3D Printing Alloys

Team Members:

Rebecca Glaser Ritij Goel Martin Hewitt Fan Meng Peisheng Wang Ruijing Yan

Graduate Student Advisor: Fuyao Yan

> <u>Client:</u> NIST, QuesTek

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1 Background

1.1 Motivation

The technology of additive manufacturing (AM), also known as 3D Printing, has the potential to revolutionize the design and manufacturing industries. As its name indicates, AM adds materials layer by layer to form complex shaped three-dimensional objects, in contrast with conventional manufacturing methods, namely reductive manufacturing, which involves machining off undesired material from regular-shaped workpieces.

Currently, additive manufacturing shows great potential as a method of fabricating different kinds of materials, and it is comparatively mature for fabricating polymers due to their low melting points. However, because of the high melting points of metals and the important role of microstructures, commercializing additive manufacturing in metals requires the resolution of several underlying problems such as porosity, inclusions, grain structures and phase distributions, particularly for those metals acting as structural parts in assemblies. Some work has been done to study the effects of different combinations of AM process parameters on the microstructure of the builds [1] [2]. Some problems, such as porosity, are much easier to solve during building, or post processing. Minimal porosity for builds can be achieved by finely adjusting the process parameters, such as laser energy, scan speed and etc., as well as by the employment of hot isostatic pressing (HIP) in the post process [2]. However, grain structures and phase properties are not as easy to control or to adjust. In most AM builds, due to extremely fast cooling rates, coarse columnar grains elongated along the building direction (as shown in Figure 1) form during solidifications [1], which inhibit AM builds from being directly used. Thus the grain structure of AM builds has to be modified during post process. Common methods of grain refinement for wrought materials usually involve recrystallizations triggered by large amounts of stored energy generated during cold/hot working. However, the nature of net-shaping of AM does not allow for any applied mechanical work on builds. Therefore, careful design of post heat treatment routes as well as of powder compositions with grain refiners are extremely important.

In this project, we desire to design post heat treatment routes and new alloys for additive manufacturing in order to refine grains and lower grain growth. In particular, the baseline materials for design are the QuesTek[®]-designed QT-Ti-2A alloys and the QuesTek[®]-designed PH-48S stainless steel.



Figure 1 Microstructure of SLM produced Ti64 [1]. Building direction is towards the top of the page. Elongated grains stretch several hundred microns in the build direction. Dark bands indicate a build layer thickness of about 50 microns.

1.2 Additive Manufacturing

Additive Manufacturing describes a process of building a three-dimensional component layer-bylayer. It begins with a 3D CAD model of a component that is sliced into thin horizontal layers on the computer. A machine then takes the sliced CAD model as input and successively traces the geometry of each layer, fabricating narrow sections of material in the geometry of the component to be built. At the end of the process, the fabricated component is net shaped and functional. Materials for AM include polymers, metals, and ceramics, usually in the form of powder, melted by the laser or electron beam and then solidified into bulk.

Additive Manufacturing of metals can be largely categorized by a process of direct metal deposition (DMD). Within DMD, there are a variety of strategies, including jet solidification, 3D welding, shape deposition manufacturing, electron beam manufacturing, and laser-based manufacturing techniques. Additive manufacturing of metal components exhibits two main advantages over conventional manufacturing techniques. First, it accelerates the process from design to market by reducing the amount of production steps. Rather than developing individualized tooling for a component, part designs are manufactured directly from CAD data in a single step to near net shape. Second, because of the layer-by-layer build process, components can be designed and built with extreme geometric complexity unattainable by conventional manufacturing. These two advantages make additive manufacturing an efficient process for creating structural prototype components as well as limited manufacturing runs in aerospace, defense, and medical technology industries [4].

1.2.1 Selective laser melting (SLM) & Laser engineered net shaping (LENS®)

Two commonly used methods for laser-based additive manufacturing are selective laser melting (SLM) and laser engineered net shaping (LENS[®]). A schematic demonstration of an SLM system is shown in Figure 2. The general SLM process begins with a part substrate fixed on the build platform. The build chamber is filled with an inert gas, commonly argon or nitrogen, to prevent

oxidation and aid in heat transfer. A roller or rake spreads and compacts the loose powders into a thin layer, usually under 100 μ m. A high-powered laser scans the powder bed in accord with geometry determined by CAD data of the component to be built, selectively melting the metal powders in a small area. The powders fuse while the laser is on, and then rapidly solidify as the laser moves away. When one layer is done, the build platform lowers an amount equal to the build layer thickness, and the next layer is prepared and scanned. This process continues layer by layer until the component is completely formed [5].



Figure 2 General schematic of an SLM system [5].

Figure 3 shows a schematic of the LENS[®] system. A metal substrate is fixed on a computercontrolled table capable of moving in the X and Y directions. The high-powered laser focuses on a small area of the substrate, with a powder delivery nozzle surrounding the laser ejecting powders by inert gas onto the localized molten pool. The added powders melt, and then rapidly solidify to build up geometry as the stage moves as specified by the component CAD file. After a single layer is complete, the laser/powder head moves upward in the Z direction, and the X-Y table creates the next profile. This process continues layer by layer until the component is completely formed.



Figure 3 General schematic of a LENS system (left) and photograph of a LENS thin-wall construction (right) [1].

1.2.2 Thermal history

Due to the layer additive nature of AM fabrication process, a complex thermal history, which involves remelting and numerous low temperature reheating cycles (as shown in Figure 4), is experienced in different regions of the deposited material, resulting in complex microstructural evolution [6]. In addition, multiple types of mass, heat, and momentum transfer that can be significantly affected by the operating conditions make additive manufacturing process much more difficult to understand [7]. Some work has been reported dealing with thermal behaviors during AM, including *in-situ* observations of temperatures and molten pools [6], multi-scale simulations considering various process parameters (as shown in Figure 5), and numerical models [7]. However, experimental measurements of temperature during AM are considered to be difficult due to localized heating and superfast melting and cooling involved [7].



Figure 4 Thermal history of LENS technique at the bottom of the first deposited layer, while additional 19-deposited layers arrive in sequence, compared with experimental data [6].



Figure 5. Molten pool size and shape of SS410 steel produced by LENS technique [7]. The molten pool size is determined by the melting temperature 1450° for different traverse speeds. a) V=2.5 mm/s, b) V=7.62 mm/s, and c) V=20 mm/s.

Different process parameter sets in additive manufacturing have great influence on material microstructures. For example, in LENS processing, with a high energy laser combined with a high powder deposition rate, the material can be held at high temperatures for a long enough time to allow grains to become coarsened and mostly equiaxed. In contrast, a lower laser energy combined with a faster scan speed produces a narrower molten pool that solidifies faster into narrow columnar grains [2]. Grain structure can also vary with height in the build direction. In steel alloys, enhanced thermal conduction near the build platform (z < 4mm) has been observed to create smaller grains than higher in the build. In Titanium alloys, β grains coarsen near the top of the part, thermal accumulation from the entire build process causes β grains to coarsen throughout [5]. For SLM titanium, a columnar grain structure again dominates the microstructures. Figure 3a shows a top view of an SLM Ti sample that exhibits a chessboard pattern caused by the 90° shift in scan direction between layers. Figure 3b shows a side view of the same sample. Long, columnar β grains oriented in the build direction span several mm [9].



Figure 6 a): Top view exhibiting checkerboard pattern characteristic of SLM Ti. b): Side view exhibiting columnar grain structures [9].

1.2.3 Problems for AM

The unique processing characteristics of AM parts can lead to the formation of microstructures that exhibit suboptimal mechanical properties. The extremely fast heating and cooling rates of small material volumes produces materials in nonequillibrium states, which can lead to segregation of compositions, and large residual stresses. The incremental layer-by-layer construction orients grains in the build direction (z-axis) and causes anisotropic properties. As the laser constructs a layer, the layers below are often re-melted or re-heated, forming the characteristic long columnar grains. Due to the nature of net-shaping of AM, it is not feasible to apply external mechanical work to reduce the grain size as would be commonly used for conventional manufacturing technology.

