcc structure are not as closely packed as in the hcp structure, thus a volume expansion during transformation is expected. This transformation of alpha to beta in pure Ti results in slight expansion of the crystal structure and thus decreases the density. The large expansion expected from the transformation of the closely packed alpha to beta structure is not realized since transformation is accompanied by a contraction in the atomic diameter. This phenomenon is known as Goldschmidt contraction. The temperature at which the transformation of alpha to beta occurs in pure Ti is referred to as Beta-transus. The addition of alloying elements can alter this temperature. Beta-transus temperature is the lowest equilibrium temperature at which the alloy consists of 100% beta-phase.
2.2. Alloying Additions

In the modern periodic table, titanium belongs to the transition group. It has several important characteristics like high inter-atomic cohesive strength, which results in high tensile strength, low thermal expansion, and a relative high melting point. This is an extremely important property for Ti and its alloys since it can provide strengthening through heat treatment. Pure titanium although very ductile has relatively lower strength compared to some of its alloys and hence finds greater engineering applications when strengthened by alloying. Selection of alloying elements is governed by the choice of phase to be stabilized or created either of the $\alpha$ or the $\beta$ phases. This behavior, in turn, is related to the number of bonding electrons, i.e. the group number of the element concerned.

- Elements with electron/atom (e/a) ratio $< 4$ stabilize the alpha-phase
- Elements with e/a ratio $= 4$ are neutral.
- Elements with e/a ratio $> 4$ stabilize beta-phase [3]

![Fig.1 Unit cell of $\alpha$ and $\beta$ phase of titanium](image)
2.2.1. Alpha Stabilizers

Alpha stabilizers are elements which stabilize and extend the α phase field to elevated temperatures during heat treatment as schematically shown in figure 2.

These elements preferentially form solid solutions with alpha-Ti, thus stabilizing the phase. Alpha stabilizers include C, O and N whose strengthening effect disappears in the range of 260°C to 425°C. Among the group of such alloying elements, Al has the most pronounced effect on microstructure and mechanical properties.

Strengthening effect of Al persists to about 538°C. Al alloys, by replacing the Ti atoms in the crystal structure, form substitutional solid solutions. Elements with smaller atomic radii like Carbon, Oxygen and Nitrogen fit into the interstitial voids of the crystal lattice thus extensively forming interstitial solid solutions. Oxygen having the smallest atomic radius has the highest interstitial solid solubility, followed by Nitrogen and Carbon, as governed by their atomic sizes.
The alpha stabilizing interstitial elements C, O and N can increase the strength, but decrease the ductility of the titanium alloy.

2.2.2 Beta Stabilizers

Group V and VI and Period IV elements of the modern periodic table that stabilize the high temperature BCC-Ti phase either in stable or meta-stable condition are classified as “Beta Stabilizers”. These elements depress the transformation temperature, thus stabilizing the beta phase at lower temperature. These elements like the alpha stabilizers also tend to form substitutional solid solutions. However, the choice and content of alloying elements has to be exercised with caution as these elements have high density and possess large atomic radii, which invariably result in problems of macro-segregation when processed through conventional bucket metallurgy routes. Vanadium is a common β stabilizer and, though less effective than molybdenum, finds extensive usage in alloys like Ti-6Al-4V.

The alloying elements that are more commonly used in titanium alloys are summarized in the table shown below:

<table>
<thead>
<tr>
<th>α stabilizer</th>
<th>β stabilizer</th>
<th>Neutral</th>
</tr>
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<tr>
<td></td>
<td>Isomorphous</td>
<td>Eutectoid</td>
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<tr>
<td>Gallium</td>
<td>Tantalum</td>
<td>Iron</td>
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<tr>
<td>Aluminum</td>
<td>Tungsten</td>
<td>Hydrogen</td>
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<td>Oxygen</td>
<td>Molybdenum</td>
<td>Nickel</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Vanadium</td>
<td>Cobalt</td>
</tr>
<tr>
<td>Carbon</td>
<td>Niobium</td>
<td>Manganese</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Antimony</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chromium</td>
</tr>
</tbody>
</table>

Table 1. Common alloying elements in titanium
2.3 Alpha Alloys

These are single phase α alloys that are solid solution strengthened by the addition of α stabilizers or neutral alloying additions. Alpha alloys are preferred for elevated temperature as well as cryogenic applications [4]. Alpha rich alloys are more resistant to creep at high temperature than α-β or β alloys. Alpha alloys exhibit poor response to heat treatment cycles as they are composed of a single phase. These alloys are strengthened by cold working, severe plastic deformation methods like cold rolling, ECAP and ECAE. The only heat treatment performed on these alloys is stress relief annealing and/or recrystallization annealing. This insensitivity of the alloy to heat treatment makes alpha alloys extremely amiable to welding and at the same time narrows down the scope of hot forging as temperature range for thermal working is narrow.

