

On the Improvement of the High Temperature Oxidation Performance of Niobium Silicidebased Alloy Systems Produced by Laser Additive Manufacture

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Abstract

There has been significant research into improving the efficiency of aerospace engines. This can be done by increasing the operating temperature of the turbine section of the engine. Turbine blades can be subjected to temperatures <1350°C. Nickel-based superalloys are the current material, but they are at the limits of their temperature capability.

Niobium silicide alloys offer a potential route to higher engine efficiencies. Binary Nb-Si alloys possess a solidus temperature near 1900°C. However, to operate in such temperatures the alloy needs to be able to resist high temperature oxidative attack. Nb-Si alloys have not proven to be resistant to oxidation thus far. If they are to replace Ni-based superalloy they will need improved oxidation performance. Processing these alloys is also challenging as the high temperature melt reacts with traditional mould materials.

This work aimed to improve the oxidation resistance of a MASC-based alloy by using uncommon elemental additions. Manufacture of the alloys in this study was done using direct metal deposition (DMD), a form of laser additive manufacture. This eliminates the need for a mould. DMD is relatively untested, so this study investigated the properties of an MASC-based Nb-Si alloy after creation by DMD. An assessment of macrosegregation was performed, which found no evidence this phenomena.

The alloy then underwent oxidation tests, comparing the results to literature source where arc vacuum melting was used. DMD marginally improved oxidation properties and changed the mechanism at 800°C. This study found a parabolic regime, followed by a linear regime. With the viability of DMD confirmed, additions of Zr (with Y) and Ta were added. At 1 at%, Zr showed minor improvements at 800°C in the linear regime. 2 at% Ta resulted in markedly improved parabolic rate constants at 1200°C. Additions of Ta show great potential in improving the oxidation resistance of Nb-Si alloys.

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1 Introduction to Gas Turbine Engines and Niobium Silicide Alloys

1.1 Gas Turbine Engines

For the past 70 years gas-turbine engines have been the primary power source for most aerospace vehicles. When compared to piston engines, gas-turbine engines do not lose propulsive efficiency when approaching the speed of sound, have reduced maintenance requirements and greater efficiency over the majority of flight plans [1]. This efficiency is achieved by greater thrust to weight ratio. Piston engines only remain economically viable where power requirements and altitude of flight are low [1].

Gas-turbine engines are commercially available in several different configurations, each suited to a specific need. Turbojets were the first gas-turbine engine to be produced. These are efficient above Mach 1 but below this speed the efficiency of these engines decreased significantly [2]. Engineers devised the turbofan engine to overcome this inefficiency at subsonic speeds. Turbofans are the most common engine found in civilian aircraft.



Figure 1 - Schematic of 2-spool Turbofan Engine [2]

In Figure 1, it can be seen that air is drawn in via the fan blades where it splits into two channels. In airflow 1, the air passes around the inner core of the engine. It then meets the air from airflow 2 in the exhaust. In airflow 2, the air is taken into the compressor, increasing the pressure of the airstream. This air then travels to the combustor. Liquid

fuel, usually kerosene, is mixed with the air and ignited. This imparts energy to the airstream which is then passed through the turbine. The blades in this section extract some of this energy, turning in the process. The turbine blades and the compressor are connected by a prop shaft. The turning of the turbine therefore drives the compressor. Once the air has passed through the turbine it exits the engine through the exhaust nozzle, mixing with the airstream from airstream. This jet of gas propels the aircraft forward [3].

The turbine section of the engine is of particular interest to the aerospace industry. This section receives the combusted air-fuel mix straight from the combustor. This gas is under high pressure, contains corrosive by-products and, most importantly, is at high temperature. This temperature can reach over 1500°C in current civilian aircraft engines [4]. This is a difficult environment for most materials to cope with. Suitable materials must be able to withstand the high temperature, whilst maintaining a significant amount of strength. They must be resistant to creep, the permanent deformation of a material at loads below its yield strength. This deformation mechanism is much stronger at elevated temperatures. They must also be resistant to oxidative attack. Like creep, oxidation is a significant problem at higher temperatures atoms have the energy to overcome the activation energy needed for reactions to occur.

1.2 Nickel-based Superalloys

Nickel-based superalloys have been the material of choice since the 1940s. Figure 2 shows that this material has excellent retention of strength at high temperature. The advent single crystal alloys significantly improved the creep resistance by eliminating grain boundaries, thereby removing one of the mechanisms which contribute to elongation. Superalloys are also resistant to oxidation, with significant amounts of aluminium and chromium helping to form stable oxide layers.



Figure 2 - Stress Rupture Strength of Common Aerospace Alloys [5]

There is great pressure on the aerospace industry to reduce emissions as ecological targets across the globe become more stringent. Lowering fuel consumption also benefits airlines by reducing fuel costs and/or increasing the number of passengers that can be transported. Efficiency improvements can be made in the turbine section of the engine, hence why it is an area of significant research. The idealised Brayton cycle, Figure 3, shows the entropy vs temperature profile as the airstream passes through the engine. Energy is extracted from the airstream as it passes through the turbine and exits the nozzle.



Figure 3 - Idealised T-s Brayton Cycle where 1 is the compressor inlet, 2 is the compressor outlet into the combustor, 3 is the combustor outlet in the turbine and 4 is the exit nozzle. [6]

The energy extracted will increase if the temperature at the turbine intake is increased. The derived equation for thermal efficiency of the Brayton cycle, Equation 1, shows that if T₃ is increased then the efficiency will increase. Therefore, increasing the temperature of the combusted gas as it enters the turbines will result in increased efficiency η_{th} .

$$\eta_{th} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

Equation 1 [7]

In the equation above the temperatures are related to the engine positions in Figure 3. Figure 4 shows the development of superalloys since their inception. There is a gradual rise in the temperature capability of superalloys, though it appears to be plateauing since single crystal alloys where introduced. This has led many researchers to suggest that superalloys are reaching the limits of their performance capability [8-11].



Figure 4 – Development of nickel-based superalloys from 1940-2010 [5]

This is shown clearly when comparing the take-off temperatures to the alloy temperature capability. Since the 1990s only complex cooling systems have enabled these alloys to continue to function in the environment. Even more recently thermal barrier coatings have become necessary for the survival of superalloys in the engine environment. These coating are made of ceramic, most often yttria-stabilised zirconia. The poor thermal conductance protects the turbine blade from the environmental conditions, as well as providing a barrier to oxidation [12].

The research above suggests that either a significant improvement in superalloys is required to improve efficiency, or that a new material is needed to replace them. With a significant improvement in superalloys looking unlikely, researchers are turning their attention to alternative materials.

1.3 Beyond Nickel-based Superalloys

Some research has been conducted into platinum group metals. These metals have high melting temperatures, well above the currently achieved engine temperatures. They are ductile at room temperature and many composition are resistant to high-temperature corrosion as they have low thermodynamic drive to form oxides [13]. However, these

alloys are dense. Pure platinum has a density of 21.45 g cm⁻³ in contrast to- 8 g cm⁻³ for superalloys. Increasing density will increase the mass of the engine, which will decrease the efficiency of the engine. But even more substantial is the cost of such alloys. Palladium and platinum retail at ~£40,000 and ~£27,000 per kilogram respectively in current markets. Nickel costs around £11 per kilogram [14]. Turbine blades are already a high-value part, costing up to £8,000 per blade with hundreds of blades in each engine. Such an increase in material costs would significantly increase the price of the engine. It is unlikely airlines could afford this increased cost, no matter the efficiency improvements achieved.

Metallic silicide systems offer a less expensive route to increased efficiency. A high solidus temperature is found for both niobium and molybdenum silicides, well above the melting temperature of current superalloys [15]. This shows that these alloys have the potential to increase the operating temperature of gas-turbine engines. Niobium and molybdenum cost £32 and £20 per kilogram respectively, significantly cheaper than any of the platinum group metals. However, both systems have issues that must be overcome if they are to achieve this potential. Intermetallic phases, such as MoSi₂ or Nb₅Si₃, are covalent structures that lack ductility. This results in alloys that have poor ductility at ambient temperature. If failure of such a material were to occur, it would be brittle in nature. This is not acceptable in a load-bearing capacity. Oxidation resistance of these alloys is also poor with neither niobium or molybdenum silicides forming protective, non-porous oxide scales. This is particularly problematic for the molybdenum silicides as the primary oxide formed is MnO₂. This oxide is volatile at elevated temperatures, preventing the formation of a beneficial oxide layer. Whilst niobium silicides also suffer from poor oxidation, the primary oxide formed, Nb₂O₅, is not volatile. Improving the oxidation resistance of either of these alloy systems would be a major step towards a new turbine blade material.

The literature suggests that it will be difficult to compensate for the volatility of the MoO_2 oxide that inhibits stable oxide growth for molybdenum silicides [16]. Niobium silicides are susceptible to pesting behaviour but the oxides formed are stable at high temperature. It should be possible to use elemental additions to reduce pesting and form a more stable oxide. It is also important to consider density. Mo has a density of 10.3 g cm⁻³ whereas Nb has a density of 8.6 g cm⁻³. If used in the same stoichiometric ratio an alloy using Nb will save 16% of the mass compared to Mo. When applied across hundreds of blades this

weight saving could contribute to improving engine efficiency. With all this in mind, the following study has chosen to focus on improving the oxidation resistance of the niobium silicide system.

1.4 Niobium-silicon binary system

To understand the potential of niobium silicide alloys for turbine blade applications, it is useful to study the binary niobium-silicon phase diagram. Figure 5 shows a binary phase diagram of the Nb-Si system, in terms of atomic weight percentage of Si from 0%-50%. Above 38% Si content only brittle silicide phases form. These compositions are not useful for the intended application.



Figure 5 - Binary niobium-silicon phase diagram from 0-50 at.% Si [17]

The eutectic point forms at 18.2 at.% Si and at a temperature of 1880°C. At temperatures below this eutectic point the sample will be solid. This is much higher than superalloy systems, with melting temperatures of the most recent systems not exceeding 1150°C. It should be noted that there is some dispute in the literature on the position of the eutectic, both in terms of composition and temperature. Upon equilibrium cooling a two phase region will form of Nb_{ss} and Nb₅Si₃. Nb_{ss} acts as the ductile phase and Nb₅Si₃ acts as the strengthening phase [18]. This type of system is common in commercially successful alloys including steels and superalloys. The equilibrium solidification sequence of hypoeutectic binary alloy is as follows with typical microstructure shown in Equation 2

$$L \rightarrow Nb_{ss} + Nb_3Si$$

Nb₃Si \rightarrow Nb_{ss} + α -Nb₅Si₃

Equation 2



Figure 6 - Typical hypoeutectic Nb-Si microstructure [19]

Figure 6 shows a typical hypoeutectic structure. No Nb_5Si_3 forms as is predicted thermodynamically. If slow cooling is used this then Nb_3Si will form and the second part of the solidification sequence will be inhibited by poor solid state diffusion. Overtime this phase will eventually decompose into Nb_5Si_3 but this will take a substantial amount of time without heat treatments to increase solid state diffusion. A hypereutectic alloy would follow a different path:

$$L \rightarrow \beta -Nb_5Si_3$$
$$L \rightarrow Nb_3Si$$
$$L \rightarrow Nb_{ss} + Nb_3Si$$
$$Nb_3Si \rightarrow Nb_{ss} + \alpha -Nb_5Si_3$$

Equation 3

In many hypereutectic alloys, the formation of Nb₃Si is not observed. This can be due to the supressing by other alloying elements or due to the rapid cooling rates often observed in manufacturing.



Figure 7 - Typical Hypereutectic Nb-Si Alloy [20]

Table 1 shows the crystal structures of the phases that form in a binary niobium silicon system. The Nb_{ss} is a cubic system with metallic bonds. All other phases are covalently bonded intermetallic phases. It can be seen that Nb₅Si₃ has several different crystal structures that can be formed. In the binary system α is the thermodynamically stable phase at room temperature. Elemental additions and non-equilibrium cooling rates can change which conformation is formed, which will be explored further later in this chapter.

Table 1 - Crystal structure of niobium silicide phases

Phase	Crystal System	Space Group	Reference
Nbss	Cubic	Im3m	[21]
Nb3si	Tetragonal	P42/n	[21]
a-Nb5Si3	Tetragonal	I4/mcm	[22]
β-Nb5Si3	Tetragonal	I4/mcm	[22]
γ-Nb5Si3	Hexagonal	P63/mcm	[22]

Nb_{ss} is always required if the alloys produced are to have reasonable ductility. The phase consists of a metallically bonded BCC structure. This is the same structure that pure Nb would form. In order for this phase to be formed Si content must be kept below the 38 at.% threshold. Of the silicide phases that can form, Nb₅Si₃ is preferred to Nb₃Si. α and β -Nb₅Si₃ have been shown to have improved creep performance in comparison to Nb₃Si. Nb₃Si is also thermodynamically unstable at ambient temperatures and will eventually decompose to α -Nb₅Si₃. Research performed on these various crystal forms of the

Nb₅Si₃.suggest that material properties of the variant, such as compressive strength, are greater at ambient temperature. However, the β variant can better retain material properties at elevated temperatures [23]. The γ variant has poor creep resistance which is caused by the increased number of slip planes in the hexagonal crystal structure. This variant is avoided where possible.

The ideal result in both hypo and hypereutectic alloys is a two phase microstructure consisting of the Nb_{ss} phase and the α -Nb₅Si₃ silicide. This results in a thermodynamically stable microstructure with the optimal material properties, such as creep resistance and strength. However, the binary system has not resulted in alloys that suitable for use in turbine blades. There is always a trade-off between ductility and oxidation resistance. Hypereutectic alloys tend to be more oxidation resistant as they contain more silicide but are less ductile for this same reason. The opposite is true for hypoeutectic alloys. Overall oxidation performance is poor, even for hypoeutectic binary alloys. Researchers have focussed on adding other elements into the binary system to improve material properties. This will be investigated in the next chapter.

2 Properties and Production of Multi-component Niobium Silicide Alloys

It is clear that the binary system is not suitable for the application of turbine blades. However, it is rare that a pure binary system is used in modern alloys. Common commercial steels will often have seven or more different elements added to optimise the steel for a particular role. The same is true of aluminium alloys and of nickel-based superalloys. Elemental additions allow a metallurgist to tailor the microstructure and mechanical properties of the alloy system to suit the required need. Niobium silicides are a relatively new alloy system and thus work is ongoing to determine the effect of various elements.

Some elements have already been studied in detail. Elements like Ti and Al have been shown to be highly beneficial to Nb-Si alloys and are present in most studies considering alloys with a good balance of material properties. The elements which have been consistently included in Nb-Si alloys and have provided benefit are discussed below, describing their effect on the Nb-Si system.

Equally important is how these alloys are processed. Whilst the high temperature capability of Nb-Si alloys make it a suitable material for turbine blade, it makes producing them a technical challenge. Temperatures above 2000°C are required to fully melt the alloy and a non-oxidative environment, such as vacuum or inert gas, is needed to prevent oxidation. Current Ni-based superalloys are produced using single crystal investment casting, but this has proven difficult to transfer to Nb-Si Alloys. The reasons for this will be discussed in the following chapter, as well as alternative methods that can be used to produce Nb-Si alloys. In particular, Laser additive manufacture will be discussed as a new way in which Nb-Si alloys can be made.

2.1 Effect of Elemental Additions

2.1.1 Titanium

Titanium was one of the first elements considered for introduction into the Nb-Si alloys. It is rare to observe a niobium silicide alloy in the literature without this element included. 3D phase diagrams of the Nb-Si-Ti system are available which show the effect of Ti on the binary Nb-Si system.



Figure 8 – Ternary Nb-Ti-Si Phase Diagram [24]

The diagram in Figure 8 shows that with increased titanium addition the solidus temperature of the eutectic continually decreases, eventually reaching a minimum of 1330°C at maximum Ti content. The production of the Nb₅Si₃ silicide is slowly inhibited as Ti content increases above 25 at.%, replaced by the formation of Ti₅Si₃. This phase is a hexagonal closed packed phase which have been shown to be detrimental to material properties. These phases are brittle and susceptible to cracking [ref]. The Nb₃Si phase is stabilised to lower temperatures. This will result in the phase decomposition into Nb_{ss} and Nb₅Si₃ will taking significantly longer as available energy for the reaction is reduced at the lower temperatures. To inhibit the formation of Ti₅Si₃ and keep the eutectic temperature >1700°C it is suggested to add no more than 25 at.% of titanium in a niobium silicide alloy [25].