1.3 Grain refinement

It is well known that a finer grain size may increase the strength and ductility of the material simultaneously. The grain size dependence of the yield strength can be expressed by the Hall-Petch relationship [10]. The commonly used method to reduce the grain size is forging at high temperatures, breaking the large grains by applied mechanical force, as well as triggering a high extent of dynamic recrystallization. However, similar with casting, AM is a net-shaping process, which has the potentiality to reduce the high costs and wastes associated with the preparation and finishing of wrought materials [11], but at the same time has the problem of coarse grains in the material. Grain refinement for AM materials is thus critically important.

Grain refinement for cast materials is usually achieved by modifying the melt before molding, such as inserting inoculations in to the melt to increase heterogeneous nucleation sites [10], which also cannot be achieved during additive manufacturing.

Acceptable ways for grain refinement in additive manufacturing are modifying powder compositions to form 2^{nd} -phase particles as grain refiners, adjusting building conditions for proper thermal behaviors, and heat treatment in the post process. In this project, only composition design and heat treatment process design for grain refinement in additive manufacturing will be considered.

1.3.1 Grain boundary pinning

Grain growth is achieved by the migrations of grain boundaries. To control the grain size, in another word, is to control the migration of grain boundaries. The Zener pinning model [12] describes the influence of a dispersion of fine particles on the movement of low- and high-angle grain boundaries through a polycrystalline material. The physical basis of the second phase particles dragging the grain boundary motion is the attractive force between the particles and the grain boundary, which is due to the reduction of total interface area upon contact of particle and grain boundary [13]. Figure 7 illustrates a grain boundary with an energy of γ per unit area intersecting with an incoherent particle with a radius of *r*. If the boundary cuts the particle radially, it exerts a force of $F = 2\pi r \gamma sin \theta cos \theta$ on the particle (where θ is the angle between the radius and the motion direction). Derivations by Zener indicate that the grain size R which can be Zener pinned is $R \cong 4r/f$ (where *f* is the volume fraction of spherical particles) [14].



Figure 7 Sketch of Zener Pinning Effect: Incoherent particle intersecting with grain boundary [12]

Several treatments have extended the original Zener pinning model afterwards. The model of Gladman, which has been quantitatively applied to the grain coarsening of austenite in steels, predicts a limiting grain size expressed by Equation 1,

$$2R = \frac{\pi}{3} \frac{\bar{r}}{f_{\nu}} \left(\frac{3}{2} - \frac{2}{Z}\right)$$
(1)

where R is the limiting grain radius, \bar{r} the mean particle radius, f_v the particle volume fraction, and Z is a grain size distribution parameter (ratio of the largest to the average grain size). Thus, the limiting grain size is proportional to \bar{r} and inversely proportional to f_v . For a given f_v , grain size is minimized by the dispersion of fine second-phase particles.

Powder compositions should be carefully adjusted to allow for the formation of second-phase dispersions from the perspective of thermodynamics. On the other hand, the corresponding heat treatment process should also be carefully rendered from the perspectives of both thermodynamics and kinetics.

Considering both thermodynamic and kinetic conditions, an appropriate grain refiner should meet the following criteria: (1) proper solvus temperature in the single high-temperature phase field of the matrix, but not too high for the homogenization process; (2) low coarsening rate constant; (3) sufficient adhesion strength with the matrix, providing enough resistance to shear localization.

1.3.2 Recrystallization

Recrystallization in metallurgy is a process by which deformed grains are replaced by a new set of undeformed (strain-free) grains that nucleate, grow, and coarsen until the original grains are entirely consumed [15], which allows for grain refinement. Plastic deformation increases the density of defects by several orders of magnitude. A certain portion of mechanical work expended during deformation is not transformed into heat but retained in the elastic distortion fields as the extra stored energy, which increases the total Gibbs free energy. The release of stored energy then provides the driving force for recovery and grain nucleation [16]. Stored energy is considered to be vitally important for the recrystallization process. It can be distinguished into two contributions. The first one is the elastic energy, connected with residual stress, i.e., grain-grain interactions. Another part of the stored energy is due to dislocation density, which is mainly localized inside the grains [17].

Experimental and modeling work [18][19] has shown that great residual stresses are locked into the parts during AM process (as shown in Figure 8) due to high cooling rates, solid-solid phase transformations or thermal shrinkage. Too much residual stress can cause component distortion, resulting in a mismatch between the final geometry and the designed geometry [20]. However, residual stress in AM builds is inevitable, due to the nature of severe thermal excursions and steep thermal gradients in AM [20]. The residual stress level in AM builds [18][19][20] is found to be higher than that in cold-rolled steels [21], so the stored energy caused by residual stress in AM can be calculated according to Equation 2 [21], and can be a considerable driving force for recrystallization. This stored energy is described by:

$$E^{el}(\boldsymbol{g}) = \frac{1}{2} S_{ijkl}(\boldsymbol{g}) \sigma_{ij}(\boldsymbol{g}) \sigma_{kl}(\boldsymbol{g})$$
(2)

where S_{ijkl} is the elastic compliance tensor.



Figure 8 Residual stress maps of Waspaloy produced by laser direct metal deposition, (a) vertical direction stresses (z direction). (b) Horizontal direction stresses (direction of beam movement) [20]

However, it is often found in some AM builds that stored energy caused by residual stress during building is not high enough to trigger a large extent of recrystallization. Since stored energy is usually more due to dislocation density, methods to increase the dislocation density in the materials, such as the martensitic transformations, are being considered. This stored energy is described by Equation 3 [21].

$$E^{disl} \cong Gb^2\rho \tag{3}$$

where G is shear modulus, b the Burgers vector of dislocation and ρ the dislocation density.

High dislocation density is inevitable in lath martensites, which accommodate the large strain induced by diffusionless martensitic transformation and subsequence interface gliding [22]. And dislocation density increases as the volume fraction of martensite increases [23], which may be achieved by cyclic austenite-to-martensite transformations. A fitted model of dislocation density

in martensite and retained austenite with the volume fraction of martensite in 17-4PH martensitic stainless steel, proposed by F. Christien et al. [24], provides a quantitative description, as shown in Figure 9 and Equation 4.



Figure 9 Dislocation density in austenite and martensite plotted vs. the fraction of martensite formed. The dotted lines fitted to the experimental points are given by Eqs.2-a and 2-b [24]

$$\rho_A = 1.2 \times 10^{15} \cdot X_M^4 \,(\text{m}^{-2}) \tag{4-a}$$

$$\rho_M = (2.03 + 2.13X_M) \times 10^{15} \,(\text{m}^{-2}) \tag{5-b}$$

1.3.3 Other heat treatment method

Recently, thermohydrogen processing, in which hydrogen is used as a temporary alloying element, is considered to be an effective method for grain refinement in titanium alloys [25]. The reaction of hydrogen with titanium is reversible, allowing hydrogen to be easily removed by vacuum annealing [26]. Grain refinement during thermohydrogen greatly depends on the interstitial hydrogen atoms accumulating along the grain boundaries during solutionizing-quenching-annealing [25].

1.4 Titanium alloys for AM

1.4.1 Phases

Pure Titanium has three equilibrium phases, i.e., the β phase (bcc), the α phase (hcp), and the ω phase (hexagonal structure). At 1 atm, the β phase forms at higher temperatures, whereas the α phase forms at temperatures below 882 °C [28]. Figure 5 illustrates a temperature-pressure phase diagram of pure titanium.



Figure 10 Phase Diagram of Pure Ti [27]

Titanium alloys are characterized as either a-, $\alpha+\beta$ -, or β -alloys, even though all commercial alloys contain both phases at operation temperatures. a-Ti alloys generally contain no more than 5% β phase, alloyed with a phase stabilizing elements. $\alpha+\beta$ -Ti represents alloys with higher β fractions (a "near-a" phase represents alloys with less than 20% in the β phase). And β -alloys are known for lack of martensitic transformation during quenching [30].

Alloying elements affecting phase compositions in titanium alloys are characterized as α -stabilizers, β -stabilizers or neutral elements. The α -stabilizers can increase the β -transus temperature, thereby increasing the temperature range in which the α phase is present. The β -stabilizers, on the other hand, decrease the β -transus temperature, and thus increase the temperature range in which the β phase is present. Neutral stabilizers slightly decrease the β -transus temperature at low concentrations and slightly increase the β -transus temperature at high concentrations. Ti-X binary phase diagrams in Figure 11 schematically show the effect of different elements on phase relations in titanium alloys.



