Modelling study of Ti64 and Ti6242 as a first approach to understand their additive manufacturing behavior

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Degree Project – E7009T

by

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Preface

The present work has been carried at GKN Aerospace in Trollhättan, Sweden, to complete my master’s degree project, as a final step before the end of my studies within my master program AMASE.

I would like to thank my supervisors, Jesper and Anna that made my stay in Trollhättan and in GKN much easier, but also my examiner in LTU, Pia Åkerfeldt who helped me find this great subject for a master thesis work.

I would also like to thank all the people from GTC that help me to understand better the software, or the project, Rosa Pineda Huitron, Ceena Joseph, Marcus Kullerstedt, Pranav Kumar and Sakari Tolvanen.

Finally, I would like to add a special thanks to my family and friends, who always supported me and my sometimes crazy choices through my education, be it in France, Sweden or Germany.

Clara De Monte
Trollhättan, June 2023
Abstract

Aerospace and aeronautics industries push forward the research to improve constantly the quality, safety, and cost of flights. The main ways of improving products are to create lighter and better components, under a highly controlled processing from the research and development to the production at a big scale.

To achieve those goals, new processes and new materials are constantly created by engineers. In this perspective, titanium alloys have been developed and studied as they provide good mechanical properties and low density. To reduce the production costs and waste due to machining, additive manufacturing has started to be implemented on the manufacturing chains. Titanium alloys seemed to react very well to additive manufacturing, but there are still some problematics that need to be answered.

The main problematic of this thesis comes from the process development cell. It has been stated that two different titanium-based alloys, Ti-6Al-4V and Ti-6Al-2Mo-4Zr-2Sn, showed the same behavior under additive manufacturing, which is not an evident statement. Therefore, the goal of this work will be to understand the behavior of those two alloys by simulations and use of key parameters in order to model the process in a proper and accurate way.
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<thead>
<tr>
<th>Symbols</th>
<th>Meaning</th>
<th>Units</th>
</tr>
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<tbody>
<tr>
<td>T</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>T_β</td>
<td>Temperature of transus $\beta \leftrightarrow \alpha$</td>
<td>K</td>
</tr>
<tr>
<td>T_m</td>
<td>Temperature of melting</td>
<td>K</td>
</tr>
<tr>
<td>ΔT</td>
<td>Undercooling</td>
<td>K</td>
</tr>
<tr>
<td>ΔT_c</td>
<td>Constitutional undercooling</td>
<td>K</td>
</tr>
<tr>
<td>ΔT_r</td>
<td>Curvature undercooling</td>
<td>K</td>
</tr>
<tr>
<td>G_L</td>
<td>Thermal gradient in liquid</td>
<td>K/m</td>
</tr>
<tr>
<td>G_{S/L}</td>
<td>Thermal gradient at the solid/liquid interface</td>
<td>K/m</td>
</tr>
<tr>
<td>Q</td>
<td>Heat</td>
<td>J</td>
</tr>
<tr>
<td>H</td>
<td>Enthalpy</td>
<td>J/g</td>
</tr>
<tr>
<td>L</td>
<td>Latent heat</td>
<td>J/(g·K)</td>
</tr>
<tr>
<td>ΔG</td>
<td>Gibbs energy</td>
<td>J/g</td>
</tr>
<tr>
<td>C_0</td>
<td>Nominal composition</td>
<td>wt%</td>
</tr>
<tr>
<td>C_L</td>
<td>Liquid composition</td>
<td>wt%</td>
</tr>
<tr>
<td>C_S</td>
<td>Solid composition</td>
<td>wt%</td>
</tr>
<tr>
<td>k_0</td>
<td>Equilibrium partitioning coefficient</td>
<td></td>
</tr>
<tr>
<td>k</td>
<td>Effective partitioning coefficient</td>
<td></td>
</tr>
<tr>
<td>f_S</td>
<td>Fraction of solid</td>
<td>wt%</td>
</tr>
<tr>
<td>m_L</td>
<td>Liquidus slope</td>
<td>K</td>
</tr>
<tr>
<td>r</td>
<td>Radius</td>
<td>m</td>
</tr>
<tr>
<td>γ</td>
<td>Interface energy</td>
<td>J/m²</td>
</tr>
<tr>
<td>R</td>
<td>Cooling rate</td>
<td>K/s</td>
</tr>
<tr>
<td>V</td>
<td>Velocity of the interface</td>
<td>m/s</td>
</tr>
<tr>
<td>D_L</td>
<td>Diffusion coefficient in liquid</td>
<td>m²/s</td>
</tr>
<tr>
<td>λ₂</td>
<td>Secondary dendritic arm spacing</td>
<td>m</td>
</tr>
<tr>
<td>Γ</td>
<td>Gibbs-Thomson coefficient</td>
<td>K·m</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Density</td>
<td>g/cm(^3)</td>
</tr>
<tr>
<td>( \eta )</td>
<td>Viscosity</td>
<td>Pa·s</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>Thermal conductivity</td>
<td>W/(K·m)</td>
</tr>
<tr>
<td>( \rho_{el} )</td>
<td>Electrical resistivity</td>
<td>Ω·m</td>
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</table>

**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Name</th>
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<tbody>
<tr>
<td>AM</td>
<td>Additive Manufacturing</td>
</tr>
<tr>
<td>BCC</td>
<td>Body-Centered Cubic</td>
</tr>
<tr>
<td>HCP</td>
<td>Hexagonal Close-Packed</td>
</tr>
<tr>
<td>Ti64</td>
<td>Ti-6Al-4V</td>
</tr>
<tr>
<td>Ti6242</td>
<td>Ti-6Al-2Mo-4Zr-2Sn-0.8Si</td>
</tr>
<tr>
<td>DED</td>
<td>Directed Energy Deposition</td>
</tr>
<tr>
<td>EBM</td>
<td>Electron Beam Melting</td>
</tr>
<tr>
<td>LMD</td>
<td>Laser Metal Deposition</td>
</tr>
<tr>
<td>SLM</td>
<td>Selective Laser melting</td>
</tr>
<tr>
<td>SDAS</td>
<td>Secondary Dendrite Arm Spacing</td>
</tr>
</tbody>
</table>
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1. Introduction

1.1 Aim of the thesis

This project is involved in the research and development group at GKN to apply additive manufacturing on the building of fan case mount rings and other engine pieces. The work will focus on two titanium alloys used for wire feeding additive manufacturing components.

In a first part, the problematic of the thesis is to understand better why those two titanium alloys (Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo) can be considered to have the same behavior during DED/AM, even though they are different by their chemical composition, and so by their properties as well.

Therefore, the aim of this thesis work will be to identify the differences of behavior between the two alloys, and in the long term, to modify the relevant parameters considering the additive manufacturing process in order to maximize the process for the specific alloy. Another goal for this thesis is to evaluate to which extend Thermocalc, the software used in this work, could be adapted for additive manufacturing purpose.

1.2 Delimitation

The project will focus mainly on evaluating different properties of the alloys provided by the company. The research work will study the behavior of the two considered alloys at high temperature to be able to compare their properties in both liquid and solid state at high temperature as well as during solidification. Therefore, there is not any deep research done on the effect of an eventual thermal cycling on the lower layers of material added to the wall by additive manufacturing, but the focus is on the top layer.
2. State of the art / Literature review

2.1 Material description

The section below will give an overview of the two materials studied in the present work, which are two titanium-based alloys, Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo.

2.1.1 Pure Titanium

2.1.1.1 Allotropic form

Titanium is a metal that shows several allotropic forms. They are called after α, β and ω. The phase α is a hexagonal close packed (HCP) phase, which is stable at lower temperatures. The phase β is a body centered cubic (BCC) phase that is stable at higher temperatures [1, 2]. And finally, the ω phase is stable only at rather low temperatures and high pressure. That last phase is not considered of interest in the rest of the discussion.

![Clapeyron diagram of titanium allotropic forms](image)

*Figure 1 – Clapeyron diagram of titanium allotropic forms [3]*

It is still interesting to mention that ω phase can appear locally at pressure, as α phase will transform to adjust to the pressure, and remain present within the structure while that pressure is released due to a hysteresis with pressure gradient. (see Figure 1). On Figure 1, there are two types of borders plotted: one based on Debye + electron model and one on Young model, which are quantum mechanics models.

At high cooling rates, which is the case for the process studied in the present work, a martensitic microstructure can appear, but contrary to the martensite phase present in steels, in titanium alloys this microstructure is composed of α phase with a nominal composition [4, 5].

2.1.1.2 Beta transus temperature

The main characteristic of titanium, and its alloys, is the β transus temperature. This temperature represents the temperature at which phase transformation occurs from α to β or inversely. For pure titanium, this temperature is at 882 °C (1155 K) [2, 6]. For an alloy, the β transus depends on the alloying elements which changes the thermodynamic properties.
2.1.1.3 Burger transformation

The transformation $\beta \leftrightarrow \alpha$ has been described by Burger with a specific mechanism [2, 4, 5]. The transformation consists of a crystallographic relationship as follow:

\[
\langle 111 \rangle_\beta \parallel \langle 11\bar{2}0 \rangle_\alpha \\
\langle 110 \rangle_\beta \parallel \langle 0001 \rangle_\alpha
\]

The relation written in brackets shows that the plane $\langle 111 \rangle_\beta$ which represents the diagonal of the BCC structure (in orange on Figure 2) should be parallel to the plane $\langle 11\bar{2}0 \rangle_\alpha$ which represents the base of the HCP structure (in blue). The relation using parenthesis represents the crystallographic planes of the structure that should be parallel during the transformation.