The resulting microstructures are strongly dependent on the cooling rate of the alloy through the phase fields as shown in figure 3. The microstructure is characterized by the presence of equiaxed α grains of which a considerable volume fraction of these grains could be of the parent β phase. Soaking in the α phase field would result in the formation of α grains, whereas soaking in the β phase filed result in completely stabilized β grains. The β-phase present above the β-transus gets transformed to alpha on cooling through that β-transus.
2.4 Near Alpha Alloys

Alpha alloys that contain small additions about 1-2 wt% of beta stabilizers have been classified as super alpha or near alpha titanium alloys. The addition of 1-2% of β stabilizing elements helps to improve the strength and workability. These alloys are a good compromise between the high strength α-β alloys and creep resistant single-phase α alloys. The most widely used commercial high temperature titanium alloys for aero-engine applications belong to this class [4].

This group of alloys, like α alloys, contain solutes that stabilize the α phase as well as small concentrations of β stabilizing elements (about 1-2% wt.) which broaden the α+β temperature range sufficiently, facilitating thermo mechanical working within α+β phase field possible. The most widely used commercial high temperature titanium alloys for aero-engine applications belong to this class. Near α alloys may also be deformed entirely within β phase field (e.g. IMI865) at temperature around 1100°C, or with more recent alloys (e.g. IMI 834) at lower temperature within α+β field. The morphology of the decomposition products from the Beta parent phase are dependent on the rate of cooling. In the β processed alloys the microstructure consists of α laths produced during transformation of large β grains during cooling. In α+β process (deformed in the α+β phase field), the prior β grain size is much smaller due to the presence of primary alpha, which helps to pin the grain boundary. The alloys when processed in the α+β phase field results in microstructure consisting of refined grains, owing to the smaller parent Beta grain (as compared to the Beta processed alloy). The grain boundary pinning resulting from the refined morphology checks grain boundary mechanisms like grain
growth and grain boundary sweep resulting in higher strength and creep resistance against pure alpha alloy.

2.5 Alpha-Beta Alloys

The alloys within the $\alpha$-$\beta$ system contain at least one alpha stabilizing and one beta stabilizing element (to a minimum of 4-6%) in their composition. These alloys retain more beta phase after solution treatment than the near $\alpha$ alloys, the specific amount depending on the quantity of $\beta$ stabilizers present and on heat treatment. $\alpha$-$\beta$ alloys can be strengthened by solution treatment and ageing. Solution treatment is usually done at a temperature in the two phase $\alpha+\beta$ field and is followed by quenching into suitable quenchant like water or oil. Quenching results in phases formed by martensitic transformation along with volumes of retained high temperature Beta phase.

The specific response depends on the alloy composition, solution treating temperature, cooling rate and hardenability of the alloy. Solution treatment is followed by ageing to precipitate $\alpha$ and produce fine mixture of alpha and beta in the retained $\beta$ or transformed $\beta$-phase [4]. Alloying elements that stabilize Beta phase strongly determine the hardenability of the alloy. Increasing $\beta$ content increases hardenability. Alloys relatively low in $\beta$-stabilizers have poor hardenability and must be quenched rapidly to achieve significant strengthening effect. Since Beta phase determines the efficiency of the hardening treatment, the strength achieved by heat treatment is a function of the volume fraction of the $\beta$-phase present at the solution treating temperature. Alloy composition and the heat treatment conditions must be carefully selected and balanced to produce desired properties in the final product. The most widely used
alloy in this class is Ti-6Al-4V, where Al stabilizes Alpha phase and Vanadium stabilizes Beta phase.

2.6 Beta Alloys

The elevated temperature Beta phase tends to stabilize at room temperature when sufficiently large amounts of beta stabilizing elements are added to titanium. These alloys are generally easily cold workable than the alpha-beta alloys, are heat treatable to high strengths, and some have superior corrosion resistance compared to the commercially pure grades. In these alloys the concentration of β stabilizing elements is high enough to produce β phase, which is, either thermodynamically stable at room temperature, or so weakly meta stable that decomposition into equilibrium α and β does not take place. Such alloys are highly cold workable and can be recrystallized at low (800°C) temperature to fine grained β structure. There are no commercially available β-alloys that are thermodynamically stable as single β-phase, and alloy can undergo α-precipitation on aging. Though weakly metastable, it is possible to age β-phase alloy to high strength through decomposition of β to fine α, β and other intermediate phases.

2.7 Near Beta Alloys

The beta alloys of the metastable β system contain about 10-15% β-stabilizers and 2-3% of α-stabilizers. High concentrations of β stabilizing solutes depress the martensitic transformation temperature below 30°C. Therefore the martensitic transformation does not complete unless subjected to cryogenic treatment. Since the β/α+β transus is significantly
below the allotropic transus of pure Ti, these alloys can be conveniently processed in the Beta phase field (about 800°C) resulting in microstructures with Meta stable Beta phase at room temperature. Thus these alloys also have excellent forgeability. The large atomic radii of the solute atoms (like W, Mo, V, Cr) retard the diffusion kinetics-nucleation and growth of α, resulting in high hardenability alloys, which may be cooled in air to produce high strength metastable-β phase. Heavier section may be quenched into water.

