Nucleation Mechanisms of Refined Alpha Microstructure in Beta Titanium Alloys

Dissertation

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Abstract

Due to a great combination of physical and mechanical properties, β titanium alloys have become promising candidates in the field of chemical industry, aerospace and biomedical materials. The microstructure of β titanium alloys is the governing factor that determines their properties and performances, especially the size scale, distribution and volume fraction of precipitate phase in parent phase matrix. Therefore in order to enhance the performance of β titanium alloys, it is critical to obtain a thorough understanding of microstructural evolution in β titanium alloys upon various thermal and/or mechanical processes. The present work is focusing on the study of nucleation mechanisms of refined α microstructure and super-refined α microstructure in β titanium alloys in order to study the influence of instabilities within parent phase matrix on precipitates nucleation, including compositional instabilities and/or structural instabilities.

The current study is primarily conducted in Ti-5Al-5Mo-5V-3Cr (wt%, Ti-5553), a commercial material for aerospace application. Refined and super-refined precipitates microstructure in Ti-5553 are obtained under specific accurate temperature controlled heat treatments. The characteristics of either microstructure are investigated in details using various characterization techniques, such as SEM, TEM, STEM, HRSTEM and 3D atom probe to describe the features of microstructure in the aspect of morphology,
distribution, structure and composition. Nucleation mechanisms of refined and super-refined precipitates are proposed in order to fully explain the features of different precipitates microstructure in Ti-5553. The necessary thermodynamic conditions and detailed process of phase transformations are introduced. In order to verify the reliability of proposed nucleation mechanisms, thermodynamic calculation and phase field modeling simulation are accomplished using the database of simple binary Ti-Mo system. Therefore, the nucleation mechanisms proposed could successfully explain the features of refined and super-refined precipitates microstructure in Ti-5553, validated by thermodynamic calculations and phase field modeling simulation.

In addition to the study of microstructure evolution in β titanium alloys upon various heat treatment conditions, another effort made in the current study is to apply various phase transformation analysis tools on titanium alloys in order to capture the initial stage of precipitation and investigate the kinetics of precipitation. Especially Electro-Thermo-Mechanical Tester (ETMT) is used to in-situ measure the physical properties change of Ti-5553 during heat treatment and therefore analyze the kinetics of phase transformation. This part of work can be treated as complementary work of the study of microstructure evolution in β titanium alloys.

In summary, refined and super-refined precipitates microstructure in Ti-5553 are studied using both modern characterization techniques and computational simulation. Nucleation mechanisms are proposed to explain all the features of two specific microstructures and
critical heat treatment conditions are figured out. Therefore, this insightful study is not only beneficial to understanding the details of phase transformation in the scientific aspect but also complement to selection of heat treatment conditions in industry area.
Dedication

This document is dedicated to my parents, Qi Zheng and Ping Li.
Acknowledgments

This was the last part I completed when I was writing my thesis, because too many times too many people’s names crowded into my mind that I wished to give my sincere thanks to. During my PhD study at The Ohio State University, I have been so lucky to study and work with many people who helped and supported me to arrive where I am at right now.

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achieved today can make them feel proud and I will spend all my life with all my effort to bring them more honor and happiness.
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Chapter 1

Introduction

The element of titanium was found in the year of 1791. After World War II, the interests in the properties of titanium alloys started attracting people’s attention[1]. Due to an excellent properties combination of strength, toughness, ductility and corrosion resistance, nowadays titanium alloys are used in wide range of fields. Chemical industry is the area that consumes largest amount of titanium due to its excellent corrosion resistance especially at the presence of oxidizing acids. Next area that titanium and titanium alloys are widely used is aero-space mainly due to its great strength to weight ratio therefore to save huge amount of fuel. Together with stainless steel and Co-based alloys, titanium alloy is one of the three main metallic biomaterials due to its high strength, low density and great corrosion resistance[2]. However the relative high cost of titanium and its alloys is still a serious problem that limits the application of titanium alloys. Therefore, further understanding of microstructural evolutions in titanium alloys upon various thermal/mechanical processes is essential to better control the cost, due to a better choice between processing, microstructure and properties relationship.
In recent years, β titanium alloys start to attract more and more attention in both aerospace area and biomedical field. Compared to the originally most widely used α/β titanium alloys, such as Ti-6Al-4V, there are several advantages of β titanium alloys[3]. Firstly, higher yield stress could be obtained in β titanium alloy; secondly, β titanium alloys could be processed in a lower temperature range and some of β titanium alloys can be cold deformable; thirdly, same level or even better corrosion resistance can be achieved using β titanium alloys[2]. In the Boeing 777, in which Ti-6Al-4V is not the dominant alloy, Ti-10V-2Fe-3Al high strength forgings, β titanium alloy, are majorly used for the landing gear structure in order to save hundreds of kilograms instead of high-strength low-alloy steel; Ti-14.7Mo-2.7Nb-3Al-0.27Si (β-21S) is used for high temperature application due to its excellent oxidation resistance with creep properties comparable to Ti-6Al-4V; Ti-15V-3Cr-3Al-3Sn is used in the environmental control system ducting, clips and floor support structure[4-6]. Although pure titanium and Ti-6Al-4V are still the dominant biomedical application materials, β titanium alloys composed of non-toxic element instead of vanadium is becoming attractive due to its mechanical biocompatibility[7, 8]. For example, molybdenum, a typical non-toxic element, is added to titanium to enhance corrosion resistance. Ti-30Mo exhibits better corrosion resistance than pure titanium in 35% HCl[9].

The properties of β titanium alloys highly depend on their internal microstructure, which in most of cases is composed of two phases, namely α phase and β phase. The volume
fraction, morphology, size scale and distribution of α phase all could influence the physical and mechanical properties of β titanium alloys significantly[2]. Therefore a complete and detail understanding of phase transformation and microstructural evolution, especially α phase related transformations, in β titanium alloys is crucial in order to better manipulate the performance of β titanium upon various requests.

The present work focuses on the study of the characteristics and transformation mechanism of refined intragranular α phase and super-refined intragranular α phase in β titanium alloys using advanced characterization techniques. The distribution and size scale of α phase is restricted and therefore could provide potential superior properties. The critical factors to obtain refined α precipitates, such as thermal conditions, heating rate and isothermal holding temperature are studied in detail. The characteristics of refined and super-refined α phase will be introduced in the aspect of morphology, composition and crystallography. Based on the characteristic of α phase and microstructural evolution path, different types of non-classical transformation mechanisms are proposed. Two β titanium alloys are primarily selected for the current study, which are both provided by TIMETAL Corporation in Henderson, NV. The first one is Ti-5Al-5Mo-5V-3Cr (wt%), a newly developed β titanium alloy for the application of landing gear in aerospace. The other one is Ti-15wt%Mo, a type of biomedical application material. Although two alloys both belong to β titanium alloys, there are
different types and amount of $\alpha$ and $\beta$ phase stabilizers in two alloys, which leads to different characteristics during phase transformations.

This dissertation is made up of 7 chapters. In the 2$^{nd}$ chapter, the physical metallurgy of titanium and titanium alloy is introduced, with an emphasis about the classical nucleation theory of $\alpha$ precipitates in titanium alloys. Chapter 3 covers all the facilities, experiment conditions and experiment procedures used in the current study. The 4$^{th}$ chapter focuses on the study of refined $\alpha$ precipitates in $\beta$ titanium alloys. The characteristics of refined $\alpha$ phase are described in details. A non-classical homogeneous transformation mechanism is proposed in titanium alloys for the first time and a new transformation path way is discussed. In the 5$^{th}$ chapter, super-refined $\alpha$ precipitate in $\beta$ titanium alloys is introduced. The electron microscope and 3D atom probe results showing characteristics of super-refined $\alpha$ phase are discussed and the critical thermal conditions to obtain super-refined $\alpha$ phase are illustrated. The influence of pre-formed metastable phase is studied using phase field modeling and the possible transformation mechanism is verified using both simulation and thermodynamic calculation. In the 6$^{th}$ chapter, results of phase transformation analysis in titanium alloys using electrical resistivity measurement are discussed. The focus is to show the application of different techniques in studying the phase transformation in titanium alloys, such as capture the initial stage of $\alpha$ precipitation during continuous heating and investigate the kinetics of $\alpha$ precipitation during isothermal aging. Finally in chapter 7, all the transformation mechanisms with critical
experiment results of refined $\alpha$ precipitates and super-refined $\alpha$ precipitates are summarized and some necessary future work is pointed out.
Chapter 2
Physical Metallurgy of Titanium and Titanium Alloys

2.1 Introduction
In this chapter, the general background of pure titanium and titanium alloys, the classical nucleation and growth theory and techniques normally used to identify and analyze phase transformations are introduced. The chapter starts from the history of titanium and the physical metallurgy of pure titanium. Different phases present in titanium alloys and category of titanium alloys will be discussed secondly. Then various types of phase transformations, especially $\alpha$ phase related phase transformations, will be introduced in detail. In the end, different techniques used in materials science to analyze phase transformations are described.

2.2 History of Titanium
Titanium is the 22\textsuperscript{nd} element in the periodic table of elements. It is a transition metal element with the mass number 47.867. Its electronic configuration is $1s^22s^22p^63s^23p^63d^24s^2[10]$. 

6
Titanium was found in the year of 1791 by British mineralogist and chemist, William Gregor in the Menachan Valley in Cornwall, England. After isolating the “black sand” known as “ilmenite” now, William removed the iron and produced impure oxide of a new element, which he named mechanite after its found location. 4 years later, Martin Heinrich Klaproth, a German chemist, isolated titanium oxide from a kind of mineral produced in Hungary known as “rutlie” independently and he named the element “Titanium” to indicate the difficulty to extract it from mineral. In the year of 1932, the “father of titanium industry”, the chemist from Luxembourg, Milhem Justin Kroll utilized TiCl4 and calcium to produce significant amount of titanium. Later, at the beginning of the World War II, he modified the method and used magnesium instead of calcium to reduce TiCl4 in inert atmosphere. This method is called “Kroll process” and is still the most widely used commercial process now [1, 11].

\[
4\text{TiCl}_4 (\text{gas}) + 2\text{Mg (liquid)} \rightarrow 4\text{Ti (solid)} + 2\text{MgCl}_2 (\text{liquid})
\]

Titanium ranks the fourth abundant element after aluminum, iron and magnesium, about 0.6% in the earth crust. However, neither pure state titanium nor ore of high concentration titanium has ever been found in nature. Besides, the processing of titanium is rather difficult. Therefore, until now, there is still no continuous process present to produce titanium like other structural metals[1].

2.3 Physical Metallurgy of Pure Titanium
Compared to other commonly practically applied metals shown in table 2.1, pure titanium exhibits the best strength to density ratio, the highest melting point and the greatest corrosion resistance. The density of pure titanium is 4.5 g/cm$^3$ and the yield strength of pure titanium can be higher than 1000MPa [2].

Pure titanium could be in two types of crystal structure, in other words there are two allotropes in pure titanium, namely $\alpha$ titanium and $\beta$ titanium. Either of two allotropes is only stable at certain temperature range. The temperature at which one allotrope transforms into the other is called transus temperature. The transus temperature of pure titanium is 882°C. Below transus temperature it is called $\alpha$ titanium and above this transus temperature it is called $\beta$ titanium[1, 2].

The crystal structure of pure $\alpha$ titanium is hexagonal close packed (HCP) structure of lattice parameter, $a$=0.295nm and $c$=0.468nm, giving a $c/a$ ratio of 1.587. The crystal structure of pure $\beta$ titanium is body centered cubic (BCC) structure of lattice parameter, $a$=0.332nm, shown in figure 2.1 [1].

The properties of pure titanium are highly dependent on the presence of two allotropes[1]. For example, both diffusion and plastic deformation properties are closely connected with the respective structure. The diffusion in HCP structure is much slower than more open BCC structure, so the creep resistance of $\alpha$ titanium is better than that of
\( \beta \) titanium; the pronounced elastic anisotropy is due to the anisotropy in HCP structure, while along c direction in HCP \( \alpha \) titanium the Young’s modulus is 145GPa and along a direction 100GPa. The elastic anisotropy in pure \( \alpha \) titanium could be weakened by polycrystallizing[2].

2.4 Phases in titanium alloys

Phase is a region of material which could be of the same crystal structure and almost same composition, and exhibit uniform properties[12]. With addition of a wide range of elements into titanium, at different temperature and pressure conditions, in titanium and its alloys there are two major equilibrium phases, namely \( \alpha \) phase and \( \beta \) phase, four important metastable phases, namely \( \alpha' \) phase, \( \alpha'' \) phase, \( \omega \) phase and \( \beta' \) phase[2, 13, 14].

2.4.1 Equilibrium Phases

a) \( \alpha \) phase

\( \alpha \) phase is of HCP structure and its structure can be represented by two atoms at (0, 0, 0, 0) and \((1/3, 1/3, -2/3, 1/2)\) positions in the unit cell. \( \alpha \) phase belongs to the space group of P6\(_3\)mmc. As mentioned in the previous section, the elastic moduli of single \( \alpha \) phase are anisotropic, but such anisotropy could be less notable in polycrystalline \( \alpha \). With different addition into titanium, the c/a ratio could be not the same. However, its value is usually smaller than the ideal HCP c/a ratio, 1.633. Therefore, the main slip system in \( \alpha \) phase is
the closed packed $<1\bar{1}20>$ direction on the prism plane \{10\bar{1}0\} rather than on the basal plane[2].

\(\alpha\) phase can be divided into various types based on different requirement. Depending on nucleation sites, \(\alpha\) phase can be divided into grain boundary \(\alpha\), intergranular \(\alpha\) and intragranular \(\alpha\). Grain boundary \(\alpha\) is the \(\alpha\) phase that nucleates at \(\beta\) phase grain boundary and grows along the boundary. It is also named as allotrimorph \(\alpha\). Intergranular \(\alpha\) nucleates at \(\beta\) phase grain boundary or grain boundary \(\alpha\) and grows into the interior of \(\beta\) phase grain. It is also named as Widmanstätten \(\alpha\). Intragranular \(\alpha\) nucleates from defects such as vacancies and dislocations or metastable phases such as \(\omega\) phases or \(\beta'\) phase in the interior \(\beta\) grain and grows within \(\beta\) grain[2].

Depending on the morphology, \(\alpha\) phase can be divided into colony \(\alpha\), basketwave \(\alpha\) and globular \(\alpha\). Colony \(\alpha\) is formed in slow cooling process and a cluster of laths morphology belonging to only one variant. Basketwave \(\alpha\) is formed in fast cooling process and different clusters of laths morphology belonging to various variants. Globular \(\alpha\) is likely to be formed in pre-worked system at triple \(\beta\) grains intersection region and of massive morphology[1, 2, 10].
Depending on the size scale and forming sequence, $\alpha$ phase is divided into primary $\alpha$ and secondary $\alpha$. In most of cases, during heat treatment and/or mechanical treatment, not all $\alpha$ precipitates form uniformly in titanium alloys. Primary $\alpha$ is the $\alpha$ phase formed in advance and always of larger size scale, while secondary $\alpha$ is formed after primary $\alpha$ and always of smaller size scale than primary $\alpha$\cite{2}. However, there is no strict difference between primary $\alpha$ and secondary $\alpha$. It is only terminology to distinct $\alpha$ phase of different size scales in the system. One thing needs to be emphasized is that preformed primary $\alpha$ has pronounced influence on secondary $\alpha$ formation. The preformed $\alpha/\beta$ interface could act as favorable nucleation site of newly $\alpha$ phase\cite{15}. This will be discussed in details in the section 2.6.1.

\textit{b) $\beta$ phase}

$\beta$ phase exhibits body centered cubic (BCC) structure, which can be defined by two atoms at (0, 0, 0) and (1/2, 1/2, 1/2) positions in the unit cell. It belongs to the space group of Im\hspace{0.2mm}3m. Compared to HCP structure, BCC structure is more open, in which atoms may vibrate more severely. Therefore, $\beta$ phase is more stable than $\alpha$ phase when the temperature is elevated. The main slip system in BCC structure is closed packed direction $<111>$ on \{110\} plane\cite{2, 10}.  
In titanium alloys, the additional elements could be divided into α phase stabilizer, β phase stabilizer and neural element. Elements like Al, B, Sc, Ga, La, Ce, C, O, N that could raise the β transus temperature are called α phase stabilizers. O and N are interstitial elements and form peritectic system with titanium; substitutional elements Al, B, Sc, Ga, La, Ce together with interstitial element C form peritectoid system with titanium. Al equivalency is used to compare the effect of different α phase stabilizers in various multicomponent systems:

$$[\text{Al}]_{\text{eq}} = [\text{Al}] + 10[\text{O}] + 0.17[\text{Zr}] + 0.33[\text{Sn}]$$

Mo, V, Ta, Mn, Cr, Fe, Ni, Cu and Si are β phase stabilizers which could reduce the β transus temperature. β phase stabilizers can be further divided into two types depending on whether or not there is eutectoid compound present at the sufficient elevated temperature (as shown in figure 2.2). Fe, Mn, Cr, Ni, Cu, and Si are called β eutectoid stabilizers, because there is eutectoid reaction present in β titanium alloys containing these elements. On the other hand, V, Mo, Nb and Ta are called β isomorphous stabilizers. In some cases, β isomorphous stabilizers are also named as β monotectoid stabilizers, because there is β phase separation present at high solute region in the β titanium alloys containing these elements, such as Ti-Mo alloy. Similar to Al equivalency, Mo equivalency is used to compare the different effect of β phase stabilizers in various multicomponent systems[1, 2, 10]:

12
\[ [\text{Mo}]_i = [\text{Mo}] + 0.2[\text{Ta}] + 0.28[\text{Nb}] + 0.4[\text{W}] + 0.67[\text{V}] + 1.25[\text{Cr}] + 1.25[\text{Ni}] + 1.7[\text{Mn}] + 1.7[\text{Co}] + 2.5[\text{Fe}] \]

The Mo equivalency of multicomponent titanium alloys can be determined using several different methods. \( \beta \) transus temperature measurement and \( \beta \) approach curve can be used to quantitatively determine the Mo equivalency of titanium alloys; while as-quenched state microstructure is good for qualitative indication of Mo equivalency of titanium alloys\[16, 17\].

1) \( \beta \) transus temperature

\( \beta \) phase stabilizer is defined as the element that could reduce \( \beta \) transus temperature after adding the element into titanium. Therefore, Mo equivalency of a multicomponent system could be determined by \( \beta \) transus temperature measurement directly which indicates the influence of all alloying elements together onto \( \beta \) transus temperature in multicomponent system. \( \beta \) transus temperature could be experimentally measured using different techniques, such as electrical resistivity measurement, differential scanning analysis and differential thermal analysis, which will be detailed introduced in the section 2.8. The measured \( \beta \) transus temperature of a specific alloy then will be compared with that of different Ti-Xwt\%Mo binary alloys. The multicomponent system will share the same Mo equivalency with the Ti-Xwt\%Mo that has the same \( \beta \) transus temperature\[17\].
2) $\beta$ approach curve

Mo equivalency of a multicomponent titanium alloy could also be determined by measuring its $\beta$ approach curve. $\beta$ approach curve is the volume fraction of $\beta$ phase in system versus temperature curve. The volume fraction of $\beta$ phase in a specific multicomponent at different temperatures could be measured by 2D or 3D image stereology technique on SEM images from materials isothermally aged at various temperatures. The volume fraction of $\beta$ phase in different Ti-Xwt%Mo alloys at various temperatures could be determined from Ti-Mo binary phase diagram or calculated directly using Thermo-Calc or Pandat software. Compared the experimentally measured $\beta$ approach curve of multicomponent titanium alloy with the calculated $\beta$ approach curve of various Ti-Mo alloys, multicomponent system’s Mo equivalency is equal to the Ti-Xwt%Mo which shares the same $\beta$ approach curve[18].

3) As-quenched state microstructure

As will be discussed in the section 2.4.2, in Ti-Mo binary system, with increasing Mo amount in alloy, different metastable phases could be present in as-quenched state alloys (shown in figure 2.3). In Ti-Xwt%Mo systems, after above $\beta$ transus temperature solution and quenching to room temperature in water: if amount of Mo is less than 4wt%, it is $\alpha'$ martensite present; if it is between 4wt% and 10wt%, $\alpha''$ martensite is present in the system; if Mo amount is between 10wt% and 20wt%, it is $\omega$ phase present; if Mo amount is higher than 20wt%, it is only $\beta$ phase present. Therefore, study of phases present at as-
quenched state microstructure of multicomponent titanium alloy using XRD or TEM diffraction pattern could provide qualitative judgment of Mo equivalency of a multicomponent titanium alloy and determine the category that it belongs to.

2.4.2 Metastable Phases

Metastable phase is the compromise of thermodynamics, the whole system is tending to the lowest gibbs free energy state, and kinetics, how fast the system could achieve the lowest gibbs free energy state\[12\]. Because only small driving force is required and no diffusion or only short range diffusion is necessary, metastable phase could be formed in short time and usually is formed before the presence of equilibrium phase.

a) \(\alpha'\) phase

\(\alpha'\) phase is a type of HCP structure martensite, the metastable phase in pure titanium, \(\alpha\) titanium alloys and near \(\alpha\) titanium alloys. It belongs to the space group \(P6_3\text{mmc}\). Actually, \(\alpha'\) phase can be treated as supersaturated \(\alpha\) phase in dilute titanium alloy. Depending on the species and content of solute, \(\alpha'\) phase exhibits different morphologies and contains different internal substructures. In Ti-Mo binary system, with increasing the Mo amount in the alloy, the morphology of \(\alpha'\) could change from massive to acicular and the internal substructure changes from dislocation to twin or fault (shown in figure 2.4a). \(\alpha'\) phase is formed in dilute titanium alloy by martensitic transformation when fast cooled from the single \(\beta\) phase temperature range. The temperature below which \(\alpha'\) martensite
could be formed is called $\alpha'$ martensite start temperature (Ms($\alpha'$)). The Ms($\alpha'$) temperature (Ms($\alpha'$)) decreases rapidly with increasing $\beta$ phase stabilizers amount into the system, which indicates $\alpha'$ phase is more difficult to form with more amount of $\beta$ phase stabilizer in multicomponent system[2, 10].

\[ b) \alpha'' \text{ phase} \]

When the amount of $\beta$ phase stabilizer increases to a critical value, $\alpha''$ phase instead of $\alpha'$ phase is formed in as-quenched titanium alloys. $\alpha''$ phase has orthorhombic structure, usually exhibits acicular morphology and contains mainly twin substructure (shown in figure 2.4b). It is formed by martensitic transformation mechanism. With increasing $\beta$ phase stabilizer amount, Ms($\alpha''$) temperature decreases rapidly and therefore $\alpha''$ phase is more difficult to form. However, the composition boundary of $\alpha'$ phase and $\alpha''$ phase formation is different for various titanium alloys. It is also necessary to point out that some authors report during $\alpha''$ phase formation, the composition within the $\alpha''$ plate is not uniform, which indicates phase separation could occur during fast cooling process within $\alpha''$ phase. Considering the speed of phase separation to occur, it could be the spinodal decomposition mode of phase separation rather than nucleation and growth mode phase separation[2, 10].

\[ c) \omega \text{ phase} \]
ω phase can be formed in titanium alloy rather than α" phase, on the condition that as-quenched titanium alloy contains even higher amount of β phase stabilizer. ω phase can be treated as a transition phase between α phase and β phase, which shows hexagonal structure. There are two types of ω phase in titanium alloys, namely athermal ω phase and isothermal ω phase. Athermal ω phase is formed during fast cooling, and its formation cannot be avoided no matter how fast the cooling rate is. Athermal ω phase is formed by diffusionless transformation mechanism and there is ω phase start temperature which decreases very fast with increasing β stabilizer amount. Isothermal ω phase is usually formed when as-quenched titanium alloys are isothermally aged or continuously aged below the ω solvus temperature. Different from athermal ω phase, there is solute diffusion occurring during isothermal ω phase formation. The morphology of isothermal ω phase may be cuboidal or ellipsoidal depending on the coherency of isothermal ω phase and parent β phase. When the misfit of isothermal ω phase and β phase is large, such as in Ti-V system, isothermal ω phase exhibits cuboidal morphology; when the misfit of isothermal ω phase and β phase is small, such as in Ti-Mo system, isothermal ω phase exhibits ellipsoidal morphology (shown in figure 2.5). The size of athermal ω particles is always small, usually from several nanometers diameter to no more than twenty nanometers diameter. Isothermal ω phase in some system, such as in Ti-Mo, is larger than that of athermal ω phase depending on the aging time and aging temperature,
while in some other systems, such as in Ti-5Al-5V-5Mo-3Cr, isothermal \( \omega \) phase is of almost the same size as athermal \( \omega \) phase\([2, 10, 19, 20]\).

d) \( \beta' \) phase

\( \beta' \) phase could form in the isomorphous/monotectoid type titanium alloys of very high amount of solute (shown in figure 2.6). It exhibits the same BCC structure as \( \beta \) phase, but has different composition. In monotectoid \( \beta \) alloy, \( \beta' \) phase could be stable at high temperature range but unstable at low temperature range. It needs to be mentioned that the terminology used here, \( \beta' \) phase, means the solute lean BCC structure phase. In some papers, \( \beta' \) is used to indicate solute rich BCC structure phase. \( \beta_1 \) and \( \beta_2 \) are also used somewhere to represent solute lean and solute rich BCC phases\([2, 3, 10]\).