![Burger transformation in titanium, superposition of the planes (110) and (0001)](image)

The transformation from the previous relationship is not completely perfect and needs some adjustments as shown in Figure 2. Atoms on the corners of the cube will shuffle to fit in the sites of the new hexagonal phase. The hexagonal base will have to rotate around the $c$-axis of the hexagonal phase of around 5º. Finally, the new base will face a compression in the $\langle 001 \rangle$ direction and a dilatation in the $\langle 110 \rangle$ direction [2].

2.1.1.4 Areas of application

Titanium is widely used due to the great ratio between the mechanical properties and the weight [7]. The density of the pure metal is 4.506 g/cm$^3$ [4]. In addition, this material has a really good corrosion resistance, as well as creep and fatigue resistance [4, 6]. Those properties lead to application in several fields such as aerospace, construction or automotive. Titanium is biocompatible, which allows also some medical applications, for example prostheses building. Generally, titanium’s good properties at high temperature make it a material of choice to be used in jet engines colder parts [7, 8].
2.1.2 Titanium alloys

2.1.2.1 Classification of the alloys

Titanium alloys are mostly split in groups according to the microstructure at room temperature. The main groups are α alloys, α+β alloys, metastable β alloys and β alloys, and are presented in Figure 3.

The classification is made by using the content of alloying elements that will stabilize either α phase or β phase more. The two alloys of interest in this work are categorized as α+β alloys, close to the border with α alloys, which means that the martensitic temperature (Ms) – the temperature at which the martensitic transformation starts – is high enough to see the formation of a martensitic microstructure during cooling [2, 4].

The alloying elements that provide information on the classification are either β-stabilizers, α-stabilizers or neutral [2]. Figure 4 shows the influence of different alloying elements on the predominant phase of the microstructure, done with Thermocalc. We can see that for α-stabilizers elements such as aluminum, the zone where the phase is thermodynamically stable is wider, and that the slope of the border between α and α+β zone is negative. For β-stabilizer elements such as molybdenum, the contrary is observed. Finally, some elements such as zirconium or tin, are neutral, and do not affect the stability of the two phases. From Figure 4, the names of the phases are not the same as the ones mentioned. The phases’ names from Thermocalc are described and explained in Appendix I – Table of the phases from Thermocalc.

Figure 3 – Schema of the classification of titanium alloys with the alloying elements [2]
2.1.2.2 Properties and microstructure of Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo

To present the two alloys used, a comparison will be made to highlight some of their differences as a first step of this work. In Table 1 and Table 2, the chemical composition considered is presented [9, 10]. The two alloys Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo are referred as Ti64 and Ti6242 in the rest of the work.

Table 1 – Chemical composition of Ti64

<table>
<thead>
<tr>
<th></th>
<th>Ti (wt%)</th>
<th>Al (wt%)</th>
<th>V (wt%)</th>
<th>Fe (wt%)</th>
<th>O (wt%)</th>
<th>C (wt%)</th>
<th>N (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti64</td>
<td>89.286</td>
<td>6.150</td>
<td>4.170</td>
<td>0.200</td>
<td>0.150</td>
<td>0.029</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Table 2 – Chemical composition of Ti6242

<table>
<thead>
<tr>
<th></th>
<th>Ti (wt%)</th>
<th>Al (wt%)</th>
<th>Sn (wt%)</th>
<th>Zr (wt%)</th>
<th>Mo (wt%)</th>
<th>Fe (wt%)</th>
<th>O (wt%)</th>
<th>Si (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti6242</td>
<td>85.66</td>
<td>6.00</td>
<td>2.00</td>
<td>4.10</td>
<td>2.00</td>
<td>0.02</td>
<td>0.13</td>
<td>0.08</td>
</tr>
</tbody>
</table>

It can be mentioned that the main elements of each alloy are different. Both alloys present a certain amount of α-stabilizers (Al and O) and of β-stabilizers (V, Mo). In addition, Ti6242 presents neutral elements, which are silicon, tin and zirconium. Even though those elements do not have a thermodynamic impact on the stability of each phase, they can still make a difference in some properties, such as the density, the beta transus, or the melting point [2, 4, 9, 10]. Another point to mention is the presence of smaller elements such as carbon, oxygen, or nitrogen. In addition to the fact that they diffuse faster as they are localized in smaller sites of the matrix, they are at risk to form some undesired species that could lead to the embrittlement of the structure. To avoid those risks, the content specified in the composition must be respected.
The two alloys differ also in their physical properties even though they stay close in their values. The main properties are summarized in Table 3 [6, 9, 10, 11, 12, 13] and compared to the alloy 718 – a nickel-based alloy –, that will be used as a reference point when Thermocalc is used to understand better if the differences found are significant or not.

All the parameters in Table 3 are from the literature and taken at room temperature. It is important to take into consideration the decrease of performance of the mechanical properties at service temperature of those two alloys, which are 600 K and up to 830 K for Ti64 and Ti6242, respectively [1, 4, 5, 15]. In the rest of the thesis work, those parameters will vary a lot compared to Table 3 as the study will focus on the phase transformation Solid – Liquid or Liquid – Solid.

An important point when comparing the two alloys is the microstructure. Indeed, it differs slightly from one alloy to the other, but as for every other material, it depends as well on the heat treatment. In this work, the cooling rate from liquid state to room temperature is extremely fast, between 600 K/s and 1000 K/s [5, 16, 17]. Commonly, for heat treatments of titanium alloys, the material is heated above the β transus, to the β phase, before cooling down the material to the α+β phase. In Figure 5, different microstructures for Ti64 are presented. Each of them present different characteristics and are achieved with different heat treatments.

<table>
<thead>
<tr>
<th>Table 3 - Physical properties of the two alloys Ti64 and Ti6242 compared with Inconel 718 at room temperature [9, 10, 14]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Property</strong></td>
</tr>
<tr>
<td>Density [g/cm³]</td>
</tr>
<tr>
<td>Beta transus [K]</td>
</tr>
<tr>
<td>Melting point [K]</td>
</tr>
<tr>
<td>Thermal conductivity [W/(m.K)]</td>
</tr>
<tr>
<td>Specific heat [J/(g.K)]</td>
</tr>
<tr>
<td>Electrical resistivity [μΩ.m]</td>
</tr>
<tr>
<td>Thermal expansion [K⁻¹]</td>
</tr>
<tr>
<td>Young's modulus [GPa]</td>
</tr>
</tbody>
</table>

In Figure 5a, the most common lamellar microstructure is represented, which is used in different applications (biomedical, aerospace) [2, 18]. Lamellae are growing with this shape because of anisotropic characteristics of the elastic energy density within the phase. The lamellas tend to grow according to a specific crystallographic direction that is the more energetically favorable. In Figure 5b, the martensitic microstructure is represented. This microstructure consists of thin α needles with a nominal composition as the diffusion cannot occur at fast cooling rates. This type of microstructure can have two names: Widmanstätten and basket weaves [19]. Mostly for additive manufacturing applications, the microstructure will be basket weaves [1, 4, 5]. In Figure 5c, the microstructure is a result from very specific heat treatments, either with ageing
or slow cooling rate that allows the α phase to grow in a globular way, or a thermomechanical
treatment to break the lamellae formed within the domain α+β. In Figure 5d, the microstructure
shows equiaxed grains that form in the same way as the previous microstructure, which means
that the material must be deformed in order to allow recrystallization to occur [2, 4].

The second alloy Ti6242 presents the same microstructures as Ti64. However, one difference
between the two alloys considering their microstructure is the thickness of α laths. According
to Davis et al. [1], the lath thickness is thinner in Ti6242 because of the alloying elements and
their ability to diffuse in the structure.

To summarize, the microstructure of titanium alloys consists of prior β grains that form and
grow above the β transus. Then, α laths grow inside the grains with a variation in their thickness
with the cooling rate (from β to α+β) and the diffusivity of the alloying elements. Finally,
smaller α grains that are formed under thermomechanical treatments such as forging or hot
rolling to allow recrystallization.

When applied to additive manufacturing, the microstructure formation is slightly different from
what is expected. To begin with, the material is completely melted and the β grains formed get
a columnar shape typical from this process. The grains are oriented in the direction of the laser
beam that is melting the material [1, 4, 5, 20, 21]. The α laths, as previously mentioned, often
form the basket weaves microstructure due to the high cooling rate of the process, which
consists of very thin needles that can be seen on

Figure 6.
2.2 Directed Energy Deposition Additive Manufacturing method

Many different additive manufacturing processes for metal exist, and they are characterized by their process parameters which can be the heating source, the scanning speed, the power of the heating source, the type of material used for the feed, and others. One can cite Selective Laser Melting (SLM), Laser Metal Deposition (LMD), or Electron Beam Melting (EBM) \[5, 11, 16, 21\] as some of the processes used nowadays. To stay in the scope of the thesis, only one type of process will be studied – as it is the one used within the company – which LMD also is known as Directed Energy Deposition (DED).

2.2.1 Process description

2.2.1.1 Description of the process

The DED process uses two different ways of feeding which are wire or powder feeding. The process is therefore quite different for those two methods.