The β-phase produced either by air cooling or water quenching is usually metastable and has a tendency to transform to the equilibrium α+β structure. After solution treatment, metastable-β alloys are aged at temperature of 450°C to 650°C to partially transform the β-phase to α. The α-phase forms as finely dispersed particles in the retained β and strength levels are comparable to or superior to those of aged α-β alloys. The chief disadvantage of β alloys in comparison with α-β alloys is that the β alloys have higher density, lower creep strength and low tensile ductility in their aged condition. The near β range of alloys incorporates the highest strength grades of Ti alloys, with yield strength in excess of 1200MPa.

2.8 Laser Engineered Net Shaping (LENS™)

Two of the upcoming technologies for direct laser deposition of the metallic components using solid free form fabrication (SFF) route are LENS™ and Directed Light Fabrication (DLF) processes. The Laser Engineered Net Shaping (LENS™) technique is being used to fabricate various types of graded alloys. It has been extensively employed to fabricate tooling parts and also in repairing the aerospace components. The LENS™ technique to fabricate near net shape alloys from a blend of metal powders using Lasers was developed by Sandia National
Labs. A CAD (computer aided design) program containing the design requirements is used to fabricate the desired components from LENS™. The alloy composition is deposited into a cylindrical shape, by uniform deposition of in-situ molten metal layers, instantly solidifying on a metal substrate. Each layer is deposited by drawing an outline of the desired shape and then filling the cross section uniformly using a rastering technique. This cycle is repeated until the part is complete, resulting in fully dense graded components.

2.9 Construction of LENS system

The LENS™ system consists of important functional sub units, that facilitate smooth deposition of the metal part. The melting system comprises of a high power Nd:YAG laser, a controlled atmosphere glove box, a 3-axis computer-controlled positioning system, and powder feed unit.

The controlled atmosphere glove box consists of mounted positioning stages. The glove box is purged with Argon gas to sterilize the sample of adsorbed atmospheric gasses. Through window mounted on the top of the glove box, the laser beam is focused into the chamber using a six-inch focal length plano-convex lens [6]. For depositing the component in LENS™, a flat metal substrate is used as a base material, on which the LENS™ part is built. A weld pool is created by focusing the laser beam on to the substrate into which the powder particles are induced to build up each layer. The substrate is moved under the laser beam and a thin cross section of the given geometry is deposited initially. This layered deposition is repeated until final part is obtained [6,7].
A considerable amount of research has been performed on the compositionally graded Ti alloys such as Ti-xV, Ti-xMo [8,9]. The Ti-6Al-4V-TiB composites, which have been in situ deposited, resulted in the precipitation of TiB but also influenced the microstructural development in the α/β matrix [10]. The grain boundary crystallography with orientation imaging microscopy has been studied in the Ti-8Al-xV alloy where grain boundary α precipitates orientation relationship with the adjacent β grains was reported. Titanium based alloys Ti-20Nb-xTa, Ti-xNb-10Zr-5Ta which are for biomedical applications are developed and the metal matrix composites such as Ni-Ti-C which are used in several engineering applications including aerospace applications due to their exceptional mechanical properties. Almost all the above alloys are compositionally graded to study various mechanical properties with varying chemical composition, which is a very economical processing technique.

2.10 Titanium – Manganese Binary System

The equilibrium phase diagram of the Ti-Mn binary system consists of twelve different phase which includes a liquid phase, six solid solutions and three line compounds. The equilibrium conditions of the various phases present in this system are stated [16]. The βTi and αTi phases are solid solutions, in which the maximum solubility of Mn in βTi is 30 at% at 1174°C and the solubility limit of Mn in αTi is ~0.4at% at 550°C, which is just above the eutectoid. The δMn is also a solid solution, which exists in equilibrium condition between the temperatures 1136°C and 1244°C. The maximum solid solubility of Ti in δMn is ~6at% at 1204°C. The γMn solid solution phase is at equilibrium between 1100°C and 1136°C and the solid solubility limit
of Ti in γMn phase is 0.6 at% Ti. The βMn solid solution is at equilibrium between 720°C and 1100°C and the solubility of Ti in this phase is 5 at% at 1148°C. The αMn is a complex cubic solid solution exists the Ti-Mn alloys at 89.5 at% Ti, upto 1148°C which is strongly stabilized in the presence of Ti. The boundary compound αTiMn is usually denoted as φ is at equilibrium at 950°C and at a composition of 50.5 at% Mn. Another line compound βTiMn denoted as ρ exists in equilibrium at 52 at% Mn, upto a temperature of 1200°C. The Laves phase, which is TiMn₂, is usually denoted as C14 starts melting at 1325°C and the TiMn₃ compound exists in equilibrium at a temperature range of 950°C-1250°C. The line compound TiMn₄, denoted, as R exists in equilibrium between 930°C and 1230°C. The composition of this line compound is 81.5 at% Mn.