Figure 11 Schematic Ti-X binary phase diagrams [28]

1.4.2 Microstructure and mechanical properties

The baseline material for titanium alloy design is the QuesTek[®]-designed QT-Ti-2A alloys, which is a near- β titanium alloy. Its microstructures at the equilibrium state can be described in terms of the morphologies and the arrangement of two phases present, a and β .

A fully lamellar microstructure is a common structure and is easiest to acquire in alpha+beta titanium alloys. It is a result of moderate cooling from the β phase field. During cooling, a phases are more likely to nucleate along the prior β grain boundaries, and then grow into the β grains to form large a colonies comprised of a lamellae, as shown in Figure 14b. This type of microstructure is characterized by relatively low tensile ductility due to large β grains and grain boundary a, moderate fatigue, and good creep and crack growth resistance [31] The important parameters for a lamellar microstructure with respect to mechanical properties of the alloys are β -grain size, grain boundary a width, a colony size and a lamellae width [31] with the latter three being reduced with increasing cooling rates [32]. The refinement of lamellar structures may improve the mechanical properties to some degree.

In addition, due to the high driving force by fast cooling, the number of nucleation sites within the β grains is increased, avoiding or thinning the grain boundary a phases. After annealing at lower temperatures for some time according to the TTT diagram (Figure 12), a phases will grow and form basketweave or Widmanstätten microstructures, as shown in Figure 14a. Basketweave microstructures are more likely to be present in the near- β titanium alloys [32]. The interlocking structure in the QuesTek[®]-designed QT-Ti-1A alloy (similar with QT-Ti-2A) significantly improves both the strength and ductility compared with commercial lamellar-structured Ti-6Al-4V alloys, as shown in Figure 13.



Figure 12 Temperature-time-transformation diagram of three β Ti alloys, relative to their β transus [28]



Figure 13 QT-Ti-1A vs. Ti64 a) Microstructures of QT-Ti-1A and Ti-64; b) RT Strength – Elongation Comparison [33]

Equiaxed microstructures, as shown in Figure 14d, are comprised of equiaxed a phases and β phases. It is the result of a recrystallization (in the two-phase field), followed by slow cooling process, so the alloy needs to be highly deformed by working. Equiaxed microstructures usually have high ductility and fatigue strength.

Bimodal microstructures, as shown in Figure 14c, exhibit similar structure with equiaxed microstructures. As its name indicates, it is comprised of both equiaxed a phases and lamellar a phases in prior β grains. Similarly, to acquire equiaxed a phases, sufficient plastic deformation is important to trigger recrystallization in the two-phase field. Then it is followed by fast cooling to transform β phase to lamellar a phase. Since bimodal structure is a combination of the lamellar and equiaxed microstructures, it exhibits the best combination of mechanical properties.



Figure 14 Typical Microstructure of Ti alloy a). basketweave; b) lamellar; c) bimodal; d) equiaxed [34][35][36][37]

In addition to diffusion-controlled transformation from β phase to a phase to form the above-stated microstructures, β phase can also transform diffusionlessly to martensites (as shown in Figure 15) during fast cooling. However, the martensites in titanium is much softer than those in steels, and cannot act as a hardening phase [32].



Figure 15 "Acicular" martensite in Ti-6Al-4V quenched from the β phase field: (a) LM (b) TEM [32]

Another diffusionless transformation product, athermal ω phase, is able to precipitate athermally over a very narrow composition range during the rapid quenching from the elevated-temperature β field of numerous titanium alloys, and cannot be suppressed no matter how rapid the quench rate is [38]. The formation of athermal ω phase may inhibit the martensitic transformation on quenching [28]. The presence of ω phase is undesirable, since it causes embrittlement [39].

1.4.3 Rate constant

The Morral and Purdy normalized coarsening rate constant can act as an indicator of transformation kinetics for α precipitates in a β matrix of an n-component alloy. The constant is defined as follows:

$$\frac{K_{mp}}{\sigma V_m} = \frac{8}{9RT} \left\{ (x_i^{\ \beta} - x_i^{\ \alpha})^T (\frac{\partial^2 G^{\beta}{}_m}{\partial x_i \partial x_j}) (D^{\beta}{}_{jk}) (x_k^{\ \beta} - x_k^{\ \alpha}) \right\}$$
(5)

In this equation, σ is the α/β interfacial energy, while V_m is the molar volume. Across a flat surface between equilibrium α and β phases, $x_i^{\ \beta} - x_i^{\ \alpha}$ is the difference in composition of element *i*. [D] is the $n \times n$ matrix of diffusivities in the matrix β phase. Normalized K_{MP} is calculated by the QuesTek's proprietary MaDe software, with the assumption that the ratio of transformed phase fraction to its final equilibrium value is 0.1 for the determination of $x_i^{\ \beta} - x_i^{\ \alpha}$ [28]. The calculations of normalized K_{MP} are performed at 200°C below the β -solvus temperature, which crosses the C-curve of the grain-boundary α phase, in order to evaluate the rate constant of grainboundary α phase formation.

1.4.4 Ms temperature calculations

For Ms temperature calculations in Ti alloys, we will use the theory of heterogeneous nucleation of martensite established by Olson and Cohen [40][41][42]. In this theory, the critical condition for martensite to nucleate is given by Equation 6.

$$\Delta G_{chem} + \Delta G_{mech} = -(W_f + G_0) \tag{6}$$

where the left-hand side is the total driving force contributed by chemical thermodynamics (ΔG_{chem}) and applied stress (ΔG_{mech}) , and the right-hand side is the critical driving force (ΔG_{crit}) which consists of a composition-dependent frictional work term W_f and a nucleation potency term G₀.

In the case of martensite formation on quenching, only the chemical driving force contributes. For $\beta \rightarrow \alpha'/\alpha''$ transformation in Ti alloys,

$$\Delta G_{chem} = G_m(\alpha) - G_m(\beta) \tag{7}$$

with fixed composition. This is calculated using the ThermoCalc software and TiGen database. By its definition, the critical driving force should equal the chemical driving force at the Ms temperature:

$$\Delta G_{chem} = \Delta G_{crit} \tag{8}$$

 ΔG_{crit} of the QT-Ti alloy system can be represented by Equation 9:

$$\Delta G_{crit} = -G_0 - \sum_i K_i x_i \tag{9}$$

where G_0 and K can be obtained by fitting experiment data, *x* is the atomic fraction of alloying element *i* [28]. This equation is analogous to the linear solution hardening law observed for Ti alloys. Therefore, the Ms temperature can be calculated by Equations 7-9.

1.4.5 Grain refinement for AM titanium alloys

Conventionally, grains in titanium alloys are refined to enhance mechanical properties via severe plastic deformation, followed by recrystallization in the two-phase field, just as stated above, to form equiaxed or bimodal microstructures. However, previous experiments have shown that the residual stress in SLM Ti-6Al-4V alloys are too low to trigger recrystallization in the two-phase field. As a result, composition modifications to form grain refiners, as well as proper heat treatment for grain refinement need to be considered.

Previous research considered boron as a solidification grain refiner for titanium alloys and titanium aluminides. Although boron has the largest growth restriction factor for solidification, its use as a practical grain-refining addition may be limited by deleterious effects such as the reduction of tensile elongation caused by the precipitation of large titanium borides. It is thus desirable to explore other potential grain refiners, such as silicides by adding some amounts of Si and Zr into the composition. In the Ti-DATA-v3 database, there are two forms of silicides, namely (Zr,Ti)₂Si and (Ti,Zr)₅Si₃. Since only one type of grain refiner is desired, a choice between the two silicides will be made according to their stability, i.e., formation energy, and rate constant.

1.4.6 Heat treatment routes

Heat treatment is of paramount importance with regards to the microstructures and therefore to the mechanical properties. The post heat treatment routes for AM titanium alloys to exhibit basketweave microstructures with silicides as the grain refiners are shown in Figure 16. All the cooling methods involved in Figure 16 are water quenching.