Ti partitions to Nb_{ss}, Nb₃Si and Nb₅Si₃, replacing Nb in the lattice of each phase. With added Ti content there is a significant increase in the fracture toughness, with values over 15 MPa m^{0.5} achieved for alloy Nb-33Ti-16Si [25], and dramatically improves the oxidation resistance of the solid solution phase, which is highly susceptible to oxidative attack. By forming Ti based oxides which pest less readily than the primary Nb oxide Nb₂O₅.

2.1.2 Chromium

Cr is often added to alloys to improve corrosion resistance as it forms a stable oxide. Cr primarily partitions to the Nb_{ss} phase if the alloy atomic concentration of Cr is <6 at.%. Small concentrations, typically less than 2 at.%, can be observed in the silicide phases. Above this threshold a C-14 or C-15 laves phase, Nb₂Cr, begins to appear in the microstructure. Most literature sources state that the C-14 laves phase is present but with little or no supporting evidence. Ternary phase diagrams show that both the C-14 and C-15 phases could potentially form [26]. More recent studies have found laves phase forming at 2 at.% in a eutectic binary alloy [19]. The laves phases have been shown to improve the oxidation resistance but at detriment to the fracture toughness, with the laves phase itself having a fracture toughness of 1 MPa \sqrt{m} [27, 28]. Cr additions also appear to destabilise the Nb₃Si phase, which is rarely present in the microstructure of alloys containing Cr.

2.1.3 Aluminium

As with Cr, Al mainly partitions to the Nb_{ss}, though Al is stable in the Nb₅Si₃ phase to a lesser extent. Al appears to supress the Nb₃Si phase and it supresses the phase more strongly than Cr does. The primary purpose of Al additions is to improve the oxidation resistance, the formation of an alumina scale seen as the optimal oxide scale at high temperature. This will be discussed in more detail in Chapter 3. With sufficient concentration aluminide phases can form, such as Nb₃Al. These do not tend to be beneficial to material properties as they possess poor ductility and result in poor creep resistance, though can increase high temperature strength [29, 30]

Al has a relatively low melting temperature of ~660°C. It is generally recommended to keep Al addition \leq 5 at.% to keep the eutectic temperature at a sufficient temperature for the intended application. Al additions of 9-10 at.% were shown to also have an adverse effect on the fracture toughness of Nb-Cr-Ti-Al alloys [28].

2.1.4 Hafnium

Hf is often added to other alloy systems as an oxygen scrubber. Hf additions are soluble in the Nb_{ss} phase but tend to partition to the silicide phases. They have been shown to stabilise the γ -Nb₅Si₃ crystal structure, if Hf at.% is at least 5% [31]. This phase has demonstrated detrimental effects on the creep properties of the Nb-Si alloys. Large concentrations of Hf lead to the formation of Hf₅Si₃, which possesses the same crystal structure as γ -Nb₅Si₃ and is also detrimental to creep resistance. This helps explain why Hf drives the Nb₅Si₃ to the γ form as Hf must be more stable in a hexagonal crystal lattice. Hf additions also tend to result in HfO₂ particles, scattered through-out samples [32]. As with Al and Cr, Hf stabilises the formation of the Nb₅Si₃ phase and supresses the Nb₃Si phase.

2.1.5 Molybdenum

In the literature molybdenum tends to be included at low atomic percentage, >5 at.%. Small additions have been shown to increase the yield strength at high temperature (1773 K) compared to binary niobium silicides. This is due to solid solution strengthening of the Nb_{ss} phase [33]. Mo addition also tends to favour the production of the β Nb₅Si₃ over the alpha equivalent. This can lead to a more brittle alloys with a lower fracture toughness [34].

2.1.6 Tin

Sn has been shown in several papers to improve the pesting behaviour of oxide scales that form at 'low' temperatures. Sn is only added in small quantities not above 2 at%. Large additions of Sn have also been found to result in formation of Nb₃Sn phase and reduce the amount of the solid solution phase, decreasing fracture toughness [31, 35]. This element is discussed in more detail in Chapter 3

2.2 Processing

2.2.1 Casting

Casting has been used to manufacture metals for thousands of years and is still relevant today. All casting techniques share the same core process; creating molten metal using heat and sometimes a catalyst, then pour the liquid metal into a pre-fabricated mould. As the metal fills the mould it solidifies, taking the shape of the mould. This mould can be that of an ingot, sheet or resemble the intend shape of a part. This is still how most metal items are produced. There are numerous types of casting, but this section will focus on investment casting as it is used to produce current Ni-based superalloy turbine blades and is most relevant to production of Nb-Si alloys [36].

Investment casting occurs in several stages. In the first stage a master pattern is produced which determines how the product will look. This can be made by a sculptor or by 3D printing. This master pattern is then used to make one or more master moulds. The master

mould/s are then used to create wax patterns which are then assembled on a 'tree' with multiple other wax patterns. This allows casting of several items in one pour. The wax pattern tree is then coated in ceramic which occurs in three steps: coating, stuccoing and hardening. During coating the tree is dipped into a fine refractory slurry; fine particles are used for a smooth surface finish after casting. Stuccoing adds ceramic particles that are coarser, as they will not affect the surface finish. Finally, the ceramic undergoes hardening where the ceramic coating cures. This is done several times to reach a suitable thickness. Once completed, the mould is then heated to melt the wax, which is poured away. A second heating, called a burnout, is performed to remove any moisture of residual wax from the mould. Now the molten metal can be poured into the mould and cooled. The solidified metal has now taken the shape of the pattern. To remove the patterns from the mould the mould is smashed or dissolved in a process called divesting. The cast components can now be taken for additional treatment [37].

Conventional casting in this manner results in Ni-based superalloy with superior creep resistance and high-temperature retention of strength, when compared to wrought alloys. This is due to the reduction in grain boundaries, caused by larger grains. However, the grains of cast Ni-based superalloys are still relatively small and there was significant investigation into the reduction of grain boundaries. Researchers found that it is possible to directionally solidify the molten metal, resulting in a microstructure with large, parallel grains which grow in the direction of the heating front. This is achieved using a Bridgman furnace, seen in Figure 9 [38].



Figure 9 – Schematic of a Bridgman furnace

The furnace has an upper heating zone and a lower cooling zone, separated by an insulating baffle. Initially, the mould is held in the heating zone with only the base in the cooling zone, sitting upon a chill plate that is water-cooled. The liquid metal is poured into the mould, as this is done the mould is slowly moved down into the cooling zone using a pulling mechanism. This creates a moving cooling front with a large temperature differential, which can be 1000°C difference over a few cm. This creates a driving force for grains to form in the pulling direction, resulting in a directionally solidified sample. This further reduces the number of grain boundaries and improved creep resistance and high-temperature strength.

Directional solidification was a big technological leap, but it is possible to remove grain boundaries entirely. The method is very similar to the creation of directionally solidified Ni-based superalloys, the key difference is the use of a pig-tail grain selector at the base of the casting. The spiral selector is able to select just one grain which is then able to grow through the remaining cast, resulting in a single crystal turbine blade with excellent creep resistance. This is the technique currently used to cast modern Ni-based superalloy turbine blades [39].

When researching materials that could replace Ni-based superalloys, it would be beneficial if turbine blades could be constructed from that material using current technology. Creating new production facilities represents a large additional investment on top of the substantial investment in investigating a new material. Aerospace, particularly civilian aerospace, has high safety standards and any new materials being introduced to a load bearing role requires years of testing before they can be introduced. Thus, there has been significant research into casting Nb-Si alloys [40, 41]

Unfortunately, the high temperature of the liquid alloy results in catastrophic interaction with most standard ceramics used in investment casting, such as alumina or silica [42]. This interaction destroys the mould, so materials such as this cannot be used. Some success has been found using yttria as a mould material. However, in Nb-Si alloys containing Hf, research has shown that hafnium is able to replace the Y atoms in the mould, resulting in reduced Hf content and Y impurities in the solidified alloy [43]. So far, there has not been a mould material that can successfully create a cast Nb-Si alloys without some interaction with the mould material. There is no suggestion in the literature that a useful mould material is on the horizon.

There are other casting techniques which have been used to study Nb-Si alloys. Optical float zone technology is able to create directionally solidified samples but is limited in the achievable size of the casting by the surface tension of the melt [44]. The shape is also limited to simple geometries, nothing complex like a turbine blade. Vacuum arc remelting has been used frequently but again is limited in the size and shape of casting that can be produced. An additional limitation of this method is that only equiaxed grains can be produced [45, 46]. Whilst other methods also exist, it is clear from these few examples that there is currently no casting method available that can produce a near-net shape turbine blade from an Nb-Si alloys on a commercial scale. Another method is needed to solve this problem.

2.2.2 Laser Additive Manufacturing

Laser additive manufacture (LAM) is the all-encompassing term given to any method that uses a laser to melt or sinter a material into a 3D construction. The general design of an instrument consists of either a moveable laser or moveable platform. The laser then heats the specified material which melts (fully or partially) and forms the 3D shape desired. Most printers work using modified CAD files called STL files. These files tell the machine how to form the shape.

The number of publications on this subject have increased dramatically over the past two decades. Statistics from Scopus show when searching the term 'laser additive manufacture' 1998 shows only 8 publications, whereas in 2018 there were 351 publications including this term [47]. The reason for this increase in interest in down to several factors. Firstly, LAM is applicable to a wide range of materials including metals, polymers and composites. Secondly, when considering parts with complex geometries that are only made in small quantities LAM can be more cost effective than casting. Figure x shows analysis of how the cost per unit of a casting technique and AM technique changes with the amount of the product made.



Figure 10 – Cost analysis of 3D printing vs injection moulding [48]

Casting shows an exponential decrease in cost per unit as the size of the production run increases. LAM shows a constant line, with cost per unit mostly independent of the size of the production run. When produced in large quantities, casting has a lower cost per unit. However, when small production runs are considered, LAM has a lower cost per unit. This make LAM suitable for products than only require a small number to be manufactured per year and for prototyping.

2.2.2.1 Direct Metal Deposition (DMD)

DMD, also known as laser metal deposition (LMD), is a recently developed additive manufacture technique. LENS, constructed in the late 1990's, is one of the earliest examples found [49].

The set-up for DMD is seen in Figure 11. A high power laser meets metallic powder at the focal point of the laser beam. This powder is then fully melted forming a melt pool. In most cases the stage moves, changing the position of the laser beam and powder feed relative to the base plate. The material solidifies once the laser beam moves, creating solid metallic structure. The base plate moves in accordance with a CAD file. Once one layer of a scan has been produced, the stage moves down in the z-direction and the next layer is created.



Figure 11- Schematic of direct metal deposition

This method of additive manufacture is theoretically applicable to any powdered material. However, most of the research has been performed with metallic powder. It is possible to create gradient material structures by varying the powder composition fed through the nozzles. This has already been used successfully in making a material that slowly changes from steel to a superalloy [50].

DMD, as with any LAM technique, as a multitude of parameters that influence the properties of the material that is produced. The complexity of the interactions between these parameters has researchers turning to artificial intelligence to develop prediction tools that would aid alloy design for such techniques [51]. A non-exhaustive list of some of the key parameters are listed in Table 2.

Laser Parameters	Scanning	Powder Properties	Material Properties
	Parameters		
Power	Velocity	Flowability	Thermal conductivity
Spot size	Layer overlap	Size distribution	Melting temperature
Spot shape	Z step-size	Absorptance	
EM wavelength	Strategy	Flow rate	

Table 2 – Some parameters that influence the properties of materials subjected to LAM processes

Laser power and spot size can be combined into one single parameter; power intensity with the unit W m⁻². This parameter determines the energy input into the area of the spot per unit time. Higher power intensity is spread over a lesser area than low power intensities, causing increased localised heating but less transmission of heat to the rest of the material. The scan speed determines the amount of time spent at a location, giving the actual energy input into an area. Faster scan speeds reduce the total energy input into an

area and result in faster cooling rates and finer microstructures. This also can increase localised residual stress.

Lasers will emit different wavelengths of light depending on the type of laser used. For example a CO₂ laser emits primarily at wavelength 10600 nm with secondary emissions between 9000-11000 nm [52]. The amount of energy absorbed by the powder will depend of the absorptance of the powder. This is the ratio of absorbed radiation to incident radiation. In a bulk solid this would depend on the absorption coefficient of the material. However in powders the radiation can travel further into the material between the gaps between the particles by both direct transport and reflection of the particles. This makes the optical penetration depth much larger in powders than in bulk materials [53]. Achieving a balanced absorptance is important in creating a good sample. If the absorptance in too low then the powder will not fully melt and a coarse, uneven sample will be produced. On the other hand, if too much energy is absorbed then certain elements of the powder will be volatized and the intended atomic composition will not be achieved.

2.2.2.2 System Assessment and Uses

Creating metallic parts using laser additive manufacture of any kind is still in its infancy. It is unlikely that it will replace casting in large production items, casting tends to become more cost efficient as the number of items in a production run increases. Most LAM systems will start out more cost efficient per item, but cost per item does not change significantly with increasing number of parts. This does mean that for small to medium production runs could be suitable to production with a form of LAM [54].

LAM does possess other benefits that can warrant its use over traditional casting. It can reduce the total time to go from design to product. When casting a new product, new master moulds need to be created and tools modified. In additive manufacture, once a CAD design is drawn then production can begin. This, however, does not account for when a new alloy is needed. A new alloy system would require the laser parameters, as seen above, to be optimised, which would take some time. It is difficult to construct complex shapes using casting, LAM is able to produce the complex geometries with relative ease. This is because casting relies on the flow of molten melt into a predefined mould. Additive manufacture is not constricted by this as metal solidification occurs rapidly before flow can occur.

Whilst LAM is good at producing near-net shapes, surface finish is often poor compared to a cast item. The melting and re-melting of material causes a bumpy finish to many LAMed items, where each layer of melting can be seen. This can be rectified by other treatments but takes away from the supposed time advantage of LAM. Porosity, introduced from trapped atmospheric gas to void formation, is a problem familiar to castings; LAM has thus far not been able to eliminate this problem and can often have worse porosity than a cast component. Again, further treatment can reduce this problem at the expense of more production time.

Another area that has not been investigated thoroughly for LAM techniques is macrosegregation. In casting of many materials such as steels and Ni-based superalloys, high concentrations of elements can segregate. This occurs whilst the metal is still liquid and is cooling, with the ejection of solutes transported by convection current a common cause of such phenomena. Macro-segregation can cause alternative phases to form in different areas of a sample, often resulting in poor material properties. It will be important to determine experimentally if macro-segregation occurs in Nb-Si alloys produced by DMD. This will be discussed further in Chapter 5, were an Nb-Si sample made by DMD is assessed for signs of macro-segregation.

3 Temperature Atmospheric Oxidation of Niobium Silicides

Oxidation of niobium silicide alloys has been the subject of numerous studies, particularly in the past 10 years [15, 45, 55-58]. As discussed in Chapter 1, oxidation properties at temperatures above 700°C remain poor for these alloys, despite the amount of research into improving them. However, the work that has been done has helped to build a comprehensive understanding of how these alloys oxidise in air at high temperature. There have also been significant improvements made in the oxidation performance, primarily by using different elemental additions. There is still a long way to go before these alloys meet the required criteria, but the improvements made suggest it will be possible to achieve an oxidation resistant niobium silicide alloy.

In order to discuss the oxidation properties of Nb-Si alloys it is important to understand the mechanisms that contribute to oxidation of metals. This chapter will discuss the fundamentals of high temperature oxidation before going into detail on studies of oxidation resistance in Nb-Si alloys. This will include the properties of binary Nb-Si alloys, how elemental additions affect the oxidation properties before finishing with a look at the theorised oxidation mechanism for multi-component Nb-Si alloys.

3.1 Fundamentals

Lavoisier's theory of combustion by oxygen was the first major leap in understanding oxidation, and it why it gets its name [59]. Oxidation was first understood as the addition of oxygen to a compound for it to combust. It is now more accurately define as the process by which a material loses electrons to another material. In many cases this is often caused by a reaction with oxygen.

When a metal reacts with oxygen it will form a covalent bond in which it will donate electrons to the oxygen molecule. When oxidation, or corrosion, is discussed a common example most people are familiar with is the rusting of iron:

$$4Fe + 3O_2 \rightleftharpoons 2Fe_2O_3$$

Equation 4 [60]

The equation above is an overall equation representing the oxidation of iron into the red rust that is often seen on untreated iron. In reality, there are numerous additional steps which occur before this product is reached. Most metals are unstable under atmospheric conditions of RTP with oxygen partial pressure of 0.2. In theory, should spontaneously react with the atmospheric oxygen to form the oxide product [60]. Ellingham diagrams, such as Figure 12, show the Gibbs free energy of a reaction at a specified temperature and/or the partial pressure of the secondary reactant (oxygen, nitrogen etc.) required for a reaction to occur at a specified temperature. In thermodynamics, Gibbs free energy determines whether a reaction will naturally occur or not. Gibbs free energy is calculated using Equation 5 [60].

$$\Delta G = \Delta H - T \Delta S$$

Equation 5 [60]

 ΔG is change in free energy, ΔH is change in enthalpy, T is temperature and ΔS is change in entropy. A negative free energy shows that the product of a reaction is more thermodynamically stable than the reactants, so the reaction will occur naturally if the need for activation energy is ignored. The more negative ΔG is, the bigger the thermodynamic driving force is for the reaction. A positive free energy shows that the reactants are more stable than the product, so the reaction will not occur naturally. Figure 12 shows an Ellingham diagram from the reaction of several metals with oxygen, along with the free energy of the reaction. It can be seen for all the metals on Figure 12 that each reaction forming the oxide has a highly negative free energy. This means that the metals shown should react completely to form the oxide product when in an atmospheric environment at room temperature.