Fig. 4 Equilibrium phase diagram of Ti-Mn system [16]
The addition of manganese to the titanium reduces the $\alpha$ to $\beta$ transformation temperature and is confirmed as a $\beta$ stabilizer element; also manganese increases the relative density of the alloy. It is clear from the above phase diagram, of the Ti-xMn system that the a and b phases are separated from each other by dashed lines, which indicates that a large domain of understanding remains unexplored as far as the accurate understanding of these alloys' metastable behavior as observed in the phase diagram is concerned.

Alloying of Ti with Mn leads to a decrease in the melting point of $\beta$-Ti from 1670°C to 1181°C [21]. At this temperature, the eutectic phase equilibrium L (39.2 at% Mn) takes place.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Crystal Structure</th>
<th>Electro negativity (Pauling scale)</th>
<th>Atomic radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>HCP &lt; 882°C, BCC &gt; 882°C</td>
<td>1.54</td>
<td>147pm</td>
</tr>
<tr>
<td>Mn</td>
<td>BCC</td>
<td>1.55</td>
<td>127pm</td>
</tr>
</tbody>
</table>

Table 2. Comparison of atomic and crystallographic properties of Ti and Mn

From the above table, difference in the electro negativities of the Ti and Mn elements is 0.01 and the % difference in the atomic radii is 13.6, which indicates that the system exhibits good solid solubility according to the Hume-Rothery rules.

Exceptional Hydrogen absorbing performance is an important property of the Ti-Mn alloy system. They attract more attention due to their specialized applications such as high hydrogen storage capacity, good hydriding – dehydring kinetics, easy activation and less expensive. The
TiMnx (x=1.5 -1.8 wt%) is the Hydrogen storage capacity of the Ti-Mn alloy which has C14 type hexagonal crystal structure.

TiMn$_2$ and TiMn$_{1.5}$ are the two useful intermetallic compounds of the Ti-Mn hydrogen storage material. The activation energy for diffusion of Mn in Ti, as calculated form the tracer impurity diffusion is 242.8kJ per mole and the corresponding diffusion coefficient is 4.3 cm$^2$ per second between 930°C and 1690°C where beta phase is stable [29]. Due to high equilibrium plateau pressure and the characterization of the hydrides by large hysteresis effect, the practical application of these alloys has been limited. Ti-Mn is a eutectic system with a partial solid solubility in the $\alpha$- and $\beta$-phases. This system exhibits eutectoid decomposition of the $\beta$ phase [11].

The application of titanium-manganese (Ti-Mn) alloys has been limited to

1. hydrogen storage tanks,
2. bio-medical implants and a very few in
3. Aerospace applications.

Ti$_8$Mn alloys were used in aerospace and later replaced by Ti64. TiMn$_2$ laves phase are used for hydrogen storage. The Ti$_2$Mn, Ti$_5$Mn and Ti$_8$Mn alloys exhibit cytotoxicity and cell proliferation of the human osteoblast and therefore have the potential for the use in bio-medical field as new bone substitutes and dental implants [12,13,14,15,16].
CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 Deposition of Ti-Mn Alloy

The initial material that was used to deposit the Ti-Mn alloy consisted of pure Ti powder and Mn powder. These powders were commercially obtained from Alfa Aesar. The compositions of the alloy are given in the table below:

<table>
<thead>
<tr>
<th>S.NO</th>
<th>Sample</th>
<th>Manganese (wt %)</th>
<th>Titanium (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti to Ti-15Mn</td>
<td>15</td>
<td>85</td>
</tr>
</tbody>
</table>

Table 3. Comparison of Ti-Mn alloy

3.2 Laser Engineered Net Shaping (LENS™)

Two powder feeders were used and independently controlled using the LENS™ computer. The first powder feeder contained pure, elemental titanium powder. The second powder feeder contained the mixture of titanium and manganese as described in the following text. Measured proportions of powders were taken in 5.6:1 ratio to compose 85% of Ti and 15% of Mn by weight. The weighed powders were placed into Nalgene bottles and tumbled in a twin roller tube mill for three hours to produce, nominally, a homogenous powder mixture. This mixture was loaded into a powder feeder attached to the LENS deposition system. The powder is carried on an inert argon gas stream and fed into the melt pool via four co-incident nozzles whose focal point is also coincident with the focused laser beam. The wavelength of laser beam was 1.06μm, generated by Nd:YAG crystal powered at 410W.