Figure 16 Heat treatment routes for AM titanium alloys

Homogenization above the β -transus temperature and below the silicide-solvus temperature can create equiaxed and homogenized β grains with fine silicides precipitated. However, due to the relatively high operating temperature, the β -transus temperature should be as low as possible on the basis of higher silicide-solvus temperature than β -transus temperature. At the same time, the homogenization and solutionizing time should be carefully tailored to reduce grain growth.

Cyclic martensitic transformations are expected to accumulate sufficient dislocation density for recrystallizations. In each cycle, the material is heated in the β +silicide phase field. Since the distortions caused by martensitic transformation in titanium alloys are less significant than those formed in steels [32], more cycles are expected to be required for a large extent of recrystallization. In addition, in order to accumulate sufficient amounts of dislocations, compositions with lower Ms temperatures would be needed to form α '-type martensite with a high dislocation density on quenching [43].

Once the β grain size is reduced, the following steps can be performed to modify the microstructures. To obtain basketweave microstructures, the material should be rapidly cooled down from above the β -transus temperature to about 200 degrees [28] below the β -transus temperature, which avoids the 'C-curve' of grain boundary α . Following annealing allows for the growth bulk α dispersed in prior β grains. In order to avoid the Ti₃Al phase and martensitic transformation, the annealing temperature should be higher than those temperatures.

1.5 Maraging steels for AM

1.5.1 Maraging steels

Maraging steels are steels which have undergone a combination of martensitic transformation and ageing treatments. The strength of such steels comes from the fine precipitates that grow during heat treatment [44]. The quenching of austenite (FCC) to martensite (BCT) corresponds to the increase in strength and toughness, properties which can be tailored by alloying elements and ageing time. Substitutional Ni, Co, Mo, and Ti are the standard alloying elements. The Ni

contributes to the η -phase (Ni₃-(Ti,Al,Mo)), finely dispersed precipitates of which are the primary strengthening mechanism in the QuesTek[®]-designed PH48S steel being considered as the baseline material for this project [45]. The resultant microstructure after a series of heat treatments is a lath martensite, with η precipitates for precipitation strengthening and with MC (M=Ti, Nb, V and Mo) carbides as grain refiners. Microstructure will be discussed more thoroughly in the heat treatment section.

In general, maraging steels, and the steel being considered in this project in particular, exhibit high strength and toughness as a result of their carefully tuned processing routes. Figure 17 illustrates the advantageous toughness of martensitic steels which have been strengthened by precipitation. Figure 18 further shows the higher fracture toughness that can be achieved from maraging steels, as compared to carbide-strengthened martensitic steels, resulting from the additional ageing for precipitation strengthening step. To maintain optimal mechanical properties, impurity concentrations, particularly sulfur, nitrogen, and oxygen, must be kept low, since the segregations of such impurities to the austenite grain boundaries decrease toughness. Carbon contents are kept low to control the amount of grain refining MC carbides.



Figure 17 Impact energy of martensitic steels [45]



Figure 18 Comparison of fracture toughness vs. strength for carbide strengthened martensitic and maraging steels [46]

1.5.2 Grain refinement for AM maraging steels

Large grains of AM builds are problematic because they provide lower strength and ductility than small grains, as given classically by the Hall-Petch relationship. Thus, small grain size should be guaranteed. For wrought materials, the grain refinement is achieved by the combination of forging to reduce the prior austenite grain size, and grain boundary pinning by finely dispersed MC particles with appropriate heat treatment routes to limit the migration of austenite grain boundaries. For AM materials, the reduction in grain size may be achieved by cyclic martensitic transformations, along with the grain pinning effect by MC carbides. Homogenization above the MC-solvus followed by annealing at sub-MC-solvus temperature enables a homogeneous distribution of fine MC particles [45].

1.5.3 Heat treatment routes

Heat treatment is an essential series of processing steps for defining the microstructure and thus mechanical properties of an alloy. Figure 19 illustrates the heat treatment procedure for PH48S steels by AM.

The initial homogenization stage serves to reduce segregation as well as to dissolute the MC carbides, so this step must be done at a temperature higher than the MC-solvus temperature. However, such a high temperature for homogenization enables high grain growth. Lowering of the homogenization temperature and time is therefore of much interest to keep small grain size and can only be achieved by lowering the MC-solvus temperature, an active area of work for this project. The holding time is primarily determined by the homogenization process, which can be estimated with DICTRA simulations using the Scheil model as input. Experimental results yield secondary dendrite arm spacing, from which cooling rates can be deduced. Arm spacing decreases with increased cooling rate [47].



Figure 19 Heat treatment routes for AM maraging steels

Reduction of prior austenite grain size is achieved by subsequent cyclic martensitic transformations. The number of austenite-to-martensite cycles depends on the volume fraction of acquired martensites, which is related with the dislocation density to trigger recrystallizations. The temperature for austenitization of each step should be higher than η -solvus temperature, preventing the precipitation of η phase at this stage, lower than MC-solvus temperature, such that some fine MC carbides precipitate out when holding, and within the austenite phase field.

The ageing step is critical as it is responsible for the precipitation of the η phase (associated with small amounts of B2-NiAl), the primary strengthening phase in this alloy, as discussed previously. The ageing temperature depends on the desired volume fraction of η phase, and the ageing time depends on the kinetics of nucleation, growth and coarsening of η phase, which can be simulated by PrecipiCalc software. However, η phase is rod-shaped. To represent η phase using PrecipiCalc, it is necessary to approximate the shape-dependent interfacial energy. Coherency transitions in PrecipiCalc have been implemented with a double hyperbolic tangent function (Equation 10) with seven controllable parameters to capture temperature and particle size dependency [48].

$$\sigma(J/m^2) = \{C_1 \tanh[C_2(T+C_3)] + C_4\}\{D_1 \tanh[D_2(R+D_3)] + 1\}$$
(10)

where C_i (i=1~4) are temperature-dependent constants and D_j (j=1~3) are size-dependent constants.

Furthermore, a two-step ageing process is used for this steel to most effectively control the precipitation process. The first ageing step occurs at a high temperature, but still below the η phase solvus temperature, and works to speed up the η precipitation process. The second ageing step, at a lower temperature ensures the desired volume fraction of precipitates and subsequent mechanical properties.

Two step ageing is a common processing method in Al-Mg-Si and Al-Zn-Mg alloys; however, in these systems a low temperature pre-ageing step is followed by a high temperature ageing step.

The lower temperature ageing step serves to form nuclei under high supersaturation and the higher temperature step selectively, via the Gibbs-Thomson effect, dissolves and grows these precipitates [49]. In the Al-Mg-Si system, such processing leads to undesirable coarse precipitates, whereas in the Al-Zn-Mg system, two step ageing yields desirable fine precipitates [50]. While this is distinct from the high followed by low temperature two step ageing to be used in the steel considered in this project, the Al systems demonstrate the control over precipitate size that can be achieved with two step ageing.

By selectively precipitating specific phases, two-step ageing allows for detailed control of the precipitation mechanism of the phase under consideration [51].

1.6 Computational tools

In the design process, a number of computational tools will be used: (1) ThermoCalc, (2) DICTRA, (3) PrecipiCalc, and (4) MaDe.

ThermoCalc is a powerful software and database package for phase equilibrium and phase diagram calculations and thermodynamic assessments using CALPHAD methods. Phase equilibria, constrained equilibria, and driving forces can be calculated as a function of composition, pressure, temperature and other user defined functions in multicomponent systems. In this project, Ti-DATA-v3 (TTTI3) and TCFE6 database will be used. ThermoCalc can also simulate solidification process using Scheil model.

DICTRA is a general software package for simulations of diffusion controlled transformations in multicomponent systems. DICTRA is interfaced with ThermoCalc, which handles all thermodynamic calculations needed by DICTRA. In this project, TIMOB12a modified with Cr (TIMOB12b) and MOBFE1 database will be used.

PrecipiCalc is a sophisticated computer program developed by QuesTek[®] to calculate threedimensional, multi-particle diffusive precipitation kinetics of multiple phases. PrecipiCalc can predict the precipitate size, number density, volume fraction, and composition of the matrix and precipitates in the system during heat treatment.