Figure 12 – Ellingham diagram of the reaction of various metals with oxygen to form metal oxides

However, this does not happen. Some metals, such as copper, have a relatively low driving force for oxidation resulting in a low reaction rate. It is important to remember that whether a reaction occurs is not only determined by thermodynamics but also kinetics. For a reaction to occur not only must there be a thermodynamic driving force but also enough energy to overcome the activation energy barrier. At low temperatures atoms do not possess much energy, so when atomic interactions occur the activation energy barrier is not likely to be overcome [61]. This is a key factor in the slow oxidation of metals such as copper in an RTP environment. However, once higher temperatures are reached it is more likely that the activation energy barrier will be overcome, hence an increased oxidation rate.

Other metals, such as aluminium, react with oxygen so quickly that they form a passivating layer of oxide which protects the metal underneath from further oxidative attack. This surface oxide acts as a barrier to the movement of electrons and charged ions. The oxide layer that forms is a covalently or ionically bonded ceramic, with no free electrons in the structure, unlike the metal beneath. This makes it much harder for electrons to pass through this layer [62]. At lower temperatures, diffusion of oxygen

through this oxide layer is also very slow, resulting in a stable oxide layer. At higher temperatures >600°C diffusion starts to play a more significant role in oxide and the surface oxide scale can begin to grow more rapidly, though still uniform with minimal cracks.



Figure 13 – Boltzmann distribution of atomic velocity (kinetic energy) at two different arbitrary temperatures [63]

The Ellingham diagram in Figure 12 shows that as temperature increases, the value of free energy change becomes less negative. From the above explanation, one would assume that as the driving force decreases so would the rate of oxide formation. However, it is well documented that increased temperature increases the oxidation rate of most substances. Atoms and molecules at higher temperatures have an increased average kinetic energy, as shown in the Boltzmann diagram in Figure 13. Once a critical temperature is reached, the interacting substances possess enough kinetic energy to overcome the activation energy and react, this is represented in figure. Activation energy is the minimum energy required for a reaction to occur. This acts as a barrier that prevents thermodynamics from taking its natural course. This means that the higher the temperature, the higher the rate of oxidation.

3.2 Oxidation Mechanisms

3.2.1 Oxide formation at elevated temperatures

Oxidation is classed as high temperature if there is sufficient energy for solid state diffusion to occur, allowing for the transport of species through the oxide layer. This tends to occur between 300-400°C, depending on the material in question. Below this

temperature, the thickness of the oxide layer is generally limited to several nanometres as quantum mechanisms, such as electron tunnelling are the only way for electrons transverse the oxide layer. Diffusion allows for oxide layers with greater thickness as the mechanisms are not limited to a certain distance.

Experimentally, three growth laws are observed in high temperature oxidation; Linear, parabolic and logarithmic. If the rate law is linear then:

$$\frac{dm_{ox}}{dt} = k_l$$

Equation 6[64]

 M_{ox} is the mass of oxide, t is time and k_1 is a linear rate constant with units kg m⁻² s⁻¹. Observation of this type of growth law indicates that the oxide layer is providing no barrier to further oxidation of the surface of the base metal. This law is observed in alloys where the oxide layer cracks and/or spallates. If this occurs there is no material inhibiting oxygen from reaching the base metal, so oxidation rate remains constant.

A parabolic rate law presents the following equation:

$$\frac{dm_{ox}}{dt} = \frac{k_p}{m_{ox}}$$

Equation 7[64]

The units for the rate constant, k_p are now $kg^2 \text{ m}^{-4} \text{ s}^{-2}$. This rate law indicates that the oxidation rate is controlled by the transport of species across the oxide layer. As the oxide layer thickness increases, transport (via diffusion) takes longer thus decreasing the rate of oxidation [64].

When a parabolic function is found the oxide film can grow either by diffusion of metal cations towards the oxide-environment interface or by diffusion of O^{2-} towards the oxide-bulk interface. It is usually a combination with one of the mechanisms dominating. For example, in Al and Si oxidation, diffusion of O^{2-} is the dominant mechanism [65]. Transport of the ions can occur via interstitial diffusion or by vacancy diffusion, shown in figure x.



Figure 14 – Diffusion of ions during oxidation via interstitials and by vacancies [64]

Equation 5 gives the parabolic oxidation function for both interstitial and vacancy diffusion where cation diffusion is the dominate mechanism.

$$k_p = 3D_i c_j M_{ox} \rho_{ox}$$

Equation 8

D is the diffusion coefficient, related to either interstitial cations or vacancy cations. C is the concentration which for interstitial diffusion is the concentration of cations at the metal-oxide interface. For vacancy diffusion it is the concentration of cations at the oxidegas interface. M and ρ are molecular mass and density of the oxide respectively.

Deviations from this mechanism are common. Wagner's theory does not account for situations where solute concentration at the relevant interface are high, nor does it consider diffusion along grain boundaries. Mechanisms need to account for such phenomena in order to reconcile theoretically derived values with experimental results [65, 66].

The summary of oxidation at high temperature given above has detailed much of the established theory, though it is. This review will now discuss the oxidation of Nb-Si alloys, relating the oxidation properties to the theory examined above.
3.3 Oxidation of Niobium Silicides

3.3.1 Oxidation of Nb, Si and Simple Nb-Si Alloys

Niobium is the primary component of Nb-Si alloys of interest. Under atmospheric pressure and at temperatures above 400°C, Nb will oxidise to form a conformer of Nb₂O₅. There are three primary conformers, α , γ and β . This is the naming convention given in [67], which has been found to vary significantly between literature sources. The crystal structure of each conformer is given in Table x. Which conformer is produced depends on the temperature of the environment. At low temperatures niobium pentoxide is amorphous but upon heating above 400° C γ is formed from an amorphous oxide. Above 830°C, γ converts irreversibly to an α/β mixture, which is coverts to α only above 1095°C. This reaction is also irreversible, showing that α is the only truly stable conformation at 1 atm of pressure. Another conformer, ε , is able form at temperatures above 1350°C but converts back to α when cooled below this temperature [67]. This oxide scale is prone to severe pesting behaviour, which is caused by two primary mechanisms. The first is the difference in thermal expansion of the oxide and the metal. This causes stresses in the oxide which can cause cracks to form. The second is the conformation changes that occur with temperature. Any conformation change will result in a volumetric change, which in the case of γ to α is +7% [67]. This also causes stress in the oxide, resulting in cracks. Nb is able to form other oxides, such as NbO and NbO₂, but when oxidised in air at high temperature, Nb₂O₅ is the primary oxide as it is the most thermodynamically stable [68].

Silicon is the other main component of all Nb-Si alloys, and under atmospheric pressure will form silica, SiO₂. As with Nb₂O₅, silica has several different temperature dependent conformations. At low temperatures, α -quartz is the thermodynamically stable structure, though amorphous forms, such as opal [69] often are often found. Above 573°C, α -quartz changes crystal structure slightly, forming β -quartz. Beyond 874°C, β -quartz changes to α -cristobalite. Heating above 1470°C will convert any α -cristobalite permanently to β -cristobalite. However, if held between 874°C and 1470°C the α -cristobalite with change to tridymite [70]. Silica scales are usually continuous and dense, protecting the alloy beneath. However, the conformation change from β -quartz to α -cristobalite has a volumetric change of ~12% [69]. If there were other stresses present in an oxide layer, or even if they are not, it is possible this could contribute to pesting behaviour.

There have been few studies performed on binary Nb-Si systems. Those that do exist, or studies on ternary systems with low amounts of a third component, have found formation of a non-protective oxide with mass gain values significantly higher than modern Nibased superalloys [71]. The oxide layer that forms mimics the microstructure beneath, with only Nb₂O₅ forming from the Nb_{ss} and a mixture of Nb₂O₅/SiO₂ forming from any silicide phases (Nb₅Si₃, Nb₃Si etc.). There is no evidence that these oxides react to form other oxide complexes. Beneath this outer oxide there is a further layer where oxygen has been able to diffuse to but has not yet reacted fully. This is known as the internal oxidation zone (IOZ). This layer is usually several times thicker than the outer oxide. The formation of such a layer indicates that diffusion of O^{2-} is primary mechanism for oxidation where parabolic functions are concerned.

3.3.2 Elemental Additions

3.3.2.1 Ti

Titanium was one of the first elements to be added to the Nb-Si system. Amongst other improvements it was found to result in improved oxidation resistance. Under high temperature oxidation at ambient pressure TiO₂ forms in the rutile configuration. TiO₂ has been detected in the oxide layers of Nb-Si alloys containing Ti [72, 73]. Also detected in Ti-containing Nb-Si alloys is TiNb₂O₇. It is thought that the TiO₂ forms and then reacts with Nb₂O₅, as shown in Equation 9.

$$TiO_2 + Nb_2O_5 = TiNb_2O_7$$

Equation 9

This maintains the high temperature monoclinic structure of the α -Nb₂O₅, incorporating the TiO₂ into the crystal; another way to write this crystal is Nb₂O₅·TiO₂. The other main Ti compound to be found in oxidation layers of Nb-Si alloys is TiNb₂O₄, thought to form from NbO₂ and TiO₂.

Ti, therefore, scrubs oxygen from the Nb_{ss} phase, helping to decrease the amount of oxygen that diffuses through the alloy. The formation of TiO_2 from Ti has a lower Gibbs energy than the formation of Nb₂O₅ from Nb. As oxygen diffuses through the Nb_{ss} phase it reacts preferably with the Ti. All of the above result in an alloy significantly more oxidation resistant than binary Nb-Si alloys. However, at high temperatures diffusion of oxygen through the rutile conformer TiO₂ is rapid [74]. This is the conformer most often detected in Nb-Si alloys containing Ti. This limits the benefit from Ti, particularly at

temperatures above 1000°C where diffusion is dominant. In addition, adding too much Ti can result in the formation of Ti₅Si₃, which is detrimental to creep properties.

3.3.2.2 Hf

Hafnium additions have also been used extensively in previous research [40, 58, 75]. Hafnium increases oxidation resistance by acting as an oxygen scrubber, forming hafnium oxide particles dispersed through-out the microstructure [56]. At high concentration, areas of HfO_2 are found in the outer oxide and it does appear that they reduce the oxidation rate constant at 1200°C.

However, it does not appear they are beneficial in preventing presenting behaviour [72]. As discussed in x, adding more than x Hf can result in the formation of γ -Nb₅Si₃ and/or Hf₅Si₃, both of which are detrimental to creep performance.

3.3.2.3 Cr

Chromium is well known for forming continuous oxide scales from its Cr_2O_3 primary oxide. When added to Nb-Si alloys Cr partitions primarily to the Nb_{ss} so this oxide tends to form from these areas. CrNbO₄ is commonly observed in Nb-Si alloys rich in Cr, though it does not tend to form a uniform layer and has no effect on the pesting behaviour of the alloy.

As discussed in Chapter 2, additions of Cr above 6 at.% can result in the formation of C14/C15 laves phase, Cr₂Nb. This phase is brittle, with a fracture toughness no greater than 1 MPa m^{0.5}. Not only is this detrimental to ductility at room temperature, it can also crack like the silicides during oxidation, allowing oxygen a direct pathway into the alloy. Even large additions of Cr do not result in the formation of a uniform oxide layer and come at severe detriment to material properties.

3.3.2.4 Al

Formation of an alumina scale, or one that mimics its properties, is the goal for any research into high temperature oxidation. Al forms Al_2O_3 under ambient pressure, forming a dense oxide with no cracks and which is able to heal should a crack appear. In niobium silicide alloys aluminium additions have been shown to reduce pesting behaviour at the medium temperature range and it also improves high temperature oxidation resistance. Aluminium also appears to help reduce the thickness of the internal oxidation layer [76, 77], the mechanism for this will be discussed later.

The main drawback of Al is its low melting temperature. The more Al added to an Nb-Si alloy the lower its solidus temperature will drop. Nb-Si alloys are intended to operate at extreme temperatures, so a significant drop in solidus temperature is unacceptable. So far, 5 at.% Al has been found to give the best increase in oxidation performance whilst maintaining a sufficiently high solidus temperature.

3.3.2.5 Sn

Tin is the most recent elemental addition to be studied for oxidation improvement. Recent work has shown that small additions of tin can eliminate pesting behaviour that occurs in the medium temperature range (~800°C). The Sn has a low affinity for oxygen so as other, more reactive elements are consumed at the IOZ/oxide boundary the Sn remains, forming a layer of NbSn₂/Sn at 800°C. This layer acts as a barrier to further oxygen diffusion. Without diffusion of oxygen the Nb_{ss} volumetric expansion is inhibited, preventing the silicides from cracking [78]. This is one of the primary causes of the pesting behaviour observed at this temperature.

At 1200°C Sn is able to react with the silicide phases and forms a layer of Nb₅Sn₂Si. This compound is detrimental to the oxidation resistance [78]. Sn also has a relatively low melting temperature, 231.9°C. Not only does this decrease the solidus temperature of the alloy, but Sn has a tendency to sublimate away from the alloy during production, so it is difficult to control the amount being added [45, 78].

3.3.3 Mechanism of Oxidation in MASC and Other Similar Alloys

Many studies have investigated the oxidation properties of Nb-Si alloys. The oxidation mechanism changes depending on the alloy composition. For example, Nb-Si alloys with high Cr content will form Cr₂O₃ oxides in the outer layer but will be confined to areas where the Nb_{ss} or Nb₂Cr phase are present [ref] However, MASC alloy is a useful starting point to understand the mechanisms present in most useful Nb-Si alloys. MASC alloy has composition Nb-25Ti-8Hf-2Cr-2Al-16Si by atomic percentage. It contains all of the elements considered important to an alloy with balanced material properties. It is likely that an alloy useful as a turbine blade will at least somewhat resemble MASC, so understanding the oxidation mechanism of MASC and similar alloys provides useful insight in how to improve oxidation resistance.

Mathieu et al attempted to refine the oxidation mechanism, which until that point had been rudimentary [22]. The primary oxide formed was TiNb₂O₇, which forms by the

reaction shown in Equation 9. This reaction has been theorised to have several steps including formation of an intermediate oxide $Ti_2Nb_{10}O_{29}$. The reaction sequence is shown in Equation 10 [79].

$$5Nb_2O_5 + 2TiO_2 = Ti_2Nb_{10}O_{29}$$
$$3TiO_2 + Ti_2Nb_{10}O_{29} = 5TiNb_2O_7$$

Equation 10

Crystallographic evidence of silicon based oxides was not found, but this was theorised to be the result of the formation of amorphous silicates. Evidence for Si-O-Si bonds as well as other silicate bonds have been found by IR spectroscopy in the same MASC alloy [58].

As with binary Nb-Si alloys, two regions of oxidation are present in MASC alloy and other similar alloys, independent of oxidation time and temperature [73, 78]. The first is an oxide scale, present as the outer-most layer. The original microstructure is maintained, with the solid solution and silicide phases oxidizing to form different oxidation products. The solid solution phase forms the TiNb₂O₇ oxide. This is alongside any Nb₂O₅ and TiO₂ that has not reacted with the intermediate Ti₂Nb₁₀O₂₉ also detected in some alloys [45]. Often undetected but likely present are oxides of Cr and Al, which partition to this phase. It is thought that the silicide phase forms amorphous silicates, along with the primary TiNb₂O₇ oxide and small amounts of TiO₂ and Nb₂O₅. Hf partitions primarily to this phase so Hf oxides are present here. This scale is always porous in nature, resulting in a linear oxidation rate. Cracking occurs due to stresses caused by different thermal expansion coefficients of the base alloy and the oxide scale, mismatches rates of oxidation between phases may also play a role [72]

The second layer was an internal oxidation zone, present between the outer oxide scale and the unaffected base alloy. Diffusion of oxygen through the solid solution phase results in a large internal oxidation layer with oxygen 'solubility' in the Nb_{ss} near 40 at.%. Whilst the Nb_{ss} can support dissolved oxygen in the matrix, the limit is around 8 at.% for pure Nb [80]. Most of the additional mass comes from nano-oxides. As oxygen diffuses through the Nb_{ss} it is able to react with the more reactive elements in the Nb_{ss}, such as Al and Ti. This is clearly visible under back-scatter SEM, where the decreased density of Nb_{ss} results in less backscattered electrons. This mass increase causes a volumetric expansion, estimated at 15%, in the Nb_{ss}. This places stress on the silicide phases, which between 700-1000°C causes cracks parallel to the surface boundary to form. At these temperatures the silicides are still brittle and easily succumb to the stress caused by the volumetric expansion of the Nb_{ss}. These cracks provide oxygen with an energetically favourable route into the sample, further increasing oxidation rates. Above 1100°C, the silicides possessed sufficient plasticity to absorb this stress without cracking. Figure 15 shows the theorised oxidation mechanism for MASC alloy at both 815°C and >1100°C.