A CAD file containing the model of the sample initiated the metal deposition. The flow rate of the powder was set at 2.57g/min. The powder was fed into a molten pool on
the substrate, where it was melted, adding volume to the molten pool. The small molten pool solidifies rapidly and a tiny alloy deposition was created. The laser scan speed was maintained at 10 in/min with hatch width of 0.018 inch and a layer thickness of 0.01 inch. The flow rates of pure titanium powder and the mixture of titanium-manganese were controlled by the computer and changed every few layers so that a digital step gradient could approximate a linear composition gradient. The glove box was purged with Argon gas with a flow rate of 3 l/min to protect the alloy deposition from contamination. The oxygen content in the glove box was maintained below 10 parts per million (PPM) to ensure no oxidation of the molten took place.

The deposition was carried out till a sample measuring 0.4-inch diameter and 1 inch high was obtained. A substrate of Ti-64 was used for all depositions. Following deposition, the specimens were sectioned using the electric discharge machine (EDM).

3.3 Thermal Processing

The then obtained cylindrical sample is sliced into six pieces using the ALLIED TechCut 5™ sectioning machine, along the length of the sample. All the six sliced Ti-Mn samples were subjected to different thermal processing. A set of three samples were subjected to
intermittent soaking processing after being held at 975°C for 30 minutes. Then, the furnace
temperature is set to 700°C and the sample is held at 700°C for 2 hours and is air-cooled. This
treatment is referred to cycle ‘A’. The same type of heat treatment is carried out on the other
two samples, with a change in the temperature being held for 2 hours at 600°C and 500°C and
then air cooled. These will be referred to as cycle ‘B’ and cycle ‘C’ respectively.

The other three samples were held in the furnace for 30 minutes with the temperature set at
975°C. Following this thermal treatment, these samples were subjected to different cooling
rates, corresponding to furnace cool, air cool and water quench. These will be refered to a cycle
‘D’, ‘E’ and ‘F’ respectively.

Fig.6a Illustration of the heat treatment procedures followed during the experiments
After heat treatment, each sample is mounted with ALLIED mounting machine using a conducting resin in order to prevent the electrostatic charge during imaging. Each mounted sample is then polished from coarse polishing to fine polishing using 120, 200, 400, 600 and 800 grit papers. In the final step of polishing, a silicon polishing cloth along with colloidal silica suspension is used to get a mirror finish. All the above-mentioned polishing steps are carried out on a semi-automatic parallel polisher.

The polished samples are cleaned in ultrasonic cleaning machine. The cleaning process is carried out in five different rounds for each sample. The first round of cleaning is with water, second round with distilled water, third round with surfactant, and fourth round with
methanol, with every round carried out for three minutes. Finally, the sample is rinsed with methanol and dried with compressed air and is kept in vacuum oven for at least two hours which ensures that the remains of the alcohol would get evaporated and also to avoid the degassing, when the sample is ready for SEM study.

3.4 Characterization of the Gradient Ti-xMn alloy

3.4.1 Scanning Electron Microscopy (SEM)

SEM is a type of electron microscope in which the images of a sample can be produced by scanning the surface of the given sample for imaging. In SEM, imaging is performed with the help of a focused beam of electrons. The interaction of the electrons with the sample, produce various signals, which are detected and carry the information of the sample’s surface topography and composition. Backscattered electron detector (EBSD) is used to generate the images of the microstructures.

3.4.2 Energy Dispersive Spectroscopy (EDS)

EDS is a technique used to determine the chemical composition of a sample using X-rays generated with the electron beam. This is an analytical technique, on which the results depend on the signals generated from the interaction volume produced with the electron beam. This is an efficient technique to determine the chemical composition of an unknown material with a fundamental principle that each element exhibits distinct “characteristic” peaks within the
spectrum. In this characterization technique, electrons or X-rays are used as the major source to determine the chemical composition of the given sample.

3.4.3 Focused Ion Beam (FIB)

FIB is used to prepare ultra thin samples for TEM studies. Site specific TEM samples were prepared using Ga+ ions to mill and thin the samples. A FEI DualBeam™ (focused ion beam/scanning electron microscope) was used to prepare the samples from pre-determined locations.

3.4.4 Transmission Electron Microscopy (TEM)

TEM is used to characterize the materials under high level spatial resolution, with the beam of electrons passing through the specimen which is thinned to electron transparent level. With the electromagnetic lenses, the electrons are focused to generate the image which is observed on a fluorescent screen, which is recorded using a CCD camera. A Philips EM420 TEM is used to study and analyze the Ti-15Mn graded samples. Electron transparent and site-specific samples for TEM study are prepared using Focused Ion Beam (FIB), a non-conventional technique.
3.4.5 X-Ray Diffraction (XRD)

XRD tests were done using the Rigaku Ultima III X-ray diffraction system with a radiation of Cu-K\(\alpha\) and a wavelength of 1.541 Å was employed to interpret the phase changes in the system. Later, the peak analysis was carried out using the Jade 7 software.