2.5 Categories of titanium alloys

Titanium alloys can be divided into four classifications: \( \alpha \) alloy, \( \alpha + \beta \) alloy, metastable \( \beta \) alloy and stable \( \beta \) alloy, depending on equilibrium phases at room temperature and metastable phases in as-quenched state (shown in figure 2.7). \( \alpha \) alloy is the titanium alloy in which only \( \alpha \) phase is stable at room temperature; \( \alpha + \beta \) alloy is the titanium alloy in which \( \alpha \) and \( \beta \) phases are both stable at room temperature and martensite \( \alpha' \) or \( \alpha'' \) phase could be present in as-quenched state; metastable \( \beta \) alloy is the titanium alloy in which \( \alpha \) and \( \beta \) phases are both stable at room temperature and no martensite but \( \omega \) phase is
formed in quenching process; stable $\beta$ alloy is the titanium alloy in which only $\beta$ phase is stable at room temperature. Both metastable $\beta$ alloy and stable $\beta$ alloy belong to $\beta$ titanium alloy. Because there is no $\alpha$ phase formed in stable $\beta$ titanium alloy, the widely used commercial $\beta$ alloys are all metastable $\beta$ alloys. Therefore, $\beta$ titanium alloy usually only refer to metastable $\beta$ alloy[1, 2].

2.6 Phase Transformations in Titanium Alloys
Almost all types of solid state phase transformations could occur in titanium alloys. The main phase transformations concerned in current study are: $\beta\rightarrow\alpha+\beta$ diffusional/displacive transformation, $\beta\rightarrow\alpha'$ or $\alpha''$ martensitic transformation, $\beta\rightarrow\omega$ shuffle transformation, and $\beta\rightarrow\beta+\beta'$ phase separation[2, 10].

2.6.1 $\beta\rightarrow\alpha+\beta$ Diffusional/Displacive Transformation
$\beta\rightarrow\alpha+\beta$ is the most important phase transformation in titanium alloys. Because the property of titanium alloys highly depends on size scale, morphology and distribution of $\alpha$ precipitates within $\beta$ phase region. Therefore, $\beta\rightarrow\alpha+\beta$ attracts most study all over the world from 1970s to now.

When the temperature of titanium alloy is slowly cooled down from single $\beta$ phase regime, $\alpha$ phase will nucleate from $\beta$ phase matrix. Depending on cooling rate and aging
temperature, $\alpha$ precipitates exhibit different morphology, volume fraction, size scale and distribution. The $\beta$ phase grain boundary is the most favorable nucleation site for $\alpha$ precipitates. A layer of allotrimorph $\alpha$ phase firstly nucleates and grows along previous $\beta$ grain boundaries. Upon further cooling, parallel widmanstatten $\alpha$ plates nucleate from $\beta$ grain boundary or grain boundary $\alpha$ layer, and grow into interior of $\beta$ grain. Widmanstatten $\alpha$ plates will belong to one single crystallographic variant upon slow rate cooling and exhibit multiple crystallographic orientations upon high rate cooling. The previous single crystallographic variant $\alpha$ precipitates are called colony $\alpha$ (Figure 2.8(a)), while the latter multiple crystallographic variants of $\alpha$ precipitates are called basketwave $\alpha$ (Figure 2.8(b)). When the titanium alloy is aged at a lower temperature within $\alpha+\beta$ phase range, tiny secondary $\alpha$ laths will nucleate from widmanstatten $\alpha$ plates and fill the retained $\beta$ phase region between $\alpha$ (Figure 2.8(c))[2, 15, 21-25].

Although $\beta\rightarrow\alpha+\beta$ phase transformation is a kind of diffusional phase transformation, it shows some characteristic of displacive transformation[26-32]. For example, $\alpha$ precipitates usually have fixed orientation relationships with the parent $\beta$ phase. The major crystallographic orientation relationship between $\alpha$ phase and parent $\beta$ phase matrix is called Burgers orientation relationship[33-36]:

$$\{0001\}_\alpha // \{011\}_\beta, \quad <1\bar{1}20>_{\alpha} // <111>_{\beta}$$
Usually the flat surface of $\alpha$ plates is parallel to $(\overline{1}100)_\alpha$ or $(\overline{1}12)_\beta$, as shown in Figure 2.8(d)[2, 37].

2.6.2 $\beta\rightarrow\alpha'$, $\alpha''$ Martensitic Transformation

Martensitic transformation occurs when the dilute titanium alloy is quenched from single $\beta$ phase temperature range to the temperature below $\text{Ms}(\alpha')$ or $\text{Ms}(\alpha'')$. With increasing $\beta$ stabilizer content, the martensite structure transforms from hexagonal ($\alpha'$ martensite) to orthorhombic ($\alpha''$ martensite). Martensitic transformation is a diffusionless transformation that no composition changes occur between parent $\beta$ phase and $\alpha'$ phase (or $\alpha''$ phase)[38, 39].

The orientation of $\alpha'$ martensite and $\beta$ matrix follows common Burgers orientation relationship: $\{0001\}_{\alpha'} \parallel \{011\}_\beta$ and $<11\overline{2}0>_{\alpha'} \parallel <111>_{\beta}$ [40]. The $\beta\rightarrow\alpha'$ transformation can be completed by expansion and contraction of parent phase structure as follows: 10% contraction along $[100]_\beta$ or $[2\overline{1}0]_{\alpha'}$, 10% expansion along $[01\overline{1}]_\beta$ or $[01\overline{1}0]_{\alpha'}$, and 1% expansion along $[011]_\beta$ or $[0001]_{\alpha'}$. $\alpha''$ martensite has orthorhombic structure, with lattice parameter between that of $\beta$ phase and $\alpha$ phase, as shown in Figure 2.9. $\alpha''$ phase and $\beta$ matrix follow the orientation relationship that $[001]_{\alpha''} \parallel [100]_\beta$, $[010]_{\alpha''} \parallel [110]_\beta$, and $[100]_{\alpha''} \parallel [\overline{1}0]_\beta$ [41].
2.6.3 $\beta \rightarrow \omega$ shuffle Transformation

Athermal $\omega$ phase is formed when metastable $\beta$ titanium alloys are fast cooled from $\beta$ phase region by displacive shuffle mechanism, in which neighboring two $\{111\}$ atoms layers of every three $\{111\}$ atoms layers displace to each other into a middle plane position, as shown in Figure 2.10 [2, 42, 43]. When the collapse of $\{111\}$ planes occurs completely, $\omega$ phase exhibits a hexagonal symmetry. Partial collapse of $\{111\}$ planes in Ti-Mo alloy has been observed by R. Williams et al [19, 20, 44]. This structure has trigonal symmetry, which may be because it is the initial state of $\omega$ phase formation [13]. The shape of athermal $\omega$ phase is usually ellipsoidal and the size of athermal $\omega$ phase is usually very small less than 10 nm. Athermal $\omega$ phase and parent $\beta$ matrix obey following orientation relationship:

$$\{0001\}_{\omega} // \{111\}_{\beta} \text{ and } <11\bar{2}0>_{\omega} // <1\bar{1}0>_{\beta}$$

Isothermal $\omega$ phase could coarsen from athermal $\omega$ phase while aging as-quenched metastable $\beta$ titanium alloys [45-47]. During coarsening process, the total number of $\omega$ particles decreases but average size of $\omega$ particles increases [10]. If the misfit between $\omega$ phase and parent $\beta$ phase is large, the morphology of isothermal $\omega$ phase is observed as cuboidal shape, such as in Ti-V alloy; when the misfit between $\omega$ phase and $\beta$ phase is
small, isothermal $\omega$ phase exhibits spherical or ellipsoidal morphology, such as in Ti-Mo alloy (shown in Figure 2.5)[48].

2.6.4 $\beta \rightarrow \beta + \beta'$ phase separation

$\beta$ phase separation usually occurs in $\beta$ titanium alloy of high solute amount. It can occur by two mechanisms: binodal chemical decomposition and spinodal decomposition. If the composition of $\beta$ titanium alloy is within the range of miscibility gap but outside the chemical spinodal curve, $\beta$ phase separation would occur by binodal chemical decomposition mechanism in which $\beta'$ phase is formed by the classical nucleation and growth mechanism. However, if the composition is within chemical spinodal curve, $\beta$ phase separation would occur by spinodal decomposition mechanism in which $\beta'$ phase is formed by composition fluctuation. Spinodal decomposition could occur faster by homogeneously diffusing a distance of 5 to 10 nm as long as the composition and temperature conditions are satisfied[12]. However, only judging from morphology, it is hard to tell the $\beta'$ phase is the product of binodal decomposition or spinodal decomposition, as shown in Figure 2.6[10, 49].

2.7 Classical Precipitation Theory and Pseudo-spinodal Decomposition Theory

In classical precipitation theory, precipitation is the formation and growth of a new phase of a different composition from parent phase matrix in all stages of its development in the
way of diffusion [50]. There are two mechanisms for a new phase to precipitate: nucleation and growth mechanism and spinodal decomposition mechanism.

A typical gibbs free energy curve in two phases equilibrium temperature range is shown in figure 2.11 in order to illustrate the process of nucleation and growth mechanism. The gibbs energy curve is plotted using Thermo-Calc software and Ti-Mo binary system at 400°C. The original composition of parent phase is Ti-25wt%Mo. At 400°C, in order to lower the total gibbs free energy of the system, product phase $\alpha$ phase, is nucleated. The driving force of $\alpha$ precipitation is:

$$\Delta G = -V\Delta G_v + A\gamma + V\Delta G_s$$

The first term $-V\Delta G_v$ is volume gibbs energy reduction if volume $V$ $\alpha$ phase replaces same volume $\beta$ phase. The second term $A\gamma$ is free energy increase due to creation of an area of $\alpha/\beta$ interface. The third term $V\Delta G_s$ is misfit strain energy increase due to product $\alpha$ phase is not perfect fit with parent $\beta$ phase. Therefore, bulk volume free energy decrease is the driving force for precipitation and on the contrary interfacial energy and misfit strain energy are the obstacle force for precipitation[12].

In order to form $\alpha$ precipitates, in $\beta$ matrix molybdenum atoms need to diffuse away from some local region to neighboring region. Then in some molybdenum lean region,
molybdenum and titanium atoms would to be rearranged and the structure will transform from BCC to HCP. The composition of product phase can be determined by common tangent line of two phases’ gibbs energy curves, as shown the blue color dot line in figure 2.11. After nucleation, precipitate will continue growth under the driving force shown in equation 2.11 until the volume fraction of product phase achieves equilibrium value.

The nucleation in solid is almost always heterogeneous rather than homogeneous, because there are usually plenty of non-equilibrium defects present which could act as favorable nucleation sites such as vacancies, dislocations, stacking faults, grain boundaries and interphase boundaries and free surfaces. Only if the driving force is huge, homogeneous nucleation could occur[12].

Besides nucleation and growth mechanism, the product phase could also be formed by gradual compositional change called spinodal decomposition rather than nucleation and growth. Spinodal decomposition only occurs on the condition that there is a negative curvature at the initial composition in the gibbs energy curve, shown in figure 2.12. In other words, the composition needs to be between two points of inflection in gibbs free energy curve. The gibbs energy curve is also dependent on the temperature. Therefore, only in the case of the alloy composition and temperature satisfy the above conditions, spinodal decomposition could occur.
If the alloy lies inside the spinodal, any small composition fluctuation off initial composition could result in a decrease of total gibbs energy (shown in figure 2.12) and therefore the product is more energy favorable. Then composition will continue diffusing away from initial composition until equilibrium compositions are achieved. Solute lean and solute rich product phases would be produced without formation of any nuclei.

Recently, a new type of decomposition mechanism, pseudo-spinodal decomposition, is discovered to successfully explain the chessboard structure in several systems, such as Co-Pt, AuCu-Pt, and NiVX (X=Co, Nb, Fe)[51-53]. Unlike conventional nucleation and growth decomposition mode in which the nuclei will jump to a different composition compared to parent phase composition, in pseudo-spinodal decomposition the composition of nuclei will gradually transform from parent phase composition to equilibrium composition value, in which the composition change is similar to that of spinodal decomposition. But unlike spinodal decomposition in which product phase shares the same structure with its parent phase, in pseudo-spinodal decomposition mode it is a nucleation and growth process and the formed nuclei have different structure from its parent phase. Therefore, the terminology of pseudo-spinodal decomposition emphasizes its similarity and difference with spinodal decomposition.

Pseudo-spinodal decomposition only occurs on the condition that the initial composition of parent phase is close to $C_0$ point at which product phase and parent phase share same
gibbs free energy, as shown in figure 2.13. If the composition of cubic structure parent phase is on the left side of $C_0$ point but very close to it, a relative small range composition fluctuation could cause the composition of local region jump to the other side of $C_0$ where product phase is more energy favorable and more stable rather than parent phase. Then the transformation from parent cubic phase to product tetragonal phase could occur in the fastest relaxation mode, a displacive crystal rearrangement maintaining the same composition as parent cubic phase. The previous stage of pseudo-spinodal decomposition is diffusionless and requires very little time to complete. After the new crystal is formed, the composition of product phase will transform to equilibrium value via diffusion. The latter stage of pseudo-spinodal decomposition is diffusional and then requires more time [51-53].

Therefore, a summary of the comparison among the conventional nucleation and growth, spinodal decomposition and pseudo-spinodal decomposition is listed in the table 2.2.

2.8 Phase Transformation Analysis Techniques

Phase transformation is the transition of system from one phase into another. There are usually physical and/or chemical properties change during the process of phase transformation. It is these physical or chemical properties that can be used in experiment to identify and analyze phase transformation, such as study the transition start temperature and transition finish temperature. Depending on analyzing different physical
and chemical characteristics of phase transformation, there are various techniques used to identify and analyze phase transformation.

2.8.1 In-situ Synchrotron XRD

The structure and/or composition of phases before and after phase transformation are usually not the same. The XRD is the most effective technique to study the structure change of the material and therefore characterize phase transitions. When charged particles are accelerated radially under electromagnetic field, the synchrotron radiation is emitted. Compared to conventional XRD, synchrotron XRD is of higher brightness and higher intensity, has smaller angular divergence of beam, better space resolution, energy resolution and even time resolution. A wide range of wavelength could be obtained down to smaller than 10 angstrom and therefore even small lattice parameter change could be detected by synchrotron XRD. Another important characteristic is that synchrotron XRD could be used to characterize the structure change of the material in real time such as during heat treatment and in situ such as at high temperature or high pressure conditions. Therefore, using in-situ synchrotron XRD could detect structure and/or composition change in material in-situ during heat treatment[54].

2.8.2 Differential Scanning Calorimeter/ Differential Temperature Analysis

Depending on the characteristics of thermal properties change in phase transformations, the phase transformation could be divided into first-order transformation, second-order
transformation and higher order transformation. The nth-order transformation is defined as:

\[
\left(\frac{\partial^{n-1}G_1}{\partial T^{n-1}}\right)_p = \left(\frac{\partial^{n-1}G_2}{\partial T^{n-1}}\right)_p
\]

\[
\left(\frac{\partial^{n-1}G_1}{\partial P^{n-1}}\right)_T = \left(\frac{\partial^{n-1}G_2}{\partial P^{n-1}}\right)_T
\]

During first-order transformation, there is discontinuous change in volume and enthalpy; while in second-order transformation, the volume and enthalpy change are continuous. The enthalpy change in phase transformation is also named as latent heat[12].

Most of solid state phase transformations belong to first order transformations. Some ordering transformations belong to second-order transformations and higher order transformations are rare.

Both differential scanning calorimeter (DSC) and differential temperature analysis (DTA) are thermal analytical technique used in experiment to measure the latent heat or enthalpy change to analyze the phase transformations. The main difference between two
techniques is that in DSC the temperature of sample and reference are kept the same while measuring heat flow difference needed to elevate the temperature of sample and reference but in DTA the heat flow to sample and reference are kept the same while measuring temperature difference between the sample and reference. Because there is a sudden change of enthalpy in the first-order transformation, phase transformation start temperature and phase transformation finish temperature can be measured as enthalpy change start temperature and enthalpy change finish temperature[55].

2.8.3 Electrical Resistivity Measurement

Electrical resistivity of material is another physical property that could be used in experiment to detect constitutional change in fast transformation, such as in quenching and aging. The main advantage of electrical resistivity measurement is its rapidity and convenience recording the data in-situ without interference of the heat treatment, and high sensitivity to phase transformations [16, 56, 57]. However, factors that could influence the electrical resistivity change in phase transformation are complicated and could affect each other. Therefore, it still needs large amount of work to experimentally determine the relationship between electrical resistivity change and specific phase transformation.

2.8.4 Dilatometry
Dilatometry is the technique to measure volume change of sample in heat treatment, such as diameter change of the sample. The heat transfer coefficient and volume thermal expansion coefficient of different phases are not the same at the same temperature. Therefore, it means that during phase transformation while a second phase is formed the volume change of sample is not the same as in the situation when there is only single phase present before phase transformation. The special change of volume or in one dimension the change of diameter could be used to indicate phase transformation[58].
Table 2.1 Crucial characteristics of titanium and titanium alloy compared with other commonly used metals and alloys[2].

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Fe</th>
<th>Ni</th>
<th>Al</th>
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</thead>
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<td>1538</td>
<td>1455</td>
<td>660</td>
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<tr>
<td>Allotropic Transformation (°C)</td>
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<td>$\gamma_{912^\circ}$ $\alpha$</td>
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<td>-</td>
</tr>
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<td>Crystal Structure</td>
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<td>fcc $\rightarrow$ bcc</td>
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<td>fcc</td>
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<td>72</td>
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<td>500</td>
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<td>Density (g/cm$^3$)</td>
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<td>7.9</td>
<td>8.9</td>
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</tr>
<tr>
<td>Comparative Corrosion Resistance</td>
<td>Very High</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Comparative Reactivity with Oxygen</td>
<td>Very High</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Comparative Price of Metal</td>
<td>Very High</td>
<td>Low</td>
<td>High</td>
<td>Medium</td>
</tr>
</tbody>
</table>

Figure 2.1 The unit cells show the crystal structure of HCP $\alpha$ phase and BCC $\beta$ phase[1].
Figure 2.2 Scheme indicates two kinds of $\beta$ phase stabilizers in titanium alloys. The left one is virtual $\beta$ isomorphous phase diagram; the right one is virtual $\beta$ eutectoid phase diagram[2].

Figure 2.3 Scheme indicates stable phases and metastable phases in titanium alloy in a virtual isomorphous phase diagram. The bold lines indicate the stable phase regions while the dotted lines indicate the metastable phase regions[59].
Figure 2.4 TEM images of (a) $\alpha'$ martensite and (b) $\alpha''$ martensite\[41\]

Figure 2.5 (a) ellipsoidal morphology isothermal $\omega$ phase (b) cuboidal morphology isothermal $\omega$ phase[48]
Figure 2.6 TEM image shows the $\beta'$ phase[3].

Figure 2.7 Scheme indicates four types of titanium alloys by a virtual isomorphous phase diagram: $\alpha$ alloy, $\alpha + \beta$ alloy, metastable $\beta$ alloy and stable $\beta$ alloy[2].
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Figure 2.11 Gibbs free energy of Ti-Mo system calculated using ThermoCalc
Figure 2.12 Phase diagram indicates miscibility gap[12].

Figure 2.13 Schematic gibbs free energy diagram indicates the thermodynamic conditions for pseudo-spinodal decomposition to occur[52]
Table 2.2 the comparison among the conventional nucleation and growth, spinodal decomposition and pseudo-spinodal decomposition

<table>
<thead>
<tr>
<th>Type</th>
<th>Condition</th>
<th>Characteristics</th>
<th>Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation and growth</td>
<td>Outside two inflection points</td>
<td>Downhill diffusion; nuclei formed; structure changed</td>
<td>Small number of large size particles</td>
</tr>
<tr>
<td>Spinodal decomposition</td>
<td>Within miscibility gap</td>
<td>Uphill diffusion; no nuclei formed; no structure changed</td>
<td>Large number of small size particles</td>
</tr>
<tr>
<td>Pseudo-spinodal decomposition</td>
<td>Close to C₀ point, on the side of parent phase is energy favorable</td>
<td>Composition fluctuation; nuclei formed; structure formed</td>
<td>Large number of small size particles</td>
</tr>
</tbody>
</table>
Chapter 3

Equipment and Experiment Procedures

3.1 Introduction

In this chapter, alloys and equipments used in current study and experiment procedure of current work will be introduced. Thermal and mechanical histories of as-received alloys are discussed first. Then all equipments including characterization tools, heat treatment facilities, phase transformation analysis tools and modeling tools used will be covered. A detailed heat treatment condition list showing thermal processes of current research is introduced with sample preparation and characterization procedure in the end.