In Figure 7, several constituents that are part of the process can be seen. The substrate is the bulk material on which the build will be deposited. The wire (or powder) is in contact with the laser at a specific angle, and the system of the wire and laser are in motion at a certain speed called the scanning speed (or welding speed). Usually for DED, the process parameters that are of main importance are the laser power, the scanning speed, the feeding rate, the direction of the feed, and for DED-w (Directed Energy Deposition with Wire), the angle at which the wire is melted \[24, 25\]. The shape of the tracks is highly dependent on the process parameters, but also on the material used itself and the substrate. During the process, some disturbance can occur, such as dripping when the wire is melted too fast, and stubbing when the wire is not fully melted. This can be avoided by adapting the process parameters to the specific feeding material according to findings from the company.
2.2.1.2 Benefits and drawbacks of the method

As every additive manufacturing method, DED is a helpful process to reduce the energy consumption by reducing the material waste during production compared to for instance machining [25, 26, 27, 28]. In addition, laser-based additive manufacturing processes are mostly used because of their efficiency. Indeed, the laser technology allows high precision of the process and more freedom in the adjustment of the parameters. Between the two DED methods, both present advantages and drawbacks [29]. Both allow design freedom and high deposition rates. With DED it is also possible to repair some parts, add metal parts on preforms, which is the case for fan blades for example, and it is also possible to use different materials in a single build. Since the feedstock material is injected directly to the heat source in DED, it is possible to build on curved surfaces [26].

However, when using powder as feedstock material, powder DED (DED-p) this fabrication method has some risks, such as explosion, fire or inhalation of the powder particles. This since the powder particles are relatively instable and small (45 µm [29]). In addition, DED-p is an expensive method mostly because of the material cost. The powder is produced with plasma atomization, which is the most expensive atomization method. On the other hand, wire DED (DED-w) has a higher deposition efficiency, and the wire feedstock is less expensive. However, the wire feed rate could be unstable causing defects, and the wire material variety (the number of alloys available) is also reduced, plus the surface finish is not as good as in DED-p and a higher dilution of the deposited material on the substrate has been reported [26, 30].

2.2.2 Laser beam

2.2.2.1 Optical description of the laser

The laser is an energy source of coherent light, which means that the source is monochromatic and so all the waves have identical frequency and wavelength [11, 27, 28]. The most commonly used lasers in the additive manufacturing field are CO₂ lasers, Nd:YAG lasers and Ytterbium-based fiber lasers [27, 31]. However, over the recent years, CO₂ lasers are replaced slowly by a new generation of laser (which Nd:YAG is part of).
CO₂ lasers consist of an electric pump, several optical devices (mirrors, lenses), and a discharge tube. The range of the wavelength of these lasers is between 9 and 11 μm, with a 10.6 μm wavelength for additive manufacturing purpose [28]. Those lasers provide a great efficiency that can go up to 20% theoretically. The power used for this laser goes from 0.1 to 20 kW. The main advantages to use them is the low cost of the system, and the high reliability that is good for higher precision in the processing [27].

Nd:YAG stands for Neodymium-Doped Yttrium Aluminum Garnet. This type of crystal is used in the form of the rod and as a solid gain medium. This gain medium is pumped by a flashlight. The output wavelength is 1064 nm, which emits in the infrared [28]. The main advantage of this laser is that the light beam is directed by optical fibers which are flexible. The power of the laser can also go up to 20 kW, which is interesting. This kind of laser slowly replaces the CO₂ lasers.

Ytterbium-based lasers (Yb-fiber lasers) are the most promising fiber lasers as they offer a great efficiency range from 10 to 30 %, which is as good as CO₂ lasers. The output wavelength of those lasers is almost of the same range of CO₂ lasers – infrared, which is of 1050 nm [28]. The laser performances in this case can be limited due to the propagation of light through optical fibers that are non-linear media. [28]

2.2.2.2 Control of the power of the beam

One of the critical parameters to control during DED is the power of the beam, since it will affect the melting of the material and its solidification afterwards. The power of the beam takes into account the average power, the power stability, the focus distance, and the wavelength stability. This parameter also highly depends on the material used as the intrinsic characteristics will change, such as melting point, but also thermal diffusivity or thermal conductivity [28].

2.2.2.3 Joule effect

The laser used in the process is a source of energy, but it does not produce heat directly. To achieve the heat of the material, the energy source will excite the material by electromagnetic waves.

The laser is a source of charged electrons in contact with the feedstock material, metallic wire, or the powder, that is conductive. It means that the charged electrons from the laser beam will transfer their energy to the lattice that creates oscillations i.e. the radiation that heat the material, which is referred to as the Joule effect. The heat generated then depends on the energy of the electrons from the laser beam, and so on the laser power. With a sufficient power to create enough radiation to increase the temperature of the material, it will melt the material [26, 32, 33]. The dissipated energy can be written as follow:

\[ Q = R \int_{t_1}^{t_2} i^2 dt \]  

Equation 1

Equation 1 is related to the power of the beam as well as to the specific heat, which allows to understand the raise of temperature from intrinsic properties of the material. Q is the dissipated energy, R the resistance of the material, i the intensity of the current implemented. From this, it is possible to calculate the value of the power of the laser beam necessary to melt the material.
2.3 Solidification and melting

The solidification process is necessary to understand as it is the phenomenon that occurs in additive manufacturing of metal when the liquid metal transforms into a solid. Getting an overview of the solidification will allow us to understand and identify better the key parameters that will influence additive manufacturing processes. In this part, solidification basis as well as melting and segregation issues will be discussed.

2.3.1 Melting parameters

During the melting, thermodynamic parameters are relevant to study. The latent heat of a system can be described as in Equation 2:

\[ L = \frac{Q}{m} \]  

Equation 2

Where \( Q \) is the dissipated energy of the system, \( L \) is the specific latent heat and \( m \) is the mass of the system. The latent heat is directly related to the enthalpy by a derivative by temperature. During the heating and the melting of the material from Equation 1, another intrinsic parameter appears of importance: the electrical resistivity.

2.3.2 Solidification process

The solidification process can be split in two parts that are the nucleation of the particles and the growth of them. To describe the solidification process, some models have been built throughout the years and are still relevant, such as the Scheil model, or Johnson-Mehl-Avrami-Kolmogorov model.

2.3.2.1 Nucleation and growth models

2.3.2.1.1 Undercooling

During solidification, a liquid transform into a solid, for this to happen, undercooling is needed to facilitate nucleation of the solid phase. According to Doru et al. [34], there are 5 types of undercooling: kinetic, thermal, constitutional, curvature and pressure. Kinetic undercooling concerns the case of pure metals and is of the order of 0.05 K, thermal undercooling is occurring when no nucleation happens, pressure undercooling requires an applied stress to the liquid. However, these types can be neglected in the case of additive manufacturing where the constitutional \( \Delta T_c \) (Equation 3) and curvature undercooling \( \Delta T_r \) (Equation 4) are of interest. According to Gu et al. [35], it is possible to neglect the curvature undercooling while the solidification front velocity is slow enough, as the curvature will be large enough to not observe any temperature gradient. Here, \( m_L \) is the liquidus slope, \( C_L^* \) is the liquid composition, \( C_0 \) is the initial composition, \( \gamma \) is the surface energy, \( \Delta S_f \) is the entropy of fusion, and \( r \) is the radius of the nucleus.

\[ \Delta T_c = -m_L(C_L^* - C_0) \]  

Equation 3

\[ \Delta T_r = \frac{\gamma}{\Delta S_f r} \]  

Equation 4
2.3.2.1.2 Nucleation

The nucleation of a phase into another phase, e.g. from liquid into a solid phase, happens when the liquid is cooled at a temperature below its melting point (undercooling). Thus, a temperature gradient between the liquid state and the equilibrium is created, that leads to a driving force to nucleate the solid phase. At this non-equilibrium state, two different growths are observed: homogeneous and heterogeneous. Homogeneous nucleation is spontaneous and happens at high undercooling. Most of the time, heterogeneous nucleation occurs, at a grain boundary, crystal defect or particles within the liquid, which represent the case of additive manufacturing. Homogeneous nucleation is therefore negligible compared to the effect of heterogeneous nucleation. Figure 8 shows an example of heterogeneous nucleation. The nucleus is using the substrate as a nucleation site. Its size depends on the different interface energies $\gamma_{SM}$, the interface energy between the substrate and the nucleus, $\gamma_{SL}$ the energy between the nucleus and the liquid, and $\gamma_{ML}$ the energy between the liquid and the substrate.

The free energy of the nucleation of a spherical nucleus, $\Delta G$, is described by a free energy of the volume of the nucleus and by the free energy of its surface. L is the latent heat of the transformation, $\Delta T$ is the undercooling, T is the temperature of the system, r is the radius of the nucleus, and the parameter $\gamma_{SL}$ represents the surface tension between the solid and the liquid.

$$\Delta G = -\frac{4\pi r^3}{3} \frac{L\Delta T}{T^2} + 4\pi r^2 \gamma_{SL}$$  \hspace{1cm} \text{Equation 5}

A critical parameter that affects this energy is the radius of the nucleus. It has a critical value under which the nucleus is not stable and will disappear, but on the other hand, above which coarsening will occur. This critical radius is showed in Equation 6, which is linked to a critical activation energy in Equation 7 [18, 36, 37].

$$r^* = \frac{2\gamma_{SL} T_m}{L\Delta T}$$  \hspace{1cm} \text{Equation 6}

$$\Delta G^* = \frac{16\pi}{3} \frac{\gamma_{SL}^3 T_m^2}{L^2 \Delta T^2} f(\theta)$$  \hspace{1cm} \text{Equation 7}

The angle $\theta$ introduced in Equation 7 is the angle between the nucleus and the substrate as shown in Figure 8. When $\theta = 0$, then $f(\theta) = 0$ and it means that the solid is completely flatten.
on the surface of the substrate, which corresponds to an ideal case where the solid starts solidification as soon as the freezing point is reached. For heterogeneous nucleation, it is good to get $f(\theta)$ as small as possible. On the other hand, if $f(\theta) = 1$, it means that the nucleation is homogeneous [18].