MaDe takes the input of thermodynamic and diffusivity values from ThermoCalc and DICTRA respectively and makes calculations in various domains in order to select the parameters for graphical design integration.

2 Team Organization

2.1 Self-introductions & Motivation

Rebecca Glaser is a junior in the Department of Materials Science and Engineering and is working with Prof. Barnett on solid oxide fuel cell anodes. Her interests are in materials for clean energy technology. She is interested in this project for its new take on steel processing and learning more about metals. Her knowledge of powder heat treatment can contribute to understanding altering of the steel used here and gives her interest in working on the heat treatment routes, like Ms temperatures and change in Ts with composition.

Ritij Goel is a junior in the Department of Materials Science and Engineering and is working with Prof. Shah on bone graft substitutes. His interests lie in biomaterials and energy materials. He is interested in this project because he is interested in learning more about metals and additive manufacturing. His experience with Thermocalc can help in performing the equilibrium calculations that may be required.

Martin Hewitt is a pre-senior in the Department of Materials Science and Engineering. His major concentration is in product design and manufacturing, and he is pursuing the Segal Design Certificate. With this project, Martin hopes to address current limitations of additive manufacturing of metals so that the technology can bring more value in prototyping and limited run manufacturing.

Fan Meng is a 1st-year PhD student in the Department of Materials Science and Engineering and working with Prof. Olson on materials design for TRIP Titanium alloys. His interest lies in understanding the overall materials designing process, learning to use calculation tools skillfully and obtaining more knowledge about titanium alloys.

Ruijing (Hazel) Yan is a junior in the Department of Materials Science and Engineering as well as Manufacturing and Design Engineering. She is working with Dr. Walton under NU-ACCESS on artwork preservation. Her interests are in polymers and materials applications. She is interested in this project because she wants to learn about the application of material science in manufacturing.

2.2 Role allocation matrix (RAM)

Within the team, roles and tasks were assigned based on each team member's interest as well as skills on each software and material properties. Team members typically volunteer to take assignments related to their field of interest and research background. Some tasks were also assigned so that team members who want to develop skills in unfamiliar areas can be paired up with team members with more experience on the subject, and thereby allowing team members to acquire new skills from each other. The chart below shows the role allocation of the team. This

| Task | Rebecca | Ritij | Martin | Fan | Ruijing |
|-----------------------------------|---------|-------|--------|-----|---------|
| Project Background | 1 | 1 | 1 | 1 | 1 |
| Ti Phase diagram | | 1 | 2 | | |
| Ti Driving Force | | 2 | | | 1 |
| Ti Ms calculation | | 1 | | 2 | |
| Ti K _{MP} calculation | | 2 | | | 1 |
| Steel Homogenization | | | | 1 | 2 |
| Steel MC Phase Diagram | 1 | | 2 | | |
| Steel PrecipiCalc | | | 1 | 2 | |
| Steel Ms calculation | 1 | | 2 | | |
| Steel Coarsening Rate calculation | 1 | | | | 2 |
| Report Writing/Compiling | 1 | 1 | 1 | 1 | 1 |

chart makes sure that everyone on the team gets relatively equal amount of work based on their preferences.

1 - Primary responsibility; 2 - Secondary responsibility

3 Property Objectives

3.1 Ti-alloys design

To design the optimum properties of titanium alloys for AM, three goals need to be achieved:

(1) Lowering the β -solvus temperature to decrease grain growth rate by adjusting the compositions, such as introducing more β -stabilizers and as well as slow diffusers (Mo) to move transformation to lower temperatures to promote the basketweave structure and lower the precipitation rate constant to minimize GB α formation on coolings.

(2) Introducing cyclic martensitic transformations and lowering the Ms temperature to accumulate sufficient dislocation density for recrystallizations.

(3) Introducing finely dispersed grain refiners (Ti-Zr-Si silicides) to restrict the motions of β grain boundaries according to the Zener pinning effect. Increasing the silicides-solvus temperature above β -transus temperature is also required.

3.2 Maraging steel design

The design of maraging steel for AM involves four main objectives:

(1) Figuring out the shortest time and lowest temperature needed for homogenization by DICTRA simulations based on measured secondary dendrite arm spacing.

(2) Introducing cyclic martensitic transformations to accumulate sufficient dislocation density for recrystallization.

(3) Choosing a best coarsening resistant MC with a lower solvus temperature to enhance grain pinning.

(4) Representing η -phase nucleation, growth and coarsening process in PrecipiCalc by properly adjusting the interfacial energy function to simulate two-step aging to get more strength from a lower temperature final age.

4 Design Approaches

4.1 System design chart



Figure 20 System chart for the proposed Ti-alloy design

The Ti systems design chart demonstrates the paradigm of materials science. Processes determine the structures which determine the properties which determine the performance of the part being produced. The process column reflects the heat treatment plot in Figure 16. Structure denotes the microstructural developments desired in this material to reach certain goals of each property, which is also denoted. The subsystems we focus on in this project are matrix and prior β grain designs.



Figure 21 System chart for the proposed maraging steel design

The steel systems design chart demonstrates the processes which inform the structures which inform the properties which inform the performance of the part being produced. The process column reflects the time vs. temperature plot in Figure 19. Structure denotes the microstructural developments desired in this material to reach certain goals of each property. The subsystems we focus on in this project are nano-precipitation and prior austenite designs.

4.2 Design flow chart

For Ti-alloy design, the main task is to adjust chemical compositions in order to refine grains and to obtain basketweave microstructures. To refine grains, we need to lower the β solvus temperature to decrease grain growth rate by adjusting the composition, such as introducing slow diffusers (Mo). To reduce the prior β grain size, cyclic martensitic transformation is introduced to accumulate sufficient dislocation density for recrystallization. At the same time, to hinder the migration of grain boundaries, the Zener pinning effect is utilized by introducing Zr and Si elements to form Ti-Zr-Si silicides as grain refiners. The silicide-solvus temperature should be designed to be above the β -transus temperature. In order to obtain the basketweave microstructures, while avoiding the formation of grain boundary α , we will increase the driving force for α phase forming from β phase by adjusting the precipitation rate constant. Besides, Ti₃Al formation temperature can also be calculated, and it can be used for setting the annealing temperature in order to avoid the formation of Ti₃Al. In this design, QT-Ti-2A alloy will be used as a baseline material.

ThermoCalc will be used to find out the optimal composition. The flow chart for Ti-alloy design is shown in Figure 22.



Figure 22 Flow Chart of AM Ti-alloy Design

For maraging steel design, the main task is adjusting the chemical compositions to refine grains. We need a best homogenization process by lowering the homogenization temperature and reducing holding time to decrease grain growth rate, on the basis of segregations having been eliminated. Since homogenization temperature must be higher than MC-solvus temperature, MC carbides with lower solvus temperature are preferable. In this design, PH-48S steel will be used as the baseline material. ThermoCalc will be used to find out the optimal composition to achieve greater grain refinement. DICTRA will be used to calculate the homogenization temperature and time. PrecipiCalc will be used to evaluate the η phase precipitation during two-step ageing. The flow chart of maraging steel design is shown in Figure 23.