3.2 Materials Used

Two different titanium alloys are used in my research, metastable $\beta$ alloy Ti-5Al-5Mo-5V-3Cr (all in wt%) and binary Ti-Xwt%Mo alloy (X=2, 8, 12, 15 and 18). All alloys were provided by TIMETAL Corporation in Henderson, NV. Some of the key process of as delivered samples include: all raw materials were prepared using arc-melter through standard arc melting technique. In order to improve their homogeneity, all materials were flipped seven times during being melted and then rolled at 2000°F after melted. As-received alloys were all homogenized again in vacuum furnace at 1100°F for 168 hours.
and furnace cooled to room temperature. Then all bulk alloys were cut into small pieces using Electric Discharge Machine (EDM) for further heat treatment.

### 3.2.1 Ti-5Al-5Mo-5V-3Cr

Ti-5Al-5Mo-5V-3Cr or Ti-5553, is modified as the derivative of VT-22 alloy [60]. Due to its high strength, great deep-hardenability and excellent corrosion resistance, Ti-5553 is a kind of promising metastable β titanium alloy with application in the field of aerospace, such as landing gear components [61, 62]. A comparison of properties between Ti-5553 and Ti-6Al-4V is shown in table 3.1. The strength, ductility and fracture toughness of Ti-5553 could be modified in a wide range due to its various internal microstructures. Especially size scale and distribution of HCP α precipitates obtained within BCC β parent phase matrix, under a number of different thermo-mechanical processes, is critical factor to manipulate mechanical properties of Ti-5553. Therefore, understanding microstructure evolution, especially α precipitation process, in Ti-5553 under specific heat treatment is critical to manipulate material for special applications [4-6].

### 3.2.2 Ti-Mo Binary Alloy

Ti-Mo binary alloy is a type of promising candidate in biomaterials field. With the population of aged people growing rapidly all over the world, the demand of biomaterials used as artificial bones, dental implants and even healthcare goods is increasing. Due to
light weight, high strength, great corrosion resistance and excellent biocompatibility, titanium alloys become one of the favorite candidates in biomaterial field. Compared to the most widely used Ti-6Al-4V, under different heat treatment conditions, β titanium alloys could exhibit even better properties, such as lower modulus, and less long-term health concern. Ti-Mo binary alloy is one of these types of β titanium alloys being studied for biomaterial application. A brief comparison of properties between Ti-Mo alloys and pure titanium and other titanium alloys is shown in table 3.2. Therefore, in order to obtain more appropriate candidate for biomaterial application, it is necessary to obtain a pronounce knowledge of microstructure evolution in Ti-Mo alloy in order to better manipulate its properties [1, 2, 9, 63-65].

3.2 Equipment

3.2.1 Mechanical Polishing tools

The standard metallurgical polishing process is applied to all samples for SEM characterization: samples were grinded on 180, 240, 400, 600, 800 and 1200 grit Allied SiC paper manually or using Allied™ MultiPrep parallel polisher. Then they were finally polished with Allied™ 0.5 colloidal silica suspension in Crystalite Mastersystem™ vibratory polisher for 24 hours. Polished samples were cleaned in Buehler Utramei™ sonic cleaning solution, distilled water and ethyl alcohol. Finally cleaned samples were stored in Fisher Scientific Isotemp™ 280A Vacuum Oven for further SEM characterization or TEM foil/3D atom probe needle preparation.
3.2.2 Characterization tools

The characteristic of microstructural evolution is studied in the aspect of morphology, structure, composition and crystallography. Depending on size scale of specific microstructure, scanning electron microscope, transmission electron microscope and three-dimension atom probe are adopted to thoroughly characterize phase transformations inside materials under various heat treatment conditions.

3.2.2.1 Scanning Electron Microscope

Three scanning electron microscopes (SEM) were used for my work, FEI Sirion™, FEI XL-30 ESEM™ and FEI Quanta™ 200. FEI Sirion™ system is a high-resolution field emission gun (FEG) SEM, with secondary electron (SD) detector, backscattered electron detector (BSD) and Energy Dispersive Spectrometer (EDS). FEI XL-30 ESEM™ is a FEG SEM with SD detector, BSE detector, EDS and Electron Backscattered Diffraction (EBSD) system. FEI Quanta™ 200 is a heated tungsten filament electron source SEM, with SD detector, BSE detector, EDS and EBSD. All high resolution BSE SEM images of current work were taken using FEI Sirion™ while necessary EBSD results were obtained using FEI XL-30 ESEM™ and FEI Quanta™ 200.

3.2.2.2 Focused Ion Beam

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Two generations of Duel Beam Focus Ion Beam (DB-FIB) were used to prepare site-specific TEM foils and 3D atom probe needles in my work. Nova™ NanoLab 600 is equipped with Sidewinder™ ion column and Sirion™ electron column. The three axis piezo-electric stage in Nova could provide ± 2 nm resolution stage movement and Sindewinder™ could provide ion beam as low as energy to 2KV. Helios™ NanoLab 600 is a newer generation DB-FIB. Compared with Nova, OMNIProbe in-situ micromanipulator is equipped for in-situ plucking out TEM foil and ion column is good to as low as 500V milling.

3.2.2.3 Transmission Electron Microscope

Three transmission electron microscopes (TEM) were used to study the crystal structure and composition in current work: Philips CM200, FEI TECNAI F20 and FEI Titan. Philips CM200 TEM is LaB₆ filament source 200kV TEM equipped with EDS. The goniometer on CM200 could be tilted of ± 45° α and ± 30° β, which makes CM200 a convenient tool for conventional TEM work, such as recording diffraction pattern and dark field image. FEI TECNAI F20 is a FEG 200KV Scanning Transmission Electron Microscop(STEM) with an X-twin objective lens of Cs=1.3mm, which has point resolution of 0.25nm. With Fischione High Angle Annular Dark Field (HAADF) detector, Z contrast HAADF image could be obtained of special resolution of 0.18nm. FEI Titan™ is a FEG 80-300kV S/TEM equipped with Cs corrector for the probe, monochromator to reduce the spread of incident beam and EDS, EELS spectrometer for
the composition analysis. With monochromator and probe aberration corrector, sub-Angstrom probe could be obtained in Titan and sub-Angstrom lateral resolution could be achieved.

### 3.2.2.4 Three Dimensional Atom Probe

Imago Scientific Local Electrode Atom Probe (LEAP 3000X HR) at Center for Advanced Research & Technology in University of North Texas was used in current study in order to obtain detail composition information at nano-scale interface region. Ions from less than 100nm diameter tip of need-shaped specimen would be field emitted and detected by the time-of-flight mass spectrometry. 0.1 nm resolution of composition measurement along the depth direction and 0.2 nm resolution in the lateral direction could be achieved. Then three dimensional atomic resolution microstructure reconstruction based on the three dimensional composition measurement could be obtained.

### 3.2.3 Heat Treatments Equipments

#### 3.2.3.1 Tube Furnace

Thermolyne 21100 horizontal tube furnace was used to complete some of quenching heat treatments. The maximum temperature of furnace is 1150°C and heating rate is 5°C/min. Furnace could be connected to flowing argon and therefore heat treatment could be completed in air atmosphere or argon atmosphere. The heat treated sample could be
pulled out and dropped into bucket full of water directly in a short time, which makes tube furnace simple and convenient for quenching heat treatment.

3.2.3.2 Drop Furnace

Lindberg drop bottom furnace was used for some quenching heat treatments. The maximum operating temperature of the drop furnace is 1200°C. The hooked sample wrapped with commercial pure titanium, to absorb oxygen and protect the sample, is hung in proper hot zone, close to the center of the furnace. Drop furnace could be back filled with inert gas argon, to even better decrease the influence of oxygen contamination. After heat treatment was complete, the hooked sample is simply dropped from hot zone to bucket of water, due to an open bottom of vertical chamber.

3.2.3.3 Electro-Thermal-Mechanical Tester

The Electro Thermal Mechanical Tester (ETMT) is developed by the National Physical Laboratories (NPL, UK) and Instron. It could be used as an accurately temperature controlled furnace and mechanical test machine in a wide range of temperatures, because the electric current passing through sample, the temperature of sample, the load and position of sample could be accurately controlled by system. Sample used in ETMT is of 40mm×3mm×1.5mm dimension, which is much smaller than that in other mechanical test equipments or other furnaces. Then one benefit to use ETMT is to reduce the cost of experiment. Sample in ETMT could be heated up by electrical resistance. An R-type
thermal couple is spot welded at the center of bar shape sample in order to in-situ measure and control the temperature of sample. Because top and bottom parts of sample are held by water cooled grips, only 2mm from the center of sample towards to either end can be treated uniform temperature hot zone region. Due to small size of hot zone region, very high heating rate and high cooling rate heat treatment could be completed using ETMT. The chamber of ETMT is connected to oil pump and flowing argon. Therefore, heat treatments could be run in vacuum condition or inert argon atmosphere. With another two platinum wire spot welded onto the sample, either is 2mm far from thermocouple in the center, electrical potential drop between two spots could be measured. The electric current passing through sample can be controlled, so electrical resistance and electrical resistivity change of sample could be in-situ measured as well using ETMT.

3.2.4 Phase Transformation Analysis Tool

As introduced in the section 2.8, during the process of phase transformations, various physical or chemical properties of material could change, which could be used as characteristic to analyze phase transformations. In current research, Electro-Thermal-Mechanical Tester at the Center for the Accelerated Maturation of Materials in The Ohio State University, Single Sensor Differential Temperature Analysis at the Welding and Joining Metallurgy Group in The Ohio State University, and Differential Scanning
Calorimetry at Clemson University were used to in-situ observe the presence of various phase transformations.

### 3.2.4.1 Electro-Thermal-Mechanical Tester

As introduced in 3.2.3.3, ETMT is capable of running accurately temperature controlled heat treatment and in situ measuring electrical resistivity change of the material. With R type thermo-couple spot welded in the center of sample, the temperature in heat treatment could be accurately recorded. With two extra platinum wires spot welded 2mm away from the centered thermo-couple (as shown in figure 3.4), the potential drop between two wires could be measured. The current passing through the sample is controlled by the system. Therefore, the temperature and the electrical resistance of the sample in the hot zone region during heat treatment could be in-situ observed.

\[
R = \frac{U}{I}
\]

\[
\rho = R \times \frac{S}{L}
\]

R and U are electrical resistance and potential drop between two measured spots. I is electric current passing through sample. S is cross section area of sample. L is the distance between two measured spots. \(\rho\) is the electrical resistivity of sample. If the change of cross section area of sample and distance between two measured spots after
heat treatment can be ignored, the measured resistance R could be used to analyze phase transformation instead of resistivity \( \rho \).

### 3.2.4.2 Single Sensor Differential Temperature Analysis (SS-DTA)

SS-DTA is designed and developed in the Welding and Joining Metallurgy lab of The Ohio State University by Dr. John Lippold and Dr. Boian Alexandrov. Compared to conventional DTA, a calculated theoretical thermal history is adopted as the reference rather than thermal history recorded from a standard sample. The temperature difference (\( \delta T \)) between the measured value \( T_m \) from experimental sample and calculated value \( T_r \) from the theory is:

\[
\delta T = T_m - T_r
\]

SS-DTA is composed of two main parts: heating chamber to heat treat samples and data record and analysis system. The heating chamber can be connected to argon and/or vacuum pump in order to provide a better protective atmosphere. The structure of SS-DTA is shown in figure 3.5. Therefore, the temperature difference versus heating temperature profile could be used to analyze phase transformation in heat treatment[66].

### 3.2.4.3 Differential Scanning Calorimetry (DSC)

Netzsch Pegasus 404 C DSC at the Clemson University was utilized for thermal analysis, which is equipped with a low temperature head and Ag wound furnace. The upper temperature limit of the DSC is 550°C and the heating rate could be adjusted from
1°C/min up to 50°C/min. Therefore, the DSC was used to study the influence of the heating rate on the microstructural evolution and identify the different transformation sequences.

3.2.5 Modeling Tools

3.2.5.1 Thermo-Calc

Thermo-Calc software is designed and developed by the department of materials science and engineering of KTH. It is a powerful program for all kinds of thermodynamic calculations, such as thermodynamic properties, equilibrium quantities, chemical driving forces and various types of phase diagrams. Thermo-Calc can handle a system as complex as up to 40 elements, 1000 species and many different solutions. It is the only software can calculate arbitrary phase diagram sections with up to five independent variables in a defined system, and the only software that can calculate chemical driving forces.

Thermo-Calc software is based on a powerful Gibbs Energy Minimizer, which can help to find the local or global minimum Gibbs Energy of system at given conditions. Linked with various databases, Thermo-Calc software has become the most powerful thermodynamic calculation packages in materials science[67].
Thermo-Calc Q version installed on the Linux workstation and Thermo-Calc R version installed on the Windows system PC are used in current work. It includes 10 public thermodynamic databases and 2 commercial thermodynamic databases of nickel and titanium.

Thermo-Calc was mainly used to:

1. Plot phase diagram of Ti-Mo phase diagram.
2. Determining β transus temperature of different Ti-Mo alloys and Ti-5553.
3. Gibbs free energy curve of different titanium alloys at various temperatures
4. The fraction of phases in different titanium alloys at various temperatures

3.2.5.2 DICTRA

DICTRA is a sister software of Thermo-Calc software, which is designed and developed by the department of materials science and engineering of KTH in Stockholm, Sweden. It is a useful engineering tool for the simulation of DIffusion Control TRAnsformation in multicomponent systems. On the condition that necessary thermodynamic and kinetic parameters are available, the software is able to solve as many as 10 components in a simulation.

DICTRA is based on a numerical solution of multicomponent diffusion equations. The program can calculate diffusion equations in various regions of a material, assuming that
thermodynamic equilibrium is held locally at all phase interfaces, which can be calculated from Thermo-Calc software[68]. However, with accurate multicomponent thermodynamics and diffusion, limited geometry in DICTRA can also help to solve many realistic problems.

DICTRA installed on Linux workstation and Windows system PC, which linked with Thermo-Calc software contains 12 public thermodynamic and kinetic databases and 2 commercial nickel and titanium database.

DICTRA was mainly used in the following fields:

1. Homogenisation of titanium alloys
2. Solidification of titanium alloys
3. Growth or dissolution of individual particles
4. Growth or dissolution of intermediate phases
5. Interdiffusion in compound materials

3.2.5.3 Pandat

Pandat software is developed by Computherm LLC. It is a program similar to Thermo-Calc to accomplish thermodynamic calculations on thermodynamic properties, equilibrium quantities and phase diagrams of various systems. But compared to the
command input environment in Thermo-Calc, there is a much user-friendly interface in Pandat software. In the current work, Pandat was used mainly in the following aspects:

1. Calculate $\beta$ transus temperature of various titanium alloys
2. Plot phase diagrams of binary and ternary titanium alloys
3. Plot $\beta$ approach curves of various titanium alloys
4. Plot gibbs free energy curves of binary titanium alloys at various temperatures

3.3 Experiment Procedures

3.3.1 Heat Treatment Conditions

The heat treatments in current study are mainly composed of two categories (shown in figure 3.6 and figure 3.7). The first set of heat treatments was aimed to study $\alpha$ precipitation in $\beta$ matrix without any possible influence of metastable phases: solution at above $\beta$ transus temperature, step quench to aging temperature, isothermally age and quench to room temperature. The second set of heat treatments was to study the influence of metastable $\omega$ phase on following $\alpha$ precipitation: solution at above $\beta$ transus temperature, quench to room temperature, heat up at different rates to aging temperature, isothermally age and quench to room temperature.

Category 1:

Ti-5553:
a) β solution + Step quench to 700°C + isothermally age at 700°C for 15 minutes/4 hours + Water quench to room temperature

b) β solution + Step quench to 650°C + isothermally age at 650°C for 1 hour + Water quench to room temperature

c) β solution + Step quench to 600°C + isothermally age at 600°C for 15 minutes/30 minutes/17 hours + Water quench to room temperature

Ti-15wt%Mo:

a) β solution + Step quench to 735°C + isothermally age at 735°C for 30 minutes + Water quench to room temperature

b) β solution + Step quench to 700°C + isothermally age at 700°C for 30 minutes + Water quench to room temperature

c) β solution + Step quench to 600°C + isothermally age at 600°C for 30 minutes/60 minutes/24 hours + Water quench to room temperature

Ti-7.5wt%Mo:

β solution + Step quench to 600°C + isothermally age at 600°C for 30 minutes + Water quench to room temperature

Ti-12wt%Mo
β solution + Step quench to 600°C + isothermally age at 600°C for 30 minutes + Water quench to room temperature

Category 2:

Ti-5553:

a) β solution + WQ + 100°C/min to 600°C + Isothermal aging at 600°C for 4 hours/17 hours + WQ

b) β solution + WQ + 50°C/min or 20°C/min to 600°C + Isothermal aging at 600°C for 2 hours + WQ

c) β solution + WQ + 5°C/min to 600°C + Isothermal aging at 600°C for 2 hours/15 hours + WQ

d) β solution + WQ + 100°C/min to 600°C to 500°C or 600°C + WQ

e) β solution + WQ + continuous heated up to 350°C, 375°C, 400°C, 500°C and 600°C at 5°C/min + WQ

Ti-15wt%Mo:

a) β solution + WQ + 5°C/min to 600°C + Isothermal aging at 600°C for 2 hours + WQ

Electrical Resistivity Measurement:

Ti-2Mo: β solution + WQ + 2°C/min to 985°C + WQ

Ti-8Mo: β solution + WQ + 2°C/min to 925°C + WQ
Ti-12Mo: $\beta$ solution + WQ +2°C/min to 923°C +WQ
Ti-18Mo: $\beta$ solution + WQ + 2°C/min to 985°C +WQ

Ti-5553:
1) $\beta$ solution + Step quench to 600°C/24hours +WQ
   $\beta$ solution + Step quench to 700°C/10hours + WQ
   $\beta$ solution + Step quench to 650°C/10hours + WQ
   $\beta$ solution + Step quench to 500°C/15hours + WQ
   $\beta$ solution + Step quench to 550°C/5hours + WQ
2) $\beta$ solution + WQ + 5°C/min to 350°C, 375°C, 400°C, 500°C and 600°C + 600°C WQ

3.3.2 Sample Preparation Procedures

3.3.2.1 SEM Sample Preparation

SEM samples were cut in the center of pro-heat treated bars and prepared following a conventional grinding and polishing route. Samples were ground on 180, 240, 400, 600, 800 and 1200 grit SiC paper and finally polished with 0.5μm colloidal silica suspension in vibratory polisher for 24 hours. The polished samples were cleaned in Buehler Utramet™ sonic cleaning solution, distilled water and ethyl alcohol. Finally, cleaned samples were stored in vacuum oven.

3.3.2.2 TEM Sample Preparation
TEM foils were prepared mainly by focused ion beam technique using Helios 600 FIB with OmniProbe. The procedure to prepare TEM foils is summarized as follows[69].

1. The polished SEM sample was set up at eucentric height, which is close to 4.2mm in Helios, and then was tilted to 52°.
2. An area of 30μm × 1.5μm was deposited with platinum to protect the surface of the foil, using 0.28nA, 30kV.
3. On either side of deposited Pt, a 34μm×5μm×0.8μm region was milled away using 21nA current, 30kV.
4. After roughly thin the foil at ±2° from 52° using 2.8nA current, 30kV, the foil was undercut with U shape pattern at 7° tilt using 2.8nA current, 30kV.
5. The foil was in situ plucked out using OmniProbe and attached to copper grit by Pt deposition.
6. The foil was thin at ±2° from 52°, from 2.8nA current down to 0.28nA current 30kV to around 100nm thick and then cleaned on both sides at 0.81Å and 5kV to eliminate amorphous layer on either side.
7. Before put into TEM, all the foils were further cleaned using 1040 Fision Low Voltage Nano-mill, at 900V 5mins on both sides and 500V 3mins on both sides.

3.3.3 Characterization Procedures
The polished samples were first studied in SEM level to obtain a general understanding of the microstructure in large size scale and then TEM foils were prepared in specific interested region to obtain detail information of microstructure.

All XHD BSE SEM images were taken on FEI Sirion™, using spot size 4, voltage of 12kV. EBSD data were collected using FEI XL-30 ESEM™ and FEI Quanta™ 200, using spot size 5, voltage of 25kV. Diffraction pattern and dark field image were taken using Philips CM200 at 200kV. HAADF STEM images and EDS spectrum were taken using FEI Tecnai F20 at 200kV. HRSTEM image were taken using Titan at 300kV. 3D atom probe data were collected using in a local electrode atom probe (LEAP™) system from Imago Scientific Instruments, using the voltage mode at a temperature of 60K, with an evaporation rate 0.2—1.0% and a voltage pulse fraction at 20% of the steady-state applied voltage.
Figure 3.1 Application of Ti-5553 in aero-space field[61]

Table 3.1 Comparison of properties between Ti-5553 and Ti-64[6]

<table>
<thead>
<tr>
<th>Property</th>
<th>Cast and HIP'ed Ti-5553 (1)</th>
<th>Cast and HIP'ed Ti-64 (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate tensile strength, MPa (ksi)</td>
<td>1159 (168)</td>
<td>910 (1320)</td>
</tr>
<tr>
<td>Yield strength, MPa (ksi)</td>
<td>1055 (153)</td>
<td>828 (120)</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>9</td>
<td>8.9</td>
</tr>
<tr>
<td>Compressive strength, MPa (ksi)</td>
<td>1138 (165)</td>
<td>897 (130)</td>
</tr>
<tr>
<td>Max shear strength, MPa (ksi)</td>
<td>690 (100)</td>
<td>655 (95)</td>
</tr>
<tr>
<td>Bearing UTS (E/d=2.0), MPa (ksi)</td>
<td>2248 (326)</td>
<td>1862 (270)</td>
</tr>
<tr>
<td>Bearing YS (E/d=2.0), MPa (ksi)</td>
<td>1931 (280)</td>
<td>1648 (239)</td>
</tr>
</tbody>
</table>

Room temperature properties. (1) Ti-5553 optimized heat treatment. (2) Standard mill anneal 843°C/2h (19-mm section size).
Figure 3.2 Application of Ti-Mo alloy in biomaterial field[7]

Table 3.2 Comparison of properties between Ti-Mo alloys and pure titanium[63].