### 2.3.2.1.3 Growth

The growth of nuclei is directly linked to the undercooling and the change in composition at the solid/liquid interface. By lowering the temperature below the freezing point, at the start of solidification, that change in the composition of the solid and the liquid can be seen in phase diagrams as the liquidus and solidus lines. This phenomenon leads to partitioning which is characterized by the partitioning coefficient at equilibrium as in Equation 8.

$$k_0 = \frac{C_L}{C_S}$$  \hspace{1cm} \text{Equation 8}

This coefficient is of high interest with the rest of the discussion concerning the segregation, and $C_L$ represents the composition in the liquid and $C_S$ represents the composition in the solid at a given temperature.

After nucleation, growth is expected, and it is dependent on the undercooling, which will be the driving force of the phenomenon [18]. Different types of growth are described by Biloni et al. [18]: planar growth, non-facetted growth and facetted growth. Planar growth occurs while the perturbations at the interface are not stable enough and disappear. On the other hand, with stable perturbation, the interface then reaches different structures: dendritic or cellular [12, 34, 35]. This perturbation can be described by the thermal gradient $G_{SL}$ of the interface. When $G_{SL} < G_L$, the thermal gradient in the liquid, the instabilities lead to a cellular structured interface, while when $G_{SL} > G_L$, the interface will lead to a planar structured interface. It means that a transition from one or the other type of microstructure is expected. This is showed by Equation 9, where $D_L$ is the diffusivity in liquid. When the ratio $G_{SL}/V$ is smaller than $\Delta T/D_L$, then the structure of the growth will be cellular to dendritic. On the other hand when $G_{SL}/V$ is bigger than $\Delta T/D_L$, then the growth will remain planar.

$$\frac{G_{SL}}{V} < -\frac{m_L C_0 (1 - k_0)}{k_0 D_L} = \frac{\Delta T}{D_L}$$  \hspace{1cm} \text{Equation 9}

As in growth theory, the velocity of the interface has a large effect on the behavior of the solidification, it is important to redefine the partitioning coefficient at non-equilibrium [18, 38, 39] with the model provided by Mehrabian [39] in Equation 10, where $R$ is the interfacial velocity, $\lambda$ is the effective diffusion coefficient in liquid at the interface – which is around ten times the interatomic distance.

$$k = \frac{k_0 + R \lambda / D_L}{1 + R \lambda / D_L}$$  \hspace{1cm} \text{Equation 10}

To get an overview about the evolution of the interface and growth with the parameters such as the velocity of the interface – which corresponds to the solidification rate –, and the thermal gradient, it is possible to refer to Figure 9.
From Figure 9, another number is introduced, which is the factor $G \times R$ that represents the degree of refinement of the structure: the larger the factor, the finer the microstructure.

![Diagram representing the evolution of the solidification structure with the thermal gradient (G) and the velocity of the interface (solidification rate R)](image)

**Figure 9 – Diagram representing the evolution of the solidification structure with the thermal gradient (G) and the velocity of the interface (solidification rate R)**

2.3.2.2 *JMAK model*

To model the nucleation and growth of a given phase, Avrami et al. have created an equation, which is known as the Johnson-Mehl-Avrami-Kolmogorov model. It expresses the recrystallized fraction as a function of time as in Equation 11.

$$x_s = 1 - \exp(-Ct^n)$$  \hspace{1cm} \text{Equation 11}

In Equation 11, $x_s$ is the fraction of solid, $C$ and $n$ are constants of the material, and $t$ is the time in second (for the case of isothermal transformation). On a point of view of solidification, the recrystallized fraction is considered to be the solid fraction of the system.

2.3.3 Segregation

2.3.3.1 *Segregations in Titanium alloys*

During cooling of titanium alloys, it is common to observe segregation, either during the solidification or after, with the appearance of $\alpha$ laths. To come back to the definition, they are caused by a variation in the composition, either in a micro-scale (dendrites) or at a larger macro-scale [41, 42]. Therefore, segregations are an issue for alloys in general as they cause instabilities in the phases formed and in the worst cases, can create brittle phases that would lead to a decrease in the mechanical properties and a risk of cracking. The segregation profile can be predicted by using some models such as the Scheil-Gulliver model. It has been said by Biloni et al. [18] that with a strong convection due to thermal gradients or solute gradients in the liquid, the system is more subjected to segregation.

From literature [1, 39, 43, 44], it has been observed that for a dendritic structure, $\beta$ stabilizers (Mo, V) are most likely to segregate within the dendrite core, and $\alpha$ stabilizers (Al, O) will consequently segregate in the interdendritic region. It is therefore interesting to model those segregations and see if some undesirable phases will appear and then lead to the embrittlement
of the structure. Thus, it has been showed that the dendritic arm spacing varies with the aluminum content inside the dendrite [43].

### 2.3.3.2 Scheil model

To describe solidification process, the Scheil-Gulliver equation is used as it is expressing solute redistribution during solidification of the alloy. That model makes some assumptions and hypothesis which are the absence of diffusion in the solid phase, a very fast diffusion in the liquid – that occurs because of the high diffusion coefficient, Marangoni convection –, an equilibrium state at the phase interface, and straight lines of the liquidus and solidus segments. It is presented in Equation 12, where $C_S$ is the composition in the solid, $C_0$ is the nominal composition, $k_0$ is the partitioning coefficient and $f_S$ is the fraction of solid.

$$ C_S = k_0 C_0 (1 - f_S)^{k_0 - 1} $$

Equation 12

This model can be adapted to non-equilibrium problems by using the partitioning coefficient $k$ defined in Equation 10 instead [18, 35]. It means that the solid composition of the solid to the cooling rate can be related, and the diffusion in the liquid. At slow cooling rates $R$ and when $D_L \rightarrow \infty$ – which are the assumptions for Scheil-Gulliver model –, Equation 10 becomes $k_0$. From Rappaz et al. [45], a model to estimate the secondary arm spacing $\lambda_2$ is given by Equation 13 and Equation 14. Indeed, the dendritic arm spacing, and more precisely, the secondary dendritic arm spacing (SDAS) is of importance to understand the segregation behavior. With a smaller SDAS value, it will be more difficult for certain alloying elements to diffuse through the liquid in the interdendritic zone.

$$ \lambda_2 = 5.5 \left( M \cdot t_{solidification} \right)^{1/3} $$

Equation 13

$$ M = \Gamma \frac{\ln \left( \sum_{i=1}^{n} \frac{m_i}{D_i} (1 - k_i)^{C_f - C_0} \right)}{\sum_{i=1}^{n} \frac{m_i}{D_i} (1 - k_i)^{C_f - C_0}} $$

Equation 14

In Equation 14, $\Gamma$ is the Gibbs-Thomson coefficient which can be estimated by 5.0e-8 for titanium alloys [18], $C_f$ represents the composition in the liquid at the base of the dendrite which can be estimated to be the composition in the dendritic core, and $C_0$ represents the nominal composition of the alloy. The sum $M$ is made on all the alloying elements of the alloy.
3. Methods

3.1 Identifying key parameters

The first part of the work is to find physical parameters that are interesting to look for considering the process used and the phase transformations that occur during the DED process. In the previous state of the art, parameters appeared to be recurrent both in the case of melting and solidification process. In the second part of the work, the focus is put onto the understanding of the solidification process, and the eventual formation of segregations in the material. Therefore, it is important to have information as well on SDAS that is calculated with the model of Rappaz et al., in [45].

Figure 10 illustrates the idea of the project to split the parameters according to the temperature range. Some parameters that will have an impact on the properties that are relevant to investigate only in the liquid alloy (viscosity and surface tension) while some are related to the solidification or the melting process only. The parameters in the center of the figure are important throughout the whole process, from the solid wire to the liquid phase, and to the solidification.

![Figure 10 – Schema of the properties investigated for the modelling of Ti64 and Ti6242](image)

3.1.1 Physical properties

3.1.1.1 Research of the physical properties

The physical parameters of the process focus on intrinsic characteristics of the studied alloys. Those parameters are listed in Table 4 according to the temperature range at which they will be of interest, both for Ti64 and Ti6242, and then for alloy 718. Its composition can be found in Appendix II – Information regarding alloy 718. This additional alloy is used as a reference so the eventual differences that occur between the two titanium alloys can be put in perspective.
Table 4 – Summary of the physical properties and the temperature range at which they are of interest

<table>
<thead>
<tr>
<th></th>
<th>Ti64</th>
<th>Ti6242</th>
<th>718</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>500 – 2100 K</td>
<td>500 – 2100 K</td>
<td>500 – 2100 K</td>
</tr>
<tr>
<td>Enthalpy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>500 – 1923 K</td>
<td>500 – 1975 K</td>
<td>500 – 1614 K</td>
</tr>
<tr>
<td>Surface tension</td>
<td>1875 – 2100 K</td>
<td>1923 – 2100 K</td>
<td>1547 – 2100 K</td>
</tr>
<tr>
<td>Viscosity</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.1.1.2 Justification physical parameters

The parameters listed in Table 4 are related to the DED process as they describe the material behavior during solidification and melting. One can notice that there are some matching properties compared with Table 3. It is of interest to compare those values with the ones from the simulation tool that will be used.