Figure 15- Oxidation Mechanism for MASC Alloy [22]

4 Experimental Procedure

4.1 Fabrication using DMD

4.1.1 Materials

Throughout all builds, elemental powder of 99.5% or greater purity was used. This powder was supplied by Sigma Aldrich. Mesh size ranged from 170 - 325 depending on the availability of powder; the mesh size for each powder used can be seen in Table 3.

Element	Mesh Size	Purity %
Nb	325	99.8
Ті	325	99.7
Si	325	99+
Cr	100	100
Al	325	99.7
Мо	100	99.9
Zr	100	99.2
Y	40	99.5
Та	100	99.9

Table 3 – Mesh Size and Purity of Elemental Powders

Intended alloy chemistries were created using this elemental powder. All the chemistries created in this study can be seen in Table 4. Stoichiometric calculations were performed to determine the weight ratio of powders, converting from atomic percentage as seen in Equation 11.

$$Wt. \%_{element} = \frac{\left(\frac{At. \%_{element} \cdot A_{r_{element}}}{N_0}\right)}{\sum_{i=1}^{n} \left(\frac{At. \%_i \cdot A_{r_i}}{N_0}\right)}$$

Equation 11

Powders were then weighed out and combined, mixing manually under an argon environment. Some of the powders, such as aluminium powder, arrived in a small amount of liquid to prevent spontaneous combustion. Therefore, the powder mix was then dried in an oven at 80°C for 3 hours to remove this liquid. Once dried the powders were placed in a MITR xxx Ball mill for a continuous period of 2 hours. This was to ensure homogeneity of the powders prior to deposition.

Alloy Name	Alloy Composition (at.%)
Chemistry A	Nb-24Ti-18Si-5Cr-5Al-2Mo
CAZ-1	Nb-24Ti-18Si-5Cr-5Al-2Mo-1Zr-0.08Y
CAZ-5	Nb-24Ti-18Si-5Cr-5Al-2Mo-5Zr-0.4Y
TCAZ-1	Nb-24Ti-18Si-5Cr-5Al-2Mo-1Zr-0.08Y-2Ta
TCAZ-5	Nb-24Ti-18Si-5Cr-5Al-2Mo-5Zr-0.4Y-2Ta

Table 4 – Composition, by at.%, of Niobium Silicide Alloys Produced by DMD

4.1.2 Method

A self-constructed direct metal deposition instrument, located in the State Key Laboratory of Solidification Processing in Xi'an, PR of China, was used to fabricate all samples. A schematic of this instrument can be observed in Figure 16.



Figure 16 - Schematic diagram of direct metal deposition (DMD) setup

The instrument was equipped with a Laserline LDF-6000. This was a continuous beam diode laser emitting primarily in the 1080 nm \pm 20 nm wavelength. The maximum achievable power was 6 kW, though the power output could be adjusted. The spot size could range between 2-5 mm with a beam parameter product of 6 mm mrad, meaning there was some divergence from a standard diffraction limited Gaussian beam. The processing parameters used to form all alloys discussed in this document are listed in Table 5.

Table 5 – Direct metal deposition processing parameters

Parameter	Value
Laser Beam Power	3000 W
Laser Spot Size	3 mm
Beam Parameter	6 mm mrad
Scanning Speed	900 mm min ⁻¹
Scanning Strategy	Cross-hatched (See Figure x)
Powder Feed Gas Flow Rate	6 L min ⁻¹

To begin the process, the alloy powder was loaded into the powder feeder, performed quickly to prevent excessive oxidation of the powders. A rectangular plate made from pure titanium was then loaded on the worktable inside the fabrication chamber. This plate measured x by y with a thickness of 10 mm. This plate was to act as the baseplate: an anchor point for the build.



Figure 17 - Cross-hatched scanning strategy employed in the manufacture of all alloys

Once loaded the chamber was the filled with inert argon gas. Argon was used to minimise the reaction of the melted metal with components of air, particularly oxygen and nitrogen. Argon possesses fully occupied valence electron orbitals. This makes forming bonds energetically unfavourable, which is why argon is often used as an inert carrier gas. An oxygen sensor was used to monitor oxygen content in the chamber, which did not exceed 200 ppm during fabrication. Before processing could begin, the STL file, a modified CAD drawing of the intended geometry, had to be loaded into the instrument. The STL file provided the instrument with the instructions on how to create the geometry. A pointing laser was used to align the processing laser with its starting position.

The titanium base plates were pre-heated before processing began to help reduce stress and prevent warping. This was done by de-focussing the processing laser and scanning over the surface of the base plate, for 5 minutes. Once this was completed the processing began, with the build constantly monitored for any sign of cracks or other defects. Once the build was finished, it was left to cool naturally to ambient temperature. Any powder that had loosely adhered to the build was removed using a stiff-fibred paintbrush. The base plates were then removed using wire erosion, performed at EDM Precision Technologies Ltd.

4.2 Post Processing

It is rare that any alloy is used directly after formation or casting. It can be difficult to achieve the intended microstructure as controlling cooling rates in all areas of the material is challenging. It is also difficult to achieve the equilibrium cooling rates that are required when attempting to achieve thermodynamically stable microstructures. Forming metals often results in defects that result in poor material performance. These defects can range from poor surface finish to porosity [81, 82].

To produce the optimal alloy, metallurgists often apply post processing treatments. These treatments improve the alloy by either improving the microstructure or reducing the size or quantity of defects. For example, a typical aluminium alloy has low tensile strength if cast conventionally with no post processing. However, certain aluminium alloys, such as 2xxx or 7xxx series, contain elements that can form θ precipitates if subjected to heat treatment. These precipitates harden the alloy and increase its strength [83].

The post processing applied to the Nb-Si alloys in this study is discussed in this section. Background is provided for each of the technics employed along with the parameters used and the reason for choosing them.

4.2.1 Hot Isostatic Pressing

Hot isostatic pressing (HIP) subjects samples to high temperatures and high pressures. The temperature and pressure used is highly dependent on the alloy system. The temperature must remain below the liquidus of the material to avoid melting; even partial melting can result in the shape of the sample changing significantly. Pressure should also be limited below the compressive strength of the alloy at the temperature employed. This is to avoid warping or cracks forming for excessive stress. Inert gas is used to apply the pressure to the sample. The most commonly used gas is argon but other gases such as helium can be used. Nitrogen is generally not suitable due to potential nitration of the sample surface [84].

The main use for this process in solid samples is to reduce the internal porosity of the sample. Most metallic materials possess some level of porosity after formation. This can enter the alloy in a number of ways, such as trapping of atmospheric gas, desorption of gas during cooling or void formation during solidification. Porosity is detrimental to the overall material properties. The strength reduces as there is less material to resist force. Pores can also act as sites for crack initiation and propagation, increasing the likelihood of fatigue failures and reducing ductility, particularly when located near the surface of the material [85]. This method can reduce the porosity by removing the gas and closing the voids. The mechanism for this is dependent on the solubility of the trapped gas in the alloy and on the position of the porosity.

After initial formation by DMD, the niobium silicide alloys were expected to have internal porosity present. This was confirmed and results are discussed in Dr Allen's thesis [86]. As pores can result in poor material performance, HIP was used primarily to reduce this porosity.

To perform the HIP an EPSI Laboratory Hot Isostatic Press was used, with argon employed as the inert gas to create the isostatic pressure. The HIP parameters used in this study are shown in Table 6. A study into the optimal HIP parameters was performed by Dr Allen, finding the parameters in Table 6 suitable for removing porosity [86]. Before samples were subjected to HIP they were checked thoroughly for cracks and surface pores. If these faults were present during HIP they could have resulted in the sample breaking inside the machine, ruining the sample and potentially damaging the press.

Table 6 – Temperature and pressure parameters used in the hot isostatic pressing of Nb-Si alloys in this study

Temperature	Pressure	Temperature	Pressure	Hold	Time
(K)	(MPa)	Ramp Rate (K	Ramp Rate	(hrs)	
		min ⁻¹)	(MPa min ⁻¹)		
1593.15	150	20	2	6	

The ramp rate for temperature and pressure were used to ramp up at the beginning of the cycle and to ramp down after the 6 hour hold time had been achieved.

4.2.2 Heat Treatment

Heat treatment is a common process used through-out the metallurgy industry. Cooling rates in primary production are rarely close to equilibrium cooling rates. This can result in phases and percentage of phases different to that suggested by the phase diagram for the material in question. There may also be desirable phases present at elevated temperatures that disappear at lower temperatures. Heat treatments are versatile processes that can potentially treat both of the aforementioned issues and others depending on the material [87].

The simplest heat treatment is an anneal. During an annealing heat treatment, the material is elevated to a high temperature and held at this temperature until close-to equilibrium phases are achieved. This temperature is often close to, but not equal to or above, the liquidus temperature of the material. Increased temperature means that solid state diffusion can occur much more readily, allowing a sample to reach its equilibrium state at that temperature. Once finished, the metal cools to room temperature.

Other, more complex heat treatments exist which can have several stages, where the length of time and temperature used will vary significantly depending on the material and the desired outcomes. Aluminium alloys are subjected to a variety of heat treatments; an alloy's designated name states the heat treatment used. Alloy 7075 is a high strength but high cost Al alloy. It is available in different tempers, three of which are 0, T6 and T7. 7075-0 has had no heat treatment and has the lowest tensile strength of the three above tempers. 7075-T6 is heat treated with an initial hold at 450°C for several hours, followed by a quench then a further heat treatment at 120°C for 24 hours. This particular heat treatment yields the highest yield strength of the three, as the heat treatment allows the formation of finely dispersed particles of eta and eta' phases. 7075-T7 is heat treated with and initial hold at ~110°C for several hours then another hold at ~170°C for 24 hrs. This

causes the eta precipitates to grow much larger and contribute less towards the yield strength of the material compared to the T6 heat treatment. 7075-T7 is called an overaged alloy because it has been aged past the point of peak hardness [88] [89].

Literature sources for niobium silicide alloys will often state that they have used a particular heat treatment of their alloy. However, most sources do not give reasons or evidence for their selection [90, 91]. In niobium silicides, as discussed in Chapter 2, α -Nb₅Si₃ is the preferred silicide. It is also the last silicide to form and is often not present. This can be caused by factors such as non-equilibrium cooling or elemental additions stabilising β or γ -silicide. DMD will not result in equilibrium cooling rates. Rapid solidification is followed by remelting as new layers are deposited. The cooling rates will not be even across the build, with faster cooling rates at the edges. A high temperature annealing heat treatment with a short time span was employed in this study. The parameters for this heat treatment can be seen in Table 7.

Table 7 – Temperature, time and ramp rate parameters used in the heat treatment of Nb-Si alloys in this study

Initial	Temperature	Hold	Temperature	Hold	Time	Ramp	Rate	(K
(K)		(K)		(hrs)		min ⁻¹)		
298 (Ar	nbient)	1773		5		5		

Once the 5 hour hold finished, the sample then cooled down to ambient temperature. The ramp rate for the cooling stage was not controlled. The intention was to heat treat the samples for a longer duration that that shown. Unfortunately, technical problems with our high temperature furnace limited the heat treatment duration.

4.3 Microstructure Analysis

Analysis of the microstructure was vital in determining the phases present, along with the morphology, elemental composition and phase fraction in the alloy. Several techniques were employed to study the microstructure, which are described in the following section.

4.3.1 Scanning Electron Microscopy

Scanning electron microscopy uses electrons to create an image of the intended specimen. In microscopy, the resolution is ultimately limited by the wavelength of the characterising radiation. For optical microscopy this limit is around 500 nm. Electrons, however, have significantly smaller wavelengths. Using Equation 12, an electron with a rest mass energy of 0.511 MeV accelerated through 15 kV will have a wavelength of ~10 pm. This is

significantly smaller than the wavelength of visible light used in optical microscopy, offering greatly improved resolution.

$$\lambda = \frac{h}{\sqrt{2meV}}$$

Equation 12

In Equation 12, λ is the wavelength, h is the Planck constant, m is the rest mass, e is the charge of an electron and V is the applied voltage. The incident electrons interact with the sample in several ways, which can be detected by components of the microscope. Secondary electrons result from the incident electron removing an electron from an orbital shell. This interaction is limited to the first few hundred nanometres of the samples and is good for identifying surface structures. Back-scattered electrons are incident electrons which have been deflected by atoms in the sample, leaving the sample in the process. This interaction can penetrate several microns into the sample and is heavily dependent on the localised density of the sample. It is also possible to detect characteristic and bremsstrahlung X-rays. The characteristic X-rays are produced when an incident electron removes an electron from an inner shell of an atom, leaving an inner shell vacancy. An electron from an outer shell then drops energy levels to fill the hole. As it does this it emits energy in the form of an X-ray. These X-rays are characteristic of the atom and can help to identify the elements present. This technique is called energy dispersive X-ray detection, otherwise known as EDS.

Two different SEMS were used to gather the SEM images and EDS data seen in this study: an FEI Quanta 650 SEM and a JEOL JSM 7900F. Both SEMs used a field emission gun to generate electrons. Images were captured in the back-scattered electron mode using a solid state copper ring detector, located underneath the electron gun. 15 kV accelerating voltage with a spot size of 5 was used. Characteristic X-rays used to identify the atomic composition of phases was detected using an Oxford Instruments Ultim Extreme detector, which both SEMs had equipped. Oxford instruments AZTEC software was used to process the data from these detectors.

Good sample preparation was important to achieve optimal images from this technique. Samples being prepared for SEM analysis were first mounted in Metprep Conductomount thermoset plastic. This was performed in a Struers mounting press using 150 MPa and 180°C for 5 mins followed by a 3 min cooling stage with water cooling. Once mounted the samples were ground using an Stuers grinding machine with a disc size of 240 mm and a rotation speed set to 250 rpm. SiC grinding papers were used starting with 80 grit then followed by 240 grit, 400 grit, 600 grit, 800 grit and finally 1200 grit. Once ground to 1200 grit the samples were then polished using the same instrument but with the rotation speed reduced to 100 rpm. Multicloth M was used, first with 6 micron diamond suspension, followed by 3 micron and finally 1 micron diamond suspension. Separate cloths were used for each suspension. After each stage of the grinding and polishing, the samples were cleaned using methylated spirit, dried, and inspected using an x optical microscope. The microscope was used to detect the presence of scratches not visible to the human eye. A sample would be deemed ready if no scratches were visible at a combined magnification of x1000 after polishing at 1 micron.

4.3.2 X-ray Diffraction

When electromagnetic waves pass through a slit, an interference pattern is observed if the width of the slit is similar in size to the wavelength of the incident light. Ordered crystal lattices act as slits, with the distance between the atomic planes acting as the slit width. This distance is on the order of angstroms, for which the appropriate wavelength electromagnetic radiation is in the X-ray region. Each crystal will exhibit an interference pattern that depends on the space group and unit cell parameters of the crystal structures present, which depends on the atoms present and the bonds they form with each other. X-ray interference patterns can, therefore, provide structural data on the crystal which has been analysed. Other factors that can alter the interference pattern are the wavelength of the incident X-ray and, if the crystal is anisotropic, the crystal orientation. X-ray analysis of the phases in the alloys investigated in this study had been conducted previously by Dr Allen and was not repeated here. This study focused on the analysis of the oxide scales produced during the oxidation tests.

X-ray diffraction was performed using a Bruker D8 Advanced X-ray diffractometer. Xrays were produced using a copper target, emitting primarily in the x wavelength. Corundum was used as the reference substance. The parameters used when conducting the tests can be seen in table x. Initial scans showed no useful information beyond 100° , so the sample was scanned between 0° and 100° .