<table>
<thead>
<tr>
<th></th>
<th>c.p. Ti</th>
<th>Ti-7.5Mo</th>
<th>Ti-9Mo</th>
<th>Ti-10Mo</th>
<th>Ti-12.5Mo</th>
<th>Ti-15Mo</th>
<th>Ti-17.5Mo</th>
<th>Ti-20Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microhardness (HV)</td>
<td>156</td>
<td>263</td>
<td>315</td>
<td>331</td>
<td>337</td>
<td>307</td>
<td>310</td>
<td>305</td>
</tr>
<tr>
<td>Bending strength (MPa)</td>
<td>884</td>
<td>1395</td>
<td>1513</td>
<td>1752</td>
<td>1440</td>
<td>1348</td>
<td>1689</td>
<td>1650</td>
</tr>
<tr>
<td>Bending modulus (GPa)</td>
<td>92</td>
<td>55</td>
<td>74</td>
<td>95</td>
<td>83</td>
<td>71</td>
<td>78</td>
<td>87</td>
</tr>
<tr>
<td>Strength/modulus ratio</td>
<td>9.6</td>
<td>25.4</td>
<td>20.4</td>
<td>18.4</td>
<td>17.3</td>
<td>19.0</td>
<td>21.7</td>
<td>19.0</td>
</tr>
</tbody>
</table>
Figure 3.3 Picture of Electro-Thermo-Mechanical Tester (ETMT)
Figure 3.4 The scheme showing the dimension of sample used in ETMT

Figure 3.5 Schematic diagram shows the structure of Single Sensor Differential Temperature Analysis (SSDTA)[66]
Figure 3.6 Schematic diagram shows the 1\textsuperscript{st} main category of heat treatments

Figure 3.7 Schematic diagram shows the 2\textsuperscript{nd} main category of heat treatments
Chapter 4

Non-classical Homogeneous Refined $\alpha$ Precipitation in $\beta$ Titanium Alloys

In this chapter, the transformation mechanisms of refined $\alpha$ microstructure in $\beta$ titanium alloys are introduced. The influence of isothermal aging temperature on $\alpha$ precipitation from $\beta$ matrix was studied using scanning electron microscopy, transmission electron microscopy and 3D atom probe. Two different types $\alpha$ precipitates were formed directly from $\beta$ matrix in Ti-5553 and Ti-15Mo while being isothermally aged at different temperature ranges. When isothermal aging temperature was high (compared to $\beta$ transus temperature), coarse $\alpha$ precipitates of irregular morphology interface were present along $\beta$ grain boundary or in the region near grain boundary; when isothermal aging temperature was selected in intermediate temperature range, refined $\alpha$ precipitates of smooth interface were present homogeneously in the interior of $\beta$ grains. In Ti-5553, the composition of refined $\alpha$ precipitates gradually shifts towards to the equilibrium value; while this type composition shift has not been observed in coarse $\alpha$ precipitates. In Ti-15%Mo, the refined $\alpha$ precipitates showed black color after etched in the optical microscope while the coarse $\alpha$ precipitates exhibited white color. Based on features of refined $\alpha$ precipitates in Ti-5553 and Ti-15Mo, a new type non-classical homogeneous
transformation mechanism was proposed to explain the microstructure in Ti-5553 and a new transformation pathway was identified to explain the refined $\alpha$ microstructure in Ti-Mo system.

4.1 Introduction

In most cases the most common phases present in titanium alloys are HCP $\alpha$ phase and BCC $\beta$ phase. The combination of two phases could influence the properties, especially mechanical properties of titanium alloys significantly. Therefore it is critical to obtain a detail understanding of $\alpha$ phase formation in $\beta$ phase matrix and then better manipulate its mechanical properties.

When the temperature drops from above $\beta$ transus temperature range to $\alpha/\beta$ temperature range, $\alpha$ phase starts to form in $\beta$ matrix. Usually, $\alpha$ phase prefers to form along $\beta$ grain boundary first, which is called $\alpha$ allotrimorph. Then widemannstatten $\alpha$ forming from $\beta$ grain bound or grain boundary $\alpha$ would nucleate and grow into interior of $\beta$ grain. Compared to the $\alpha$ allotrimorphs and widemannstatten $\alpha$, intragranular $\alpha$ is the hardest and almost usually the last to form within the $\beta$ grain. However, the formation of $\alpha$ allotrimorph usually brings serious problems to degrade its properties. For example, the precipitate free zone (PFZ) formed in the region near $\alpha$ allotrimorph could lead to the non-uniform of mechanical property. The crack would like to form in the PFZ and results in the materials to fail. Therefore, it is important to obtain homogeneous
intragranular $\alpha$ within $\beta$ grain to provide uniform properties from grain boundary region to the interior of $\beta$ grain.

It is reported in several $\beta$ titanium alloys, two types of $\alpha$ precipitates were found when materials were aged in different temperature ranges. In 1970s, in Ti-14wt%Mo-6wt%Al and Ti-11.6wt%Mo $\beta$ titanium alloys, C. Rhodes et al. [70] reported when materials were aged in the temperature range between 400°C and 650°C, type 1 $\alpha$ precipitates formed at beginning and then this type 1 $\alpha$ precipitates were replaced by type 2 $\alpha$ precipitates after a long time isothermal aging; when alloys were aged at the temperature region higher than 650°C, type 2 $\alpha$ would form directly rather than type 1 $\alpha$. It was also pointed out that type 1 $\alpha$ phase obeyed Burgers orientation relationship with parent $\beta$ phase while type 2 $\alpha$ phase did not. The difference of two types of $\alpha$ precipitates was attributed to Mo composition difference at different aging temperature range or at different aging time while being aged at same temperature. At a higher aging temperature or longer aging period, in some local region of $\beta$ matrix Mo could diffuse away and form some solute lean regime. Therefore, type 2 $\alpha$ is formed at the nucleation site containing a lower amount of Mo while type 1 $\alpha$ is formed at the nucleation site containing a higher amount of Mo. However, no composition analysis was provided in Ti-14wt%Mo-6wt%Al or Ti-11.6wt%Mo $\beta$ titanium alloys to support this explanation. In 1980s, E. S. K. Menon et al. [71] found two different types $\alpha$ plates in Ti-6.6at%Cr system when the material was aged.
at various temperatures. Ill-shaped $\alpha$ precipitates called normal $\alpha$ plates appeared at high aging temperature while perfectly formed $\alpha$ precipitates called black plates occurred on the condition that the alloy was aged lower than a characteristic temperature. But both two types’ $\alpha$ phases were reported obeying Burgers orientation relationship with parent $\beta$ phase. Based on the characteristic of Ti-Cr phase diagram, it was proposed that normal $\alpha$ precipitates occur when $\alpha$ phase equilibrates with Ti-rich $\beta$ phase while black plate $\alpha$ phase occurs when it maintains equilibrium with Cr-rich $\beta$ phase. However, there was no composition measurement provided to verify the proposed mechanism, such as characterize solute lean and solute rich $\beta$ phase. In 2000s, similar results were reported in Ti-4.5Fe-6.8Mo-1.5Al $\beta$ titanium alloy. S. M. C. van Bohemen et al. [72] found that two types of $\alpha$ precipitates were formed when the alloy went through a similar single step aging process. Primary $\alpha$ plates were formed on $\beta$ grain boundary when the alloy was aged at 735°C on the other hand “bainitic” $\alpha$ plates were formed when it was aged at 615°C. The above phenomenon was explained by that bainitic $\alpha$ plates formed by partitionless mechanism with no volume change while primary $\alpha$ plates formed by partitioning mechanism with volume change based on the result of composition analysis. However, the reason why $\alpha$ precipitates may form by different mechanisms when the alloy was aged at different temperature range still remains a problem. There is not a complete set of theory to explain above phenomena in all materials. Therefore, the transformation mechanism, especially the nucleation mechanism of the second type $\alpha$
formed at lower temperature range which is of much finer size scale, is of great interests and still needs to be studied in detail.

In this chapter, Ti-5553 and Ti-15Mo, two types characteristic β titanium alloys, are selected to study microstructure evolution especially α precipitation while being aged at different temperature ranges. The features of structure and composition change during transformation are introduced first. Based on these features, different transformation mechanisms are proposed and will be discussed in details.

4.2 Experiment Procedure

Raw material of Ti-5553 alloy in the size of ~ 15 mm diameter cylinder was provided by TIMET Corporation. The raw material was sectioned into ~ 10 mm slices using EDM. All sectioned samples were heat treated in two neighboring tube furnaces. One of the furnaces was used for above β transus solutionizing and the other one was used for aging in α+β temperature range. All samples were solutionized at 1000°C (β transus around 845°C) for 30 minutes and pulled out from the first furnace into the second one quickly. Then samples were step quenched to 700°C, 650°C and 600°C and isothermally held for different times. Finally all samples were water quenched to room temperature in order to preserve the microstructure obtained after isothermal thermal aging.
Raw material of Ti-15Mo bulk sample in the size of 50mm×40mm×3mm was provided by TIMET Corporation. Then the raw material was cut into 40mm × 3mm × 1.5mm bars to be heat treated in ETMT. All samples were solutionized at 1000°C for 30 minutes and then step quenched to 735°C, 700°C and 600°C. Samples were isothermal annealed for various time to study the transformation kinetics and finally fast cooled to room temperature.

Samples for SEM studies, TEM studies and 3D atom probe studies were prepared following the routine described in chapter 3. These samples were investigated using FEI Sirion™ FEG SEM operating at 12kV, Philips CM200 TEM, at 200kV, FEI Tecnai TEM at 200kV and LEAP system with an evaporation rate of 0.2 – 1.0 % and a pulsing voltage at 20% of the steady-state applied voltage.

4.3 Results and Discussion

4.3.1 Ti-5553

4.3.1.1 Formation of Refined Intragranular α Phase

Microstructure of Ti-5553 aging at 700°C is shown in figure 4.1. After 4 hours aging at 700°C, coarse size scale grain boundary allotrimorph α and intergranular widmanstatten α were present. Allotrimorph α nucleates from β grain boundary and grows along β grain boundary. In some part of region, the α/β interface is smooth while in other regions, the α/β interface is irregular. PFZ is present in some region near grain boundary.
Intergranular $\alpha$ nucleates from $\beta$ grain boundary or grain boundary $\alpha$ and grows into the interior of $\beta$ grain. The size of intergranular $\alpha$ is more than 50$\mu$m long and some of them are more than 100$\mu$m. The $\alpha/\beta$ interface is of irregular shape. The formation of $\alpha$ phase at 700°C is consistent with classical nucleation theory. Grain boundary and preformed interface are favorable nucleation sites of precipitates to further release the total gibbs free energy of system.

The microstructure of Ti-5553 aged at 650°C is shown in figure 4.2. After only 1 hour, grain boundary $\alpha$, inter granular $\alpha$ and intragranular $\alpha$ are all formed in the material. The size scale and morphology of $\alpha$ precipitates change a lot compared to the microstructure formed at 700°C. The size of $\alpha$ precipitates within $\beta$ grain is more uniform, between 2$\mu$m to 5$\mu$m long, no matter it is formed in the interior of $\beta$ grain or near grain boundary region. The size of $\alpha$ precipitates suddenly drops from more than 50$\mu$m long down to less than 5$\mu$m long. The $\alpha/\beta$ interface is smooth and no longer of irregular shape. The kinetics of $\alpha$ precipitation is much faster than that is at 700°C as only after one hour the volume fraction of $\alpha$ phase is much higher than that at 700°C, which means 650°C is more close to nose temperature in the TTT diagram.

The microstructure of Ti5553 aged at 600°C for various time periods are shown in figure 4.3 and figure 4.4. After 30 minutes aging at 600°C, refined $\alpha$ precipitates were
uniformly formed in β grains. The size of α precipitates is around 5μm long. Three α variants prefer to form triangle shape cluster. Even after 17 hours aging at 600°C, a long time coarsening process, the size of α precipitates still does not increase to the size of α precipitates formed at 700°C and the volume fraction of α precipitates still does not change. It means at 30 minutes aging, the volume of α phase in the system almost achieves equilibrium value.

Obviously, compared the microstructure formed at 600°C with that at 700°C, the size scale, morphology and distribution of α precipitates are completely different. A type uniformly distributed refined α precipitates are formed at 600°C. The size of intragranular α precipitates is uniform but much smaller than those formed at 700°C. Even after a long time aging, the size of α precipitates is still much finer than that of 700°C.

As is well known, the second phase or metastable phase, such as ω phase or β' phase in titanium alloys is regarded as kind of possible favorable nucleation sites for α precipitates. But 600°C is much higher than the widely believed ω phase solvus in Ti-5553 (between 400°C and 500°C). It means that in step quench heat treatment, there is no way for ω phase to form and therefore, ω phase is not the reason that causes the suddenly formation of refined uniform intragranular α phase. In the Ti-Mo binary phase diagram,
there is a possible phase separation present. Using the current Mo equivalency of Ti-5553, which is around 9wt%, at 600°C Ti-5553 is outside miscibility gap and therefore, phase separation should not be present in the system at 600°C. Then β' phase could not influence the sudden nucleation rate increase either. Therefore, the formation of α phase at 600°C in Ti-5553 is directly from β matrix. There is a sudden increase in the nucleation rate and decrease in the size scale of α precipitates.

4.3.1.2 Characteristics of Refined α Precipitates

In order to study the transformation mechanism of refined α precipitate, a thorough description of characteristics of refined α phase is summarized in following aspects:

1. Temperature dependence of refined α phase

The refined α phase is formed while being step quenched from above β transus to intermediate temperature range and isothermally aged at same temperature. When sample is step quenched and isothermally held at 700°C, coarse α phase is formed. It is consistent with classical nucleation theory, because coarse α precipitates first form along grain boundary and grow along grain boundary. When sample is step quenched to 650°C and 600°C, there is a sudden increase of nucleation rate of intragranular α phase, which cannot be explained by classical nucleation theory. Judging from the size scale and
uniformity of $\alpha$ precipitates, it indicates that all $\alpha$ precipitates are formed almost at the same time without influence of grain boundary.

Based on these experimental results, there appears to be a substantial difference between morphology and size scale of $\alpha$ precipitates, nucleation density and the kinetics of $\alpha$ precipitation, between the annealing temperatures of on the one hand 700°C, and on the other hand 650°C and 600°C. This suggests that there is possible a change in the mechanism of $\alpha$ precipitation between annealing step-quenched samples at 700°C and 650°C.

2. Structure of refined $\alpha$ phase

In order to determine the structure of precipitates formed in intermediate temperature range, Ti-5553 sample step quenched to 600°C and held for 15 minutes was characterized in transmission electron microscope. The results are shown in figure 4.5a and 4.5b. In $[110]$ $\beta$ zone axis diffraction pattern, $\alpha$ reflections are present. In the corresponding dark field image selecting reflection belonging to $\alpha$ phase, it is confirmed that the size of $\alpha$ phase suddenly drops to hundreds nanometers long and its interface is smooth. Above results clearly indicate that there are BCC and HCP crystal structures present in the system. Therefore it is reasonable to conclude that $\alpha$ phase forms directly with the HCP crystal structure from $\beta$ matrix.
3. Composition of refined $\alpha$ phase

The compositions of $\alpha$ and $\beta$ phase across $\alpha/\beta$ interface at nanoscale were studied using 3D atom probe in isothermally aged Ti-5553 samples. The focus was to determine whether the chemical composition of as-formed $\alpha$ phase is at or close to equilibrium, indicating a classical nucleation mechanism, or the composition changes as a function of holding time at temperature following step-quenching implying a non-classical nucleation mechanism.

The 3D atom probe results of compositional variations during isothermal aging at 600°C are shown in figure 4.6. Figure 4.6a shows the composition at $\alpha/\beta$ interface in Ti-5553 isothermally aged at 600°C for 15 minutes. Al amount increases to content of 13 at% in $\alpha$ phase region from on average around 7 at% in $\beta$ phase region. On the other hand, $\beta$ phase stabilizers, V amount drops from around 9 at% in $\beta$ phase region to less than 2 at% in $\alpha$ phase region; Cr amount drops from around 5 at% in $\beta$ phase region to less than 1 at% in $\alpha$ phase region; Mo amount drops from more than 4 at% in $\beta$ phase region to around 3 at% in $\alpha$ phase region. In figure 4.6b, the composition across $\alpha/\beta$ interface region in Ti-5553 after 17 hours isothermal aging at 600°C is shown. Al amount in $\alpha$ phase region continues to grow to the content around 16 at% while in $\beta$ phase region its content drops to around 6 at%. The same gradual composition variations happen to $\beta$
phase stabilizers too. In $\alpha$ phase region, V amount drops to around 2 at%, Cr amount drops to less than 2 at% and Mo amount drops to less than 1 at%. If only aluminum is considered near $\alpha/\beta$ interface region, its profiles at 15 minutes, 30 minutes and 17 hours aging at 600°C are shown in figure 4.6c. In the precipitated $\alpha$ phase, the amount of Al changes from around 13 at% at 15 minutes to around 14 at% at 30 minutes and finally to around 16 at% after 17 hours aging. The above results clearly indicate that the composition of $\alpha$ precipitates at the initial stage of its precipitation is far from equilibrium composition and with continuous isothermal aging its composition is driven towards to the equilibrium value by diffusion.

Therefore, in summary the characteristics of refined $\alpha$ precipitates are:

1. A refined dispersion of $\alpha$ precipitates in $\beta$ matrix can be effected by heat-treatment in the absence of previously claimed heterogeneous nucleation sites. No other obvious heterogeneous nucleation pathways were identified.

2. The formation of refined $\alpha$ precipitates is significant temperature dependent, associated with the phase transformation such that over a 50°C temperature decrease in the aging temperature following step-quenching from above $\beta$ transus, the nucleation rate jumps by several orders of magnitude.
3. At the initial stage of precipitation, HCP structure has been formed in the product phase. It indicates the structure change in phase transformation has completed.

4. The composition of product phase gradually changes towards to the equilibrium value during isothermal aging. At the initial stage of precipitation, the composition of product phase is far from equilibrium, which indicates the composition change is not in the same pace as its structure change.

4.3.1.3 Mechanisms of Refined $\alpha$ Precipitation

Based on previously summarized features of refined $\alpha$ precipitates, it appears that this transformation involves a mechanism of homogeneous nucleation without influence of any metastable phases. Secondly this phenomenon is heavily dependent on isothermal aging temperature. The sudden increase of nucleation rate is hard to be explained by the increase of undercooling using classical nucleation and growth mechanism. What’s more, the structure of product phase will form prior to the composition of product phase arriving equilibrium, which indicates there may be a displacive or diffusionless component of transformation before diffusion occurs. Therefore, a new non-classical homogeneous nucleation mechanism which could explain all the above features is described in the following part.
The proposed precipitation mechanism is inspired by the pseudo-spinodal decomposition concept that was recently proposed by Ni and Khachaturyan, which has been introduced in section 2.7. Pseudo-spinodal decomposition occurs on the condition that the composition of material is located not far from the intersection point of parent phase and product phase in gibbs free energy versus composition curve. The transformation of pseudo-spinodal decomposition is composed of three stages:

1. Local composition shifts from the side that parent phase has lower gibbs free energy than product phase to the side that parent phase has higher gibbs energy than product phase via composition fluctuation.

2. In the local region that product phase is more energy favorable, parent phase transforms to product phase via the fastest transformation path, diffusionless transformation.

3. The composition of product phase gradually changes toward to equilibrium value via diffusion.

Therefore, in current Ti-5553 system, at 700°C the composition is still far from the intersection point of α phase and β phase in gibbs free energy curve, which in other words means composition fluctuation is not enough to drive composition to the other side
of intersection point (shown in figure 4.7). Then the total gibbs free energy of the system can only be reduced by the classical nucleation and growth mechanism. On the other hand, because the intersection point of $\alpha$ phase and $\beta$ phase in gibbs free energy curve would be highly depend on temperature, at 600°C the composition of Ti-5553 could be close to the intersection point, which indicates that pseudo-spinodal decomposition could occur (shown in figure 4.8).

The phase transformation mechanism at 600°C is summarized in Fig. 4.9. Thus, the alloy composition, lies close to $c_0(T)$, such that a small compositional fluctuation, shown in red in the figure, may result in the composition in some local region jumps to the solute lean side of $c_0(T)$. As a result, the energy barrier for transformation would be markedly reduced in these local regions and they would be favorable to direct transform into the product $\alpha$ phase. The composition of precipitated $\alpha$ phase would be the same as that of parent $\beta$ phase and so far from equilibrium. Continued isothermal aging at the temperature of precipitation would be accompanied by diffusion of solute so that the compositions of $\alpha$ and $\beta$ phases would continually change towards equilibrium.

This proposed mechanism could fully explain the four features listed in section 4.2.1.2.
1. The compositional instability within β matrix due to compositional fluctuation is intrinsic to the given alloy system and does not involve heterogeneous pathways.

2. The thermodynamic conditions for pseudo-spinodal decomposition is strongly dependent on temperature, because nucleation will only occur on the condition that the alloy composition is within a small deviation from the given c0(T). For a given alloy, c0(T) is influenced by temperature.

3. The equilibrium crystal structure is expected to form as soon as the composition shifts to the side that product phase is more energy favorable. Because the energy barrier is reduced, the transformation would occur via the fastest mode, which is possible diffusionless displacive transformation.

4. The initial composition of product phase in the proposed mechanism is far from equilibrium and therefore will continually change towards the equilibrium value to decrease the total energy of system.

### 4.3.1.4 Thermodynamic Calculation

The previous discussion presented above is based on schematic gibbs free energy plots. In order to verify the proposed transformation mechanism, the gibbs free energy of Ti-Mo system were calculated using Thermo-Calc, considering that Mo-equivalency is used to represent the composition of alloy Ti-5553, to evaluate thermodynamic conditions Ti-5553 satisfy at various temperature. Thus, calculations of G-X plots for Ti-Mo alloys at
700°C and 600°C are presented in Fig. 4.10(a) and 4.10(b), respectively. The Mo equivalency for the composition of alloy Ti-5553 is \( \approx 10 \); for the case of 700°C (Fig. 4.10(a)), there is a reasonable difference between the alloy composition and \( c_0(T) \), whereas for the case of 600°C (Fig. 4.10(b)), the alloy composition is much closer to \( c_0(T) \). These calculations validate the arguments made above using schematic diagrams and confirm that at 600°C Ti-5553 satisfies the thermodynamic conditions of pseudo-spinodal decomposition.

### 4.3.1.5 Discrepancy on Mo Equivalency of Ti-5553

As introduced in chapter 2, there are several methods in experiment to determine Mo equivalency of a specific alloy besides using the equation to calculate its value. However, different methods to calculate Mo equivalency of Ti-5553 do not provide consistent result. In current work, \( \beta \) transus temperature and as-quenched condition microstructure were utilized to study Mo equivalency of Ti-5553.

1. \( \beta \) transus temperature

The experimentally measured \( \beta \) transus temperature of Ti-5553 could be compared with that of various Ti-Mo alloys to obtain the Mo equivalency of Ti-5553. There are two available experimentally determined \( \beta \) transus temperatures. The first one is the reported experiment determined \( \beta \) transus temperature for commercially used Ti-5553. Its value is
around 845°C--855°C[60]. The other one is the value measured from current material by electrical resistivity measurement using ETMT.

The electrical resistivity change of Ti-5553 during continuous heating process is shown in figure 4.11. The detail explanation related to electrical resistivity measurement will be discussed in chapter 6. In the curve, there are three inflection points. The first and second inflection points in relative low temperature range, between 300°C and 450°C, are related to ω phase and α phase formation. In high temperature range, around 870°C, another inflection point is identified which is due to α to β transition. Therefore the temperature of the 3\textsuperscript{rd} inflection point in electrical resistivity change curve could be treated as the β transus temperature.