Figure 23 Flow Chart of Maraging Steel Design

5 Results

5.0 Final Composition and Processing Design

Titanium alloy

In wt%: Ti-4.2Al-2.8V-1.65Cr-2Fe-10Mo-1.5Zr-0.15Si

Table 1 Comparison between baseline alloy QT-Ti-2A and our design alloy

| | Ms | β solvus | $K_{MP}(\alpha \text{ from } \beta)^*$ [m ² /(J/mole)/s] |
|----------------|-------|----------|--|
| Baseline Alloy | 638°C | 863°C | 8.6e-20 |
| Our Design | 177°C | 730°C | 5.3e-22 |

*Rate constant were calculated at 200°C below β solvus temperature

Steel

In wt%: Fe-8Cr-8.73Ni-7.4Co-1.6Mo-0.3Ti-0.38Al-0.01Nb-0.02C

| Table 2 | Comparison | between | baseline | alloy | PH-48S | and | our | design | alloy |
|---------|------------|---------|----------|-------|--------|-----|-----|--------|-------|
|---------|------------|---------|----------|-------|--------|-----|-----|--------|-------|

| | Baseline Alloy | Our Design |
|----------------------------|----------------|---------------|
| Homogenization temperature | 1250-1350°C | 1250-1350°C |
| Homogenization time | 100-23 minutes | 95-23 minutes |
| Ageing temperature 1 | 450°C | 550°C |
| Ageing time 1 | 3 hours | 30 minutes |
| Ageing temperature 2 | N/A | 450°C |
| Ageing time 2 | N/A | 9 hours |

5.1 Ti Design

5.1.1 Ms Temperature Target

High dislocation density is desired for high stored energy inducing recrystallization. The dislocation density of martensite in steels usually reaches maximum for $Ms \le 300^{\circ}C$. Diffusion controlled recovery is responsible for lower dislocation density above 300°C. Therefore, we can find the temperature when diffusivity of Ti in beta phase is the same as that of Fe in austenite or ferrite at 300°C. We can then adjust Ms to that temperature to obtain high dislocation density.

The diffusivity of Fe at 300°C in PH-48S steel was retrieved from MOBFE database using DICTRA. The diffusivities of Fe in austenite and ferrite are 2.46e-34 and 4.46e-30 m²/s respectively. The temperature when diffusivity of Ti in beta phase is the same with that of Fe in austenite or ferrite at 300°C was retrieved from TiMOB12b database. 130°C and 180°C (shown in Figure 24) are corresponding temperatures for the diffusivity of Ti to reach 2.46e-34 and 4.46e-30 m²/s. Therefore, the Ms temperature should be lowered to near 180°C (130°C is optimal).



Figure 24. Diffusivity of Ti in beta phase in QT-Ti-2A alloy

The Ms temperature was calculated, as explained in 1.4.4, using the Olson-Cohen Model. The K values used are displayed in Table 3:

Table 3 K values of alloying elements in Titanium alloys[28][29]

| Element | G_0 | Fe | Мо | Cr | V | Al |
|---------|-------|-------|------|------|------|-----|
| K | 71 | 16714 | 6951 | 4290 | 2441 | 472 |

The Ms temperature of the baseline composition, based on the Olson-Cohen model, is approximately 638 °C, as shown by Figure 24.



Figure 24 The Ms temperature of the baseline material is approximately 638 °C, calculated using the Olson-Cohen model.

5.1.2 Influence of Fe and Mo content on the phase fields of titanium alloys

The phase diagrams within the QT-Ti-2A system with variable Mo or Fe content were calculated to determine the effect of Mo or Fe on phase fields, more specifically the β -solvus temperature and Ti₃Al formation temperature. Figure 25 and Figure 26 show that an increase in Fe results in a lower β -solvus temperature and an increase in Mo shows slightly lower β -solvus temperature. From this phase diagram, it is thus evident that Mo and Fe act as β -stabilizers in this system. A lower β -solvus temperature allows for homogenization at a relatively lower temperature, which helps decrease the grain growth rate. It is also found that the Ti₃Al-solvus temperature is quite low, so it can be easily avoided during annealing. However, TiM and C15 formation temperatures increase with the Fe content. The amount of Fe in this alloy system is thus limited.



Figure 25 Phase diagram with variant Mo mass fraction and temperature, with 2.8 wt% V, 4.2 wt% Al, 0.35 wt% Fe and 1.65 wt% Cr held constant



Figure 26 Phase diagram with variant Fe mass fraction and temperature, with 2.8 wt% V, 4.2 wt% Al, 1.45 wt% Mo and 1.65 wt% Cr held constant

5.1.3 Influence of Fe and Mo content on the rate constant of α phase growing from β phase

The coarsening rate constants of Fe and Mo in the baseline alloy were calculated. These elements help lower the Ms temperature of this alloy. Thus, their influence on the coarsening rate must be understood. Both Mo and Fe lower the rate constant of the overall alloy. Figure 27 illustrates the effect of Mo and Fe on the baseline alloy on the coarsening rate. The rate constant drops abruptly with a small addition of Mo. However further additions cause the rate constant to drop linearly. Adding Fe causes the rate constant to initially drop linearly, but then taper off. Ultimately, the reduction in coarsening rate constants with the addition of Mo is more rapid than that of Fe by about one order of magnitude.



Figure 27 Coarsening rate constants as a function of Mo and Fe composition. Baseline composition held constant.

5.1.4 Ms temperature adjustment by adding Fe and Mo

To lower the Ms temperature, Fe and Mo (two elements with high K values) are considered. However, the addition of Fe decreases the temperature difference between β -solvus and TiM or C15 phase formation temperature. Mo has no such effect. As a result, more Mo can be added relative to Fe. A design objective in this step is to lower Ms to near 180°C and the temperature difference between β -solvus and TiM or C15 phase formation temperature larger than 200°C. After several trials, we found that with 2wt% Fe and 10wt% Mo, the Ms temperature lowers to 177°C and the temperature difference between β -solvus and TiM becomes about 250°C (shown in the step diagram, Figure 28).



Figure 28 Step diagram with 2.8 wt% V, 4.2 wt% Al, 2 wt% Fe, 10 wt% Mo and 1.65 wt% Cr

5.1.5 Selection of silicides for Titanium alloys

In order to decrease the grain size of the AM titanium alloys, silicides are introduced as grain refiners. The grain refiners help reduce grain sizes in accordance with the Zener pinning effect. There are two types of silicides — $(Ti,Zr)_5Si_3$ and $(Ti,Zr)_2Si)$ — available in the Ti-DATA-v3 (TTTI3) database. A ternary phase diagram of Zr, Ti, and Si was plotted in Figure 29 using the OQMD database [53]. Two forms of silicides in the phase diagram were found to be related with the two silicides in OQMD database: Ti₅Si₃ and Zr₂Si.

To find out the more suitable silicide for this application, the formation energies of these two silicides were first evaluated, according to the OQMD database. The more negative the formation energy is, the more stable the silicide. Table 4 shows the formation energy of the two silicides, Ti_5Si_3 and Zr_2Si . It was found that the formation energy of Zr_2Si is slightly smaller than that of Ti_5Si_3 , without the considerations of the solution effect.



Figure 29 Ternary Phase Diagram of Ti-Zr-Si system

| Silicide | Formation Energy (kJ/mol) |
|---------------------------------|---------------------------|
| Ti ₅ Si ₃ | -737.8 |
| Zr ₂ Si | -800.0 |

Table 4 Formation Energy of the Two Types of Silicides [53]

In addition, the two silicides were compared in terms of which provides the lower rate constant. Rate constants were calculated with either fixed Si composition or fixed Zr composition in the phase diagram. From these calculations, the trends of Si and Zr composition on the rate constant can be observed on the resulting plots.



(a)

(b)





Figure 31 Rate constant with (Zr,Ti)₂Si at fixed (a)Zr composition, (b)Si composition

From these plots, it can be observed that the effect of adding Si and Zr is mostly consistent across different compositions. The calculation also suggests that $(Zr, Ti)_2Si$ is able to get the lower rate constant. As shown in Figure 30(a), the lowest rate constant, 4E-19[m²/(J/mole)/s], occurs when Zr composition is 8.4% and Si composition is 0.12%. This rate constant is approimately half of the lowest rate constant that $(Ti, Zr)_5Si_3$ can get within the allowed compositions, which is 8.5E-

 $19[m^2/(J/mole)/s]$ as shown in Figure 31(b). Because of this result, (Zr, Ti)₂Si was chosen over (Ti, Zr)₅Si₃.

5.1.6 Influences of Zr and Si on the phase fields of titanium alloys

Using the composition generated from 5.1.4, Ti system isothermal sections were plotted with varying Si and Zr. These isothermal sections clarify the effects of Si and Zr on the β -solvus temperature and silicide-solvus temperature, as well as what composition ranges result in the formation of the respective silicide. The two possible silicides are $(Zr,Ti)_2Si$, which is a solution of Ti in Zr₂Si, and $(Ti,Zr)_5Si_3$, which is a solution of Zr in Ti₅Si₃. The isothermal sections generated using Thermo-Calc-4.0 are shown below. The β -transus temperature is confirmed to be between 700 °C and 780 °C, as no α phase is present at 780 °C.