3.5 Mechanical Testing: Vickers Micro Hardness

The micro hardness tests were performed on the six Ti-Mn alloy samples using a SHIMADZU Vickers micro hardness tester at a load of 200g for 10 seconds. The hardness tests were carried out at ambient temperature (RT). Constant indent spacing was maintained as 1mm. The hardness was measured along the longitudinal section of the sample through the alloy chemistry gradient. The number of indentation varied between 23-29 depending on the individual sample size.
CHAPTER 4
RESULTS AND DISCUSSIONS

4.1 Continuous Cooling Studies – Water Quenching, Air Cooling, Furnace Cooling

Figures 7-9 show the influence of cooling rate on the microstructures of various compositions produced along the Ti-xMn gradient. Figures 7(a-d) show backscattered scanning electron micrographs for the water quenched gradient. As can be seen in figs. 7(a,b), at low Mn concentrations (~3.0 and ~4.5, respectively) the microstructure is comprised of a titanium martensite. The scale of the martensite is very refined, suggesting that either a highly refined α’ (hcp) martensite or the α” (orthorhombic) martensite is present. This is surprising as a coarse lath-like α’ martensite can be observed in the Ti-xMo and Ti-xV systems at similar solute levels. However, the unusual crystal structure of elemental Mn (space group 217, I-43m) which has a lattice parameter of ~8.9Å and 58 atoms per unit cell distributed as differently ‘sized’ atoms due to local differences in their valence, suggests that the somewhat variable valence state of the Mn leads to either a disruption in the regularity of the long-range atomic displacements associated with the bcc->hcp martensitic transformation or an early symmetry disruptions (the cause of α” martensite) not expected by the atomic size.
Figure 7(c,d) show unusual microstructural features that are observed along the Ti-xMn water quenched specimen. In figure 7(c), features in the Ti-xMn water quenched specimens exhibit unique microstructural evolution; for example, subgrain boundaries are present in the microstructure, and appear to be decorated by a unknown microstructural feature. As one would expect a region transitioning between a fully martensitic (α’ or α”) structure and a mixed β+(α’ or α”) structure, such a region is not necessarily surprising. However, in titanium alloys the three-phase (β, α’ or α”, ω) region is typically a very narrow composition region and very
difficult to capture – thus, this result is unexpected. Further, the preferential occurrence of a martensite along a subgrain boundary is somewhat unexpected. The cause is unknown, but is likely attributed to either small differences in composition at subgrain boundaries or differences in the degrees of lattice strain at subgrain boundaries that might more easily result in the formation of a martensite. One consequence of fig. 7(c) is that it is possible to preliminarily assess the composition above which the beta phase is ‘fully’ stabilized in water-quenched specimens. This assessment is important as the well-known “Moly equivalency” equation, given in the equation below, is based upon compositions above which titanium martensites are no longer stable. However, in the conventional form (enclosed by \{\}), Mn is not given, owing to the fact that this system has often been neglected. If one assesses complete beta to be between 7.5 and 8.0 wt% Mn (based upon micrographs from ~7wt%Mn and ~8wt%Mn of Fig.8 ), a new term could be added with the prefactor of ~1.1 to 1.2 wt%Mn, as noted by square brackets at the end.

\[
\{\text{Mo Equiv. =1.0 Mo+0.67 V+0.44 W+0.28 Nb+ 0.22 Ta+ 1.6 Cr+ 2.9 Fe} \ [+ 1.33\text{Mn}]\]