The calculated β transus temperatures for various Ti-Mo alloys using Pandat software are listed in table 4.1. Compared the experimentally determined β transus temperature of Ti-5553 with the values of various Ti-Mo alloys, it is mostly close to that of Ti-3wt%Mo. Therefore judging from β transus temperature aspect, Mo equivalency of Ti-5553 is close to 3wt%.

2. As-quenched condition microstructure

With increasing molybdenum amount in Ti-Mo alloys, different product phase could be present in as-quenched state from above β transus solution, such as α’ phase, α” phase, ω
phase and β' phase. Therefore as-quenched state microstructure could be used roughly determine the Mo equivalency of specific alloy.

Dark field TEM image and diffraction pattern from the as-quenched state Ti-5553 are shown in the figure 4.12. In [110] BCC zone axis diffraction pattern, ω reflection is present. In the corresponded dark field image, athermal ω particles of which sizes are no more than 10 nm are homogeneously distributed in β phase matrix.

As-quenched state microstructures of Ti-Xwt%Mo have been reported in the paper by R. Davis[41]. HCP structure α' phase is present up to around 4wt%Mo and then orthorhombic structure α" phase is present up to around 10wt%. If molybdenum amount in Ti-Mo alloy is higher than 10wt%, ω phase is formed in as-quenched state.

Compare as-quenched state microstructure of Ti-5553 to the above results, it is similar to the Ti-Mo alloy containing at least 10wt% Mo. Therefore judging from the as-quenched state microstructure, Mo equivalency of Ti-5553 is at least 10wt%.

Therefore, it needs to be point out that Mo equivalency is a very controversial method to describe or evaluate the influence of various elements within titanium alloy. Especially, if there are any α phase stabilizers, such as Al and O, in the system, Mo equivalency is even less important or effective. What is more, there is not a single experiment that can
be utilized to determine the Mo equivalency of a specific alloy. Mo equivalency of a specific alloy measured from different methods could be not consistent with each other. In current study, Mo equivalency of Ti-5553 is treated as the value close to 10wt% based on its as-quenched microstructure.

4.3.2 Ti-Mo

The proposed mechanism of precipitation of refined α from β phase in previous section, involving compositional fluctuations, is expected to apply to a more general group of titanium alloys rather than be restricted to the present alloy system under discussion. Thus, the mechanism is expected to be relevant to any potential phase transformation where the sample composition is sufficiently close to the appropriate $c_0(T)$. Ti-Mo is a simple but characteristic monotectoid titanium alloy. As a simple binary system, the gibbs free energy curve is available for either α phase or β phase in all temperature ranges. So Ti-Mo is a proper candidate to study refined α precipitates and verify the pseudo-spinodal decomposition mechanism, except that there is controversy whether there is miscibility gap or not in Ti-Mo system. In current study, the experimentally reported phase diagram by Furuhara et al in the year of 1998 was used as standard reference[49]. The phase diagram plotted using the Pandat 7 software and its Ti-Mo binary database was compared with Dr. Furuhara’s phase diagram to verify its eligibility to plot its gibbs free energy curves. The plotted phase diagram using Pandat and experimental reported phase diagram are shown in Figure 4.13. It is noticed in the phase
diagram, there is monotectoid temperature which is around 690°C--710°C. Therefore, the isothermal annealing temperatures were selected above and below this monotectoid temperature range.

4.3.2.1 Formation of Refined α Phase

Ti-10wt%Mo is the first candidate selected in current work, because Mo equivalency of Ti-5553 in the previous part is treated as 10wt%. The microstructure of Ti-10wt%Mo step quench from above β transus temperature and isothermally aged at 700°C and 600°C are shown in figure 4.14 and figure 4.15. After 5 minutes aging at 700°C, allotrimorph α is present at β grain boundary and few number of intergranular α form at allotrimorph α and grow towards to the interior of β grain. But there is no intragranular α found in the interior of β grain. After 30 minutes isothermal aging at 700°C, a few number of coarse intragranular α precipitates are present and α/β interface is of irregular morphology. When the aging temperature drops to 600°C, after 5 minutes, large number density of intragranular α are present. The formed α precipitates prefer to form triangle shape cluster and their interfaces are smooth. After 30 minutes aging at 600°C, the volume fraction of α precipitates increases and smooth interface refined α precipitates still remain triangle shape cluster. Judging from the number density, morphology and size scale of α precipitates in Ti-10wt%Mo, coarse intragranular α formed at 700°C is similar to the conventional α in Ti-5553 formed at high temperature range while refined α
precipitates formed at 600°C is similar to those pseudo-spinodal type α precipitates formed in Ti-5553 at intermediate temperature range. The above results indicate in Ti-Mo system, when the average composition of material is close to that \( c_0(T) \), a different type of α phase does form and it could be formed by pseudo-spinodal decomposition mechanism.

The second candidate is Ti-15wt%Mo, a system that is some distance away from \( c_0(T) \) at both 700°C and 600°C. The microstructure of Ti-15wt%Mo step quenched from above β transus temperature range to 735°C and isothermally aged for 30 minutes is shown in figure 4.16. After 30 minutes aging at 735°C, very few number of coarse size scale intragranular α precipitates are present. The α/β interface is of irregular morphology. When the isothermal aging temperature drops to 700°C (shown in figure 4.17), after 30 minutes holding, more intragranular α precipitates are present in β matrix and α precipitates still have irregular interface. Based on the size scale, morphology and distribution of α phase, α precipitates formed at 735°C and 700°C belong to the same type. When the isothermal aging temperature continues decreasing to 600°C, refined α precipitates are formed (shown in figure 4.18). The density of α precipitates suddenly increases and α/β interface changes to smooth morphology. After longer time holding at 600°C, α precipitates grow, intersect with each other and form triangle shape cluster. Compared the morphology and size scale of microstructure in Ti-15wt%Mo with that in Ti-5553, coarse intragranular α formed at 735°C and 700°C are similar to conventional α
in Ti-5553 formed at high temperature range while refined α precipitates formed at 600°C is similar to those pseudo-spinodal type α precipitates formed in Ti-5553 at intermediate temperature range. Results in Ti-15wt%Mo indicate that even though the average composition is way off the $c_0(T)$, refined α precipitates still could form in material. However, there is no convincing result showing the thermodynamic database of Ti-Mo is reliable except that the plotted phase diagram using this database is consistent with the experiment reported one. As mentioned in the beginning of this section, there is a controversy whether there is miscibility gap in Ti-Mo alloy. Therefore, the plotted phase diagram using the current Ti-Mo database may be questionable and the plotted gibbs energy curve and calculated $c_0(T)$ are in doubt.

Then the third step of current work in Ti-Mo is to study in what kind of composition range that refined α precipitates could be formed while being aged at 600°C. Ti-7.5wt%Mo and Ti-12wt%Mo were selected to be step quenched from 1000°C and isothermally aged at 600°C for 30 minutes. The microstructure of Ti-7.5wt%Mo and Ti-12wt%Mo are shown in figure 4.19 and 4.20. In both two alloys, refined α precipitates of high nucleation density are present in the interior of β grain. Therefore, it means in Ti-Mo system, refined α precipitates not only occur in the alloy whose composition is close to $c_0(T)$ but also occur in Ti-Mo of a wide range composition.

**4.3.2.2 Characteristics of Refined α Phase**
1. Temperature dependency

The refined $\alpha$ precipitates are formed when Ti-Mo is step quenched from above $\beta$ transus temperature to an intermediate temperature range and isothermally aged. When isothermal aging temperature is around 700°C, irregular shape coarse $\alpha$ precipitates are present; when isothermal aging temperature is as high as 600°C, refined $\alpha$ precipitates of smooth interface are formed. Therefore, in order to obtain refined $\alpha$ precipitates the isothermal aging temperature has to be selected within an intermediate temperature range. Based on the sudden nucleation rate increase and morphology change of $\alpha$ phase, there seems to be transformation mechanism change between 700°C and 600°C.

2. Composition

The composition of refined $\alpha$ precipitates formed in Ti-15wt%Mo at 600°C for 30 minutes and 24 hours were studied using STEM EDS shown in figure 4.21 and figure 4.22. After only 30 minutes isothermal aging at 600°C, Mo amount in $\alpha$ precipitates has already dropped to around 0.5wt%; while after 24 hours isothermal aging at 600°C, the average Mo amount in $\alpha$ precipitates is almost the same, which is around half weight percent. The calculated equilibrium composition of $\alpha$ precipitates at 600°C using Pandat is less than 0.1wt%. Therefore, considering accuracy of STEM EDS, the composition of $\alpha$ precipitates formed at 600°C in 30 minutes is close to equilibrium.

3. Etching Effect
The optical microscope images of etched Ti-15wt%Mo and Ti-8wt%Mo are shown in figure 4.23 and figure 4.24. Ti-15wt%Mo sample was β solution at 1000°C for 30 minutes, then step quenched to 600°C and isothermally aged for 30 minutes, BSE image clearly indicates the presence of large number of refine α precipitates in the interior of β grain. While in the optical microscope image, these refine α precipitates show black color and on the contrary β matrix is of white color. In order to study the etching effect of coarse α precipitates, a Ti-8wt% sample was β solution at 1000°C for 30 minutes and slow cooled to 600°C and held for 30 minutes. Coarse grain boundary α, irregular shape intergranular α and intragranular α are present in BSE SEM image with some fine scale secondary α plates in remained β matrix. In optical microscope image, all coarse size scale α precipitates including grain boundary α, intergranular α and intragranular α show white color but fine scale secondary α shows black color. Therefore, based on the etching effect, refined α precipitates formed in Ti-15wt%Mo intragranularly and secondary α in Ti-8wt%Mo shows different contrast in optical microscope compared with coarse irregular shape grain boundary α, intergranular α and intragranular α.

Compared the characteristics of microstructure in Ti-Mo and Ti-5553 after similar step quench plus isothermal aging heat treatments, two types α precipitates based on their size scale and interface morphology were found in both two systems depending on selection of different isothermal aging temperatures. Different contrast shown in optical
microscope images also indicates there are intrinsic differences between coarse \( \alpha \) precipitates and refined \( \alpha \) precipitates. However, in Ti-Mo the composition of refined \( \alpha \) and coarse \( \alpha \) are both close to the equilibrium values at initial stage of their formation, unlike the characteristic of refined \( \alpha \) in Ti-5553 that gradually approaches equilibrium composition. The presence of refined \( \alpha \) precipitates in Ti-Mo occur in a wide range of compositions not only restricted in the system whose average composition is close to \( c_0(T) \).

4.3.2.3 Discussion
As introduced in the section 4.1, there are three set of theories proposed to explain the transformation mechanism of refined \( \alpha \) in titanium alloys. The first set of theory to explain the above phenomenon is that two types of \( \alpha \) phases are equilibrium with two different \( \beta \) phases, one is solute lean \( \beta \) phase and the other is solute rich \( \beta \) phase. This theory could explain the temperature dependency of the refined \( \alpha \) microstructure completely. Further more, this mechanism also explains the results why coarse \( \alpha \) precipitates and refined \( \alpha \) precipitates both obtain almost close to equilibrium value composition at the initial stage of \( \alpha \) precipitation. Because no matter solute redistribution within \( \beta \) matrix is formed due to \( \beta \) phase separation in the whole \( \beta \) matrix region or local non-uniformity of composition caused by thermal fluctuation, it is heavily related to the temperature. And \( \alpha \) phase is formed by classical nucleation and growth mechanism, in
which process the precipitates have near equilibrium composition. In the Ti-Mo binary phase diagram, monotectoid transformation could occur between 690°C and 713°C. In the monotectoid transformation, $\beta \rightarrow \beta_1 + \alpha$, $\beta$ phase of different solute amount is able to be formed. Based on the phase diagram, the solute lean $\beta$ phase contains less than 20wt% Mo while the solute rich $\beta$ phase contains more than 80wt% Mo. At temperature higher than monotectoid temperature, the formed $\alpha$ precipitates is equilibrium with solute lean $\beta$ phase; while at temperature lower than monotectoid temperature, the fine scale $\alpha$ precipitates are equilibrium with solute rich $\beta_1$ phase. However up until now, there are no solidified results proving the conclusion whether the solute rich $\beta$ phase could possibly exist in the Ti-Mo system has been reported or observed in current study. Long time isothermal aging heat treatments were applied to Ti-15wt%Mo (24 hours at 600°C) and Ti-2wt%Mo (7 days at 600°C), but no $\beta$ phase of solute higher than 40wt% Mo has ever been observed in $\alpha$/$\beta$ interface neighboring region. Besides composition, another characteristic feature of solute rich $\beta$ phase is its lattice parameter. With increasing solute content into $\beta$ matrix, the lattice parameter of $\beta_1$ phase will deviate from its original value of solute lean $\beta$ phase. In Ti-Mo binary alloy, using Vegard’s law: The lattice parameter of solid solution composed of two elements of same structure is equal to the linear superposition of their individual lattice parameter:

$$a_{Ti-Xwt\%Mo} = X\% \times a_{Mo} + (100-X)\% \times a_{Ti}$$
The lattice parameter of BCC structure Ti-X at%Mo is therefore equal to the linear superposition of the lattice parameter of BCC structure pure titanium (3.32 angstrom) and BCC structure pure molybdenum (3.15 angstrom). Therefore the lattice parameter of solute rich $\beta_1$ phase of composition 80wt%Mo(66.62 at%Mo) is 3.21 angstrom and the lattice parameter of solute lean $\beta$ phase of composition 10wt%Mo(5.25 at%Mo) is 3.31 angstrom. In the conventional 200kV TEM of which the wave length is 0.0251 angstrom and camera length is 2915.76 mm, the distance between the 110 reflections of two lattices is only 0.97 mm which is hardly to tell using naked eyes. Therefore unless using high energy synchrotron XRD, it is hard to characterize the lattice parameter change in Ti-Mo using conventional TEM or XRD techniques. The lack of evidence showing the presence of $\beta_1$ phase could possibly be due to the slow kinetics of $\beta_1$ phase formation. If the gibbs free energy change from solute lean $\beta$ phase to solute rich $\beta_1$ phase is low and the diffusion of molybdenum is low, then the metastable state of $\alpha + \beta$ phase could be kept for a very long time. Therefore, it may take very long time for the solute rich $\beta_1$ phase to form in the Ti-Mo binary system and explain the reason why no solid proof supporting the presence of $\beta_1$ phase has ever been found. Although this mechanism could explain some features of refined $\alpha$ precipitates, no convincing results have ever been found to fully validate this mechanism.

The second set of transformation mechanism explains that refined $\alpha$ precipitates are diffuseless $\alpha$ formed in intermediate temperature range. The reported transformation
mechanism is similar to para-equilibrium phenomenon in Fe-Cr system. Near \(\gamma/\alpha\) interface region, only fast diffuser carbon achieves equilibrium on both sides of the interface, but slow diffuser chromium stays almost the same level across the interface. As it is well known, carbon in Fe-Cr is an interstitial element which could diffuse several magnitudes faster than chromium which is a substitutional element. However in most of cases solutes considered in titanium alloys are all substitutional elements, the mobility of which cannot be as different as carbon and chromium in Fe-Cr system. In current study, based on compositional measurement in Ti-15wt%Mo using STEM EDS, in intermediate temperature range, molybdenum amount in the formed \(\alpha\) precipitates is at really low level and almost close to the equilibrium. The results indicate that diffusion has already occurred during initial stage of refined \(\alpha\) precipitation in Ti-Mo alloy. There is no diffusionless \(\alpha\) precipitates found in Ti-15wt%Mo alloy even though the material is isothermally aged at intermediate temperature range. Therefore, the second set of transformation mechanism does not applied to the microstructure in Ti-Mo alloy.

The third set of transformation mechanism is pseudo-spinodal decomposition mechanism. The thermodynamic condition for pseudo-spinodal decomposition to occur is that the average composition of material at isothermal aging temperature in the gibbs free energy curve is close to \(c_0(T)\), where the molar gibbs free energy of parent phase and product phase are the same. However, the gibbs free energy curve of Ti-Mo at 600°C is shown in figure 4.10. The \(c_0(T)\) point is between 9 and 10wt%. So, Ti-15wt%Mo is more than 5
wt% away from \( c_0(T) \). This composition difference is so enormous that it is hard to drag the composition from the solute rich side of \( c_0(T) \) to the other side by the way of composition fluctuation. And one important characteristic of pseudo-spinodal decomposition is the composition of product phase will approach the equilibrium composition gradually. Judging from the composition measurement using STEM EDS, the molybdenum amount in \( \alpha \) precipitates at 600°C from 30 minutes to 24 hours (shown in figure 4.21 and figure 4.22) stays almost the same value, lower than 1wt%. It indicates based on the current experimental results, the composition of \( \alpha \) precipitates formed in Ti-15wt%Mo isothermally aged within intermediate temperature range is close to its equilibrium value. Therefore, Ti-15wt%Mo at 600°C does not satisfy the thermodynamic condition of pseudo-spinodal decomposition mechanism and the features of refined \( \alpha \) precipitates in Ti-15wt%Mo is not consistent with the characteristic of product by pseudo-spinodal decomposition.

None of the previous three sets of mechanisms can individually explain the microstructure in Ti-Mo alloy completely. But each of three mechanisms provides kind of hint and can explain part of observed features of microstructure in Ti-Mo alloys. Such as, the presence of refined \( \alpha \) microstructure is present in Ti-Mo alloy of a wide range composition can be explained by \( \beta \) phase separation due to the width of miscibility gap. The temperature dependency and a sudden increase of nucleation can be predicted using pseudo-spinodal decomposition mechanism.
Therefore, a new transformation pathway is proposed combining β phase separation and pseudo-spinodal decomposition mechanism. Besides thermal compositional fluctuation, phase separation especially spinodal decomposition could provide the other type of composition instability within β phase matrix. Then the composition shift from solute rich side of \( c_0(T) \) to the other side can be accomplished not only by local compositional fluctuation but also phase separation. After the stage of phase separation is complete, if the composition of solute lean β phase is on the side of \( c_0(T) \) where product phase is more energy favorable, then in the solute lean β phase region α precipitates could directly form by the fastest transformation mode; if the composition of solute lean β phase is close to \( c_0(T) \) but still on the side of \( c_0(T) \) where parent phase has lower gibbs free energy, the refined α precipitates could be formed by the pseudo-spinodal decomposition mechanism, in which the composition could continue shifting due to thermal fluctuation.

The phase transformation mechanism in Ti-Mo alloys at 600°C is summarized in figure 4.25. The average composition of alloy lies in the miscibility gap such that spinodal decomposition may result in the composition in some local region shifts to the solute lean side of \( c_0(T) \) or the regime close to \( c_0(T) \) in which pseudo-spinodal decomposition could happen. Then the energy barrier for transformation would be markedly reduced in these local regions. Therefore, large number density of refined α precipitates could be formed in the interior of β phase matrix.
Recently, using high energy synchrotron XRD, phase separation was characterized in the ternary alloy Ti-20Mo-5Al (all in wt%), shown in figure 4.26. [200] β peak was split when Ti-20Mo-5Al was isothermally aged at 400°C for 5 hours, which indicates the presence of two BCC lattices of slightly different parameters. Because Mo equivalency of Ti-20Mo-5Al is 15wt%, synchrotron XRD result in Ti-20Mo-5Al indicates β phase separation could possibly to occur during isothermal aging. However, more experiment work still needs to be done in Ti-Mo alloy in order to verify whether or not there is β phase separation occurring in this system.

4.4 Conclusion

The microstructure in two different β titanium alloys, Ti-5553 and Ti-15Mo, isothermally aged at different temperature ranges were studied using SEM, TEM and 3D APT. The main conclusions are summarized in the followings:

1. Two different types of α precipitates were formed in both alloys. During high temperature aging, coarse size scale, irregular shape α/β interface α precipitates are present; while during intermediate temperature aging, refined smooth α/β interface α precipitates are homogeneously present within β grains.

2. In Ti-5553, the composition of refined α formed in the intermediate temperature range slowly and gradually achieves equilibrium value. In Ti-15wt%Mo, the composition of
refined $\alpha$ formed in the intermediate temperature range stays almost the same from 30 minutes to 24 hours isothermal holding.

3. A new type non-classical homogeneous transformation mechanism, pseudo-spinodal decomposition, could be applied to Ti-5553 under the condition that the Mo equivalency of Ti-5553 is around 10wt%. Around 600°C, the composition of Ti-5553 is close to the $C_0$ point in the gibbs free energy curve. Therefore, causing by the composition fluctuation, the composition of some local region could shift to the other side of $C_0$ point where the molar free energy of $\alpha$ phase is more favorable than that of $\beta$ phase. It will cause a rapid structure change from BCC to HCP without any composition change. With long time aging, the composition of new HCP structure $\alpha$ phase will slowly achieve equilibrium as shown in the result of atom probe.

4. Mo equivalency of Ti-5553 is a controversial problem. There is not a convincing method to experimentally determine the Mo equivalency of a specific alloy. Using different experimental methods, the measured Mo equivalency of Ti-5553 is not consistent with each other.

5. The formation of refined $\alpha$ precipitates is present in a wide range of Ti-Mo alloys while being isothermal aged in the intermediate temperature range. A sudden increase of
the nucleation rate, a decrease of $\alpha$ precipitate size and a change of interface morphology are the common characteristics.

6. A new transformation pathway is proposed in Ti-Mo alloys. $\beta$ phase separation could happen first and cause local compositional instability in $\beta$ matrix. Then the pre-formed local compositional instability could assist the following pseudo-spinodal decomposition. Spinodal decomposition could act as the precursor of refined $\alpha$ precipitates in Ti-Mo alloys.
Figure 4.1 Microstructure of Ti-5553 step quenched from 1000°C to 700°C, isothermally held for 4 hours and water quenched to room temperature.
Figure 4.2 Microstructure of Ti-5553 step quenched from 1000°C to 650°C, isothermally held for 1 hour and water quenched to room temperature.
Figure 4.3 Microstructure of Ti-5553 step quenched from 1000°C to 600°C, isothermally held for 30 minutes and water quenched to room temperature.
Figure 4.4 Microstructure of Ti-5553 step quenched from 1000°C to 600°C, isothermally held for 17 hours and water quenched to room temperature.
Figure 4.5 Microstructure of Ti-5553 step quenched from 1000°C to 600°C, isothermally held for 15 minutes and water quenched to room temperature. (a) bright field and dark field images (b) [110] β zone axis diffraction pattern
Figure 4.6 The composition across α/β interface in isothermally aged Ti-5553 at 600°C

(a) 15 minutes  (b) 17 hours  (c) Al amount across α/β interface after various times
Figure 4.6 Continued
Figure 4.7 Schematic gibbs free energy curve of $\alpha$ and $\beta$ phase at 700°C

Figure 4.8 Schematic gibbs free energy curve of $\alpha$ and $\beta$ phase at 600°C
Figure 4.9 Schematic gibbs free energy curve indicates the stages of pseudo-spinodal decomposition mechanism in Ti-5553
Figure 4.10 Gibbs energy curve of Ti-Mo system at temperature 700°C(a) and 600°C(b)
Figure 4.11 Relative resistance via temperature change during continuous heating in Ti-5553

Table 4.1 Calculated $\beta$ transus temperature of various Ti-Mo alloys

<table>
<thead>
<tr>
<th>wt%</th>
<th>$K$</th>
<th>$^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-2Mo</td>
<td>1131.3</td>
<td>858.1</td>
</tr>
<tr>
<td>Ti-8Mo</td>
<td>1065.6</td>
<td>792.5</td>
</tr>
<tr>
<td>Ti-12Mo</td>
<td>1025.9</td>
<td>752.7</td>
</tr>
<tr>
<td>Ti-15Mo</td>
<td>997.9</td>
<td>724.7</td>
</tr>
<tr>
<td>Ti-18Mo</td>
<td>971.2</td>
<td>698.1</td>
</tr>
</tbody>
</table>
Figure 4.12 Microstructure of as-quenched state Ti-5553 (a) [110] β zone axis diffraction pattern (b) corresponding dark field image using ω reflections
Figure 4.13 Phase diagram of Ti-Mo binary alloy. (a) Pandat calculated phase diagram
(b) experimental reported phase diagram
Figure 4.14 Microstructure of Ti-10wt%Mo step quenched from 1000°C to 700°C, isothermally held for 5 minutes (a) or 30 minutes (b) and water quenched to room temperature.
Figure 4.15 Microstructure of Ti-10wt%Mo step quenched from 1000°C to 600°C, isothermally held for 5 minutes (a) or 30 minutes (b) and water quenched to room temperature.
Figure 4.16 Microstructure of Ti-15wt%Mo step quenched from 1000°C to 735°C, isothermally held for 30 minutes and water quenched to room temperature.