Figure 32 Isothermal sections of the Ti alloys with varying Si and Zr, with 2.8 wt% V, 10 wt% Mo, 4.2 wt% Al, 2 wt% Fe and

1.65 wt% Cr held constant

The four phase fields of interest are labeled. In the alloy design, it is important to have a single type of silicide. As the alloy cools from very high processing temperatures, it is desired that it

crosses from the single- β phase to the β +(Zr,Ti)₂Si and avoid precipitating (Ti,Zr)₅Si₃. This defines a region of interest for the alloy composition, as shaded in Figure 33.



Figure 33 Isothermal sections of the Ti Alloy system with varying Si and Zr, with 2.8 wt% V, 10 wt% Mo, 4.2 wt% Al, 2 wt% Fe and 1.65 wt% Cr held constant. Acceptable compositions are indicated by the shaded area.

5.1.4 Phase fraction of silicides

The phase fraction of $(Zr,Ti)_2Si$ needs to be adjusted to 0-1% as a grain refiner to refine β phase according to Zener pinning effect. By adjusting Zr and Si content, the phase fraction of $(Zr,Ti)_2Si$ can be adjusted to 0-1% when it has 2wt%Zr and 0.15wt%Si at 780°C. At this stage, small adjustments can be done to obtain lower silicide rate constant. The trends of rate constant with variant Zr or Si content were generated using MaDe, as shown in Figure 34. It shows that the rate constant decreases as Zr and Si content increases. Zr content was slightly reduced to 1.5wt%. This corresponds to a silicide phase fraction of approximately 0.2% at 780°C. The step diagram of final composition was shown in Figure 35.



Figure 34 Rate constant K_{MP} of variant Si or Zr content with 2.8 wt% V, 4.2 wt% Al, 2 wt% Fe, 10 wt% Mo, 1.65 wt% Cr, and 1.5wt% Zr (for variant Si) or 0.15wt% Si (for variant Zr) held constant



Figure 35 Step diagram with 2.8 wt% V, 4.2 wt% Al, 2 wt% Fe, 10 wt% Mo, 1.65 wt% Cr, 1.5wt% Zr and 0.15wt% Si

5.2 PH-48S maraging steel

5.2.1 PH-48S maraging steel step diagram

A step diagram of PH-48S steel was plotted using ThermoCalc 4.0, as shown in Figure 36. The composition used in this diagram is PH-48S powder composition (wt%): Fe-11.1Cr-8.7Ni-7.4Co-1.6Mo-0.61Ti-0.38Al-0.012C. From this diagram, MC (TiC) carbide solvus temperature of this system is about 1211 °C.



Figure 36 Step diagram of PH-48S steel

5.2.2 MC (M=Ti,Nb)-solvus temperature for the maraging steel

Phase diagrams for Ti-C and Nb-C within the PH-48S system were plotted over a range of temperatures in order to understand the effect of alloying elements (M and C) on the MC solvus temperature. Figure 37 illustrates that the solvus temperature is much more sensitive C content in the Nb-C and V-C systems than in the Ti-C system, i.e., small changes in M content or C content yield larger changes in the solvus temperature. An MC with a lower solvus temperature is desired because it would allow for lower homogenization temperature to prevent huge grain sizes, so NbC



may be a good replacement of TiC in this maraging steel system since the solvus temperature can be tailored by altering C content. In order to lower the NbC-solvus temperature, C content and Nb content in the steel composition should be controlled at a relatively low level.



Figure 37 Ti-C, Nb-C, and V-C phase diagrams at different temperatures with the composition (wt%) Fe-11.1Cr-8.7Ni-7.4Co-1.6Mo-0.38Al (FCC_A1 for Austenite, and FCC_A1#2 for MC)

5.2.3 Influence of MC (M=Ti,Nb) on Ms temperature for the maraging steel

A high Ms temperature, above at least 50°C [45], is desired to help with the complete martensitic transformation. Figure 38 shows the initial variation of Ms temperature with Ti and C content to be on the range from 30-60°C. This was intended to gauge the effects of Ti and C on the Ms temperature in the original alloy such that when designing their influence was known. The Ms temperature decreases with increasing C content. The Ms temperature of the new alloy (in wt%: Fe, 8Cr, 8.73Ni, 7.4Co, 1.6Mo, 0.3Ti, 0.38Al, 0.01Nb, 0.02C) is 298°C.



Figure 38 Ms temperatures (in °C) for Ti-C ranges and 11.1 wt%Cr, 8.7 wt%Ni, 7.4 wt%Co, 1.6 wt%Mo, 0.38 wt%Al held constant

5.2.4 MC (M=Ti, Nb) coarsening rate for the maraging steel

The coarsening rate constants for MC (M=Ti, Nb) carbides in the austenite matrix within the austenite+MC phase field are evaluated using MaDe software. Plots of at the solutionizing temperature (800 °C) within this double phase field for all three systems are shown in Figure 39. While the coarsening rate constants of the Ti-C, Nb-C, and V-C systems are on the same order of magnitude for the same temperature, the Ti-C and Nb-C coarsening rates are lower than that of V-C, though not largely. More importantly, the Nb-C system shows a minimum for certain compositions, whereas neither Ti-C nor V-C show minima within the ranges being investigated. The difference is not overwhelming; however, the small decrease in coarsening rate by using Nb-C as the MC in this steel is advantageous particularly when considering that the multiple heat treatment steps give plenty of time for coarsening to occur. Due to the lower coarsening rate, similar Ms temperatures, and greater flexibility with solvus temperatures, Nb-C is a good candidate for the replacement for Ti-C as the MC in this maraging steel. Particularly since V does not seem to influence the coarsening rate of the three metals being considered, except at very high T concentrations, and it does not allow for optimization, by minimization, of the coarsening rate.



Figure 39 Coarsening rate constant for MC (M=Ti, Nb) carbides in austenite matrix at 800 °C and 1000 °C, with 11.1 wt% Cr, 8.7 wt% Ni, 7.4 wt% Co, 1.6 wt% Mo, 0.38 wt% Al held constant

5.2.5 Maraging Steel Step Diagrams with Updated MC Carbide

Now that Nb-C has been determined as the optimal MC carbide for this steel, a composition must be picked such that the solvus temperature is minimized. To recall: a lower solvus temperature allows for a lower homogenization temperature. ThermoCalc 4.0 was used to generate step diagrams to find the most favorable composition. The best Nb and C contents are found to be 0.01 wt% and 0.02wt%, respectively. Figure 40 shows the resulting step diagram for this composition and should be compared with Figure 36 which depicts the step diagram of the steel's original composition. The MC carbide solvus temperature is 1200°C, 10°C below that of the original alloy and therefore satisfying the design requirement of lowering the solvus temperature.



Figure 40 Step diagram with new alloy composition

Furthermore, the Cr and Ti contents in this alloy were decreased. Since Ti is no longer being used as the M in the MC carbide, such a high concentration is no longer necessary, though it is still necessary for the n phase and remains in solution in the MC carbide. Decreasing Ti content was found to aid with decreasing the MC carbide solvus temperature. Additionally, increasing the C content to minimize the coarsening rate was found to introduce undesired phases at lower temperatures, namely the μ and σ phases (also called TCP phases), which are detrimental to ductility and are to be avoided. A major element in both μ and σ phases was determined to be Cr. Figure 34 shows the phase diagram with various Cr content, and from this it was deduced that Cr content must be less than 8.wt% to eliminate the σ phase at 450°C, a temperature of interest for ageing. According to the patent [45] the lower limit of Cr content is around 8wt%, that is the minimum value of any of the alloys introduced. Since this is a stainless steel alloy, the Cr content must be kept high enough that a stable chromic oxide layer can form on the surface; however, it must also be low enough to eliminate the σ phase. Additionally, the undesired p phase is also present in the step diagram (Figure 40). Lowering the Cr content lowers the p phase solvus temperature such that it will not be an issue during the ageing steps. Changing the Cr content did not significantly affect the MC carbide solvus temperature. While 8.5 wt% Cr is the upper limit of Cr content, at this composition, the σ and p phase solvus temperature are comparable to 450 °C, the ageing temperatures, thus the 8wt% Cr was chosen to be safe and avoid these undesired phases. Figure 41 shows the phase diagram for Cr in this system.