There are two microstructural features that are observed in fig. 7(d). The first is the fact that most of the beta grains are fully β-stabilized. The second is the fact that there are coarse, dark features that appear in some of the grains near boundaries. The precise nature of these phases are unknown, but are likely oxygen-stabilized alpha phases that are observed only near the very edges of the specimen in composition regions highly enriched in Mn.
Figures 8 and 9 show the backscattered electron micrographs for the air-cooled specimen and furnace-cooled specimens. When considering the two figures together, a few important observations can be made. The first is that the scale of the basket weave microstructure formed in the air-cooled specimens is highly refined at Mn concentrations of approximately 4wt%Mn, whereas similar compositions in the furnace-cooled specimens exhibit a coarse colony microstructure. Such features are analogous with the influence of V on the microstructures in Ti-6Al-4V. At compositions above ~6wt%Mn, the microstructure contains highly refined alpha precipitates in a beta matrix in the air-cooled material, and above a composition of ~7.5% Mn, the microstructure appears to be fully beta stabilized. Both the highly refined alpha laths and the fully beta stabilized microstructures have the highest hardness levels for the air-cooled specimens (~350 Vickers), far exceeding even the highest hardness levels in the furnace cooled specimens (~270 Vickers). The highly refined alpha and the retention of a fully beta microstructure at the relatively low solute levels (indeed, even below the amount required for complete beta stability in water-quenched Ti-Mo gradients) points to Mn as being a potentially slow diffusing species in solid titanium. This is an interesting observation, as the Ti-Mn alloys have largely been ignored, as they are prone to very large compositional fluctuations within the liquid phase during conventional melt-based practices.
Fig. 8 Back scattered SEM micrographs from Ti-xMn Lens gradient, heat treated from room temperature to 975°C for 30 min and then Air cooled (cycle ‘D’).
Fig. 9 Backscattered electron micrographs recorded from Ti-xMn Lens gradient, heat treated from room temperature to 975°C for 30 min and then Furnace cooled (cycle ‘E’).
FIB specimens were prepared from regions with nominally complete β-stability as observed using the SEM for the water quenched Ti-xMn gradient. This was done in order to assess the presence of the ω phase using the TEM. The diffraction patterns revealed strong ω reflections, which would explain the very high hardness observed (~450 Vickers hardness) for any region containing either β or β+(α’ or α”), as the β phase would be expected to contain ultrafine ω precipitates. However, a very surprising result was observed, in addition to the ω reflections. Figure 10 shows a [012]β zone axis of a FIB foil that has been carefully placed onto a pure Al nano grained film that is used as an internal calibration standard. As the d-spacing for the standard sample is known, so the camera length (sample-to-camera) can be determined, and therefore used to find the d-spacing of the unknown sample i.e., Ti-Mn in our study. From the diffraction pattern obtained and shown in fig. 10, the lattice constant of β-Ti was calculated and a value of 3.607Å was obtained. This is a surprisingly large lattice parameter, as the lattice parameter of pure β-Ti is 3.32Å, and the reported values of Ti-12.3Mn are less than this [30]. In order to understand what may be occurring, a more representative method of the sample, X-Ray diffraction experiment was conducted, and the results are shown in fig. 11. Based on Bragg’s law equation (nλ=2d sinθ), calculations of the lattice parameter from the XRD data, the lattice parameter of this same region of the specimen obtained (~12wt%Mn) is 3.24Å. Clearly, there is a discrepancy between the lattice constant calculations from both experiments, though both values are considered to be accurate as an internal calibration was used for the TEM, which is prone to experimental issues when determining d-spacing. Interestingly, although the lattice parameter may change, the position of the ω reflections remains exactly at the 1/3 and 2/3 g=112 positions. Although the precise origin of this difference in experimental observation
is not known, three possible explanations are given. The first possible explanation is one of stress relaxation of TEM thin films. Such stress-relaxation has been known to occur in TEM thin films and result in loss of symmetry or changes in crystal structures. It would be surprising that stress relaxation would result in a lattice change of ~10% and the constraint provided in-plane in the TEM specimen. However, Mn does desire to undergo a reduction in symmetry in its elemental form. The second possible explanation is that Ga+ ions are used to prepare these thin specimens. It is possible that Ga+ ions may induce a phase change or trigger internal bulk stress relaxation. The third possibility is that there are very rapid transient temperature fluctuations when TEM foils are prepared using the FIB. It is possible that such temperature excursions result in such a change. Much more work is needed to understand this interesting observation and it will be left to future research efforts. For instance, conventional TEM sample preparation should be done to study the probable effects of sample preparation on lattice parameter changes.

Fig. 10 Omega phase observation in the diffraction pattern from TEM study on Ti-xMn sample subjected to cycle ‘F’ heat-treatment with an internal calibration standard.
In addition to the unusual discrepancy in the d-spacing as determined using these two different approaches, TEM has been used to reveal other features present in the water-quenched Ti-xMn sample. The TEM micrographs are shown in fig. 12(a-d). Figures 12(a,b) show the martensite that is present in ~3wt%Mn (equivalent to fig. 7(a)). Figure 12(c) is from ~6wt%Mn (equivalent to fig. 7(c)), and clearly shows the coexistence of a beta matrix and martensite laths. In addition, fig. 12(d) is a [113]β zone axis diffraction pattern showing the presence of athermal ω following the water quench.
Fig. 12 Transmission electron micrographs taken from along the Ti-xMn gradient.
4.2 Two-Step Isothermal Histories (Direct Aging)

While continuous cooling can reveal aspects of microstructural evolution in highly controlled laboratory environments, they do not always result in the greatest balance of properties. Thus, the practice in industry is to, at times, execute more complex direct aging experiments. Additionally, in the recent times, researchers have discovered an unusual phase transformation route – so named ‘pseudospinodal’ – in titanium alloys that results in highly refined alpha laths in a parent beta matrix [1]. Both the industrial practice and the newly identified ‘pseudospinodal’ have motivated the direct aging studies of the Ti-xMn gradients. All three specimens were β-solutionized and directly step-cooled to the aging temperature (i.e., 500°C, 600°C, and 700°C) and held for two hours and then air-cooled. Selected ‘representative’ backscattered SEM for each of these three direct aging treatments are shown in Figs. 13-15 which correspond to 700°C, 600°C, and 500°C respectively.