The oxide scales were not suitable for grinding and polishing as was done for the samples in Dr Allen's X-ray study. The oxides were brittle and flaked easily, with often only a thin layer remaining on the sample surface. This made it difficult to achieve a flat surface and to remove the oxide layer from the sample surface. Instead the spallated oxides were prepared as powders. The oxide scales were first removed from the underlying metal and brushed into a pestle and mortar. They were then ground until particles were fine, with individual particles difficult to distinguish. Following this they were ground for a further 5 mins to ensure a small particle size and minimal chance of anisotropic particle alignment, which would affect the resultant diffraction pattern. The prepared powder was then poured into the sample holders, shown in fig x. A flat surface was essential for a good diffractogram and this was achieved by using a glass slide to compress the powder. This formed a flat surface that was level with the top of the sample holder. Once completed, the sample was then ready for X-ray diffraction. The X-ray diffractogram was then analysed in Bruker's EVA software, with peaks matched using crystallographic open database [92-96].

4.3.3 Muon Spectroscopy

Techniques such as EDS and X-ray Fluorescence are popular and widely used in the analysis of elemental composition, and can provide accurate atomic compositions of a given sample. However, both these techniques require significant sample preparation for optimal results. Whilst the technique itself is non-destructive, the sample preparation can be. These techniques can also only analyse near surface structures, which may not be reflective of the whole sample. Further preparation of samples would be required to build an accurate representation of an alloy.

Negative muon spectroscopy can analyse materials without the requirement for sample preparation, preventing potential destruction of important elemental evidence. A negatively charged muon acts like an electron, the key difference being that a muon is more massive than an electron. When negatively charged muons interact with a material, they replace an electron in a given orbit. This muon will then drop orbital levels towards the atomic nucleus, releasing high energy X-rays as the muon loses energy. Just as in EDS, the energy of the X-rays emitted indicate a particular energy change, such as a K α line. In EDS the energy of X-ray produced is usually between 1-20 KeV, whereas in muon spectroscopy X-rays have energies ranging between 0.1-8 MeV. The high mass of the incident muons and the high energy of the resultant X-rays means sample analysis can occur much deeper into materials, with analysis up to 1 cm into dense materials such as copper shown to be viable [97].

Negative muon spectroscopy was carried out at the ISIS Neutron and Muon Source using the CHRONUS instrument, part of the RIKEN RAL muon spectroscopy facility. A material reference of known atomic composition was required for full analysis. This was created using elemental powders, with the atomic composition of Chemistry A, seen in Table 4. The powders were weighed using a Mettler Toledo ME104E analytical balance in an argon atmosphere. They were then sealed in a glass vessel and mixed in an x mixer for two hours to ensure homogeneity of the powder. The powder was then transferred to an aluminium foil packet under argon, with all open ends subsequently sealed. The actual samples required no preparation other than removal from the baseplates, which was done by EDM Precision Technologies using wire erosion.



Figure 18 – Schematic of the negative muon spectroscopy set up

Figure 18 shows the experimental setup. Samples were hung in an aluminium foil packet perpendicular to the line of the muon beam. Detection of this foil was minimal and could easily be accounted for. Sites, or spots, for analysis were marked on the foil and lined up with the muon beam path using a pointing laser. High energy and low energy X-ray detectors were placed at 45° angles from the sample surface. Detectors were also placed behind the sample, but the sample detectors were not useful for this experiment. A lead collimator that reduced the beam width to 15mm was place in the muon beam outlet to control the size of the area analysed. Muon momentum of 50 MeV/c was used for all

spots except for the internal spot, number 4. Higher momentum of 100 MeV/c was used to allow the beam to penetrate further into the sample. Once ready, the samples were subjected to negative muon analysis for 12 hours per spot. This was the time with which no further spectrum changes could be detected in the reference powder. Any beam downtime was accounted for, so each spot was analysed for the same amount of time. The location of the spots analysed can be seen in Figure 19.



Figure 19 – Location of spots analysed by negative muon spectroscopy

4.4 Thermal Properties

Understanding the nature of the microstructure can provide insights into how a material may behave. However, it is not currently possible to reliably relate the microstructure to material properties. To know the properties, mechanical, thermal or electrical testing must be conducted. The thermal tests conducted for this study are detailed in the following section.

4.4.1 Oxidation

As discussed in Chapter 3, oxidation resistance at high temperature is a key area to improve for niobium silicide alloys, so measuring this property was essential to this study. The most common way to quantify high temperature oxidation resistance is to subject the sample to a pre-defined oxidative environment for a set period of time. More complex heating cycles, such as cyclic oxidation, can also be performed. The mass change is then measured either after the test or is tracked over the course of the test. It is important to measure the surface area of the sample beforehand so that the oxidation rate constant can be calculated. This calculation will change depending on whether a linear or parabolic function is observed, as described in Chapter 3.

Oxidation resistance in this study was found using isostatic heating in air, performed in an Elite TS1200 furnace. Each alloy was tested at 800°C and at 1200°C. 10 samples were prepared for each test, with one sample removed every 10 hours, resulting in a test 100 hours in length. Samples were prepared by cutting cuboids of dimensions ~ 4 mm x 4 mm x 10 mm. These cuboids were then ground to an 800 grit finish. This was in order to be comparable to the oxidation observed in Geng et al [75]. The 10 samples were then cleaned in methylated spirit using a sonic bath to remove any surface contamination. Exact dimensions, measured using callipers, were used to calculate the surface area of each sample. The initial mass of each sample was placed in individual bags with the surface area and initial mass recorded, along with a number. This number indicated in what order the samples were to be removed from the furnace. They were then placed in individual alumina crucibles and put into the furnace. The furnace was then switched on and the test commenced. The parameters used can be seen in Table 8.

Run	Start	Hold	End	Hold	Ramp rate
	Temperature	Temperature	Temperature	Time (hrs)	(°C min ⁻¹)
	(°C)	(°C)	(°C)		
1	25	800	25	100	5
2	25	1200	25	100	5

Table 8 – Heating parameters during the heat

When removing the samples, the crucible was placed on a heat proof mat and an alumina lid was quickly placed over the top. Removing the samples from a high temperature furnace into air caused thermal shock in the oxide layer, which resulted in a violent spallation, hence the need for a lid. This was left to cool before the mass was re-measured using the Mettler Toledo ME104E analytical balance.

Cross-sections of some samples were analysed using SEM, as described in 4.3.1. Oxide and internal oxidation zone thicknesses were measured using the FEI software. A minimum of 9 measurements taken from 3 separate locations on the sample were used to obtain average values.

5 Assessment of Macro-segregation in Nb-Si Alloys using Negative Muon Spectroscopy

5.1 Introduction

The primary focus of this research is to improve the oxidation properties of Nb-Si alloys. To achieve optimal oxidation properties from an alloy, it is important that the chemistry is uniform. Uniform chemistry will result in an alloy that, in theory, will oxidise evenly across the surface and provide the best conditions for forming a dense, stable oxide layer. However, metal processing comes with the inherent risk of a phenomena called macrosegregation.

Macro-segregation is a major cause of defects in metallic materials. Macro-segregation was first noted in cast ingots, where areas of a steel ingot were noted to be rich or poor in certain elements [81]. These defects cause non-uniform material properties which can weaken the material. More recently, welds have been investigated for macro-segregation with some evidence that welds with poor mixing can be susceptible to macro-segregation [98].

Laser additive manufacture is a series of laser welds which are used to build a geometry. After deposition of one layer, a subsequent layer is formed on top. This partially remelts the initial layer, resulting in mixing and eventual fusion of these layers. Macrosegregation of elements has not been investigated in this type of manufacture. It is likely that the turbulent mixing conditions that exist in the weld and the short time in the liquid state have convince researchers this is not worth investigating. Most researchers use prealloyed powder when investigating the variations of laser additive manufacture [55, 99, 100]. This further reduces the risk of macro-segregation as the elements have already been mixed.

However, when researching alloy compositions it is more cost effective to use elemental powders. This makes it easier to vary the chemical composition for alloys without committing to the purchase of large quantities of powder for a single alloy system. However, using elemental powders relies on the effective mixing of the powders to produce a homogenous powder. If this is not achieved then the resulting product will have variable properties where the elemental composition is different, similar to the effects of

macro-segregation. Our case study is a niobium silicide alloy produced by direct metal deposition using elemental powders.

To determine the macro-segregation in the niobium silicide alloy, negative muon spectroscopy will be employed. This uncommon technique aims negative muons, produced by protons colliding with a carbon target, at the desired sample. As discussed in Chapter 4, these muons act as heavy electrons and displace electrons in the outer shells of atoms present in the sample. The muon then travels down energy states towards the nucleus, releasing high energy x-rays as it falls down each energy modified state. This provides a characteristic x-ray spectrum, just as would be observed in EDS. A schematic of this can be observed in Figure 1. The advantage of this technique is the high energy of the x-rays produced.

In EDS the energy of the x-rays produced are on the order of 1-30 KeV. In negative muon spectroscopy, due to the greater mass of the muons, the x-rays produced are on the order of 0.2-10 MeV. This allows much deeper penetration into the sample, up to 1 cm in dense materials such as iron. It is possible to control the penetration depth of the analysis by controlling the momentum of the muons. This circumvents the need for sample preparation, which can cause damage. Even light elements with mass greater than lithium can be detected using this technique, providing the ability to assess the oxygen content of the samples if present in the required concentration.

5.2 **Results and Discussion**

5.2.1 Macro-segregation Analysis

5.2.1.1 Muon Spectroscopy

Figure 2 shows the muon spectrogram of spot 3. Only the high energy detector spectrogram was shown, with the low energy detector spectrograms available in the appendix 1.1. Elements niobium, titanium and silicon were detectable on each spectrum. The peak positions of key energy levels used for identification of the elements and in the subsequent analysis are labelled for each element. This was the M_a transition peak for Nb (231.5 KeV), the L_{α} transition peak for Ti (189.5 KeV) and finally the K_{α} transition peak for Si (400 KeV). These peaks were selected as they were detectable in both the high energy and low energy detectors and were strong emission peaks. Though the samples also contained aluminium, chromium and molybdenum, it was not possible to detect these elements reliably. The low concentration of these elements and high background noise both contributed to this difficulty.



Figure 20 – Negative muon spectrograph of the centre spot (spot 3) of the sample of Chemistry A with the primary peaks for Nb, Ti and Si labelled



Figure 21 - Muon count, relative to NbMa peak, of titanium and silicon in the reference powder and spots 1-4

Figure 4 shows the ratio of peak height of the silicon K α peak and titanium L α peak relative to the niobium M α peak for each spot analysed. There was a clear difference between the relative peak ratios observed for the reference powder and the sample. Titanium content appears higher and silicon content appears lower when comparing the sample to the reference powder. The powder had not undergone any manufacturing process, so had not been subjected to the losses that can occur. Some elements are volatile and will evaporate away from a surface, such as Cr [101].



Figure 22 - Graphical presentation of linear relationship of peak ratios. C is assumed to be 0

Use of a reference powder meant it was possible to calculate a factor that related the peak ratio to the elemental ratio of two elements, given we had a known composition and known peak ratio from our results. The reference powder had composition Nb-25Ti-18Si-5Cr-5Al-2Mo, the same as Chemistry A before manufacture. With only Nb, Ti and Si detectable, the atomic composition was normalised concerning only those elements finding a ratio of 51.13Nb:28.41Ti:20.45Si. Further normalising showed an Nb:Ti ratio of 9:5 and an Nb:Si ratio of 5:2. The decimal value of this ratio was then divided by the decimal value of the peak ratio, the output was the factor m from the linear algebraic expression y=mx+c. A graphical representation was plotted and shown in Figure along with values of m. Previous research has showed that composition is linearly proportional to the X-ray fluorescence values, from which the peak ratio is determined [97, 102]. This means that this relationship will also be roughly linear in nature. With the value of m determined for Nb:Ti, Nb:Si and Ti:Si it was now possible to calculate the ratio of Nb:Ti:Si for all the other spots analysed. Figure 23 shows the normalised composition for each spot.



Figure 23 – Normalised concentration of Nb, Si and Ti, measured by negative muon spectroscopy

We observed no significant difference in elemental distribution of Ti or Si between spots 2-4, labelled as the diagram in Figure 23 shows. This strongly suggested that there was no significant macro-segregation in the xy plane, if the build direction is taken as the z direction. So although some of the differences appeared relatively large in Figure 21, once the composition was calculated the majority of these differences reduced in apparent magnitude. Research has shown that although macro-segregation can occur in laser welding, it was only observed when there was poor mixing of the weld pool [Refs]. In additive manufacture a deposited layer solidifies, as in a weld, but is then remelted as new material is deposited above, mixing with this new material. This turbulent environment appeared to have thoroughly mixed the liquid, and resulted in an even distribution of elements.

The scan strategy played a key role in achieving this mixing of elements. A cross-hatched scan strategy, as seen in Figure 17, was employed. The direction of travel of the laser beam, and therefore deposition, is always perpendicular to the previous layer. This is likely to increase the uniformity of elemental distribution, as convection currents

generated by the melt pool acted in perpendicular directions. With partial remelting of each layer, the elements get tumbled in several different directions before finally solidifying permanently.

Spot 1 appeared to show minor composition differences, with a reduction in Si concentration and an increase in Ti concentration. Spot 1 was located at the top of the build where the process ended. This part of the build cools rapidly and the top layers are not remelted. This rapid cooling could make some elemental segregation in this area more likely. The turbulent flows in the melt pool would act over decreased timespan. There is a distinct lack of mixing that other parts of the sample do not experience. There is also the possibility of residual, partially melted powder, both sinking into the melt pool before it solidifies and sticking to the surface.

Only Spot 5 showed a significant difference in elemental composition, with decreased Ti content. This spot was located at the base of the build, ~4 mm above the titanium base plate, as shown in Figure 19. In castings, macro-segregation occurs whilst the alloy is liquid. Castings often remain liquid for sufficient time to allow mechanisms such as convection currents or solute partitioning to occur, resulting in macro-segregation. However, in this process solidification occurred rapidly with only a short periods in the liquid state. This would not have given much time for such effects to occur. Also, as discussed above, the turbulent melt pool during remelting and remixing suggested that during the liquid stage a uniform distribution of elements is achieved. It was thought unlikely that solid state diffusion had a significant effect. During processing the build was subjected to high temperatures as melted material was deposited. High temperatures do increase the rate of diffusion, as shown in Fick's first law of diffusion in Equation 13.

$$J = -D\frac{\partial C}{\partial x}$$

Equation 13

However, the temperature of the build decreases with distance to the top layer, with the temperature gradually decreasing over this distance. Whilst the bottom of the geometry would be heated for more time, an estimated final temperature of less than 400°C would not result in significant effects from solid state diffusion. Therefore, the most probable cause of this difference lay in the elemental distribution of the powder before formation.

The elemental powders were mixed thoroughly in the required ratios as stated in the experiments section. However, once loaded into the hopper for distribution into the DMD instrument, there would have been further mixing. When beginning a build, the hopper was turned on as the instrument warmed up, which took 5 minutes in total. This resulted in vibrations from the hopper, shaking the powder. When particles of a similar size are mixed in this way, more dense particles will tend to sink towards the bottom and less dense particles rise to the top. With a density of 4.51 g cm^{-3} , titanium is less dense than niobium, at 8.57 g cm⁻³ [103]. It is thought that this short time of additional mixing could have resulted in a reduced titanium content in the bottom of the powder feed. This, in turn, resulted in reduced titanium content in the initial part of the build. This would suggest that silicon content should also have been reduced at this stage. However, silicon was only available at the time in a smaller particle size than the niobium and titanium. Size is also an important factor in mixing of powders [104]. When particles of the same density are mixed, the smaller particles segregate towards the bottom of a given container. Not only this, but the high surface free energy of the silicon powder could have encouraged it to stick to nearby particles, which may have helped to prevent the same mixing segregation observed for titanium.

5.2.2 Microstructure and EDS

Muon spectroscopy is potentially a powerful analysis tool and has seemed to provide sensible results. However, this technique is in its infancy and is not established as a standard analysis. EDS works on the same principle as negative muon spectroscopy, but uses electrons rather than muons to induce emission of X-rays. Therefore, an EDS assessment of spots 3 was completed to qualify the results from the negative muon spectroscopy.



Figure 24 - Microstructure of as-formed Chemistry A used for negative muon spectroscopy

Figure 24 shows microstructure image equivalent to spot 4. The image was typical of a MASC-based Nb-Si alloy, with an Nb_{ss} and two Nb₅Si₃ structures, β and γ , forming a three phase system. A large pore was observed towards the left of the image, this was ignored for elemental analysis. The micrographs showed clear signs of micro-segregation in the Nb_{ss} phase, thought to be an uneven distribution of Ti. There were also pores present, which were theorised by Allen to be primarily trapped gas pores [86].