Figure 4.17 Microstructure of Ti-15wt%Mo step quenched from 1000°C to 700°C, isothermally held for 30 minutes and water quenched to room temperature.
Figure 4.18 Microstructure of Ti-15wt%Mo step quenched from 1000°C to 600°C, isothermally held for 30 minutes(a)/ 60 minutes(b) and water quenched to room temperature.
Figure 4.19 Microstructure of Ti-7.5wt%Mo step quenched from 1000°C to 600°C, isothermally held for 30 minutes and water quenched to room temperature.

Figure 4.20 Microstructure of Ti-12wt%Mo step quenched from 1000°C to 600°C, isothermally held for 30 minutes and water quenched to room temperature.
Figure 4.21 Composition analyses across α/β interface in Ti-15wt%Mo step quenched from 1000°C to 600°C, isothermally held for 30 minutes and water quenched to room temperature
Figure 4.22 Composition analyses across α/β interface in Ti-15wt%Mo step quenched from 1000°C to 600°C, isothermally held for 24 hours and water quenched to room temperature.
Figure 4.23 Microstructure of Ti-15wt%Mo step quenched from 1000°C to 600°C, isothermally held for 30 minutes and water quenched to room temperature. (a) BSE SEM image before being etched (b) optical scope image after being etched
Figure 4.24 Microstructure of Ti-8wt%Mo containing coarse α phase (a)BSE SEM image before being etched (b)optical scope image after being etched
Figure 4.25 Schematic gibbs free energy curve indicates the stages of transformation pathway in Ti-Mo alloy
Figure 4.26 High energy synchrotron XRD result of Ti-20Mo-5Al (wt%) isothermally aged at 400°C from 0 minute to 318 minutes.
Chapter 5

ω Phase Assisted Super-refined α Precipitation in β Titanium Alloys

In this chapter, the influence of ω phase on following α precipitation and the transformation mechanism of super-refined α precipitates will be discussed. The influence of heating rate before material arrives the peak isothermal aging temperature on the final microstructure in Ti-5553 and Ti-15wt%Mo is studied using scanning electron microscopy, transmission electron microscopy and 3D atom probe. In Ti-5553 two types of α precipitates of different morphology, size and distribution are obtained when various heating rates are adopted. Triangle shape cluster refined α plates are present in the interior of β phase grain after fast heating up such as at the rate of 100°C/min, while even refined α or what we called super-refined α precipitates could be formed homogeneously within β phase matrix after slow heating such as at the rate of 5°C/min. These two types α precipitates only coarsen but do not transform into each other even after long time isothermal aging. More experiment results indicate that previous microstructure difference occurs during continuous heating before summit isothermal aging temperature is achieved. During fast continuous heating, refined α precipitate are formed and at the
initial stage of $\alpha$ precipitation, $\alpha$ precipitates prefer to form the [11\overline{2}0]/60’ type $\alpha/\alpha$ boundary and consist 3 variants triangle cluster, which is expected to be more energy favorable when elastic interaction energy is taken into consideration. During slow continuous heating, super-refined $\alpha$ precipitates are formed with the presence of pre-formed isothermal $\omega$ particles which could influence the stress field and chemical compositional filed in the nearby region and therefore provide potential favorable $\alpha$ nucleation sites that could compete with grain boundary. However, in Ti-15wt%Mo, after being heat treated in a similar thermal history, slow continuous heat up, super-refined $\alpha$ microstructure has not been observed. Therefore, in Ti-5553 heating rate does play very critical role of determining the final size and morphology of $\alpha$ precipitates and this influence occurs during the process of continuous heating, but similar phenomenon is not present in Ti-15wt%Mo binary alloy.

5.1 Introduction

Due to its high strength and great deep-hardenability, Ti-5553 is a kind of promising metastable $\beta$ titanium alloy with the application in the field of aerospace, such as the landing gear components[6, 60, 61]. The strength, ductility and fracture toughness of Ti-5553 could be modified in a wide range due to its various microstructure, especially the size scale and distribution of HCP $\alpha$ precipitates obtained within BCC $\beta$ parent phase matrix, under a number of different thermo-mechanical processes[73]. Therefore,
understanding microstructural evolution in Ti-5553 under specific heat treatment is critical to manipulate the material for special applications.

The microstructure of isothermally aged Ti-5553 has been studied in previous research of Hamish group. Nag et al. have shown that refined α precipitates and isothermal ω particles could co-exist in Ti-5553 while aged at 350°C for 2 hours and nano-scale ω particles may act as favorable nucleation sites for α precipitates[74]. In the following study, it is also reported when Ti-5553 was aged at high temperature, 600°C, triangle cluster α plate of far from equilibrium initial composition were formed[75], which was named by many other researchers, type 1 α [70], black plate α [71] and bainitic α [72].

As it is well known, besides isothermal aging temperature, heating rate adopted before achieving summit isothermal temperature is another important factor that can influence the final microstructure. Recently, a type of fine scale α precipitates is reported in several different β titanium alloys when they are heated up to aging temperature at relative low heating rate, such as heating TIMETAL-LCB at the rate of 0.25°C/s and heating Ti-15-3 at the rate of 0.01°C/s[76]. The formation of fine scale α precipitates were assumed to be related to isothermal ω formation, but no direct experimental result was shown to verify ω particles were present during continuous heating process. It is also worthy to point out that it is reported a type of orthorhombic structure phase (which was labeled as α” phase, the same as people labeled for orthorhombic structure martensite) could be formed in
heating process prior to fine scale $\alpha$ precipitation. However, no TEM diffraction pattern or image has ever been provided and the indexed XRD result shown in their work is not consistent with the simulated XRD result using software Desktop Microscopist. Therefore, the microstructural evolution during fine scale $\alpha$ precipitation needs to be studied in details.

With the excellent processing equipment and advanced characterization techniques, the microstructural evolution of Ti-5553 during accurately temperature controlled heat treatment could be investigated down to nano scale level in transmission electron microscope. Therefore, there are at least three motivations for this paper:

1. Describe characteristics of $\alpha$ precipitates obtained in Ti-5553 during various heat treatments.
2. Provide direct experimental results and propose transformation mechanism that could explain the microstructure evolution.
3. Study the critical heat treatment condition to obtain different types of $\alpha$ precipitates.

### 5.2 Experimental Procedure

Ti-5553 raw material was provided by TIMET Company. The chemical composition of raw material measured using wet chemistry is listed in Table 5.1, which shows Ti-5.67Al-4.92V-5.00Mo-3.04Cr (in wt%). The as-received Ti-5553 block was then cut into
the 1.5mm×3mm×40mm bars using Electrical Discharge Machine, of which dimension the sample could fit to be electrical resistance heated in Electrical-Thermal-Mechanical-Tester (ETMT). Due to the small size of sample and resistance heating capability of ETMT, various heating rates of a wide range could be achieved. All heat treatments were completed in ETMT under vacuum condition. Same β solution processes were applied to all the samples, 1000°C (\( T_\beta \) of Ti-5553 is 855°C) solutionized for 30 minutes and fast cooled to room temperature. As-quenched state microstructure was observed using transmission electron microscope to verify the above β-solution process guaranteeing no α precipitates left in samples. After β-solution, all as-quenched samples were thermal processed in four different groups: The 1st set of samples were going through a continuous heating plus short time isothermal aging process to study characteristic of final microstructure, especially the size and distribution of α precipitates in β matrix. As-quenched samples were heated up to 600°C at the heating rate of 100°C/min, 50°C/min, 20°C/min and 5°C/min and held for 4 hours or 2 hours before fast cool to room temperature. The 2nd set of samples were going through a continuous heating plus long time isothermal aging process in order to study the microstructure of near equilibrium. As-quenched samples were heated at the rate 100°C/min to 600°C and held for 17 hours or 5°C/min to 600°C and held for 15 hours before fast cooled to room temperature. The 3rd set of samples were going through a continuous heating process at various rates in order to separate the influence of continuous heating and isothermal heating on final microstructure. As-quenched samples were heated up to 600°C at the heating rate of
100°C/min, 20°C/min, 5°C/min and 2°C/min and without any time holding directly cooled to room temperature. The 4th set of samples were going through continuous heating process to various temperatures in order to detail study of microstructural evolution. As-quenched samples were heated up to 500°C and 600°C at the rate of 100°C/min and to 350°C, 375°C, 400°C and 600°C at the rate of 5°C/min.

SEM samples were cut in the center of pro-heat treated bars and prepared following a conventional grinding and polishing route. The polished samples were characterized in FEI Sirion FEG scanning electron microscope operating at 12KV. For detailed microstructure study, site-specific TEM foils were prepared using Focused Ion Beam technique, specifically FEI Helios Nanolab 600 system. TEM characterization work was completed on Philips CM200 microscope and FEI Tecnai F20 microscope operating at 200KV. For composition analysis, atom probe needles were prepared using Focused Ion Beam technique, specifically the FEI Nova 200 NanoLab. These needles were used for 3D atom probe tomographay studies in a local electrode atom probe (LEAP™) system from Imago Scientific Instruments, using voltage mode at a temperature of 60K, with an evaporation rate 0.2—1.0% and a voltage pulse fraction at 20% of steady-state applied voltage.

5.3 Result and Discussion
5.3.1 Microstructure of As-quenched State Ti5553

Microstructure of as-quenched state Ti-5553 is shown in figure 5.1. In back scattered SEM image, only β grains without any α precipitates are clearly seen. In TEM diffraction pattern, additional ω reflection could be observed in [110] β zone axis diffraction, which is located at 1/3 and 2/3 of {112} positions. In the corresponding dark field image using ω reflection, homogeneously distributed ω particles of size less than 10 nm diameter are present through whole β grain. These ω particles present during fast cooling are formed by the {111} planes collapse mechanism and labeled as athermal ω or ω$_{ath}$.\cite{19, 77}

Above result verifies that 30 minutes at 1000°C guarantees that all α precipitates have dissolved into β matrix and the cooling speed in ETMT is sufficient to avoid any α phase precipitation but to form athermal ω phase. Therefore, the initial microstructure of Ti-5553 before aging is composed of remained β phase and nano-scale athermal ω particles:

$$\beta \rightarrow \beta + \omega_{ath}$$

5.3.2 Microstructure after Continuous Heating plus Isothermal Aging

5.3.2.1 Microstructure after Different Rate Heating plus Short Time Isothermal Aging

Microstructure of Ti-5553 after heated up to 600°C at 100°C/min and held for 4 hours before fast cool to room temperature indicates the presence of high volume fraction of refined α plates within β matrix, shown in Figure 5.2. In the interior of β grains, primary α plates are likely to form triangle shape cluster and smaller size secondary α could form
within primary $\alpha$ triangles region which could be explained by the mechanism of sympathetic nucleation. High angle annular dark field (HAADF) image shows that the length of primary $\alpha$ plate could be as long as 2000nm and secondary $\alpha$ plate is of 500nm long or even shorter. In $\beta$ grain boundary neighboring region, even coarser $\alpha$ plates of more than 5$\mu$m long are present. At grain boundaries, grain boundary allotriomorphic $\alpha$ and intergranular Widmanstätten $\alpha$ precipitates are both observed.

Microstructure of Ti-5553 after heated up to 600°C at 50°C/min and held for 2 hours before fast cool to room temperature is shown in Figure 5.3. Generally, the microstructure is similar to the ones shown in Figure 5.2. Primary $\alpha$ plates of triangle shape cluster are present in the interior of $\beta$ grain and even larger size $\alpha$ precipitates are present in the grain boundary neighboring region. In HAADF image, the length of $\alpha$ plate could range from several hundred nanometers to thousands of nanometers. Therefore, when the heating rate is decreased to 50°C/min, the microstructure does not change, especially the morphology and distribution of $\alpha$ precipitates are almost the same.

Microstructure of Ti-5553 after heated up to 600°C at 20°C/min and held for 2 hours before fast cool to room temperature indicating the presence of another type of much finer scale $\alpha$ is shown in Figure 5.4. In the interior of $\beta$ grain, a large number of super-refined $\alpha$ precipitates are distributed homogeneously, which indicates a sudden increase
of nucleation rate. The HAADF image shows the length of all these $\alpha$ plates is almost the same, of around 200nm, which could indicate that all $\alpha$ precipitates are formed at the same time. Even at grain boundary neighboring region, the size of $\alpha$ precipitates does not increase. It means compared to grain boundary, there are possible other more favorable homogeneous nucleation sites within $\beta$ grain.

The microstructure of Ti5553 after heated up to 600°C at 5°C/min and held for 2 hours before fast cool to room temperature is shown in Figure 5.5. In general the microstructure shown in both BSE SEM images and STEM HAADF image are similar to those shown in Figure 5.4. Around 200nm long super-refined $\alpha$ plates are homogeneously distributed within $\beta$ grain, no matter it is at the region near grain boundary or in the interior of $\beta$ grain.

**5.3.2.2 Microstructure after Different Rate Heating plus Long Time Isothermal Aging**

Two different types of $\alpha$ precipitates in Ti-5553 were obtained while being aged at the same temperature, the next question needs to be answered is whether two types $\alpha$ precipitates would converge into one after long time aging. Therefore, a 2nd group of heat treatments are to extend the holding time at the same aging temperature in order to study and compare the microstructure closer to equilibrium of different heat treatments.
Microstructure of Ti-5553 after heated up to 600°C at 100°C/min and held for 17 hours and 5°C/min and held for 15 hours before fast cool to room temperature are shown in Figure 5.6. Obviously, the microstructure of two heat treatments do not belong to the same type, super-refined α precipitates even after a relative long time isothermal aging and coarsening still do not grow into the size compatible to that of refined α precipitates and the size of super-refined α precipitates are still nearly uniform. The number density of super-refined α precipitates at the 5°C/min rate heat treatment is still much higher than that at the 100°C/min rate heat treatment. Another point is that after long time aging, the volume fraction of α precipitates in either heat treatment is similar to each other. Therefore, it could be claimed that the homogeneously distributed super-refined α phase is relative stable.

Therefore, combined all above results together, depending on heating rate before arriving the summit isothermal aging temperature, there are two different types of microstructure obtained in Ti-5553 and characteristics of two different types α precipitates are summarized as follows:

1. Heating rate equal to or higher than 50°C/min: refined α plates are present in the interior of β grain. Primary α plates of around 2000nm long prefer to form triangle shape cluster and secondary α plates form within the triangle shape primary α. The size of α precipitates near grain boundary region is larger than
that in the interior of $\beta$ grain. The microstructure is similar to the one obtained in step quench process by pseudo-spinodal decomposition mechanism.

2. Heating rate equal to or lower than 20°C/min: super-refined $\alpha$ precipitates of around 200nm long size homogeneously distributed within $\beta$ grain. The size of all $\alpha$ precipitates are almost the same which could indicate of large amount of $\alpha$ precipitates are formed simultaneously. The ratio of length of $\alpha$ lath to thickness is much smaller than that of previous case, which indicates the morphology of $\alpha$ precipitates change.

Based on above results, it is concluded that during low rate heating process, there are more nucleation sites in the interior of $\beta$ grain which could compete with other classical favorable nucleation sites such as grain boundaries and dislocations and the number density of these nucleation sites is really high within $\beta$ grain. Secondly, the kinetics of $\alpha$ phase precipitation process is not related to its location in $\beta$ grain. As long as the nucleation starts, large amount of $\alpha$ precipitates are formed simultaneously and the contact between different precipitates could retard further growth of each single precipitate and then results in all super-refined $\alpha$ precipitates of almost uniform size. During high rate heating process, $\alpha$ phase precipitates near grain boundary and in the interior of grain are significantly different from each other. The kinetics near the grain boundary is much faster which means grain boundary is the preferred nucleation site.
Therefore, it is necessary to have a detailed study of the initial stage of \( \alpha \) precipitation in continuous heating process plus isothermal aging to analyze what kind of nucleation sites are present in the interior of \( \beta \) grains adopting various heating rate.

### 5.3.3 Microstructural Evolution during Continuous Heating

In order to separate the influence of first stage continuous heating and second stage isothermal heating on final microstructure, a 3\(^{rd}\) group heat treatments were done, in which as-quenched samples were heated up using various heating rates, 100°C/min, 20°C/min, 5°C/min and 2°C/min, to 600°C and directly cooled to room temperature without any isothermal holding.

The microstructures of above heat treatments are shown in figure 5.7, figure 5.8, figure 5.9 and figure 5.10. In [113] or [110] \( \beta \) zone axis diffraction patterns of all the heat treatment conditions, extra reflections of HCP \( \alpha \) phase are present. In the corresponding dark field images, \( \alpha \) precipitates of different size and number could be clearly observed. So no matter what kind of heating rate is adopted when the temperature arrives at 600°C, \( \alpha \) precipitates have already formed in \( \beta \) matrix.

When the heating rate is as high as 100°C/min, there are only a small number of \( \alpha \) plates present. The size of \( \alpha \) plates is around 500nm long and the volume fraction of \( \alpha \) phase is relative low. In its diffraction pattern, there are extra reflections belonging to hexagonal
ω phase present. It indicates in remained β phase region, there are ω phase formed. Due to small amount of α precipitates formation, the composition of β phase region, especially the region far from the α precipitates is still close its initial composition, at which in the fast cool process athermal ω phase could form. Therefore, in the continuous heating process using 100°C/min rate, there are few number of refined α plates formed and in the final quenching process, there are fine scale athermal ω phase formed.

When heating rate is 20°C/min, compared to the previous microstructure there are larger number of α plates present while the size of α plates drops to around 120nm long. In [110] β zone axis diffraction pattern, extra reflections, besides α reflection, are off the 1/3 and 2/3 {112} positions, indicating they are not belonging to ω phase. When the heating rate is 5°C/min, [110] β zone axis diffraction pattern is similar to previous case, while the corresponding dark field image shows the density of α plates continues increasing and the size of α plates keeps decreasing. When heating rate is as low as 2°C/min, the number density of α plates is the highest while the size of α plates decreases to the value lower than 100nm.

Therefore, the 3rd group results show that the number density difference and size difference of α plates present after continuous heating plus isothermal aging heat treatments have already occurred during the first stage continuous heating process. When
the temperature arrives at the summit isothermal aging temperature, the higher the heating rate adopted the smaller number of $\alpha$ precipitates are formed in $\beta$ matrix and the larger size $\alpha$ precipitates are of.

5.3.4 Microstructure Evolution during Fast Heating Process

In order to study the reason that causes the above differences, a 4$^{th}$ group of heat treatments were done to study the detailed transformation sequence during continuous heating process, while using 100°C/min or 5°C/min to heat up as-quenched samples to various temperatures and cool to room temperature fast.

The microstructure of as-quenched Ti-5553 heated up at 100°C/min, to 500°C and directly cooled to room temperature are shown in figure 5.11. In [110] $\beta$ zone axis diffraction pattern of sample arriving at 500°C, only extra $\omega$ reflections are observed but no $\alpha$ reflection is present. In the corresponding dark field image, there are large amount of $\omega$ particles distributed in $\beta$ matrix. In Ti-5553 the formation of $\omega$ phase is fast during quenching process and therefore the reflection spot of athermal $\omega$ phase is sharp and clear. The size of isothermal $\omega$ particles in Ti-5553 is similar to that of athermal $\omega$ particles. Therefore, no matter depending on the intensity of the diffraction pattern or the morphology of the particles in the dark field image, the $\omega$ phase present in this aged sample cannot be identified for sure whether it belongs to athermal $\omega$ phase or isothermal $\omega$ phase. However, 500°C is higher than the widely-believed $\omega$ phase solvus temperature.
in Ti-5553 (around 400°C), so the \( \omega \) phase present is considered to be formed in the final quenching process, which means the pre-formed athermal \( \omega \) phase has been dissolved into \( \beta \) matrix during continuous heating. No \( \alpha \) precipitates have been formed in Ti-5553 when as-quenched sample is fast heated up to 500°C, neither present in diffraction pattern nor dark field image. Therefore, in the continuous heating at the rate of 100°C/min, when the temperature arrives at 500°C, all the pre-formed athermal \( \omega \) particles have dissolved into \( \beta \) matrix but no \( \alpha \) precipitates have formed yet.