Figures 13(a-e) show clearly, and not surprisingly, that as the Mn content increases the volume fraction of α decreases and β increases. Figure 14(a-e) show the same trend, although with a larger fraction of α and a lower fraction of β at the equivalent compositions as the locations shown in figs. 13(a-e). This is rationally explained as the hcp α is a more stable structure at lower temperatures, and can be demonstrated by applying the lever rule to any composition at either 700°C or 600°C. Figure 15(a-e) shows the microstructures for the gradient directly aged at 500°C. This gradient also contains only two phases, the α and β phases, which is not what is expected for the system at equilibrium – i.e., it is not what is expected given the phase diagram. The phase diagram indicates that the two stable phases below ~550°C are hcp α and the intermetallic α-TiMn. The fact that there are no obvious morphological changes to the
Fig. 13 A series of back scattered SEM images from Ti-xMn Lens gradient, heat treated from room temperature to 975°C for 30 min and held at 700°C for 2hrs and then Air cooled (cycle A)
two phases suggest that the Ti-Mn system is a very sluggish system when it comes to diffusion and phase transformation. The Ti-Cr system is similarly sluggish when it comes to precipitating the intermetallic phase – indeed, although a thermodynamically stable phase, TiCr₂, is not often observed <5wt%Cr.
Fig. 14 A series of back scattered SEM images from Ti-xMn Lens gradient, heat treated from room temperature to 975°C for 30 min and held at 600°C for 2hrs and then Air cooled (cycle ‘B’).
Fig. 15 A series of back scattered SEM images from Ti-xMn Lens gradient, heat treated from room temperature to 975°C for 30 min and held at 500°C for 2hrs and then Air cooled (cycle ‘C’).
Figures 13-15 show the backscattered SEM micrographs for compositions up to 8wt%Mn. While this is a useful composition range to explore some aspects of microstructure, such as phase fraction, observations of the complex phase mixtures of alpha and beta occurring at a composition of ~10-12wt%Mn, as shown in fig. 16. In this figure, two different compositions directly aged at 600°C are shown. When comparing these two images with figure 14, it is clear that the scale of the microstructure is more highly refined. Sub-regions of these micrographs have been extracted and are shown with greater detail. As a comparison, a similar alloy of the coupon directly aged at 500°C is shown.

![Fig.16 Comparison of backscattered electron micrographs of the 600°C and 700°C direct aged specimens.](image)
It is interesting that the 500°C direct age has regions that are coarser than the 600°C direct age while having other regions that appear at an equivalent scale. Interestingly, the 500°C direct age lies below the invariant temperature for the β→α+TiMn eutectoid reaction. The fact that the 500°C sample was held below the eutectoid explains the variation in the degree of supercooling there by free energy change that results in a microstructure containing both coarser and highly refined alpha laths. The coarser laths have their origins in the high temperature decomposition (975°C) of beta, where growth dominates nucleation. The secondary decomposition occurring during the step treatments (500°C) is observed to have resulted in secondary alpha in the form of the fine scale laths. This may be explained by higher nucleation than growth at lowered transformation temperatures – 500°C. These features are detailed in fig. 17.

![Fig.17 Backscattered electron micrographs with highly localized differences in the α-lath size. Local compositional inhomogenities are probable sources of such differences.](image)
CHAPTER 5

CONCLUSIONS

The significant experimental observations, of this work are as follows:

1. Manganese is a more potent β-stabilizer than Mo, as designated by the content beyond which β is stable upon water quenching. This is consistent with other monotectoid forming elements. The precise value, previously not established, has been added to the Mo-equivalency equation.

2. There is an extended compositional range at room temperature between the $M_{\text{start}}$, $M_{\text{finish}}$, and Martensites can be observed to preferentially form along subgrain boundaries at compositions lying between the $M_s$ and $M_f$ compositions.

3. The size of the martensite appears to be smaller than that observed in other work for the Ti-xMo system. The appearance is highly suggestive of a martensite that is being distorted by the solute.

4. There is an apparent conflict in the lattice parameter as measured by a calibrated TEM experiment and a Bragg-Brentano X-Ray Diffraction experiment. The origin of this difference is not known, though three potential causes are given.

   - Stress relaxation in TEM foils
   - $\text{Ga}^+$ ions
   - Temperature artifact
5. The kinetics of the Ti-Mn system appear to be very sluggish, and at intermediate temperatures below the invariant temperature and for solute levels up to 10wt%Mn, the intermetallic TiMn is not observed.

6. There appears to be a difference in the distribution of the laths at temperatures above and below the invariant reaction.
CHAPTER 6

FUTURE WORK

1. TEM diffraction or X-ray diffraction, and perhaps precession electron diffraction is necessary to determine the precise nature of the martensite present.

2. Care in preparation of TEM specimens, including Ar+ cryomilling, is suggested to eliminate preparation as a cause.

3. Studies of kinetics for the precipitation of TiMn should be conducted to determine precisely how sluggish this reaction is.

4. More detailed assessments of the microstructures needs to be conducted, including both TEM and possibly local electrode atom probe.
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