5.2.2.1 Phase analysis

Figure 25 shows EDS maps of the image in Figure 24





Figure 25 - EDS maps of NbMa (top left), SiKa (top right) and TiLa (bottom) peak transitions also used in the muon spectroscopy

The maps show a uniform distribution of elements, other than where Si and Ti have partitioned preferably to a particular phase. A series of analyser analyses were performed to determine the average chemical composition of this area. The average result can be seen in Table 9.

Table 9 - Composition, by atomic %, of the sample analysed by EDS

Nb	Ti	Si	Al	Cr
51.29	24.96	18.72	3.07	2.26

This lead to an Nb:Ti:Si ratio of 54.00:26.28:19.71, or in other terms and alloy with 54% Nb, 26.28% Ti and 19.71% Si. This compared to a relative composition of 55.36Nb-30.58Ti-14.07Si. The Nb content matches well, with both the EDS and muon data showing similar relative concentration. The is just over 4 at.% difference between the Ti and Si concentrations. EDS, even when using several sites, was only able to measure a relatively small area. The area the muons measure was 2.5 mm in diameter so would include a larger portion of the sample. This is likely the biggest factor in the discrepancy observed.

4 at.% was a relatively small difference, especially when compared to composition difference between the spots. Spot 1 and spot 4 had a Si compositional difference of over 5 at.%, and this looked minor in Figure 23, even though this was discussed at length.

5.3 Conclusions

There was a clear difference in the composition of the main sample and the reference powder. This is most likely to result from the processing, silicon powder lost during various stages of powder preparation and on travel through the DMD instrument. Si is not likely to have volatised away. There was no apparent macro-segregation visible in the X-Y plane of the build, despite strong evidence of macro-segregation in the microstructure. Rapid solidification caused this micro-segregation but was also the reason no macro-segregation was observed, with remelting and remixing in perpendicular directions also likely to have inhibited macro-segregation.

Small deviations in composition were observed at spots 1 and 5, the top and bottom of the build respectively. It was though that poor mixing and rapid solidification at the top of the alloy contributed to the slight changes in normalised composition. The reduction of titanium in at the base of the build is most likely to have resulted from non-uniform distribution of elements in the powder. This was caused by vibrational mixing in the hopper before laser forming began.

The chemical composition detected by EDS did not agree entirely with the negative muon results. However, the discrepancies were relatively small at around 4 at.% difference from the Ti and Si relative concentration. This was less than the difference between spot 3 and spot 1 Ti and Si content, where even this only was a minor change. The Nb relative concentration agreed to within 2 at.%,

With minimal changes in relative composition through-out the tests spots and with a good agreement with the EDS results suggest that DMD will be a suitable technique to create Nb-Si samples that are mostly free from large-scale elemental segregation.

6 Effect of 3D Printing on the Properties of Niobium Silicide Alloys

6.1 Introduction

With niobium silicide alloys proving difficult to produce by conventional investment casting, AM could offer an alternative means of production. There are few examples of niobium silicide alloys being produced by additive manufacture in the literature [55, 105]. There are not currently enough sources to determine the viability of additive manufacture for niobium silicides. As shown in Chapter 2, there are numerous parameters where even small changes can affect the resulting alloy. Understanding the effect of each parameter enables researchers to optimise each one, producing the optimal build. Many of these parameters including laser power, laser spot size and gas flow rate are being investigated by Mr Qian and a detailed study of these parameters will be included in their thesis.

However, this chapter, and the following chapter, focussed on a set of standard parameters that were investigated by both Dr Feitosa and Dr Allen's theses, and are listed in Table 5 [86, 106]. These standard parameters have been shown to result in uniform and regular microstructures that showed good response to post-processing treatments. Other parameters that were attempted resulted in either less desirable microstructures or faults during laser formation, such as hot-cracking or layer-spreading. Because the DMD method used required elemental powders, oxygen contamination during powder preparation, loading and forming is a likely. Small concentrations of oxygen can have a detrimental impact on materials properties including oxidation resistance [100]. As discussed in Chapter 3, niobium silicides will need to be resistant to oxidative attack at temperatures >1350°C to become a viable alternative to nickel-based superalloys. It is one of the major challenges yet to be overcome in niobium silicide research. With this in mind, the study set out to quantify the effect of DMD on oxidation properties of the alloy Chemistry A.

Chemistry A was formed standard set of parameters listed in Table 5, followed by a HIP treatment and a heat treatment, shown in table y and table z respectively. The composition of Chemistry A is defined in Table 4. The composition of this alloy is typical for a niobium silicide alloy with balanced properties. This alloy chemistry was taken from Geng et al, named JG3-HT in the source [107]. JGC-HT was produced using vacuum arc

remelting, providing this study with a reference processing technique to compare to. The microstructure and oxidation properties were investigated, providing data to compare AM with vacuum arc remelting. . Chemistry A alloy was oxidised according to the procedures in Chapter 4. The literature values for vacuum arc melted Chemistry A was used as a reference point.

6.2 Results and Discussion

6.2.1 Post-Processing Microstructure

Figure 26 shows the microstructure of Chemistry A after all processing was completed. This includes the laser forming, hot isostatic press and heat treatment. It should be noted a detailed study of the alloys after laser forming and after hot isostatic pressing was produced by Dr Allen and will not be repeated here [86].



Figure 26 – Microstructure of Chemistry A after heat treatment for 5 hrs at 1500°C, captured using backscattered electron SEM

There is a uniform morphology with four distinct phases observed. Nb_{ss} formed the matrix, producing the lightest coloured phase due to the high relative density of the phase. Two silicides were produced, β -Nb₅Si₃ and γ -Nb₅Si₃. In the alloy produced by Geng et al, only the β -silicide was formed [107]. The alloy was heat treated for a longer period which would aid in changing any γ -silicide to β -silicide. The γ -silicide was the darker of the two phases due to increased Ti content. Elemental analysis of the phases, shown in Table x, showed a significant segregation of Ti to the γ -silicide compared to the β -silicide. The γ -silicide has a similar crystal structure to Ti5Si3, shown in Table 1. Below 882°C,

pure titanium is most thermodynamically stable in the HCP A3 crystal, so this element is likely to segregate preferably to phases in the HCP configuration [108].



Figure 27 – Binary thermodynamic assessment of the Ti-Nb binary alloy system [109]

Finally, a small amount of a dark phase rich in Ti was formed. This phase was thought to be an α -Ti phase. The α -Ti phase shows high Ti content with only small quantities of other elements consistently present. The binary Nb-Ti phase diagram in Figure 27 shows that small quantities of α -Ti can form over most Nb:Ti ratios. This phase resided inside or at the grain boundaries of the Nb_{ss} and was not observed forming inside either silicide. This supports the idea that this phase formed from the Nb_{ss} rather than from either silicide.

Phase	Phase composition (at.%)						Fraction
	Nb	Si	Ti	Al	Cr	0	%
Nbss	65.6	-	22.3	4.8	7.3	-	39.70
α- Nb5Si3	47.0	33.8	16.7	2.3	0.2	-	53.42
γ- Nb5Si3	40.2	33.0	22.9	2.8	1.1	-	7.44
Tiss	3.8	0.3	61.5			34.2	0.41

Table 10 – Phase composition and phase fraction of Chemistry A after heat-treatment

Further evidence for this came from the EDS analysis performed on Chemistry A using the Bruker dual detection system attached to the Zeiss SEM. This analysis consistently showed the presence of titanium, oxygen and small amounts of niobium. Importantly, oxygen content was too low to suggest the phase was entirely TiO₂. On average, it appeared this phase possessed a Ti:TiO₂ ratio of 3:1. The presence of oxygen in this phase did suggest, however, that this phase was acting as an oxygen scrubber. As can be seen in the Ellingham diagram in figure x, formation of TiO₂ from Ti has a lower Gibbs energy than Nb₂O₅ formation from Nb. When oxygen diffuses through the matrix, Ti will more readily react, forming TiO₂ oxide. Such a phase had not been report in the paper by Geng et al or in other literature for similar alloys [107, 110, 111]. The high titanium content of Chemistry A could contribute to the formation of this phase.

6.2.2 Oxidation Behaviour at 800°C

6.2.2.1 Appearance and Microstructure Morphology

Figure 1a-c shows the progression of oxidation at 800°C for Chemistry A. After 20 hrs of oxidation, a darkening the surface was observed, forming a dark grey scale. After 100 hrs a patchy oxide was formed with areas of golden oxide inter-dispersed with dark grey areas. The change in colour is theorised to be due to a conformation change of the oxide from low temperature conformation γ to a combination of high temperature conformations, α and β , in an irreversible reaction [67]. Oxide product formed from the 100 hr sample was relatively soft, forming a powder-like substance where it has spalled. Oxide still adhered to the substrate was continuous but easily broken.

When observed under SEM, Figure 28a, a thin oxide layer was seen, which appeared to mimic the microstructure of the bulk. Beneath this was an internal oxidation zone (IOZ), observable through a darkening in contrast of the Nb_{ss} phase and cracking in the silicide blocks. This IOZ was 10 μ m ± 1 in thickness. This agrees with previous research performed by Mathieu et al [112], whereby this darkening of the Nb_{ss} was attributed to the formation of nano-oxides by the more reactive elements such as Ti, Cr and Al.



Figure 28 – Microstructure of Chemistry A after a) 20 hrs and b) 100 hrs at 800°C in static air, captured using backscattered electrons SEM

Figure 28b showed an oxide similar in thickness to the 20 hr sample. However, this was caused by spallation of the oxide. The IOZ increased in thickness to 40 μ m, which is to be expected, with the same darkening of the Nb_{ss} observed. At 800°C there was not enough energy available for oxides that form to move and coalesce into larger phases. Beyond the boundary of the IOZ the bulk microstructure appeared unchanged at both time-scales. However, EDS analysis of the α -Ti phase, shown in Table 11, after 100 hrs shows much higher oxygen content. Increased oxygen content was detected up to 400 μ m from the oxide/IOZ interface. This shows that oxygen had been able to diffuse far into the sample, reacting with the α -Ti when it reached the phase. Diffusion along grain boundaries, has been shown to be more rapid than volume diffusion in many materials
including niobium [113]. Short circuit diffusion theory also showed that this type of diffusion is common in metal corrosion [65]. It is possible that the oxygen diffused rapidly through the sample along the grain boundaries until it reaches the α -Ti phases, reacting when it arrived. Diffusion of oxygen through TiO₂ is also rapid at high temperature so when oxygen reached a fully reacted α -Ti phase it would pass through quickly [74].

Table 11 - Phase composition of the alpha Ti phase after 100 hrs oxidation at 800°C

Phase Composition (at.%)					
Nb	Si	Ti	Al	Cr	0
6.9	1.5	32.6	0.5	0.3	58.3

6.2.2.2 Oxide Scale Components

The SEM images in Figure 28 showed a small but dense oxide layer at the surface with separate oxide systems appearing to form from each bulk phase. EDS analysis, seen in table x, shows that the oxide areas formed from Nb_{ss} are rich in Nb and Ti, suggesting formation of TiNb₂O₇ oxide. The oxide areas formed from the silicides were high in Si content which suggested either a complex Nb-Ti-Si oxide, or the formation of SiO₂ alongside other Nb and Ti based oxides. EDS could not look into the chemical composition of the complex formations described above. It was not possible to detect oxide phases forming from the α -Ti, with no areas showing spikes in Ti content. This is likely to be caused by the reaction of TiO₂ and Nb₂O₅ to form the more complex oxides.

X-ray diffraction after 100 hours shows the presence of 4 main oxide components; TiNb₂O₇, Nb₂O₅, TiO2, and finally intermediate compound Ti₂Nb₁₀O₂₉. The results of the XRD can be seen in Figure x. The powder pattern produced contained broad peaks with relatively low counts per second and high background. Firstly, this indicated that there was a transition occurring in the oxide. This would explain the change in oxide scale colour from dark grey to golden. It is thought that a transition could have occurred from amorphous forms of Nb₂O₅ and TiNb₂O₇ into high temperature conformers α/β .

Secondly, the XRD results could explain why SiO₂ was not detected in any of its common crystal forms. SiO₂ is known to exist in amorphous forms at temperatures below 500°C, such as opal or opal CT [69], but is not generally observed at 800°C. However, research has shown that amorphous silica coating can remain stable up to 1000°C, with no

crystallisation observed after 5000 hrs at 800°C [114]. It is, therefore, highly likely that SiO₂ was present in an amorphous form. This has been observed in other Nb-Si alloys, with IR spectroscopy confirming the presence of Si-O-Si bonds [58].

As noted in Chapter 4, the 20 hr sample did not produce enough oxide for XRD analysis. This showed that Chemistry A oxidised in a similar manner to JG3, the reference alloy made by vacuum arc melting, forming similar oxide products. However, in the reference alloy SiO_2 was detected, suggesting that Chemistry A from this study possesses a mechanism that either prevented or slowed the crystallisation of SiO_2 , though this mechanism is not understood yet.

6.2.2.3 Mechanism

The mass gain per unit area vs time graph in Figure 29 shows an initial parabolic regime until 30 hours, followed a linear regime that lasted until the test ended. The rate constant for each regime is shown in table x. When the linear regime was compared to the value obtained by Geng at el for JG3-HT, there did not appear to be a significant difference in values. They also obtained a parabolic rate constant but for the as cast JG3. Although not a direct comparison and to be used with caution, the values obtained are again, similar in magnitude. The comparison cannot be assumed direct because as cast samples tend to perform better under oxidative conditions.



Figure 29 – Mass gain per unit area vs time plot showing the oxidation curve of Chemistry A at 800°C over 100 hrs.

The parabolic regime gave way to a linear regime at 30 hrs. The values for the rate constants can be seen in Table.

Table 12 – Oxidation rate constants for Chemistry A after 100 hrs oxidation at 800°C. JG3 values are included for comparison

Sample	Parabolic Rate	Linear Rate	Critical
	Constant k _p (g ² cm ⁻	Constant kı (g cm ⁻	Oxidation Time
	⁴ s ⁻²)	² s ⁻¹)	(hrs)
Chemistry A	5.910x10 ⁻¹²	1.877x10 ⁻⁸	30
JG3-HT (ref) [107]		8.000x10 ⁻⁸	-
JG3-AC (ref) [107]	2.5x10 ⁻¹¹		-

This is further evidence that supports the theory of a transition from amorphous to β/α Nb₂O₅/TiNb₂O₇. It appears that after 30 hours of oxidation a critical point is reached. Once this point, named the critical oxidation time (COT), is reached enough energy is available for the conformation change of the primary oxides. Oxidation of Nb-Si alloys

causes stresses in the oxide layers that form, which increase of the oxide grows. In these samples it may be possible that once the COT was reached there was sufficient stress energy available for the atomic repositioning to occur. The change in structure was accompanied by the volumetric change discussed in Chapter 3. So once the transition occurred the outer oxide stated forming cracks and spallation product. Once cracks began to form the rate controlling step changes from diffusion through the outer oxide layer to direct surface reaction with oxygen. The new crystal configuration of the primary oxides proved to be detrimental and was not able to heal these cracks and prevent further cracks from occurring.

The presence of the critical oxidation time and the appearance of a think oxide layer in Figure 28a showed that it was likely that during initial oxidation, a dense, uniform oxide layer was present and prevented direction reaction of oxygen with the surface material. This may be a mechanism that could be manipulated to either prolong or indefinitely extend the oxidation time before the COT is reached.

Based on the above results and drawing on previous literature research a mechanism for oxidation of Chemistry A was devised, shown in Figure 31 – Microstructure of Chemistry A after a) 20 hrs and b) 100 hrs at 1200°C in static air, captured using backscattered electron SEMFigure 31.



Figure 30 - Oxidation mechanism at 800°C for Chemistry A

Figure 30 is based on the mechanism described by Mathieu et al [112] with some modifications, taking into account the parabolic to linear change that was observed. Firstly a layer of dense, amorphous oxide forms at the oxide/sample interface. This results in protection of the oxide from direct reaction with oxygen, but diffusion still occurs. This means an IOZ is still able to form. This causes expansion in the Nb_{ss} due to nano-oxides which results in cracking of the oxides. Stresses build up in the oxide due to mismatch grow-rates of the individual phases and mismatch in thermal expansion. This strain puts the oxide layer in a higher energy state. Eventually, the internal energy from the stresses are sufficient to cause a conformation change in the primary Nb₂O₅/TiNb₂O₇ oxides, crystallising from an amorphous formation into either the α or β forms, or a mixture of the two. This has been termed the COTT in this study. The volumetric change associated with this transformation causes spallation, linking surface cracks with the internal cracks from the silicides. There after a linear regime takes over, with the crystalline oxides more susceptible to stresses causing constant formation of cracks and spallation.