To understand the thermodynamic of the system, the enthalpy is necessary as it provides information such as the latent heat of the system, the specific heat, and some information about the temperature range for which solidification occur for each alloy. The temperatures listed in Table 4 come from the enthalpy evolution with temperature, and the highest temperature of 2100 K comes from Kelly et al. [46].

The parameters in the liquid phase should be studied as they will contribute to the material tendency to drip or stub. This is the case for viscosity and surface tension. During additive manufacturing processes using wire, just like in welding, the molten material is subjected to Marangoni convection, which is the dominant convection effect. That type of convection is related to the difference of surface tension between the substrate and the fluid. It is characterized by the Marangoni number Ma, as in Equation 15.

$$Ma = \frac{L_e \frac{\partial \gamma}{\partial T}}{\kappa \eta \frac{\partial T}{T}}$$  

Equation 15

From the Marangoni number, the thermal conductivity $\kappa$, which is another intrinsic parameter that appears to be interesting to investigate, but not only in the liquid phase, as it could impact the heating of the material as well. Another important parameter is the electrical resistivity of the system, as it is the parameter that will influence the heating by Joule effect from Equation 1, and so the melting of the material. In addition, electrical resistivity is of interest, since it shows the $T_B$ of titanium alloys.
3.1.2 Solidification properties

The solidification is described in detail in section 2.3.2. From this, some key parameters are extracted and summarized in Table 5. The main reason to use those parameters is to extract information about the SDAS, and to compare this value with the simulation results about microsegregation. It is also necessary to keep in mind that those parameters are used at non-equilibrium. Therefore, the surface tension from this part might differ from the surface tension from the previous part about physical properties that might focus on equilibrium.

Table 5 – Summary of the solidification properties and the temperature range at which they are of interest

<table>
<thead>
<tr>
<th>Composition evolution</th>
<th>Ti64</th>
<th>Ti6242</th>
<th>718</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling rate</td>
<td>500 – 2100 K</td>
<td>500 – 2100 K</td>
<td>500 – 2100 K</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>1875 – 1943 K</td>
<td>1923 – 1975 K</td>
<td>1547 – 1614 K</td>
</tr>
<tr>
<td>Liquidus slope</td>
<td>1875 – 2100 K</td>
<td>1923 – 2100 K</td>
<td>1547 – 2100 K</td>
</tr>
<tr>
<td>Partitioning coefficient</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Latent heat</td>
<td>1875 – 2100 K</td>
<td>1923 – 2100 K</td>
<td>1547 – 2100 K</td>
</tr>
<tr>
<td>Surface tension</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The first parameter to get is the composition evolution of the liquid and the solid with temperature. From this, by using the cooling rate and the diffusion coefficient in liquid, it is possible to calculate the effective partitioning coefficient $k$ from Equation 10. Latent heat is of interest as well since it then is possible to compare its value to the one obtained at equilibrium previously. Finally, with liquidus slope, it is possible to evaluate the SDAS. The last parameter to be studied, that requires a deeper study, according to the state of the art, is the velocity of the interface.

3.2 Simulation methodology

3.2.1 CALPHAD method

CALPHAD stands for calculation of phase diagrams. The method consists of using thermodynamics and phase equilibria of a certain system and to extrapolate that information for multicomponent systems. It is a useful method, frequently used in industries, to better understand the behavior of a given alloy, which most of the time is complex, when many alloying elements are involved.

The methodology is to collect phase and thermodynamic information at equilibrium of a given system, and then to with models, describing the properties of that system. The parameters described are adjusted to fit the model by including other information, such as new coexisting phases. With this method, it is then possible to predict phases from the phase diagram in specific regions where it is difficult to obtain certain measurements, for instance at high temperature.
3.2.2 Thermocalc

Thermocalc is a software that uses the CALPHAD method in order to build phase diagrams, but it can also carry out diffusion calculations, precipitation calculations, and predict some properties of the considered material.

3.2.2.1 Equilibrium module

Equilibrium calculator allows the user to perform equilibrium and non-equilibrium calculations with a fixed set up. The user can fix temperature, pressure, moles, and composition of a considered material, but also its thermodynamics properties such as the activity, chemical potential, enthalpy or entropy.

The module can perform several calculations:

- Single equilibrium,
- One axis equilibrium,
- Grid,
- Phase diagram.

Single equilibrium calculates the properties at a specific set of conditions. One axis equilibrium is the one used in the present work and allows to show the properties with a variation of one of the conditions, with plot or table as a result. Grid makes two conditions vary at the same time with the same step. Finally, the phase diagram calculation makes two conditions vary to follow phase boundaries and generate a phase diagram.

In the present work, the equilibrium module is used to model property diagrams and phase diagrams.

3.2.2.2 Scheil module

Scheil module allows to get the properties during the solidification assuming different conditions such as the cooling rate. This module also presents four types of calculations: the classic Scheil-Gulliver module, the Scheil calculation with fast diffusers, the Scheil calculation with back diffusion and the solute trapping.

- The classic Scheil-Gulliver model assumes to have infinitely fast diffusion in liquid, and no diffusion in solid, and the solid/liquid interface is at equilibrium.

- Scheil calculation with fast diffuser assumes the same as the Scheil-Gulliver model except that the fast diffuser elements have their diffusion coefficient put as infinite in solid.

- The back diffusion calculation considers that in the primary phase, diffusion in liquid is infinite but diffusion in solid is calculated from the mobility database, and the interface solid/liquid is at equilibrium.

- The solute trapping model assumes that one primary phase forms dendrite, and solute trapping happens in this solid phase. The amount of solid phase and the dynamic liquidus depend on the solidification rate and the solute trapping. The dynamic solidus is calculated for complete solidification.
Scheil module is used for many occasions, and in the present work for example, it helps to understand which of phases are formed in order to implement them in DICTRA calculations. It can also be a useful tool for AM, especially the Scheil with Solute Trapping as it is constructed for this purpose, following a model of rapid solidification. This module will help to have all the data necessary to build the SDAS model used in Equation 14, to make it possible to discuss the SDAS with microsegregation.

3.2.2.3 DICTRA

DICTRA is an add-on module to Thermocalc that is made to run diffusion model analysis using a mobility database. The calculation is based on CALPHAD method and makes some numerical calculations to reach multicomponent solutions.

This module is used in this work to model the microsegregations within the matrix of the considered alloy, as from previous studies, it has been showed that Ti6242 demonstrates larger microsegregations than Ti64. The goal for the present study, is to use this module to compare the microsegregation behaviors of the alloying elements in both alloys in order to understand the composition evolution during solidification, and therefore, with a comparison with the phase diagram, understand to which extend some phases are more likely to form with new local compositions.
4. Results

4.1 Physical properties

The physical properties were modelled by Thermocalc software and equilibrium module using the one axis equilibrium calculation. The system was defined by the chemical composition in Table 1 and Table 2, with the database TCTI4 available for the version 2022a of the software. The phases that were allowed to form during those simulations were BCC_B2, HCP_A3 and LIQUID (see Appendix I – Table of the phases from Thermocalc, after running a Scheil simulation to see which phases were going to form. In addition, a last check from the datasheets about the database used in the simulation was done to make sure that the correct phases were selected. As previously mentioned in methodology, alloy 718 is used as a reference for comparison between the two titanium-based alloys to identify significant differences.

4.1.1 Similarities between the two alloys

4.1.1.1 Density

The density evolution with temperature gives a hint on the phase transformation that could occur during the cooling of the material. Thermocalc calculates the density of a given material using the molar volume and inverting it.

From Figure 11, it can be seen that the density decreases with increase of temperature. This tendency is the same for both alloys. One can notice the change in the curve at $T_B$ for both alloys. However, the behavior of Ti6242 is different from Ti64. On the other hand, the fall in the slope at high temperature represents the melting of the alloy and is similar for both cases.

![Figure 11 – Evolution of the density of Ti64 and Ti6242 with the temperature using Thermocalc simulation](image-url)
4.1.1.2 Electrical resistivity

Electrical resistivity is calculated following the same database as density and its evolution is presented on Figure 12.

![Electric resistivity of Ti64, Ti6242 and alloy 718](image)

*Figure 12 – Evolution of the electrical resistivity with temperature of Ti64 and Ti6242 compared with alloy 718 using Thermocalc simulation*

Before the beta transus, the two alloys are behaving in a different way, as the increase in resistivity of Ti6242 is higher than Ti64. On the other hand, at temperatures above the beta transus, while the two alloys show only beta phase, the two curves overlap. Finally, during melting, the two alloy start to act in a very different way. These affirmations are reinforced by the tendency of alloy 718 that is completely different. In addition, it seems like Ti64 behavior at high temperature is not predicted well, as both Ti6242 and alloy 718 experience a drop in their resistivity during the melting.