Using 100°C/min rate, it only takes one minute for the temperature to arrive at 600°C from 500°C. Both diffraction pattern and STEM HAADF image have clearly shown the presence of \( \alpha \) precipitates. \( \alpha \) reflection is present in both \([110]\) and \([111]\) \( \beta \) diffraction patterns, which indicates the formed \( \alpha \) phase obeys Burgers orientation relationship with \( \beta \) matrix. The number density of \( \alpha \) precipitates is very few but the size of \( \alpha \) precipitates is coarse. The length of \( \alpha \) plate is over 200nm in general and some of plates are as long as 500nm. Two \( \alpha \) variants like to form check-mark shape cluster while three \( \alpha \) variants prefer to form triangle shape cluster. Based on \([111]\) \( \beta \) zone axis diffraction pattern, in the above cluster the composed two or three \( \alpha \) variants share the same \([1120]\) direction and their (0001) basal planes rotate 60° from each other. Therefore, the type of \( \alpha/\alpha \) boundary is:

\[
\text{Axis/Angle Pair: } [1120]/60°
\]
It has been reported that based on statistical analysis of large amount of EBSD data, in pure titanium and one β titanium alloy, Ti-4.5Fe-6.8Mo-1.5Al, α/α boundaries show a strong preference of axis angle pair [1120]/60° compared to randomly calculated variants distribution.[25, 78] However, due to the space resolution of EBSD technique, their analysis above cannot be applied to study the variant selection at the initial stage of α precipitation directly. In our experiment result, based on the density and size of α plates shown in HAADF image, the microstructure captured is more close to the initial stage of α precipitation compared to results shown in previous reported work. Current results indicate that as long as α precipitates are formed in β grain interior, the triangle cluster is preferred to be formed by three α variants in which every two variants share [1120]/60° type α/α boundary. Furthermore, the simulation of α precipitation process using phase field modeling supports our experiment result. After the first α plate is formed within β grain, considering the elastic interaction energy between the preformed α plate and nucleating ones, the nucleating α plate likes to precipitate from the broad surface of the preformed one and two α plates would form the [1120]/60° type α/α boundary.[79-81]
Therefore, during fast continuous heating process, a small number of $\alpha$ plates are formed directly in $\beta$ matrix without the formation of isothermal $\omega$ particles. The pre-formed $\alpha$ plate would influence the following $\alpha$ precipitation due to elastic interaction and then result in $[11\bar{2}0]/60^\circ$ type $\alpha/\alpha$ boundary and three $\alpha$ variants triangle shape cluster at the initial stage of $\alpha$ precipitation. The transformation sequence in fast heating process is:

$$\beta + \omega_{\text{ath}} \rightarrow \beta \rightarrow \beta + \alpha$$

### 5.3.5 Microstructure Evolution during Slow Heating Process

Microstructure of as-quenched Ti-5553 heated up at 5°C/min, to 350°C, 375°C, 400°C, 500°C or 600°C and without any holding time directly cooled to room temperature are shown in figure 5.13 — figure 5.17. When the temperature arrives at 350°C, only $\omega$ reflections could be observed in $[110]$ $\beta$ diffraction pattern. In the correlated dark field image, isothermal $\omega$ particles are homogeneously distributed in $\beta$ phase region and the size of isothermal $\omega$ particles are around 10 nm. The coarsening of isothermal $\omega$ particles in Ti-5553 is different from what is reported in the Ti-18wt%Mo in which the diameter of the $\omega$ particles increase from 10 nm to around 100 nm.[19, 77] The result indicates the diffusion of elements of Al, V, Mo and Cr is more complicated in Ti-5553 which could restrict the coarsening process of isothermal $\omega$ particles, especially the growth of $\omega$ particle size. As mentioned in previous part, it cannot be identified in Ti-5553 whether formed $\omega$ phase belongs to athermal $\omega$ phase or isothermal $\omega$ phase just based on
diffraction pattern or dark field image. Therefore 3D atom probe tomography was used to study the composition of formed \( \omega \) particles. The 3D atom probe reconstruction of 160nm long region containing 80at\%Ti iso-concentration surface with vanadium atoms (red color spot) and the composition profile of Ti, Al, V, Mo and Cr across \( \omega/\beta \) interface are shown in figure 5.18. The 80at\% titanium iso-concentration surface clearly indicates that there are titanium rich regions of 10 nm diameter which are in grey colors. Compare the titanium rich region in 3D atom probe with isothermal \( \omega \) particles in dark field image, not only the size but also the shape of titanium rich region is similar to that of isothermal \( \omega \) particles shown in dark field image. Therefore, it can be concluded that using 3D atom probe tomography, isothermal \( \omega \) phase is captured in the aspect of composition. Then the proximity histogram is plotted, using gray color particles all of which particles are fully within the reconstruction region and not connected to each other. The composition profile indicates not only the \( \beta \) phase stabilizers Mo, V and Cr but also \( \alpha \) phase stabilizer Al is rejected from isothermal \( \omega \) phase into \( \beta \) phase matrix. Near \( \omega/\beta \) interface, there are different elements rich regions, such as aluminum rich region and chromium rich region but none of these element rich regions overlay with the other. The result verifies that the complicated diffusion of the elements of Al, V, Mo and Cr in Ti-5553 could restrict coarsening of isothermal \( \omega \) particles, especially the growth of the \( \omega \) particles size. Therefore the size of isothermal \( \omega \) phase is not increasing much compared to that of athermal \( \omega \) phase. The above results indicate composition is the main difference between athermal \( \omega \) phase and isothermal \( \omega \) phase in Ti-5553. After hexagonal structure athermal
\(\omega\) phase was formed in the quenching process, in the following continuous heating, all elements except titanium and oxygen are rejected from \(\omega\) phase into \(\beta\) phase matrix and the presence of different small element rich pockets around the \(\omega\) phase could restrict the growth of isothermal \(\omega\) phase. Therefore, a type of hexagonal structure titanium rich isothermal \(\omega\) phase of the 5 to 10 nm diameter size is formed in the continuous heating process and then the transformation sequence is up to 350°C as follows:

\[
\beta \rightarrow \beta + \omega_{\text{ath}} \rightarrow \beta + \omega_{\text{iso}}
\]

In the sample that is heated up to 375°C, both \(\omega\) and \(\alpha\) reflections are observed in [110] and [113] \(\beta\) diffraction patterns, which indicates the presence of isothermal \(\omega\) phase and \(\alpha\) phase in \(\beta\) phase matrix. Using the correlated \(\omega\) and \(\alpha\) reflections, \(\omega\) particles and \(\alpha\) precipitates could be clearly shown in dark field image. Two phases could be distinguished by their morphology: \(\omega\) particles are more close to spherical shape on the contrary \(\alpha\) precipitates exhibit more lenticular morphology. The number density of formed \(\alpha\) precipitates is large and the size of formed \(\alpha\) precipitates is only around 20nm long. It is noticed that in many cases shown in the image there are contacts between the \(\omega\) particles and \(\alpha\) plates, shown in figure 5.14, which provides clearly indication that \(\alpha\) plates formation could be associated with the preformed isothermal \(\omega\) particles, which could provide more nucleation sites within the \(\beta\) phase matrix. The relative large number of \(\omega\) particles could provide much higher number of nucleation sites for \(\alpha\) precipitates.
and small spacing between neighboring $\omega$ particles could restrict the growth of formed $\alpha$ plates. It is also necessary to point out that in [100] and [111] $\beta$ diffraction patterns in which $\omega$ reflection should be overlapped by the $\beta$ reflection there are additional reflections present besides $\alpha$ reflection. Similar diffraction pattern was reported in the work of Nag etc, in which the diffraction pattern was explained by the chemical ordering of the $\omega$ particles.[74] It indicates that during Ti5553 was continuously heated up from 350°C to 375°C, the structure of the isothermal $\omega$ phase transforms from disordered hexagonal structure to ordered $D8_\beta$ structure. Therefore, ordered structure isothermal $\omega$ particles of the 5 to 10 nm diameter size and large number of super-refined $\alpha$ plates of 20 nm long are present during continuous heating process and then the transformation sequence is as follows up to 375°C:

$$\beta \rightarrow \beta + \omega_{a\text{th}} \rightarrow \beta + \omega_{i\text{so}} \rightarrow \beta + \omega_{i\text{so}} + \alpha$$

When final temperature is equal to or higher than 400°C, only $\alpha$ reflection could be seen in [110] and [111] $\beta$ diffraction patterns which means $\alpha$ precipitates obeying Burgers orientation relationship with $\beta$ matrix form in the Ti-5553. Large numbers of super-refined $\alpha$ plates from 20 to 50 nm long are present at 400°C and the size of $\alpha$ plates grows to more than 100nm long when temperature arrives at 600°C. $\alpha$ plates do not form triangle shape cluster but are uniformly distributed in the $\beta$ matrix. The size of $\alpha$ plates are almost the same, which indicates most of $\alpha$ plates are formed simultaneously and no
secondary α precipitates are present in Ti5553 during slow heating process. Therefore, only α plates are present when the temperature equal to or higher than 400°C and α plates grow to more than 100 nm long during continuous heating and the transformation sequence is as follows up to 600°C.

\[ \beta \rightarrow \beta + \omega_{\text{ath}} \rightarrow \beta + \omega_{\text{iso}} \rightarrow \beta + \omega_{\text{iso}} + \alpha \rightarrow \beta + \alpha \]

In order to study the influence of the stress field and chemical compositional field around \( \omega \) particle and/or within \( \omega \) particle onto α precipitation, the transformation from hexagonal structure \( \omega \) phase to HCP α phase is studied using phase field modeling. As suggested by experimental observation, elastic energy might play a significant role for the morphology of α precipitates. In order to analyze the elastic interaction between \( \omega \) and α phases quantitatively, a phase field model [82] was applied to determine the stress distribution around an \( \omega \) particle and the elastic interaction between \( \omega \) and α. Based on experimental measurement of lattice parameters of \( \beta \) and \( \omega \) phases (\( a_\beta=0.3263\text{nm}, a_\omega=0.4454\text{nm}, c_\omega=0.2863\text{nm} \)), the principal transformation strains are determined to be -0.034, -0.034 and 0.0133. With the elastic constants \( C11=97.7 \text{ GPa}, C12=82.7 \text{ GPa}, C44=37.5 \text{ GPa} \) for \( \beta \) matrix (under the assumption of homogeneous modulus) [reference for Ti64], the equilibrium shape of a coherent \( \omega \) particle was obtained[82], which has an ellipsoid shape along \(<111>\) direction. Furthermore, the stress field around an \( \omega \) particle and the elastic interaction energy[83, 84] between the existing \( \omega \) particle and an α
The formation of the isothermal $\omega$ phase during aging at 375°C would result in solute redistributions around $\omega$ particles in the $\beta$ matrix leading to formation of $\alpha$ stabilizer lean or rich regions. To analyze the effect of this chemistry variation on the nucleation process of $\alpha$ phase, below we calculate contributions from the chemical free energy to the driving force for nucleation. From the Gibbs free energy database employed in the current study, the chemical driving force for nucleation of $\alpha$ from $\beta$, $\Delta G_f$, in Ti-Mo system can be calculated as:

$$\Delta G_f = G^\beta (\overline{c}_{Mo}) + \frac{\partial G^\beta}{\partial \overline{c}_{Mo}} \left( \overline{c}_{\text{nucleus}}^{\text{nucleus}} - \overline{c}_{Mo} \right) - G^\alpha (\overline{c}_{Mo})$$

where $\overline{c}_{Mo}$ is the average composition of the matrix phase, $\overline{c}_{\text{nucleus}}^{\text{nucleus}}$ is the composition of the nucleus, $G^\beta$ and $G^\alpha$ are the molar Gibbs free energy of $\beta$ and $\alpha$ phase respectively from the thermodynamic database. The results are shown in Fig. 5.19c. It is seen that the
chemical driving force for nucleation increases from $1 \times 10^8 \text{J/m}^3$ to $2 \times 10^8 \text{J/m}^3$ when concentration of Mo decreases from 18 wt% to around 7.5 wt%, which is comparable with the extra nucleation driving force caused by the elastic interaction between $\omega$ particles and $\alpha$ nuclei.

In summary, during slow continuous heating at the rate of 5°C/min, solute lean isothermal $\omega$ phase is formed in $\beta$ matrix up to the temperature 350°C and then transform to ordered $\omega$ phase. Isothermal $\omega$ particles could influence stress field and chemical compositional field in nearby $\beta$ matrix and therefore provide more favorable $\alpha$ nucleation sites in $\beta$ matrix which could compete with classical nucleation site; at 375°C, the detectable super-refined $\alpha$ plates of around 20nm long uniformly precipitate within $\beta$ grain. After temperature passes by 400°C, all isothermal $\omega$ particles have disappeared and only $\alpha$ plates around 20 to 50 nm long are present uniformly in $\beta$ grain. Between 400°C and 600°C, formed $\alpha$ plates grow and the length of $\alpha$ plates increases from around 20nm to more than 100nm. The transformation sequence during slow heating process is as follows:

$$\beta \rightarrow \beta + \omega_{sth} \rightarrow \beta + \omega_{iso} \rightarrow \beta + \omega_{iso} + \alpha \rightarrow \beta + \alpha$$

5.4 Ti-Mo
Similar heat treatment was applied to simple binary Ti-15wt%Mo system in order to verify the influence of ω phase on α precipitation. Ti-15wt%Mo was β solution at 1000°C for 30 minutes, fast quenched to room temperature, heated up at 2°C/min to 600°C, isothermally held for 2 hours and finally fast cooled to room temperature. The heating rate selected is the lowest heating rate used in Ti-5553 system, in which heat treatment super-refined α precipitates were present. The isothermal temperature used is the same as in the step quench heat treatment introduced in chapter 4 in order to compare the final microstructure. The microstructure is shown in figure 5.20. In the interior of β grain, refined α precipitates of triangle shape cluster are present. Based on its size scale and morphology, the microstructure obtained in Ti-15wt% after a slow continuous heating process is more close to refined α precipitates obtained in Ti-5553 rather than the super-refined α precipitates formed in Ti-5553.

As introduced in chapter 2, with increasing the amount of β phase stabilizer in titanium alloy, the ω phase formation and dissolution temperature could decrease. If the molybdenum equivalency of Ti-5553 is around 9wt%(same value used in chapter 4), in Ti-15wt%Mo ω phase could dissolve into β matrix at an even lower temperature and it could occur much earlier than α precipitation. It means in Ti-15wt%Mo during continuous heating, the pre-formed isothermal ω phase could dissolve into β matrix first and concentration of β matrix could turn to be uniform in a short time. Therefore, the
preformed isothermal \( \omega \) phase could not influence the following formation of \( \alpha \) precipitates during slow continuous heating and the microstructure of refined \( \alpha \) phase obtained stays the same as that in step quench heat treatment in which \( \alpha \) precipitation is not influenced by metastable \( \omega \) phase.

### 5.4 Summary and Conclusions

This chapter describes the characteristics of a type of super-refined \( \alpha \) precipitates obtained under specific heat treatment in Ti-5553. The phase transformation sequence during this microstructural evolution is investigated using transmission electron microscopy and 3D atom probe. The role of metastable \( \omega \) phase acting in the following \( \alpha \) precipitation is studied. The structural, morphological and crystallographic characteristic of super-refined \( \alpha \) precipitates at the initial stage of precipitation is studied in details.

More specifically, the following conclusions could be achieved:

1. Refined \( \alpha \) precipitates are formed in the high heating rate continuous heating plus isothermal aging process, while super-refined \( \alpha \) precipitates are formed in the low heating rate continuous heating plus isothermal aging process. Both two types microstructure are stable and would not transform to the other after long time isothermal aging.

2. Both two types \( \alpha \) precipitates found obey Burgers orientation relationship with \( \beta \) matrix.

3. The critical heating rate to obtain two types \( \alpha \) precipitates is between 20°C/min.
and 50°C/min.

4. The transformation sequence in high heating rate continuous heating process is:
\[ \beta + \omega_{ath} \rightarrow \beta \rightarrow \beta + \alpha \]. \( \alpha \) precipitates are formed from \( \beta \) matrix without the influence of \( \omega \) phase and following nucleating \( \alpha \) precipitates would like to form from the broad face of preformed \( \alpha \) plates. \([11\overline{2}0]/60^{\circ}\) type \( \alpha/\alpha \) boundary and three \( \alpha \) variants triangle shape cluster are present at the initial stage of \( \alpha \) precipitation.

5. The transformation sequence in low heating rate continuous heating process is:
\[ \beta \rightarrow \beta + \omega_{ath} \rightarrow \beta + \omega_{iso} \rightarrow \beta + \omega_{iso} + \alpha \rightarrow \beta + \alpha \]. Solute lean isothermal \( \omega \) phase is formed in advance and will result in the precipitation of very fine scale \( \alpha \).

6. The formation of \( \omega \) particles would influence the stress field and chemical compositional field in neighboring \( \beta \) matrix and therefore affect following \( \alpha \) precipitation.
Table 5.1 The composition of the as-received Ti5553 measured using wet chemistry

<table>
<thead>
<tr>
<th>O</th>
<th>N</th>
<th>Al</th>
<th>V</th>
<th>Mo</th>
<th>Cr</th>
<th>Fe</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.179</td>
<td>0.0025</td>
<td>6.7</td>
<td>4.92</td>
<td>5.00</td>
<td>3.04</td>
<td>0.48</td>
<td>BALANCE</td>
</tr>
</tbody>
</table>

Figure 5.1 SEM image, dark field images and correlated diffraction patterns from the as-quenched state Ti-5553.
Figure 5.1 Continued
Figure 5.2 Microstructure of Ti-5553 after heated up to 600°C at 100°C/min and held for 4 hours before fast cool to room temperature
Figure 5.2 Continued
Figure 5.3 Microstructure of Ti-5553 after heated up to 600°C at 50°C/min and held for 2 hours before fast cool to room temperature

Continued
Figure 5.3 Continued
Figure 5.4 Microstructure of Ti-5553 after heated up to 600°C at 20°C/min and held for 2 hours before fast cool to room temperature
Figure 5.4 Continued
Figure 5.5 Microstructure of Ti-5553 after heated up to 600°C at 5°C/min and held for 2 hours before fast cool to room temperature
Figure 5.5 Continued
Figure 5.6 Microstructure of Ti-5553 after heated up to 600°C at 100°C/min and held for 17 hours and 5°C/min and held for 15 hours before fast cool to room temperature.
Figure 5.7 Microstructure of as-quenched Ti-5553 heated up to 600°C at the rates of 100°C/min and without any holding time directly cooled to room temperature
Figure 5.8 Microstructure of as-quenched Ti-5553 heated up to 600°C at the rates of 20°C/min and without any holding time directly cooled to room temperature
Figure 5.9 Microstructure of as-quenched Ti-5553 heated up to 600°C at the rates of 5°C/min and without any holding time directly cooled to room temperature
Figure 5.10 Microstructure of as-quenched Ti-5553 heated up to 600°C at the rates of 2°C/min and without any holding time directly cooled to room temperature
Figure 5.11 Microstructure of as-quenched Ti-5553 heated up to 500°C at the rates of 100°C/min and without any holding time directly cooled to room temperature.
Figure 5.12 STEM HAADF image of as-quenched Ti5553 heated up to 600°C at the rates of 100°C/min and without any holding time directly cooled to room temperature
Figure 5.13 Microstructure of as-quenched Ti-5553 heated up at 5°C/min, to 350°C and without any holding time directly cooled to room temperature
Figure 5.14 Microstructure of as-quenched Ti-5553 heated up at 5°C/min, to 375°C and without any holding time directly cooled to room temperature
Figure 5.15 Microstructure of as-quenched Ti-5553 heated up at 5°C/min, to 400°C and without any holding time directly cooled to room temperature
Figure 5.16. Microstructure of as-quenched Ti-5553 heated up at 5°C/min, to 500°C and without any holding time directly cooled to room temperature.
Figure 5.17 Microstructure of as-quenched Ti5553 heated up at 5°C/min, to 600°C and without any holding time directly cooled to room temperature
Figure 5.18 3D atom probe reconstruction of 160 nm long region containing 80at%Ti iso-concentration surface with vanadium atoms (red color spot) and the composition profile of Ti, Al, V, Mo and Cr across \( \omega/\beta \) interface
Figure 5.19 Extra driving force of $\alpha$ precipitation due to $\omega$ phase formation. (a) the stress field of $\omega$ particle in neighboring $\beta$ matrix. (b) Elastic interaction energy iso-surface ($-9 \times 10^4 \text{kJ/m}^3$) between a pre-existing $\omega$ particle and an $\alpha$ nucleus. (c) extra driving force of $\alpha$ precipitation due to chemical change in $\beta$ matrix.
Figure 5.19 Continued

DATABASE:USER
N=1., P=1.01325E5, T=648.15;

Nucleation Driving Force (J/mol)

Weight Fraction of Mo W(Mo)
Figure 5.20 Microstructure of Ti-15wt% after heated up to 600°C at 2°C/min and held for 2 hours before fast cool to room temperature
Chapter 6

Phase Transformation Analysis in Titanium Alloys

In this chapter, experiment results of using ETMT to capture the initial stage of $\alpha$ phase nucleation during continuous heating and study the kinetics of $\alpha$ precipitation during isothermal aging in Ti-5553 and Ti-Mo will be discussed. Electrical resistivity measurements of Ti-5553 during continuous heating using various heating rates indicate that $\alpha$ nucleation temperature increases while elevating the heating rate. The TTT diagram of Ti-5553 is plotted using electrical resistivity measurements during isothermal aging at various aging temperatures and it shows that the kinetics of $\alpha$ precipitation is fastest at 650°C, which is the nose temperature in TTT diagram of Ti-5553.

6.1 Introduction and Motivation

As introduced in previous chapters, various transformation pathways are present in titanium alloys upon different heat treatment conditions. Within this field, the most attractive phase is $\alpha$ phase, because the morphology, size scale and distribution of $\alpha$ precipitates within $\beta$ phase could all affect mechanical properties of titanium alloys. The pre-formed metastable phases such as $\omega$ phase in system have significant influence on
newly formed phases. In order to obtain a better and thorough understanding of \( \alpha \) phase nucleation in titanium alloys, a careful and detailed study of composition and structure change at initial stage of \( \alpha \) nucleation is required. Therefore, in current study Electro-Thermo-Mechanical Tester is used attempting to capture the initial stage of phase transformation in titanium alloys and then investigate the kinetics of precipitation.

It has been reported in multiple papers that electrical resistivity measurement is efficient and effective technique to detect \( \omega \) phase related transformation in titanium alloys. Electrical resistivity measurement is known to be sensitive to minor constitutional change or structural change in quenching, continuous aging and isothermal aging treatments \([16, 85-87]\). The measured electrical resistivity curve in Ti-12wt%Mo reported by F. Sun \textit{etc.} indicates that isothermal \( \omega \) phase formation, nano scale intragranular \( \alpha \) phase precipitation and grain boundary \( \alpha \) precipitation all could be detected by electrical resistivity change during continuous heating\([85, 86]\). However, in their work there was no characterization results provided to verify the explanation of inflection points in electrical resistivity curves showing the microstructure at certain critical temperatures. Instead, the inflection points in the electrical resistivity curve are interpreted due to temperature range at which they are present. For example, the first inflection point in electrical resistivity curve was explained by isothermal \( \omega \) formation, because it was located in the temperature range where isothermal \( \omega \) phase could form when the material was isothermally aged. The microstructure in sample after heat treated using the same
heat treatment in which electrical resistivity was measured has not been investigated yet. Therefore, similar continuous heat treatments as introduced in the previous papers were adopted in current study to analyze phase transformation sequence in Ti-5553 and Ti-Mo systems and corresponding TEM work were completed trying to better explain the inflection point in electrical resistivity curve.

It is also reported the transformation kinetics during isothermal aging in some near β titanium alloys Ti-5Al-2Sn-2Cr-4Mo-4Zr-1Fe or α/β titanium alloy Ti-6Al-2Sn-Zr-6Mo could be studied using electrical resistivity measurement[16]. The amount of transformation can be detected by electrical resistivity measurement on the assumption that resistivity is proportional to volume fraction of different phases and therefore TTT diagrams of these materials could be plotted. Ti-5553 samples were step quenched from above β transus temperature and isothermally aged at various temperatures in α/β temperature range in order to study the kinetics of α precipitation in titanium alloys.