Figure 41 Cr phase diagram

5.2.6 Minimizing the impact of the µ phase

The phase diagram also shows that the μ is still present at both 450°C and 550°C, candidates for the two-step ageing temperatures. To further understand the contributions from the μ phase, the driving force and coarsening rates of the μ phase, undesired, and η phase, desired as the primary strengthening precipitates, were compared. While the coarsening rates, Table 5 for the μ phase are an order of magnitude higher than that of the η phase, at 450°C and 550°C, the driving force for μ is so significantly lower than η (Figure 42) that the existence of the undesired phase in the step diagram is acceptable since it is much less likely to precipitate out than the desired η phase. The driving force diagram also shows that the driving forces go to zero at 600°C, thus the ageing temperatures must be below 600°C. Therefore the 450°C and 550°C ageing temperatures determined from the step diagram are still viable based on the driving force.



Figure 42 Driving force for μ and η phases for the final alloy composition. Dashed lines indicate relevant temperatures.

Table 5 Coarsening rates of μ and η phases at relevant temperatures. The units are $[m^2/(J/mol)/s]$.

| | 450°C | 550°C |
|---|----------|----------|
| μ | 1.25e-27 | 2.22e-25 |
| η | 8.31e-29 | 3.4e-26 |

5.2.7 Solidification and homogenization simulations for the maraging steel

The Scheil model embedded in TCC was used to simulate the solidification process. In this model, elements in the liquid are assumed to have infinitely large diffusivity, while those in the solid are assumed to have no diffusivity. For PH-48S maraging steel, the solid phase is single austenite (fcc) when the mole fraction of solid is 0.95 (T=1300 °C). For our final AM steel design, austenite (fcc) is also the only solid phase, as shown in Figure 43.



Figure 43 Fraction of Solid Phase for PH-38S Steel and our design steel

The homogenization time is simulated by DICTRA using the single phase model. The diffusion distance in the DICTRA simulation is the secondary dendrite arm spacing, which is 7 μ m in this case, as shown in Figure 44. The composition distribution in DICTRA simulation is obtained from the Scheil model composition output file.



Figure 44 SEM image of dendritic structures of PH-48S by LENS®

The homogenization temperature should be higher than MC solvus temperature to fully dissolve the MC carbides. The MC solvus temperatures of PH-48S and our final design steel are approximately 1211°C and 1200°C respectively, according to the step diagrams (Figure 36 and Figure 40). Thus, we chose 1250, 1300 and 1350°C for homogenization temperature tests.

Diffusion curves of all the elements in PH-48S are shown in Figure 45. Co is the slowest diffuser, i.e., rate-controlling element, in both PH-48S and our final design steel. Therefore, Co was used

to find the homogenization time at each chosen temperature. The homogenization time required each temperature is shown in Table 6.



Figure 45 Diffusion curve of all elements in PH-48S at 1250 °C

| Temperature (°C) | 1250 | 1300 | 1350 |
|------------------|------|------|------|
| PH-48S | 100 | 65 | 23 |
| Our design | 95 | 43 | 23 |

5.2.8 Determination of Aging Temperature and Time

The maraging steel step diagram with updated MC carbides (Figure 46) was used to identify proper two-step aging temperatures. The first aging step will have a higher temperature to accelerate the

nucleation of the η -phase precipitates. As seen in the driving force diagram, the η phase driving force becomes negative above 600°C, so 550°C was chosen in calculations. The second aging step will have a lower temperature to allow η -phase growth while minimizing coarsening of the matrix. 450°C was chosen to avoid other undesirable precipitate phases.



Figure 46 Zoomed in step diagram of final alloy composition.

Aging times were investigated using PrecipiCalc. Initially, aging times were determined for singlestep aging at both 450°C and 550°C in order to optimize input model parameters and find a point of comparison for the two-step process. Lattice parameters of the matrix and precipitate phase were determined from literature.

| Table 7 Lattice parameters of BCC iron and N | ï31 | Гi |
|--|-----|----|
|--|-----|----|

| Phase | Lattice Constant (m) |
|-------------------------------------|-----------------------------------|
| Matrix (BCC Iron) | 2.88E-10 [52] |
| Precipitate (η, Ni ₃ Ti) | a = 5.093E-10, c = 8.276E-10 [54] |

Additionally, the model was executed with nuclei on dislocations as our cyclic martensitic transformation is designed to leave the material with a high dislocation density. The model specified a dislocation density of $5E15 \text{ m/m}^3$ which is typical of lath martensites [55]. The initial results indicated that nucleation of coherent particles was not feasible due to the large difference in lattice parameter, thus calculations proceeded with only incoherent precipitates considered. Due to time constraints, precipitates were approximated as spherical (C4=0.2) Single-step aging simulation results are summarized in Figure 47.



Figure 47 Single-step aging results at 450C (blue) and 550C (red).

The single-step aging simulation results indicate, as expected, that the η particles grow much faster at 550°C than at 450°C. At 550°C, the equilibrium volume fraction 0.012 is reached in 40 minutes. At 450°C, it takes ~20 hours to reach the same phase fraction.

In order to shorten the overall aging time, a two-step approach was adopted. In the simulation, the material is held at 550°C for just long enough to surpass critical radius before air cooling to 450°C. The high-temperature step accelerates nucleation while the low-temperature step serves to continue the development of the target volume fraction. The two-step aging simulation results are summarized in Figure 48.



Figure 48 Two-step aging results with temperature profile indicated.

The two-step aging simulation holds the alloy at 550°C for 30 minutes and at 450°C for the remainder. Equilibrium volume fraction of 0.12 is reached in approximately 9.5 hours total. The two-step process reached the target volume fraction in half the time of the 450°C single-step and reduced the amount of time at 550°C by 25% compared to the 550°C single-step. However, there are several remaining problems with the PrecipiCalc model. A number of the results are not physically realistic, such as the angstrom-scale nuclei in both sets of simulation results. Additionally, the calculated required ageing times are longer than would be desirable in an alloy system. Much of the problem stems from an inability to optimize the parameters of the interfacial energy equation (Equation 10). In the simulation, precipitates are modeled as spherical instead of rod-like due to a lack of experimental data to fit the interfacial energy equation constants. The PrecipiCalc simulation does illustrate the approach taken to two-step aging and serves as a proof of concept. Further optimization of PrecipiCalc input parameters defines a large part of future work necessary to lower the aging time of the η phase precipitates.

5.3 Conclusion

This project focused on designing new compositions and heat treatment routes for titanium alloys and steel for additive manufacturing applications. Various computational methods were used to produce phase and step diagrams, simulate coarsening, precipitate growth, homogenization, and diffusion, and deduce solvus and Ms temperatures.

In the AM Titanium alloy design, Fe and Mo were added to lower the Ms temperature to obtain sufficient dislocation density for recrystallization. Additionally, the addition of Mo and Fe can lower the β -solvus temperature and rate constant for α growing from β , which helps to decrease the grain growth rate and obtain basket-weave microstructure respectively. (Zr,Ti)₂Si was introduced to refine β phase (in accordance with Zener pinning effect). The final design composition yields a significantly lower Ms temperature, lower β solvus temperature and lower rate constant for α growing from β than baseline material QT-Ti-2A alloy.

In the AM steel design, Nb was chosen as the optimal M for the MC carbide grain refiners. From the coarsening rate diagrams, the best Nb and C contents were chosen to decrease both MC coarsening rate and MC carbide solvus temperature. Furthermore, a homogenization temperature and time were chosen based on DICTRA simulations. Ageing temperatures were chosen based on the final alloy's step diagram and ageing time was chosen based on PrecipiCalc simulations of η phase coarsening. The final designed material exhibits a lower MC carbide solvus temperature, which allows for the lowering of the homogenization time and temperature as compared to the baseline material. Comparing the single step and two-step ageing for the final composition, the two-step ageing is considerably faster, showing the benefits of this processing procedure.

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