4.1.1.3 Thermal conductivity

The thermal conductivity is a parameter that helps to follow the tendency of the material to conduct heat during an increase of temperature. The two titanium alloys follow the same trend all along the heating and experience a small change at high temperature.
Figure 13 – Evolution of the thermal conductivity with temperature of Ti64 and Ti6242 compared with alloy 718 using Thermocalc simulation

Once again, it seems that it is Ti64 that acts differently, as both alloy 718 and Ti6242 experience a raise during the melting. Those results should be considered carefully as they might be subjected to the size of the database. Similary, looking at the thermal conductivity at very high temperature, it could as well be an issue from the database or the complexity of gathering accurate measurements at high temperatures.

4.1.1.4 Viscosity

The viscosity is a parameter that requires to be investigated during the melting or solidification in order to understand the convection system within the melt. From Figure 14, it is clear that the two alloys present the same behavior, both for equilibrium calculation and during solidification. The curves show a small decrease with temperature, which is explained by the increase of the amount of liquid in the melt, which causes the fluid to be less viscous. The viscosity investigated was the dynamic viscosity, which takes into account the cooling and solidification rates. Therefore, it is interesting to compare both the results with Scheil-Gulliver method and at equilibrium, to notice further differences between the viscosity data for those two calculation methods.
4.1.2 Differences between the two alloys

4.1.2.1 Enthalpy

The enthalpy of the two titanium alloys follows the same trend, which is an increase with temperature. In Figure 15, the enthalpy here is normalized by its value at 300 K. The three alloys behave the same. The beta transus at around 1250 K is visible on the curves by a change on their inflection. A small difference between the two curves of 3% was calculated. It is visible from that plot that Ti64 melts at a lower temperature than Ti6242, but the energy required to the melting shows up to 6.5% difference.

During the melting of the alloys, even though the curves follow the same trend, they are not perfectly parallel, and the latent heat – which can be calculated from the enthalpy data by doing a derivation – shows some differences. It is therefore easier to melt Ti6242 than Ti64. To have information concerning the feed rate, one can multiply the enthalpy value by the density at room temperature, as $\Delta H_{\text{volume}} = \Delta H_{\text{mass}} \times \rho_{\text{alloy}}$. We get a difference of 7% difference that makes a difference.

Figure 14 – Evolution of the dynamic viscosity with temperature of Ti64 and Ti6242 compared with alloy 718 using Thermocalc and Scheil simulation
4.1.2.2 Surface tension

The surface tension plotted in Figure 16 demonstrates the biggest difference between the two alloys. It has been plotted within the temperature range of solidification. The two alloys behave in the same way but with a difference in their value, both for equilibrium and Scheil calculations.

Figure 16 – Evolution of the surface tension with temperature of Ti64 and Ti6242 compared with alloy 718 using Thermocalc and Scheil simulation
The surface tension of Ti6242 is clearly higher than the surface tension of Ti64 when compared to the reference alloy 718. Quantitatively, the difference is of about 30%. Not only that the surface tension impacts the Marangoni convection described in Equation 15, but it might also affect the DED process in itself, which will be studied further in the discussion section.

4.2 Solidification properties

The solidification properties have been extracted from Thermocalc software using two different calculation methods: DICTRA and Scheil module with Solute Trapping calculations. The databases used were TCTI4 and MOBTI4 with the version 2022a of Thermocalc. On a first step, the solidification fraction was plotted with temperature to understand which solidification calculation method should have been used for the collection of data.

From Figure 17 and Figure 18 it can be seen that the solidification behavior for DICTRA is behaving differently from any other calculation method, even though the closer calculation method seems to be solute trapping. DICTRA is supposed to be the most accurate for this kind of simulation as the inputs can be adjusted to fit the cooling rate the best to the AM process, but its behavior from this diagram seems to be off the trend. However, for the following discussion, the results are extracted from the solute trapping method, as more properties suitable for the Secondary Dendrite Arm Spacing (SDAS) can be extracted from this type of calculation (see Equation 14).
4.2.1 Properties to evaluate the SDAS

This part will show the data collected to build the model from Equation 14 to get the SDAS for the two alloys, to better understand their behavior during solidification. The solute trapping module was set up using a scanning speed \( v_{\text{scanning}} \) and an angle \( \alpha \) between the scanning direction and the interface solid/liquid. With those two sets of data and using the formula: \( R = v_{\text{scanning}} \cdot \cos(\alpha) \), Thermocalc is calculating the solidification rate \( R \). However, the solidification rate was estimated from previous simulations in the company as around \( 4 \times 10^{-2} \) m/s. The data entered in the software were therefore a scanning speed of \( 4 \times 10^{-2} \) m/s and an angle of 0.

4.2.1.1 Diffusion coefficient

As shown in Figure 19, the diffusion coefficient within the solidification range stays quite consistent for all the alloying elements in both alloys. It can be noticed that the diffusion coefficient in liquid of aluminum changes slightly from one alloy to the other. Vanadium diffusion coefficient decreases during the solidification.

The main alloying elements in Ti6242 are showing diffusion coefficients relatively similar to the ones in Ti64. It could be interesting to note that tin is an element that could diffuse almost as fast as vanadium. Despite the different alloying elements in the two alloys, one can say that aluminum diffusion coefficient is pretty similar in both cases.
4.2.1.2 Liquidus slope

Liquidus slope is extracted from the composition evolution with temperature directly from the Solute trapping simulation, and DICTRA simulation. What can be noted from Figure 20 is the numerical instabilities of the values close to the end of the solidification (from 77%) in the DICTRA case. They have been reduced by arranging the time step as 1.0E-12 and a maximum increase from one time step to the other at 1.01 in the option for DICTRA simulation.
To understand the difference between the Scheil calculation (using Solute trapping) and the DICTRA calculation, a comparison of the liquidus slope in both alloys was done. For Ti64, we can notice that the behavior of O is completely different than for the other elements, with an increase in the liquidus slope values. However DICTRA and Scheil calculations are showing a behavior that is similar. On the other hand, for Ti6242, the results show singularities as the composition of Al in Ti6242 is almost constant with small variations in Scheil calculations, and the same issue is spotted for Sn in DICTRA (Figure 21a). By removing them in Figure 21b, one can see that the behavior for Scheil and DICTRA is similar as well. The goal after that was to compare those results with the microsegregation results, and as previously mentioned,
DICTRA is not the most relevant calculation method for that. Therefore, the results from solute trapping will be kept.

The liquidus slope is almost considered constant for Mo and Zr, and is decreasing for Al. The elements with a close-to-constant liquidus slope through the solidification are the β-stabilizers. The evolution of the liquidus slopes for the α-stabilizers (Al) show a clear decrease. On the other hand, the alloying elements considered neutral follow their own trend.

4.2.1.3 Partitioning coefficient

Partitioning coefficient is calculated from the composition results from DICTRA simulation for the classic version (k0) and the dynamic version (k) (see Equation 10). The solidification rate is given by previous simulations done at the company and the interatomic distance is considered to be around 4E-10 m.

![Partitioning coefficient for the main alloying elements in Ti64](image)

*Figure 22 – Comparison between the equilibrium partitioning coefficient and the dynamic partitioning coefficient for each alloying element in Ti64*

For the first alloy Ti64, the partitioning coefficient on Figure 22 does not show significant difference between the equilibrium and dynamic version. However, for the rest of the work, the dynamic behavior will still be considered instead of the equilibrium coefficient to keep accuracy with the model used to calculate the SDAS.

For the second alloy Ti6242, it can be seen that the partitioning coefficient is slightly closer to 1 for a given solid fraction, which can be seen by a small shift up for Mo and down for Zr, as predicted by Equation 10.
Figure 23 – Comparison between the equilibrium partitioning coefficient and dynamic partitioning coefficient for each alloying element in Ti6242

4.2.1.4 SDAS

The plots seen in Figure 24 and Figure 25 are built from the model of Equation 14. On Figure 24, there is a clear difference between the two titanium alloys due to the behavior of Sn in Ti6242. The case of Sn will be further discussed in 5.2.1 SDAS model limitation.

Figure 24 – Evolution of the Secondary Dendrite Arm Spacing of Ti64 and Ti6242
Due to numerical instabilities, Sn has been excluded from the model for SDAS in the case of Ti6242 as this element does not show any segregation (see Figure 27d), and is a neutral alloying element in titanium alloys. Therefore, its influence on the SDAS during solidification should be minor. The new curve is shown in Figure 25. The two alloys show a different trend, where Ti64 values keep increasing with the solid fraction, and Ti6242 values are almost constant throughout the solid fraction.

Ti64 is showing a growth in the SDAS which is different from Ti6242. The spacing values are also different from one alloy to the other (about 2.5 µm for Ti6242 and from 15 to 30 µm for Ti64), which is almost one order of magnitude greater for Ti64 than for Ti6242.

### 4.2.2 Properties to evaluate the microsegregations

The microsegregations were evaluated using a DICTRA simulation for solidification. The simulation for Ti64 was run with a simplified alloy to make it possible to run the simulation in a proper way. The three main alloying elements were used in the system: Titanium, Aluminum, and Vanadium. The simulation allows the formation of three phases: BCC\_A2, HCP\_A3 and LIQUID. One can notice that the phase used for β is different from the phase used during the previous simulations for Scheil and Equilibrium. It is of importance because the software might not recognize BCC\_B2 as the β phase for diffusion calculations.