With the combination of ETMT and TEM, in-situ electrical resistivity change in titanium alloys during heat treatments could be measured and microstructure of titanium alloys at different stages of heat treatments could be characterized. Therefore, the qualitative relationship between electrical resistivity change and phase transformation could be established. In this chapter, the electrical resistivity curve of Ti-12wt%Mo was studied first to verify the reliability of ETMT to measure electrical resistivity and study phase
transformation during continuous heating. Then the transformation sequence in Ti-5553 during various heating rates continuous heating was studied using ETMT. The last part focuses on α precipitation kinetics in Ti-5553 during isothermal aging at various temperatures.

6.2 Experimental Process

All samples were heat treated in ETMT with electrical resistivity measurement. The measurement process has been introduced in section 3.2.4.1. The experimental measured values are raw electrical resistance of the sample between two platinum wires region. The change of cross section area before and after the heat treatment and the distance between two platinum wires can be ignored. Therefore, the electrical resistance change in heat treatment could be used to identify phase transformation instead of electrical resistivity. The relative resistance or relative resistivity is defined as the electrical resistance at time T (R_T) divided by the electrical resistance at initial time zero (R_0):

$$R_{relative} = \frac{R_T}{R_0}$$

Then relative resistance is the quantity used in experiment to indicate the resistivity change of titanium alloy in heat treatment. Relative resistance versus temperature curve is used in continuous aging heat treatment to indicate the transformation temperature, while relative resistance versus time curve is used in isothermal aging heat treatment to indicate the embryo time in isothermal heat treatment.
6.3 Reliability of ETMT to Analyze Phase Transformation

The relative resistance change in Ti-12wt%Mo during continuous aging at the rate of 5°C/min has been reported by F.Sun etc. using their home-made facilities, shown in figure 6.1[85]. Depending on the slope change of curve, relative resistivity curve is divided into different regimes below β transus temperature: below 451K (178°C), the slope is negative and relative resistivity continuously decreases; between 451K (178°C) and 600K (327°C), the slope is positive and relative resistivity continuously increases; between 600K (327°C) and 840K (567°C), the slope changes to be negative again and relative resistivity continuously decreases; between 840K (567°C) and β transus temperature (around 755°C), the slope turns positive and relative resistivity continuously increases.

Using ETMT, the exact same heat treatment was repeated using the same Ti-12wt%Mo alloy. The result measured in ETMT is shown in figure 6.2. The curve could also be divided into 4 regimes below β transus temperature region: below 530K (257°C), the slope is negative and relative resistivity continuously decreases; between 530K (257°C) and 610K (337°C), the slope changes to be positive and relative resistivity starts to increase; between 610K (337°C) and 890K (617°C), the slope is negative and relative resistivity is going down; between 890K (617°C) and β transus temperature (755°C), the slope turns to be positive and relative resistivity is going up.
Compared the relative resistivity curve obtained from ETMT with the reported curve, first of all, they all show the same overall trend and contain the same number of inflection points, which means two curves both show the same starting microstructure and same numbers of phase transformations during continuous aging below $\beta$ transus temperature. Secondly, locations of the inflection points are not exactly the same in two curves, which indicates that transformation temperatures detected are not exactly the same. This may be because the compositions of two materials are not completely the same, especially different heat treatment atmosphere could lead to significant different oxygen contamination into material which could impact the transformation temperature seriously.

Generally speaking, ETMT could qualitatively repeat the reported data and analyze same transformations such as isothermal $\omega$ formation and $\alpha$ precipitation in Ti-12wt%Mo during continuous heating. But transition temperatures need to be further studied using other characterization techniques, especially using TEM.

### 6.4 Transformation in Continuous Aging

After $\beta$ solution and quench to room temperature, with different amount of $\beta$ phase stabilizer in the alloys, different phases could be present in as-quenched condition titanium alloys. In the following same rate continuous aging process, the trends of
relative resistance changes versus temperature are not the same for different initial microstructure and therefore relative resistance versus temperature curve is capable of indicating starting microstructure, in other words as-quenched condition microstructure, and different phase transformation sequences present in various systems.

6.4.1 Athermal α Phase Analysis

The curves of relative resistance versus temperature in Ti-2wt%Mo, Ti-8wt%Mo, Ti-18wt%Mo are shown in figure 6.3, 6.4 and 6.5. In the resistance versus temperature curve of Ti-2wt%Mo, below β transus temperature (around 858°C), there is only one inflection point. The slope of curve is positive and the relative resistance keeps increasing until reaching around 800°C. Above 800°C, the slope of curve is negative and the relative resistance starts to decrease until it arrives β transus temperature. In the resistance versus temperature curve of Ti-8wt%Mo, compared to that of Ti-2wt%Mo, there are more inflection points in the curve below β transus temperature (around 795°C). The slope of curve is positive and the relative resistance is increasing until the temperature arrives at 475°C. Between 475°C and 600°C, the slope of curve is negative and the relative resistance decreases. Above 600°C, the slope changes to positive again and the relative resistance keeps increasing. In the relative resistance versus temperature curve of Ti-18wt%Mo, compared to the previous two curves, the trend of relative resistance curve is completely different and there are more inflection points in the curve. Starting from room temperature, the slope of curve is negative and relative resistance keeps decreasing until
around 300°C. Then the slope changes to be positive and the curve starts to increase until around 505°C. Between 505°C and 610°C, the slope of curve is negative and the relative resistance is decreasing. Above 610°C the slope of the curve turns to positive and curve starts to increase again.

Based on the above results, there are two factors that can be used to indicate that there is athermal ω phase formed in the starting microstructure. Firstly, it is the number of inflection points. Different starting microstructure has different routine to achieve equilibrium microstructure, so there are different amount of phase transformations present during continuous aging process. Secondly, it is the slope of the relative resistance curve near room temperature. Only in Ti-18wt%Mo (also in Ti-12wt%Mo discussed in the previous section), the slope of the curve is negative, while in the other two curves the slope is positive near room temperature. This negative slope of resistance versus temperature is not consistent with the normal situation, the higher the temperature the higher the resistance. Therefore this phenomenal named as negative temperature dependence effect is an indication of presence of athermal ω phase in titanium alloys.

TEM characterization work was completed to verify the as-quenched state microstructure of previous introduced three different titanium alloys. As shown in figure 6.6, the diffraction shows the plate morphology phase belongs to HCP structure. Therefore, it is α’ martensite present within as-quenched Ti-2wt%Mo. The diffraction shown in figure
6.8 indicates the plate morphology phase in which there are stacking fault present is of orthorhombic structure. Therefore, it is the $\alpha''$ martensite within the as-quenched Ti-8wt%Mo. In the water quenched Ti-18Mo, in the (110) $\beta$ zone axis diffraction pattern shown in figure 6.9, besides $\beta$ reflection, there are extra reflections at 1/3 and 2/3 \{112\} positions which indicates it is hexagonal structure $\omega$ phase. Judging from the size scale of $\omega$ particles in dark field image, it is athermal $\omega$ phase formed in as-quenched Ti-18wt%.

Therefore, the characterization of as-quenched condition microstructure using TEM verifies that three different types relative resistance curve are corresponding to three different types of initial microstructure. The negative temperature dependence effect can be used to indicate the presence of athermal $\omega$ phase in titanium alloys.

6.4.2 $\alpha$ Precipitation Analysis in Ti-5553

As introduced in chapter 5, as-quenched Ti-5553 was heated up to 350°C, 375°C, 400°C and 500°C at the rate of 5°C/min and fast cooled to room temperature. Below 350°C, there is only isothermal $\omega$ phase in $\beta$ phase matrix; at 375°C, both isothermal $\omega$ and super-refined $\alpha$ precipitates are present in $\beta$ phase region; at temperature equal to or higher than 400°C, there is only $\alpha$ phase present in $\beta$ phase regime. Therefore, based on the TEM characterization result, $\alpha$ precipitation starts around 375°C in Ti-5553 during the rate of 5°C/min continuous heating.
The resistance versus temperature curve in Ti-5553 heated up at the rate of 5°C/min and fast cooled to room temperature is shown in figure 6.9. There are two inflection points below 500°C, one of which is around 380°C and the other is around 450°C. Combined the TEM results and the resistance measurement together, the first inflection point which is around 380°C in resistance curve could indicate actually the refined α precipitation.

In order to verify the indication of α precipitation in Ti-5553 using resistance versus temperature curve, similar measurements are obtained using the heating rate of 20°C/min, 50°C/min and 100°C/min, shown in figure 6.10. They all show that there are two inflection points in the resistance curve and both two inflection points move to higher temperature direction with the elevated heating rate. Further more, as discussed in chapter 4, when the heating rate is even higher, there is no time for isothermal ω phase to grow and the α precipitation will nucleate from the β region directly. Then the presence of the first inflection point, in the fast continuous heating such as at the rate of 50°C/min and 100°C/min, cannot be due to isothermal ω phase formation and therefore could indicate α nucleation. What is more, based on the resistance curve during continuous aging at 100°C/min, α phase nucleates at the temperature close to 600°C, which is consistent with the TEM work result shown in chapter 5. In Ti-5553 at 600°C, there are only a few number of α precipitates and the volume fraction of α precipitates is very low, which showed that it is only the initial stage of α precipitation and α nucleation only occurs for a really short time.
Therefore, in Ti-5553, using resistance versus temperature curve, besides indication of the presence of athermal \( \omega \) phase by negative temperature dependence effect, \( \alpha \) nucleation could be indicated by the first inflection point, at which the slope changes from negative to positive. Another important point has to be pointed out that the trend of resistance curve in Ti-5553 is different from the results obtained from Ti-12wt%Mo and Ti-18wt%Mo. When The Ti-12wt% and Ti-18wt%Mo were continuous heated up to the temperature close to the shown first inflection point. In TEM results, only isothermal \( \omega \) particles were observed in the sample rather than any super-refined \( \alpha \) precipitates. Therefore, it means unlike Ti-5553, in which the first inflection is clearly indicating \( \alpha \) precipitations, in Ti-Mo binary system, the first inflection point in resistance versus temperature curve has no relationship with \( \alpha \) precipitation.

6.5 Transformation Kinetics in Ti-5553 during Isothermal Aging

Electrical resistivity measurement not only is applicable in continuous heating process but also could indicate phase transformation present in isothermal heating process. Time-Temperature-Transformation curve is used to indicate the kinetics of precipitation in isothermal treatment. Therefore, electrical resistivity measurement could be used to plot the TTT diagram and help to capture the initial stage of precipitation in titanium alloys during isothermal treatment.
A basic assumption in this work is that the electrical resistivity of superposition of electrical resistivity of $\alpha$ phase and electrical resistivity of $\beta$ phase:

$$
\rho_{sys} = \rho_\alpha \times f_{\alpha} + \rho_\beta \times f_{\beta}
$$

$\rho_{sys}$ is the resistivity of the system, $\rho_\alpha$ and $\rho_\beta$ are the resistivity of the $\alpha$ phase and $\beta$ phase, $f_{\alpha}$ and $f_{\beta}$ are the volume fraction of $\alpha$ phase and $\beta$ phase.

Therefore, electrical resistivity change or relative resistance versus time curve in isothermal treatment can be used directly to indicate the volume fraction of $\alpha$ phase or $\beta$ phase change versus time during isothermal treatment.

Ti-5553 is used to study the kinetics of $\alpha$ precipitation when isothermally aged at various temperatures. After $\beta$ solution at 1000$^\circ$C for 30 minutes, the samples were step quenched to 800$^\circ$C, 750$^\circ$C, 700$^\circ$C, 650$^\circ$C, 600$^\circ$C, 550$^\circ$C and 500$^\circ$C, held for 5 hours and fast cooled to room temperature.

The relative resistance curve of Ti-5553 isothermally aged at 500$^\circ$C, 550 and 600$^\circ$C are shown in figure 6.11. In all plots, curves follow sigmoidal shape. It takes around 5000 seconds at 500$^\circ$C to reach maximum value, 1200 seconds at 550$^\circ$C, and 900 seconds at 600$^\circ$C to arrive maximum value. The results show the higher the temperature in this range, the faster the relative resistivity reaches maximum.
The relative resistance curve of Ti-5553 isothermally aged between 600°C and 700°C, between 700°C and 800°C are shown in figure 6.12 and figure 6.13 respectively. Between 600°C and 700°C, it is at 650°C, the relative resistance reaches maximum value in the shortest time, around less than 500 seconds. At temperature of 700°C, it reaches the maximum value around 2000 second, while at 600°C it reaches the maximum around 900 seconds. When the temperature is higher than 700°C, it takes even longer time for relative resistance to reach maximum. At 750°C, the time is more than 4000 seconds while at 800°C, the time is even longer, as long as 8000 seconds.

Therefore, 650°C is the temperature electrical resistivity reaches maximum fastest. When temperature is higher than 650°C, the higher the temperature the slower it reaches the maximum; when temperature is lower than 650°C, the lower the temperature, the slower the relative resistance reaches the maximum.

Based on our assumption, the resistance reaches maximum equals to volume fraction of $\alpha$ phase arrives the equilibrium. Then the relative resistance curve could show that at different temperatures, the speed of $\alpha$ phase reaching equilibrium is different. It is at 650°C, the kinetics of $\alpha$ phase precipitation is fastest, which is the nose temperature in the TTT curve. While the temperature is higher than the nose temperature, the kinetics is slower because of less driving force and less nucleation rates; while the temperature is
lower than that nose temperature, the kinetics is slower due to slower diffusion. All relative resistance curves are summarized in figure 6.14. 5% phase transformation and 95% phase transformation time could be roughly read from figure 6.14 and plotted into figure 6.15. Then figure 6.15 can be treated as the TTT diagram of Ti-5553 during isothermal treatment.

Therefore, TTT diagram of Ti-5553 can be plotted using electrical resistivity measurement on the condition that considering precipitation of new phase is the dominant factor of changing electrical resistivity and the variation of electrical resistivity is proportional to fraction of precipitated phase. $\alpha$ precipitation in Ti-5553 is fastest at 650°C and it is consistent with experiment results shown in chapter 4.

**6.6 Summary and Conclusions**

This chapter discusses using electrical resistivity measurement to study the transformation sequence during continuous heating and transformation kinetics during isothermal aging in titanium alloys. The main conclusions are summarized:

1. The negative temperature dependence effect of electrical resistivity can be used to indicate the presence of athermal $\omega$ phase at as-quenched state titanium alloy.
2. The slope change of electrical resistivity in Ti-5553 during continuous heating can be used to indicate the nucleation of $\alpha$ precipitates.

3. The electrical resistivity measurement in the isothermal aging can be used to study the kinetics of $\alpha$ precipitation and plot TTT diagram.
Figure 6.1 Reported relative electrical resistivity curve of Ti-12wt%Mo during continuous heating. [85]

Figure 6.2 Measured relative electrical resistivity curve of Ti-12wt%Mo during continuous heating using ETMT
Figure 6.3 Measured relative electrical resistivity curve of Ti-2wt%Mo during continuous heating using ETMT

Figure 6.4 Measured relative electrical resistivity curve of Ti-8wt%Mo during continuous heating using ETMT
Figure 6.5 Measured relative electrical resistivity curve of Ti-18wt%Mo during continuous heating using ETMT

Figure 6.6 Microstructure of as-quenched Ti-2wt%Mo
Figure 6.7 Microstructure of as-quenched Ti-8wt%Mo

Figure 6.8 Microstructure of as-quenched Ti-18wt%Mo
Figure 6.9 Resistance versus temperature curve in Ti-5553 during the rate of 5°C/min continuous heating

Continued

Figure 6.10 Resistance versus temperature curve in Ti-5553 during continuous heating (a) at the rate of 20°C/min (b) at the rate of 50°C/min (c) at the rate of 100°C/min
Figure 6.10 Continued
Figure 6.11 Relative resistivity versus time curves of Ti-5553 isothermally aged at 500°C, 550°C and 600°C.
Figure 6.12 Relative resistivity versus time curves of Ti-5553 isothermally aged at 600°C, 650°C and 700°C
Figure 6.13 Relative resistivity versus time curves of Ti-5553 isothermally aged at 700°C, 750°C and 800°C
Figure 6.14 Relative resistivity versus time curves of Ti-5553 isothermally aged at  
500°C, 550°C, 600°C, 650°C, 700°C, 750°C and 800°C
Figure 6.15 TTT diagram of Ti-5553
Chapter 7
Summary and Future Work

The primary focus of present study is to investigate the influence of instability within $\beta$ matrix on $\alpha$ precipitation, involving two aspects, compositional instability and structural instability. Current experimental and simulation results validate that refined $\alpha$ precipitates could be formed in some $\beta$ titanium alloys due to compositional instability in $\beta$ grain; on the other hand that super-refined $\alpha$ precipitates can be formed due to compositional and structural instability within parent $\beta$ phase. A non-classical homogenous refined $\alpha$ nucleation mechanism was proposed in titanium alloys for the first time. A new transformation pathway that $\beta$ phase spinodal decomposition occurs prior to refined $\alpha$ precipitation and acts as precursor of refined $\alpha$ precipitates was discussed in details. $\omega$ assisted super-refined $\alpha$ precipitation in $\beta$ titanium alloy was studied systematically by experiment and computational simulation.

The first aspect of instability, compositional one, could be caused by thermal fluctuation and/or spinodal decomposition within $\beta$ matrix. If at proper combination of temperature and concentration, the initial overall concentration of $\beta$ matrix could be close to $C_0$. Then
a small amplitude concentration fluctuation could cause pseudo-spinodal decomposition to occur, which leads to a non-classical homogeneous \( \alpha \) nucleation. Combined with advanced electron microscopy and 3D atom probe technique, experimental results indicating each stage of pseudo-spinodal decomposition are characterized in Ti-5553. The characteristics of refined \( \alpha \) precipitates, product of pseudo-spinodal decomposition, are fully studied. Especially, TEM diffraction pattern and 3DAP result indicate during the formation of refined \( \alpha \) precipitates, structural change completes prior to compositional change. Further thermodynamics calculation using Thermo-Calc software provides direct evidence of its necessary thermodynamics conditions. Therefore, the compositional fluctuation or the concentration instability in some local region could lead to the formation of refined \( \alpha \) precipitates in Ti-5553 via pseudo-spinodal decomposition mechanism.

Similar studies were conducted in various Ti-Mo binary systems. Similar morphology refined \( \alpha \) microstructure not only occurs in the system that is close to \( C_0 \) concentration but also in the system that is fairly far away from \( C_0 \), which indicates thermal fluctuation is not the only way for local concentration to shift away from its initial value. If the concentration is within miscibility gap, spinodal decomposition could happen to lower the total gibbs energy, which also leads to the change of local composition in \( \beta \) matrix. Although up until now, no convincing experimental results showing phase separation could happen in Ti-Mo system have ever been reported. The synchrotron XRD results of
Ti-20Mo-5Al provide clear evidence indicating the presence of phase separation in this 15wt% molybdenum equivalency system, which indicates the possibility of phase separation in Ti-15wt%Mo binary system. Therefore, the pre-occurred \( \beta \) phase spinodal decomposition in titanium alloys could also shift the local composition in \( \beta \) grain to the regime close to \( C_0 \) point, cause pseudo-spinodal decomposition and assist \( \alpha \) precipitation.

The presence of isothermal \( \omega \) particles can change not only concentration but also structure in \( \beta \) grain and therefore can be treated as compositional plus structural instability within \( \beta \) matrix. In Ti-5553 system, super-refined \( \alpha \) precipitates were formed with the presence of isothermal \( \omega \) particles in \( \beta \) matrix while without \( \omega \) particles only refined \( \alpha \) precipitates nucleated. 3DAP result clearly shows the rejection of not only \( \beta \) phase stabilizers Mo, Cr and V, but also \( \alpha \) phase stabilizer Al from \( \omega \) particles into \( \beta \) matrix. The thermodynamic calculation verifies the concentration change in \( \beta \) phase may provide an extra chemical driving force of \( \alpha \) precipitation. The structure change of \( \omega \) phase could also apply an extra stress field on the nearby \( \beta \) matrix and therefore provide an extra driving force of \( \alpha \) precipitation due to elastic interaction. Therefore, the presence of \( \omega \) particles in \( \beta \) matrix could cause the local concentration and structure instability in \( \beta \) matrix and then provide extra driving force for super-refined \( \alpha \) precipitation.
The current study not only provides some insights in the aspect of phase transformation mechanisms in titanium alloys, but also gives some clue in the aspect of practical heat treatment condition selection. First of all, aging temperature plays an important role to determine final $\alpha$ microstructure. If aging temperature is too low, below $\omega$ phase start temperature, then $\omega$ particles could form in titanium alloys and then influence following $\alpha$ precipitation; if aging temperature is too high, thermodynamic conditions for pseudo-spinodal decomposition may not be satisfied and then homogeneous refined $\alpha$ precipitates could not form. Secondly, heating rate before arriving peak isothermal aging temperature also plays significant role on final microstructure. Low heating rate could provide the opportunity for isothermal $\omega$ phase to form during continuous heating and then influence the following super-refined $\alpha$ precipitation while high heating rate will result in $\omega$ dissolution earlier than $\alpha$ precipitation and then refined $\alpha$ precipitates would be formed. Therefore, in order to better manipulate the final microstructure in titanium alloys, appropriate selection of aging temperature and heating rate to arrive the peak aging temperature are of significant importance.

A brief summary of conclusions obtained in current study about nucleation mechanisms of refined $\alpha$ precipitates due to instability with $\beta$ matrix:

1. Compositional instability
   - Heat treatment: Step-quenching from above $T_\beta$ and then isothermal aging
• Microstructure: Refined α precipitates homogeneously distributed in β matrix
• Transformation mechanism: Pseudo-spinodal decomposition or β phase spinodal decomposition promoted α precipitation

2. Compositional and structural instability
• Heat treatment: Quenching from above $T_\beta$ and then continuous heating up (plus isothermal aging)
• Microstructure: Super-refined α precipitates homogeneously distributed in β matrix
• Transformation mechanism: ω phase assisted super-refined α precipitation

As discussed in previous chapters, there are still plenty of questions within the scope of current research area that need to be answered in future work:

1. The reliability of phase separation in Ti-Mo binary system still needs experimental results to validate. Ti-Mo system is widely treated as a simple characteristic monotectoid/isomorphous type titanium alloy. In both reported and calculated phase diagram, there exists miscibility gap. However, up until now, no convincing experimental results including structural analysis using XRD spectrum or diffraction pattern and compositional analysis using EDS or 3DAP have ever been reported to validate the presence of molybdenum rich β phase in Ti-Mo system. Without necessary experimental
data, all the current calculation and simulation using the database which is constructed based on the presence of miscibility gap could be misleading.

2. The differences between refined $\alpha$ precipitates and super-refined $\alpha$ precipitates need to be studied in details. Currently, two types $\alpha$ precipitates are distinguished by morphology, size scale and nucleation density. In the crystallography aspect, both two types $\alpha$ phase are HCP structure and obey Burgers orientation relationship with parent $\beta$ phase. However, not enough information about the composition of super-refined $\alpha$ precipitates has been collected. With more 3DAP work on super-refined $\alpha$ precipitates, a thorough comparison between two types $\alpha$ microstructure will be beneficial to detailed understanding of their nucleation mechanisms.
References


68. *Dictra Manual*.