6.2.3 Oxidation Behaviour at 1200°C

6.2.3.1 Appearance and Microstructure Morphology

At 1200°C golden oxide formation was observed after 20 hrs and was a continuous formation on the surface. This would suggest either that there was no transformation between conformers or that the transformation occurred earlier than 20 hrs of oxidation, yet the 10 hour sample also showed only golden oxide formation. To test this another sample was added for one hour of oxidation, with only the golden oxide formed. The same, continuous oxide was observed for 100 hrs oxidation time, but there was significantly more oxide product, as was expected. This evidence suggested no conformation change occurring and that the initially formed primary oxide remained unchanged through-out the test. The oxide product formed at 1200°C, though fractured, was harder than the product formed at 800°C. This is likely due to increased crystallinity, as crystalline solids tend to be harder and more brittle than amorphous solids. It was difficult to find areas of adhered outer oxide scale for both 20 hr and 100 hr samples, shown in Figure 31. This was because of severe pesting once samples were removed from the furnace, induced by thermal shock.



Figure 31 – Microstructure of Chemistry A after a) 20 hrs and b) 100 hrs at 1200°C in static air, captured using backscattered electron SEM

The IOZ was thicker than the 800°C sample at both timescales, 50 μ m ± 5 at 20 hrs, 128 μ m ± 11 at 100 hrs. This was not unexpected as the increased energy available to oxygen atoms allowed the atoms to more easily overcome the energy barrier to volume diffusion. Rather than forming nano-oxides, as seen at 800°C, the nano-oxides appear to agglomerate into discrete precipitates that form inside the Nb_{ss}, comprised primary of Tibased oxides when analyses by EDS. This is likely to be caused by the increased energy available to the atoms and compounds, which allowed them to overcome the energy barriers to diffusion, eventually encountering other oxide particles and coalescing. Oxide particles are not miscible in the Nb_{ss} matrix and would be at a lower energy state when in an oxide phase, which helped to drive the coalescence of the particles. This may have increased the number of grain boundaries present, which could have assisted in increasing the diffusion rate of oxygen because, as discussed before, diffusion along grain boundaries is more rapid.

6.2.3.2 Oxide Scale Components

SEM images showed the oxides to be porous in nature, a known property of Nb-based oxides [67, 68]. Close inspection showed complex formations in each 'phase'. Spheroidal formations observed in the oxide formed from the silicides, hence known as the silicide oxide. The size of the spheroids increased towards the oxide surface. This could be caused by partitioning of the oxides present in this 'phase'. A mixture of light and dark amorphous areas in the oxide formed from the Nb_{ss}, hence known as the Nb_{ss} oxide. This is theorised to be dark areas of TiO₂, with the primary Nb₂O₅/TiNb₂O₇ oxide in the lighter phase. EDS was not able to conclusively confirm this as the phase size was too small, the EDS spectrum containing contributions from surrounding phases. Porosity was present primarily in the Nb_{ss} oxide, though there was some present in the silicide oxide. This porosity was present from near the oxide/IOZ interface, suggesting porosity forms quickly as the oxide is formed.

XRD, performed on Chemistry A subjected to a 100 hr heat treatment at 1200°C, found similar components to the 800°C. The XRD peaks for Chemistry A at 1200°C were much sharper and had more counts per second than the 800°C sample obtained. This indicates that no conformation changes were occurring and that most, if not all components of the oxide were crystalline in nature. It was now possible to detect silica, present in the cristobalite form, though it is unclear whether it is the α or β form. The study by Coley et al found that above 900°C and after 5000 hrs, all amorphous silica has crystallised [114].

Sufficient energy was present at 1200°C to ensure the silica product formed was crystalline.

6.2.3.3 Mechanism

Figure 32 shows the mass gain per unit area over time for Chemistry A at 1200°C. Rather than the two stage parabolic to linear curve observed at 800°C, now a single parabolic curve was detected. This was evidence that the rate controlling process for the entire experiment was diffusion of oxygen through the outer oxide layer.



Figure 32 - Mass gain per unit area vs time plot showing the oxidation curve of Chemistry A at 1200°C over 100 hrs Though the oxide spallated away after removal from the furnace, it was firmly attached before this point, with no dislodging observed we handling the samples. The evidence suggests that a continuous oxide scale formed, preventing the direct reaction of oxygen with the sample surface. This has been observed in several other Nb-Si alloys including JG3-HT [107, 115]. The value of the rate constant can be seen in Table 13

Table 13 - Oxidation rate constants for Chemistry A after 100 hrs oxidation at 1200°C. JG3 values are included for comparison

Sample	Parabolic Rate Constant	Linear Rate Constant
	k _p (g cm ⁻² s ⁻¹)	kı (g cm ⁻² s ⁻¹)
Chemistry A	1.343×10^{-10}	-
JG3-HT (ref chem) [107]	-	6.7x10 ⁻⁷

Interestingly the mechanism appeared to have altered at 1200°C when compared to the reference chemistry, with a linear regime observed for JG3-HT. The reason for this change is unclear. However, in the study by Geng et al, the data appears to curve, particularly towards the start of the data. It is also possible that in the reference data, a parabolic function may have been present. However, this is the judgement made by the research team and the curve was close to a straight line that would be expected for a linear regime [107].

Compared to an alumina or silica scale, the parabolic curve changes slowly and did not indicate complete protection. The porous nature of the scale that formed, shown well in Figure 31a, meant that oxygen could be transported more rapidly through the voids and gases present. Secondly, whilst the cracking and pesting seen at 800°C is much reduced, there was still evidence of cracks forming in the oxide layers. These cracks would also allow oxygen an easier pathway through the oxide.

6.3 Conclusions

Conclusions on the heat treated microstructure remain similar to A. Allen [86]. However, new insights into the formation of α -Ti phase, along with formation of TiO₂ show that Ti acts in a more thorough oxygen scrubbing mechanism that previously considered.

Oxidation at 800°C showed a two phase oxidation curve, with an initial parabolic function that lasted until a critical oxidation time was reached at 30 hrs, then followed a linear function for the remaining test. The reference alloy only exhibited a linear function. The change in regime, alongside colour changes observed in post oxidation images at 20 and 100 hrs, suggested a transition occurring in the oxide. This was thought to be an amorphous Nb₂O₅/TiNb₂O₇ changing to crystalline α/β forms. The linear obtained for Chemistry A compares favourably with the reference alloy JG3-HT, with some improvements likely due to reduced heat treatment time.

At 1200°C, a parabolic rate constant was observed. This was thanks to the formation of a continuous oxide scale that adhered to the surface until spalling after the test finished. Chemistry A, again, compared favourably to JG3-HT as the later was determined to have a linear rate constant.

Overall, this part of the study appeared to confirm that for alloys with chemistry similar to JG3-HT, such as Chemistry A, manufacture by DMD did not result in poorer oxidation performance. Whilst there were some microstructural changes and differences in oxidation mechanism, the impact was either neutral or, in some case, of minor benefit to the alloy. This meant the next stage of the study was able to progress with relative confidence in DMD as a method of manufacture.

7 Effect of Zr, Y and Ta on the Properties of Niobium Silicide Alloys

7.1 Introduction

With the effect of additive manufacture on the performance of chemistry A assessed, the study now moved on to improving oxidation properties. Elemental additions of Zr, Y and Ta were added, as described in Chapter 4.

Zr is commonly used in other alloying systems, such as steels or superalloys, in small quantities (>> 1 at.%). It is not used to improve oxidation resistance but as an impurity scrubber, removing elements such as O, S and N from the melt. Zr has potential as a useful element to increase oxidation resistance. At temperatures above 1000K the Gibbs energy of formation for Equation 14 becomes lower than for Equation 15 [116].

$$Zr_s + O_{2g} = ZrO_{2s} \ \Delta G_{1200 K} = -871.5 \ kJ \ mol^{-1}$$

Equation 14

$$2Al_s + 1.5O_{2_g} = Al_2O_{3_s} \ \Delta G_{1200 K} = -863.4 kJ \ mol^{-1}$$

Equation 15

Formation of an alumina layer is considered the Holy Grail for an oxidation resistant alloy, as discussed in Chapter 3. A lower Gibbs energy for zirconia formation means an oxide film should form quickly to protect the alloy. However, Gibbs free energy is not the only consideration when choosing an element to improve oxidation resistance. Many oxide, like Nb₂O₅, have several conformations that are stable at different temperatures. When these rearrangement include a volumetric change, this can induce stresses into the oxide and cause spalling. Zirconia undergoes several reversible conformation changes as temperature changes, which are shown in Figure 33.



Figure 33 - Temperature-dependant conformation changes of zirconia [117]

The conformation change at 1440 K has a density change with an associated volumetric change [118]. This causes cracking and spallating of any oxide film, which is poor for oxidation resistance. However, research into thermal barrier coatings has shown that by adding yttria to the zirconia it is possible to stabilise either the tetragonal or cubic forms. A 4 at.% addition of yttria will stabilise the tetragonal form and an 8 at.% addition stabilises the cubic form [119]. Another factor in the poor oxidation resistance of niobium alloys is the disparity in thermal expansion of the base metal and the oxide layer, as described in Chapter 3. Tetragonal stabilised zirconia has a similar thermal expansion coefficient to pure niobium, which is the same BCC structure as the Nb_{ss}. It will always be difficult to match the expansion of the silicide phases, which show anisotropic expansion coefficients. However, matching the thermal expansion of the Nb_{ss} could assist in reducing spallation of the oxide layer. From the above information tetragonal-stabilised zirconia has the potential to help improve the oxidation resistance of the alloy.

Tantalum is a common addition to nickel-based superalloys, with additions of up to 4.18 at.% [5]. The additions are tantalum are primarily used to promote the formation of γ ' and are not considered important in oxidation resistance. The primary tantalum oxide that forms at high temperature is Ta₂O₅, which exhibits the same monoclinic crystal structure as Nb₂O₅ and undergoes similar conformation volumetric changes [67]. As a result, cracking and spallation of this oxide occurs in Ta alloys and it would appear this addition would not be beneficial to oxidation resistance. However, BCC Ta has a lower oxygen diffusion coefficient than BCC Nb, with the relative values shown in Table 1 [120].

Table 14 – Oxygen diffusion coefficient in pure Nb and pure Ta

Material	Oxygen diffusion coefficient (cm ² s ⁻¹)
Nb	3.17x10 ⁻⁴
Та	2.05x10 ⁻⁴

Additions of Ta may prove beneficial if they can slow the diffusion of oxygen, which is the primary oxidation mechanism when oxidation above 1000°C is considered. The alloys investigated are listed in Table x. The values obtained for Chemistry A were used as a reference point to compare the effect of the elemental additions on the oxidation performance of these alloys.

7.2 Microstructure after Post-processing

7.2.1 Effect of additions of Zr, Ta and Y

Figure x shows the microstructure of alloys CAZ-1 and CAZ-5 after heat treatment. These, and all other alloys in this chapter, were analysed after laser forming and post HIP by both A. Allen and L. Feitosa in their respective theses and will not be discussed here [86, 121]. Heat treated alloys were also discussed by A.Allen, but are discussed here again to relate the oxidation data to the initial microstructure and to include the new theories on the α -Ti phase.





Figure 34 - Microstructures of CAZ-1 (top left), CAZ-5 (top right), TCAZ-1 (bottom left) and TCAZ-5 (bottom right) after HIP and HT, captured using backscattered electron SEM

CAZ-1 maintains a similar microstructure to Chemistry A with the Nb_{ss}, β Nb₅Si₃, γ -Nb₅Si₃ and α -Ti all presented by this alloy. The amount of γ -Nb₅Si₃, the darker of the two silicides, has increased and accounts for x% of the phase fraction. More γ -Nb₅Si₃ remained after heat treatment, whereas Chemistry A only maintained small quantities of this silicide. Zr is in the same column, of the periodic table as both Ti and Hf. When present in sufficient amounts, these elements promote the formation of γ -silicide. It is likely that Zr behaves in a similar way to these elements and promoted the formation of γ -silicide.

Further evidence is provided by CAZ-5, where after heat-treatment there was only γ -Nb₅Si₃. The increased amount of Zr further promoted the stabilisation of the γ -silicide, with 5 at.% enough to prevent the α or β -Nb₅Si₃ formation entirely. CAZ-5 had a significantly different morphology to Chemistry A, with angular blocks of γ -Nb₅Si₃ in an Nb_{ss} matrix. It is unlikely that such formations would be beneficial to fracture toughness as the larger, elongated silicide blocks would be more susceptible to cracking when under load. Angular phases can also result in stress concentrations because of the sharp edges and corners. No α -Ti was present in CAZ-5 which was thought to be caused by the dominance of γ -Nb₅Si₃. This silicide is able to accommodate a higher at.% of Ti than the α or β silicides, shown clearly by the EDS analysis and in literature sources [refs]. With no excess Ti solidified in the Nb_{ss}, there was no drive for the formation of the α -Ti phase seen in Chemistry A and CAZ-1.

Additions of Ta, shown in Figure x, appear to have little effect on the microstructure of CAZ-1, with few differences noted in TCAZ-1. However, when comparing TCAZ-5 to CAZ-5, it was clear that Ta additions had promoted stabilisation of the β -Nb₅Si₃. The microstructure reverted back to one more similar to Chemistry A, though without the α -

Ti phase. When studying the EDS it could be shown that whilst Ta partitions primarily to the Nb_{ss}, it also partitioned in significant quantity to the β -Nb₅Si₃. Whereas it was not reliably detectable in the γ -Nb₅Si₃, showing Ta had preference for the β -Nb₅Si₃ and would be likely to stabilise that phase.

7.3 Oxidation Behaviour at 800°C

7.3.1 Appearance and Microstructure Morphology

Oxidation of all chemistries at this temperature resulted in samples that looked similar to Chemistry A when visually inspected, with a dark grey scale formed after 20 hrs, followed by a patchy golden oxide scale after 100 hrs. Images of these are not shown here as there were no differences to compare that were visible by eye. This initially indicated that there was little difference in the oxide scale formed at this time. After 100 hours, the golden oxide layer developed by the alloys easily spallated into a fine-powder. This showed immediately that the additions of Zr and Ta had not prevented pesting behaviour after 100 hours oxidation.

After 20 hours oxidation all chemistries showed an oxidation microstructure typical of Chemistry A, with a thin or barely present outer oxide and an IOZ several micrometres thick. Inside this IOZ the silicide phases were cracked and the Nb_{ss} showed the typical darkening due to ingress of oxygen.



Figure 35 – Microstructures of CAZ-1 (top left), CAZ-5 (top right), TCAZ-1 (bottom left) and TCAZ-5 (bottom right) after 20 hrs oxidation at 800°C, captured using backscattered electron SEM

The formation of cracks are one of the primary causes of spallation at 800°C. None of the new elemental combinations were able to prevent this from occurring. Zr additions, as shown by EDS in table x, partitioned exclusively to the silicide phases, with no detectable levels in the Nb_{ss}. Zr was not able to scrub oxygen from this phase and reduce the IOZ. Ta did partition into the Nb_{ss}, the lower value for oxygen diffusion coefficient suggested this may assist in slowing down the formation of the IOZ. This did not occur and expansion of Nb_{ss} was able to crack the silicides. It would appear that a uniform layer that is resistant to oxygen needs to form at the interface between the oxide and the bulk material, as happens with additions of Sn [57].

After 100 hours the thickness of the outer oxide appeared the same thickness, though this was due to spallation of the oxide rather than a reduction in alloy oxidation. The IOZ had grown in depth from several micrometres to over 40 micrometres in most cases.



Figure 36 - Microstructures of CAZ-1 (top left), CAZ-5 (top right), TCAZ-1 (bottom left) and TCAZ-5 (bottom right)after 100 hrs oxidation at 800°C, captured using backscattered electron SEM

7.3.2 Oxide Scale Components

X-ray diffraction showed that CAZ-1 was similar to Chemistry A. If zirconium-based oxides were present it was not possible to detect them. This suggested little change to the outer oxide scale with either Zr-based oxides present in small quantities or Zr forming

small amount of complex oxides. EDS mapping of this alloy showed Zr detected throughout the oxide layer. With the affinity of Zr to the silicide phases, particularly the γ conformer, it was unexpected to find no concentration of Zr where the silicide oxide formed. Transport of Zr-based oxides must occur in the oxide layer, allowing them to spread through the layer. Y was not able to be detected, the concentration far below the limits of current EDS instruments.



Figure 37 - X-ray diffractograms of all alloy chemistries after 100 hrs oxidation at 800°C. Phase identification is identical to Chemistry A unless otherwise labelled.

CAZ-5 showed signs of ZrO₂, either in the cubic or tetragonal form. This suggested the either via additions of Y or via another mechanism any ZrO₂ present had been stabilised

to either the tetragonal or cubic conformer. This is discussed further when 1200°C oxidation is considered.