The conditions of the simulation were a planar simulation at the micrometer scale and using a composition in mass percent. The main region was considered to be the liquid and therefore the composition at the beginning was considered to be the nominal composition (see in Table 1) for V and Al, and a balance for Ti. The hypothesis for this simulation was to keep the concentration in liquid constant while editing the composition profile. The width of the studied
region was 100 µm, based on the results from SDAS model in previous section, and was meshed
doing a grid of 100 points with a geometric type and a ratio of 1.05. At the left boundary of the
main region, BCC_A2 phase was allowed to form. The thermal profile is described in the The
settings for this simulation can be found in Table 6.

Table 6. Finally, the options chosen in the timestep was 1.0E-12 and the factor used to get
maximum increase from one timestep to the other was set to 1.01. The settings for this
simulation can be found in Table 6.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2100</td>
</tr>
<tr>
<td>0.1</td>
<td>2000</td>
</tr>
<tr>
<td>0.3</td>
<td>1900</td>
</tr>
<tr>
<td>5.0</td>
<td>1000</td>
</tr>
<tr>
<td>10.0</td>
<td>500</td>
</tr>
</tbody>
</table>

4.2.2.1 Composition evolution with the distance

Figure 26 and Figure 27 show the microsegregation behavior of the two alloys. The Y-axis
shows the relative concentration, which is the concentration within the material divided by the
nominal concentration, in this way, all the graphs show the same axis and it is possible to
compare them. The X-axis shows the distance through the drawn region. Different
concentration profiles are plotted on the same graph to show the evolution during solidification.
At 0 µm, it is β phase which will form. According to the thermal profile in The settings for this
simulation can be found in Table 6.

Table 6 and the solidification behavior from Figure 17, the end of solidification for Ti64 is
evaluated at 0.8 s.

From Figure 26, Al behavior demonstrates that this element is not likely to form
microsegregation during solidification. On the other hand, V shows higher composition
gradients, which are up to three times higher than the nominal composition close to the end of
the solidification. Also, the solidification rate slows down strongly after 0.5s, as all the
interfaces solid/liquid are almost overlapping.
Modelling study of Ti64 and Ti6242

Figure 26 – Concentration profile of a) Al; and b) V in Ti64 alloy using DICTRA simulation at different times

For the second alloy Ti6242, five elements were followed during solidification. The first element Al in Figure 27a shows the same behavior as in Ti64, which is the absence of composition gradient. Mo, a β-stabilizer, in Figure 27b on the other hand shows a concentration doubled in solid phase and divided by two at the interface solid/liquid, which makes the composition inside solid at 4wt%. Zr is a neutral element and demonstrates in Figure 27c an increase of its concentration at the interface, and a lower concentration in the solid. Sn in Figure 27d, another neutral element, shows the opposite behavior of Zr in solid, and a lower concentration at the interface, and compared to other elements like Mo, Zr and Si, it is not significant.
Figure 27 – Concentration profile in Ti6242 of a) Al; b) Mo; c) Zr; d) Sn; and e) Si using DICTRA simulation at different times

The last element that was studied was Si. Its curve (Figure 27e) is of interest as it behaves in a different way. Close to the interface but in the solid phase, the composition is twice as low as the nominal composition, while on the other side of the interface the composition shows a big increase, up to four time the nominal composition.

4.2.2.2 Study of the phase diagram

The information given in the previous section about the microsegregation is not enough to evaluate a risk of microsegregation. However, it is interesting to associate the composition found at the interface with the phases that could be brittle according to the phase diagram. Thus, the phase diagrams of V, Mo, Zr and Si will be presented. The following compositions are evaluated: up to 12 wt% for V, 4 wt% for Mo, 8 wt% for Zr and 0.32 wt% for Si.
From Figure 28, the elements V, Mo and Zr do not show any phase that is not α, β or liquid, which means that no brittle phase are at risk of formation during the solidification. On the other hand, from the phase diagram Ti-Si, there is a risk of forming Ti$_3$Si.

*Figure 28 – Phase diagrams of the binary systems a) Ti-V; b) Ti-Mo; c) Ti-Zr; d) Ti-Si*
5. Discussion

5.1 Physical properties

5.1.1 Impacting parameters

5.1.1.1 Discussion about the important parameters

5.1.1.1.1 Enthalpy

As previously mentioned in Section 4.1.2.1, the enthalpy curves demonstrate a difference of 3% on the temperature, and 6.5% on the enthalpy between Ti64 and Ti6242. It means that Ti6242 is easier to melt as the energy required must be raised at a lower value than Ti64. From an economical point of view for a future production application, the cost of the process is advantageous for Ti6242. However, the quality of this result is highly dependent on the alloying elements added for the simulation. For example, it is difficult to identify the end of melting with the enthalpy curve, and in addition, alloy Ti6242 is more expensive to produce than Ti64, so even though it seems like the process for Ti6242 seems less expensive, the cost of the raw material is still important (Ti6242 is twice as expensive as Ti64).

In addition, as mentioned shortly in the results part, the volumetric enthalpy presents a difference of 7% between the two alloys, making Ti6242 easier to melt again. The volumetric enthalpy can be used to evaluate the capacity of melting a certain volume of material, which is what is used in the wire feed rate. A lower volumetric enthalpy means that the feed rate could be increased slightly.

5.1.1.1.2 Electrical resistivity

The main differences between the two alloys occur before the transus temperature. The electrical resistivity of Ti6242 is much higher than for Ti64. Therefore, according to the law describing Joule effect stated in Equation 1, the heat of Ti6242 will be much higher than the heat in Ti64 for a same current flow. The current is a parameter that can be changed during the process as it is an input, so two solutions can be stated. Either the current is reduced for Ti6242 which creates a process more economically friendly for this alloy, or the wire can be pre-heated for Ti64 to make sure that the two alloys start their heating process in the same condition.

The difference between the two alloys is unneglectable according to the simulation results. A remaining question is the limitation of the software to evaluate the properties of the two alloys. We already know that a scarcity of data for Ti6242 exists, and the behavior in the curve from Figure 12 could be verified using a measure of the electric resistivity through a test. Using thermocouples on a titanium sample heated in a small furnace, it is possible to follow this evolution and make sure that the values are right.
5.1.1.3 Surface tension

From the Section 4.1.2.2, the software came up with a large difference between the surface tension of the two considered alloys (about 30%). This property affects a lot the process as the wire is melted simultaneously as the substrate melt pool. In the results part, the quantitative difference has been pointed out already, but to understand to which extend the two titanium alloys are acting differently, a comparison with some other materials from literature can be done as well. For example, from Berg [47], the surface tension of different materials has been summarized in Table 7, and it shows that a difference of 0.3 J/m² between Ti64 and Ti6242 makes a big difference.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>T (K)</th>
<th>Surface tension (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>1</td>
<td>0.00016</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>19</td>
<td>0.0024</td>
</tr>
<tr>
<td>Oxygen</td>
<td>90</td>
<td>0.0132</td>
</tr>
<tr>
<td>Water</td>
<td>293</td>
<td>0.0727</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>1074</td>
<td>0.114</td>
</tr>
<tr>
<td>Zinc</td>
<td>633</td>
<td>0.877</td>
</tr>
<tr>
<td>Iron</td>
<td>1793</td>
<td>1.7</td>
</tr>
</tbody>
</table>

From Figure 30, the difference of behavior is described by a capillary bridge between the wire and the substrate, for different thicknesses and heights. The surface tension can be seen as the interface energy between two media. The capillary bridge from a material with a high surface tension can tolerate a longer distance between the wire and the substrate, and is less likely to drip. From the results of this study, it is clear that the surface tension of Ti6242 increase the capability of this alloy to avoid dripping. Another statement could be that the height at which
the wire is situated from the substrate must be adapted to avoid dripping and stubbing risks. Getting the wire too close to the melt pool on the other hand could make stubbing effect happen.

![Figure 30 – Impact of the surface tension on the capillary bridge of Ti64 and Ti6242 for different heights of the wire](image)

### 5.1.1.2 Conclusion

The study of the physical properties allows us to start the discussion about the possibilities to adjust the DED-w process in a way to make it more energy efficient. Indeed, the results of electrical resistivity and enthalpy present some evidence that it requires less energy to melt Ti6242. The higher electrical resistivity before the beta transus shows that in the end, the Joule effect will cause the alloy to heat up faster than Ti64, and along the enthalpy curve, Ti6242 presents lower results than Ti64. Thus, these parameters lead to the conclusion that Ti6242 might be more cost effective to print than Ti64, likewise it indicates that Ti6242 has a higher flexibility in terms of process parameters, as it is less prone to instabilities such as dripping.

### 5.1.2 Limitations due to the software

![Figure 31 – Comparison of the density evolution with temperature for each phase of the two titanium alloys](image)
On the results about density evolution with temperature, it has been said that the behavior of Ti6242 before beta transus was different from Ti64. Further research highlighted that the problem was not only related to the density of the alloy but also to the density of each phase specifically as seen in Figure 31. For Ti64, BCC – which is the phase with the lowest packing structure coefficient – is the densest, which is physically incorrect. On the other hand, for Ti6242, BCC density curve is always under HCP density curve, which is physically correct. Further information can be found in Appendix III – Discussion about the density issue.

After this study and reaching the support team for Thermocalc, it came up that there was a scarcity of the density data for Ti6242. The possibility of plotting properties for the version of Thermocalc used in the present work (version 2022a) was very new at that moment, and therefore the database needed some update.

This problem encountered with density might at some degree also impact the evaluation of other properties in the present work, even though nothing noticeable was found in the work. Therefore, it appears necessary to make it possible to compare the results from the software with other results for different studies or tests.

5.2 Solidification properties

5.2.1 SDAS model limitation

By looking at the model presented in Equation 14, some sources of divergence, as found in Ti6242 in Section 4.2.1.4 can be discussed. The denominator going towards zero makes the model diverge. It can be caused by:

- \( m^l \to 0 \)
- \( D^l \to \pm \infty \)
- \( k^l \to 0 \)
- \( C^f \to C^l_0 \)

In the case of Al in Ti6242, the reason was the singularities seen in the liquidus slope line, as seen in Figure 21, and the dynamic partitioning coefficient getting also close to 1, as seen in Figure 23. Another problem with this dynamic partitioning coefficient is when the correction coefficient \( R^l A / D^l \) (see in Equation 10) is getting much bigger than the equilibrium partitioning coefficient, then the dynamic partitioning coefficient will see its value getting closer to 1 as well, which might cause the model to experience divergence as well. However, the evaluation of the SDAS is a useful information that can be implemented in the DICTRA simulation. Its value is indeed interesting as it can be used directly as an input in the diffusion module which is the width of the liquid region. In this way, it makes the simulation of microsegregations more trustable.

5.2.2 Microsegregation calculations

5.2.2.1 Influence of Ti₃Si

During the alloy design stage, some chemical elements have to stay under a certain percentage to avoid the formation of undesirable phases. However, the variations in chemical composition of the alloy during the solidification process can be thermodynamically favorable to the
formation of those undesirable phases. From the results, one phase is formed in Ti6242 which is Ti₃Si. From Tavares et al. [48], it has been shown that silicon can impact the mechanical properties of some titanium alloys. From Zhao et al. [15], the content of Si in the alloy can change the properties as Si will spread differently in the matrix.

As exhibited in Figure 32, the microstructure of the titanium alloy is impacted by the content of Si. With a content lower than 0.09 wt%, Si is dissolved in the matrix smoothly. Higher than that, precipitation of silicide begins first at the grain boundaries and then spreads inside the grains as well with even higher content. Due to the microsegregations, locally, the Si content can be up to 0.3 wt%, so the risk of forming Ti₃Si at the grain boundaries cannot be neglected. This precipitation is observed during the heat treatments, and mostly during aging, which is an important data to note while performing post heat treatment on the additive manufacturing products.

No study has been performed to check the mechanical properties of an alloy with presence of Ti₃Si species. However, for a future work it might be interesting to look at the influence of Si on the mechanical strength of different alloys, and to which extend this type of silicide can precipitate.

**5.2.2.2 Limitation of DICTRA**

During the thesis, it was difficult to adjust the parameters in DICTRA. In addition, the phases selected within the system definer are highly important while running the simulation. The software can be very sensitive to the phases allowed to form, as mentioned previously about the phase β in Section 4.2.2.

It was also difficult to run the simulation for a multicomponent alloy, as for Ti6242. Most of the time during the work, the simulation was crashing at some point which made difficult to access the results of the simulation. Surprisingly, adding some elements such as Si during the solidification calculation made DICTRA work better as the database already had some information about Ti6242, which contain Si. On the other hand, running a simulation that supposed to be simplified with only the “main elements” Ti, Al, Mo, Zr and Sn made the simulation fail.

Some discussions were initiated with Thermocalc support team about it and with the same set up and project, that team was able to run it. Thus, it can be concluded that the computational environment used to run those diffusion simulations might affect the success of the simulation.
6. Future work

This thesis work opens new possibilities of research, both to understand better the software and its limitations, and to evaluate better the risks of embrittlement of the structure. Some ideas are listed below to continue this work.

➢ Evaluate the precipitations of titanium silicides using the module TC Prisma from Thermocalc

➢ Evaluate the impact of titanium silicides on the mechanical properties of Ti6242

➢ Compare the results obtained with experimental results: electric resistivity, enthalpy, density measurements

➢ Adjust the simulations of microsegregation to take a distance that is known as dendrite arm spacing

Some further investigations should be done to evaluate the precipitations of titanium silicides and the impact on the mechanical properties on the titanium alloys. It would be recommended as well to perform some tests in order to compare the experimental data obtained with the results from the Thermocalc simulations.
7. Conclusions

The main questions to answer in this thesis work have been separated in two bullets:

- How to maximize the process to make it the most effective possible for each alloy?
- To what extend Thermocalc is a useful tool for Additive Manufacturing purpose?

The main results from this work have been discussed already in previous parts and will be summarized below.

First of all, Ti6242 is slightly easier to melt than Ti64 (6.5%) and has higher surface tension. A lower energy necessary to the melt of the wire means that it is possible to increase the feed rate for a similar laser setting and still have a stable process. On a second place, the surface tension might have an impact on the process parameters. This physical property fixes the maximum height at which the wire should be to avoid dripping, which can be a significant improve to a better quality component. Ti6242, with the same process parameters than for Ti64, is a material that will provide a stable process for longer considering the feeding rate. The conclusion on the finding about physical properties is that the differences spotted counteract each other, but still for the same process parameters, Ti6242 might be more stable than Ti64.

The evaluation of the microsegregations in both titanium alloys shows interesting results that could be seen in relation with the diffusion coefficient and the partitioning coefficient as well. From the differences in their values for each element in each alloy, microsegregations are therefore observed and may lead to the thermodynamics conditions of forming brittle phases such as intermetallic phases, like titanium silicides in the case of Ti6242.

Finally, the SDAS model from this work has been previously used in other studies to model the microstructure of titanium alloy components from DED-p. The study of the microsegregations coupled to SDAS is a powerful method to improve our understanding of the microstructure. The SDAS modelling result can be implemented into DICTRA simulation to get an accurate simulation of the solidification process. Even though some limitations of the model have been found, the model can be useful in future works as well.
References


8. Appendix I – Table of the phases from Thermocalc

Presentation of the phases used in Thermocalc to get the results from this thesis.

Table I a – Description of the phases names and modules used for the simulation

<table>
<thead>
<tr>
<th>Phases name</th>
<th>TC name</th>
<th>Database</th>
<th>Module</th>
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<td>BCC_B2</td>
<td>TCTI4</td>
<td>E(1), S(2)</td>
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<td></td>
<td>BCC_A2</td>
<td>MOBTI4</td>
<td>D(3)</td>
</tr>
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<td>Alpha</td>
<td>HCP_A3</td>
<td>TCTI4, MOBTI4</td>
<td>E, S, D</td>
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<tr>
<td>Liquid</td>
<td>LIQUID</td>
<td>TCTI4, MOBTI4</td>
<td>E, S, D</td>
</tr>
</tbody>
</table>

[1] : Equilibrium
[3] : DICTRA

9. Appendix II – Information regarding alloy 718

Table II a – Composition of alloy 718 used in the physical properties simulation

<table>
<thead>
<tr>
<th>Alloy 718 composition (wt%)</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Nb</th>
<th>Mo</th>
<th>Ti</th>
<th>Al</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balanced</td>
<td>19.0</td>
<td>18.0</td>
<td>5.00</td>
<td>3.00</td>
<td>0.85</td>
<td>0.50</td>
<td>1.00</td>
<td></td>
</tr>
</tbody>
</table>
10. Appendix III – Discussion about the density issue

From the first density simulation, a difference between the behavior of Ti64 and Ti6242 has been spotted. This difference gained our interest and we decided to investigate it further to understand better why such a difference was observed.

In a first part, we knew Thermocalc had some limitations due to the database and therefore we used another software based on CALPHAD methodology (JMat Pro) to investigate further. Comparing the density of the system for both alloys, there is a difference for Ti6242 with Thermocalc. The calculations for Ti6242 seem wrong, and it might be interesting to know if it is caused by $\alpha$ or $\beta$ phase.

![Comparison between JMat and TC for density evolution](image)

*Figure III a – Density comparison between Thermocalc and Jmat Pro for Ti64 and Ti6242 system*

While focusing on BCC phase, we can see that the curves for Ti64 are pretty similar but the main difference is spotted for Ti6242 once again. The density of $\beta$ phase evaluated with Thermocalc is lower than the one evaluated by JMat Pro. In addition below the beta transus, the density of $\beta$ seems to increase a lot because of the diffusion of $\beta$-stabilizers and $\alpha$-stabilizers in their respective phases.
On the other hand, HCP estimations for both softwares are the same below the beta transus. But a remaining question is why Thermocalc is evaluating the density of α phase at a temperature higher than the beta transus which marks the transformation start.
Finally, comparing one phase to the other for each alloy, it appears that in the case of Ti6242, the evolution of BCC and HCP is normal, as BCC is less close-packed than HCP with a packing factor of 0.68 for BCC and 0.74 for HCP. For that reason, the density of BCC should always be lower than for HCP.

Figure III d – Density comparison between BCC and HCP in a) Ti6242; b) Ti64

However, for the case of Ti64, BCC is always above HCP, which means that α is always lighter than β. Above the beta transus, this error can be considered acceptable as α is not supposed to exist, as seen with the simulation of the phase fraction for the alloys.

Just to understand better the behavior of the two alloys under the beta transus, the evolution of phase fraction with temperature has been collected. It shows that the amount of BCC phase decreases rapidly and therefore, to stay stable at room temperature, the phase needs to see its composition increase in β-stabilizers, which are V and Mo for Ti64 and Ti6242 respectively. Those elements being heavier, it could explain why BCC is heavier than HCP below the beta transus, but not above it.

Figure III e – Phase fraction evolution for a) Ti6242 and b) Ti64