7.4 Mechanism

Oxidation curves of all alloys are shown in Figure 38, including Chemistry A for reference. All curves follow the same general pattern as the Chemistry A curve, an initial parabolic regime which is followed by a linear regime after a critical time is reached. As before, this suggested an initial diffusion controlled, in turn suggesting formation of a protective outer oxide before a change in mechanism whereby direct reaction with the surface became the primary reaction mechanism.



Figure 38 - Mass gain per unit area vs time plot showing the oxidation curve of all chemistries at 800°C over 100 hrs This change suggested an oxide with cracks and prone to spallation, just as Chemistry A alloy showed. The rate constants can be seen in Table.

Alloy	Parabolic Rate	Linear Rate Constant	COTT (hrs)
	$Constant k_p (g^2 cm^{\text{-}4} s^{\text{-}}$	$k_p (g \text{ cm}^{-2} \text{ s}^{-1})$	
	²)		
CAZ-1	5.910x10 ⁻¹²	1.296x10 ⁻⁸	30
CAZ-5	5.046x10 ⁻¹²	2.399x10 ⁻⁸	40
TCAZ-1	4.917x10 ⁻¹²	2.621x10 ⁻⁸	40
TCAZ-5	4.860x10 ⁻¹²	2.993x10 ⁻⁸	50
Chemistry A	4.959x10 ⁻¹²	1.877x10 ⁻⁸	30
(ref)			

Table 15 – Oxidation rate constants and critical oxidation transition times for all alloy chemistries during oxidation at $800^{\circ}C$

CAZ 5 showed a small benefit in the linear regime, with a reduced rate constant. The small addition of Zr meant that no strong microstructural changes occurred. The small additions of Zr were able to scrub oxygen whilst not impacting other oxidation pathways. EDS did show that Zr partitioned to the silicide, so it was unlikely that Zr was scrubbing the Nb_{ss} phase. However, other research has demonstrated that the reaction front between the oxide and the metal only occurs once the silicides have been consumed. The Zr additions may have prevented the front from moving as quickly as it normally does by preferentially reacting with the oxygen. It is thought that this was also occurring in CAZ-5. However, the poorer oxidation performance was caused by the enlarged silicide blocks. These larger silicides were more susceptible to cracking, with stress concentrations more pronounced. The images in Figure 35 and Figure 36 appear to support this, with larger and deep cracks shown in the CAZ-5 images.

TCAZ alloys exhibited linear rate constants significantly worse than the reference, Chemistry A. TCAZ-1 showed heavy cracking in the IOZ layer after both 20 and 100 hrs at 800°C. TCAZ-5 also showed severe IOZ cracking and had the largest of the linear rate constants. Clearly, Ta additions have a negative impact on the cracking of silicides in the IOZ. The mechanism for this is not yet understood.

Interestingly, the elemental additions appeared to have an impact on the value of the COTT, the values for which can be seen in Table 15. The addition of 1 at.% Zr did not impact the COTT. Minimal changes in the microstructure and XRD pattern suggest Zr at

this concentration had minimal influence of the resultant alloy. So it was expected for no impact here. CAZ-5 did, however, show an improvement of 10 hours in the COTT. In Chapter 6 it was suggested that the COTT was the result of a change in oxide conformation. Additions of Zr at 5 at.% may have stabilised this low temperature amorphous oxide, which then required increased energy before crystallising. This suggest that Zr interacts with the primary oxides of Nb₂O₅/TiNb₂O₇. This could be via incorporation of ZrO₂ into one of the primary oxides. Alternatively it is possible...

TCAZ-1 and TCAZ-5 also showed an improvement in this transition, resulting in a COTT of 40 hrs and 50 hrs respectively. This clearly shows that Ta has a stronger beneficial influence of the COTT than Zr additions, increasing the transition temperature with 2 at.% additions. It is well-known that Nb and Ta form similar oxide systems, with the Ta₂O₅ crystal conformers similar to those of Nb₂O₅. It is also known that Nb₂O₅ and Ta₂O₅ can form oxide complexes, such as $2Nb_2O_5 \cdot Ta_2O_5$, which forms an I4/m tetragonal structure [67]. Formation of such complexes was not confirmed, with lack of data available on the crystallographic open database or elsewhere [93]. However, it does suggest that Ta oxides incorporated into the primary oxide structure, making the resulting oxides more resistant to the conformation change.

The overall oxidation mechanism was very similar to that proposed for Chemistry A in Chapter 6 for low alloy chemistries CAZ-1 and TCAZ-5.

7.4.1 Oxidation Behaviour at 1200°C

7.4.1.1 Appearance and Microstructure Morphology

When the chemistries were oxidised at 1200°C for 20 hrs, a golden-coloured oxide formed over the whole surface of the material. This was true of all the chemistries tested. The oxide was a solid layer, not powder-like as the samples were at 800°C. This solid layer catastrophically spallated into small fragments when removed from the furnace due to thermal shock. This closely mimicked the observations for Chemistry A.

After testing for 100 hrs significant oxidation was observed. The oxide layer remained golden suggesting a similar configuration of the primary oxides after both 20 hrs and 100 hrs. No dark grey scale was observed at this temperature, again behaving in a similar manner to Chemistry A

After 20 hrs under oxidation all samples exhibited microstructures with a deep IOZ over x microns in depth. This showed that the increased energy available at this temperature allowed oxygen to diffuse greater distance into the materials. Some samples showed remaining outer oxide in places, but this was not consistent across all areas, with all chemistries showing areas with spallated oxide and areas where oxide remained. The outer oxide still resembled the microstructure beneath, with areas of Nb-rich and Si-rich oxides forming.



Figure 39 Microstructures of CAZ-1 (top left), CAZ-5 (top right), TCAZ-1 (bottom left) and TCAZ-5 (bottom right)after 20 hrs oxidation at 1200°C, captured using backscattered electron SEM

Despite some spallation after removing from the furnace, all the chemistries maintained at least some of the other oxide layer. This suggests that adherence of the oxide scale on this time scale is good and likely helps prevent direct reaction of oxygen with the surface.

When CAZ-5 was inspected at a higher magnification, the silicides near the surface appeared to undergo a complex oxidation process. Formation of sub-micron areas of a dark phase appeared to form before incorporation into the oxide. This resulted in a highly porous oxide phase forming from the silicide. The γ -silicide has higher content of Ti that an α or β -silicide. The dark areas forming are likely to be area of titanium rich oxide that form before assimilation into the oxide layer. This is not dissimilar from the formation of areas of Ti-rich oxides that form in the Nb_{ss}, which can also be observed in this alloy and the others.



Figure 40 – High magnification microstructure of the outer oxide and IOZ for CAZ-5 after 20 hrs at 1200°C, captured using backscattered electron SEM

After 100 hrs at 1200°C severe oxidation had resulted in significant 'consumption' of the Nb_{ss} located in the IOZ, with large areas of Ti-rich oxides present on all areas of this phase. The depth of the IOZ had only increased marginally, which suggested that equilibrium reaction rate of oxygen with the materials was achieved quickly, not long after 20 hrs.



Figure 41 - Microstructures of CAZ-1 (top left), CAZ-5 (top right), TCAZ-1 (bottom left) and TCAZ-5 (bottom right) after 100 hrs oxidation at 1200°C, captured using backscattered electron SEM

All the samples now lost the majority of their surface oxide when spallation occurred. The CAZ-5 sample did have some remaining oxide, but this was not a uniform coating and significantly spallation product was produced. Lack of surface oxide made EDS analysis a challenge for these samples, so data is included where it was possible to get results.



Figure 42 - X-ray diffractograms of all alloy chemistries after 100 hrs oxidation at 1200°C. Phase identification is identical to Chemistry A unless otherwise labelled.

7.4.1.2 Oxide Scale Components

XRD patterns for the chemistries gave similar results to chemistry A, particularly for alloys CAZ-1 and TCAZ-1. For these alloys there were no changes in the crystal structures that were detectable.

As with at 800°C, the Zr concentration was too low to have a significant impact on the oxide components. EDS point analysis did not detect Zr in the oxides of these two alloys, so it was clear that Zr had not agglomerated into areas of ZrO_2 . Ta was likely to have incorporated into the Nb-based primary oxides. This would not be likely to significantly alter the XRD patterns observed and was not detected in this study. It may be possible to use Rietvield analysis to refine the peaks and potentially detect the presence of Ta_2O_5 incorporated into the Nb primary oxides.

CAZ-5 and TCAZ-5 both showed signs of small amounts of ZrO_2 in either a cubic or tetragonal structure. As with 800°C, it was not possible to determine which conformer was present. The X-ray diffractograms also showed that some peaks, located at 18.5 and 24.3 either disappeared or where severely reduced in peak height. Nb₂O₅ was the compound responsible for these peaks. High Zr content seems to have reduced the amount of this compound that was present. This strongly suggests that either Zr or ZrO₂ catalyses the reaction of Nb₂O₅ and TiO₂, which forms TiNb₂O₇, as shown in equation and equation.

EDS mapping performed on CAZ-5 and TCAZ-5 appear to show Zr and Y agglomerating to similar areas in the microstructure. This would make the stabilisation of ZrO_2 more likely as Y₂O₃ would also form in these areas. This means that formation of stabilised ZrO₂ oxides was possible in this alloy system, though which form was stabilised is hard to determine from the XRD pattern. It is not thought that other oxides where formed with Zr at this stage.



25µm



Figure 43 - EDS mapping of CAZ-5 after 20 hrs oxidation at 1200°C showing agglomeration of Zr and Y to similar areas in the IOZ

7.5 Mechanism

Figure 44 shows the oxidation curves of all chemistries when subjected to 1200°C for 100 hrs, Chemistry A is added in for reference.



Figure 44 - Mass gain per unit area vs time plot showing the oxidation curve of all chemistries at 1200°C over 100 hrs All chemistries demonstrated a single, parabolic regime, indicating the presence of a continuous oxide that protected the oxide to at least some extent. The parabolic functions confirm that diffusion of oxygen was the rate-controlling step at this temperature.

Alloy	Parabolic Rate Constant k _p (g ² cm ⁻⁴ s ⁻²)
CAZ-1	1.644x10 ⁻¹⁰
CAZ-5	1.667x10 ⁻¹⁰
TCAZ-1	8.333x10 ⁻¹¹
TCAZ-5	1.134x10 ⁻¹⁰
Chemistry A	1.343x10 ⁻¹⁰

Table 16 – Parabolic rate constants for all alloy chemistry during oxidation at $1200^{\circ}C$

The CAZ alloys showed similar oxidation performance to Chemistry A, with CAZ-5 producing the largest rate constant, which can be seen in Table blah. This was a clear indication that increasing Zr resulted in slightly reduced oxidation performance. The large silicide blocks were again, likely to be partially responsible. The large silicides meant that there were also large areas of Nb_{ss} exposed to the oxide interface, allowing

oxygen a large distance to diffuse over readily, before eventually being slowed by a silicide phase.

TCAZ alloys showed markedly improved resistance to oxidation at this temperature. The best performing alloy was TCAZ-1. This alloy was less hindered by the zirconium additions so could produce better results. A potential explanation for this can be found in the introduction for this chapter. EDS shows that Ta partitions to all phases, with a slight preference to the Nb_{ss}. When Nb and Ta mix, Ta can occupy the same lattice positions as Nb, it does not sit interstitially [122] As explained at the start of this chapter, diffusion of oxygen is slower through Ta than through Nb. So with Ta in the Nb_{ss} crystal, the diffusion of oxygen through the Nb_{ss} was inhibited. Evidence for this can be seen when comparing the thickness of the IOZ. CAZ-1 exhibited an IOZ thickness of 151.2 μ m ±7.6. TCAZ-1, on the other hand, exhibited IOZ thickness of 126.8 μ m ± 8.0. This means that the IOZ for TCAZ-1 was just over 16% thinner than the CAZ-1. This is likely to be the primary contributing factor to the marked improvement in parabolic rate constant induced by Ta additions.

7.6 Conclusions

The primary finding in this chapter was the good oxidation resistance, relative to Chemistry A, of alloy TCAZ-5 and particularly TCAZ-1, which showed a parabolic rate constant almost 50% of the Chemistry A rate. This was only found at 1200°C, with Ta seemingly inhibiting the diffusion of oxygen through the Nb_{ss}. This improved oxidation resistance does not quite reach the desired target of 25 μ m surface loss at 1325°C over 100 hrs. But it does show that Ta has great potential as an element useful for high temperature oxidation. It would, however be recommended that it is used with an alloy that promotes good oxidation properties around 800°C, such as Sn. This is because Ta performed poorly at this temperature, with severe cracking of the silicides and large rate constants observed.

Small additions of Zr provided minor benefit to the oxidation resistance at 800°C, with CAZ one with the lowest linear rate constant. This was likely due to the scrubbing effect of Ti, holding up the reaction front and preventing the consumption of both Nb₅Si₃ and Nb_{ss}. Higher Zr concentrations were detrimental and Zr provided no benefit to oxidation properties at 1200°C.

Perhaps the most interesting finding was the ability of both Ta and Zr to change the value of the COTT, both elements able to increase the time before the regime changed from parabolic to linear. Ta had the stronger impact, with just 2 at.% increasing the COTT by 10 hours. This suggests that there may be a way to alter the COTT more significantly, either prolonging the transition further or, ideally, preventing it from occurring. If this could be achieved that would mark a big leap forward for the oxidation properties of Nb-Si alloys.

8 Concluding Statements

8.1 Conclusion

This study began with a two stage assessment in the viability of DMD as a production method for the production of oxidation resistant Nb-Si alloys. The first stage was an investigation into macro-segregation, to determine if additively manufactured material undergoes the elemental distribution defects seen in many casting techniques. This part was a success, with no signs of significant macro-segregation observed. There were areas with minor differences but nothing that would prevent the use of DMD as a production technique. The results found in this section are not just applicable to Nb-Si alloys but also the additive manufacture community. Few studies have been performed in this area and this was the first

The second stage looked into the comparison of two similar alloys; one made by DMD and a literature reference alloy which was produced by a casting method, in this case vacuum arc remelting. As with the first stage, this was successful in confirming the viability of DMD as a method of production. Oxidation rate constants for Chemistry A were marginally better than those of JG3-HT. This may have resulted from the reduced heat treatment time of Chemistry A, but it does take away from the conclusion that alloys with chemistry similar to JG3 can be produced with DMD.

The primary aim of this study was to find new Nb-Si alloys that were more resistant to oxidative attack at high temperature. Not all the alloys investigated achieved this. Zr did have a small benefit at 800°C when at low concentration. However, this addition was not able to prevent silicide cracking at 800°C, and hence not able to stop spalling behaviour. Zr also proved to have no benefit at 1200°C, both concentrations proving marginally detrimental to oxidative behaviour. The other primary addition, Ta, performed poorly at 800°C, with poor linear rate constant and severe cracking in the IOZ and oxide layer. This is not yet understood but it may be linked to an increased amount of Nb_{ss} phase. There was, however, considerable success at 1200°C with both TCAZ alloys, particularly TCAZ-1, showing improved performance compared to chemistry A. This was thanks to the improved resistance to diffusion of oxygen through the Nb_{ss}.

Overall, despite Zr not performing as well as was hoped, improvement to the oxidation resistance of Nb-Si alloys was gained. There was also some interesting mechanism at

play, with a parabolic to linear transition occurring in the 800°C sample. This, as far as the writer is aware, has not been observed before.

In short, this study has shown that DMD is able to produce Nb-Si alloys that are at least as oxidation resistant as a cast counterpart. This can be done without fear of uneven elemental distribution, as the macro-segregation study found no significant evidence of this occurring. Finally, whilst continued investigation of Zr may be questionable, using Ta additions showed minor but significant improvement in the high temperature oxidation resistance of a MASC-based Nb-Si alloys.

8.2 Future Work

As with any study, there were exciting avenues that could not be explored for various reasons. Listed below are areas that may yield interesting results and that would have been explored in this study had there been sufficient time:

- It would have been beneficial to investigate the oxide layers using TEM. Whilst XRD is a powerful tool for analysis of crystal structures, it is not able to identify their location. Equally, EDS or atom probe can identify location of particular ratios of atoms but does not provide information of the atomic arrangements, TEM would be able to do this, with the crystal patterns detected where you point the electron beam. This would help build a more in-depth picture of the structure of the outer oxide.
- 2) One thing this study did not achieve was to analyse the effect of these additions on the material properties, such as fracture toughness, tensile strength and creep. Fracture toughness is of primary concern as this is often the property that is weakened at the expense of improved oxidation resistance. I would recommend to anyone picking up this research to start with material property measurements, particularly for fracture toughness.

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