CHARACTERISATION OF ATI 718PLUS PRODUCED BY WIRE-ARC ADDITIVE MANUFACTURING PROCESS: MICROSTRUCTURE AND PROPERTIES

BY

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ABSTRACT

ATI 718Plus is a $\gamma'$-strengthened variant of the extensively used Alloy 718 which was developed in a bid to enhance the operating temperatures of Alloy 718, in aero-engines and power-plants. To facilitate the application of this alloy, several studies have been performed to investigate the microstructure and properties of ATI 718Plus produced by using the conventional processes that are used to manufacture Alloy 718. However, there is the lack of detailed information on the microstructure and associated properties of the ATI 718Plus produced by additive manufacturing (AM). This research work is therefore carried out to comprehensively characterise the microstructure and the corresponding properties of ATI 718Plus produced by wire-arc additive manufacturing (WAAM), which is a low-cost but high deposition AM technique.

Extensive segregation of the alloying elements is observed in WAAM ATI 718Plus. Alloying elements like Nb, Ti, and Mo significantly partitioned into the interdendritic regions of the deposit promoting the formation of secondary phase particles, identified as the detrimental Laves phase and MC-type carbides. The segregation of Nb and Ti also prompted the inhomogeneous precipitation of strengthening phase ($\gamma'$ and $\gamma''$ precipitates) within the deposit.

In the as-processed condition, WAAM ATI 718Plus display an inferior dynamic impact resistance compared to the wrought ATI 718Plus. This is attributed to the presence of solidification constituents and the inhomogeneous distribution of the strengthening phase precipitates. Similarly, WAAM ATI 718Plus, in the as-processed condition, exhibits a significantly lower hot corrosion resistance in comparison to the wrought alloy. The depletion of Nb and Mo in the dendrite core regions, decreases the local corrosion resistance of the alloy, leading to accelerated degradation of the as-processed alloy.
Based on the understanding accrued from electron microscopy and spectroscopy techniques and in corroboration with thermodynamic calculations, post-deposition heat treatment is developed to improve the microstructure of the additive manufactured alloy. The post-deposition heat treatment comprises a homogenisation treatment prior to the application of the standard heat treatment and aging. A significant improvement is observed in the dynamic impact response and the hot corrosion resistance after subjecting the WAAM ATI 718Plus to the newly developed post-deposition heat treatment procedure.
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DEDICATION

I dedicate this thesis to my Dad, Elder Michael B. Asala and my Mum, Mrs. Roseline B. Asala

for all of their sacrifice to help me succeed.
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CHAPTER 1

1 INTRODUCTION

1.1 Background Information

The need to improve the reliability and performance of aero-engines and land-based power generation gas turbines has necessitated the development of high-temperature superalloys. These alloys are designed to withstand stringent operational conditions in service. A nickel (Ni)-based superalloy called Inconel 718 (typically referred to as Alloy 718) is the most widely used superalloy for structural components in aero-engines. The relative manufacturing ease of Alloy 718 along with its adequate strength and ductility in temperatures of up to about 650°C have been attributed to its widespread use and applications. However, an appreciable loss of strength occurs at temperatures above 650°C due to the instability of the main strengthening phase, $\gamma''$, which precipitates at high temperatures [1]. When higher temperature requirements exceed the capacity of Alloy 718, more expensive and difficult to fabricate alloys, such as Waspaloy (General Electric) and René 41 (Pratt & Whitney) are usually used as a substitute [2]. Unfortunately, the higher cost of the raw materials and difficulty of fabricating these alloys significantly increase the cost of the components.

The demands for increased efficiency and performance of aero-engines and land-based power generation gas turbines mean that they are operated at high service temperatures. Therefore, it is imperative to use a low-cost yet higher-temperature replacement for Alloy 718 while maintaining relatively good processability. To address this need, ATI 718Plus was developed by Allegheny Technologies Incorporated (UNS N07818) [3] and designed with improved thermal stability of approximately 55°C above that normally stipulated for Alloy 718. The improved stability was achieved through significant modification to the composition of Alloy 718 which allows for the replacement of the metastable $\gamma''$ (D0$_{22}$ BCT) precipitates in Alloy 718 with the more stable $\gamma$ (L1$_2$, "bcc").
ordered face-centered-cubic) precipitates as the main strengthening phase in ATI 718Plus. Thus, ATI 718Plus is beginning to serve as a higher temperature substitute for Alloy 718 for aerospace applications [4].

Metal additive manufacturing (AM), the industrial version of 3D printing, has gained significant attention in the manufacturing industries in the last few decades as the production of complex components requires improvement in quality and material utilization. This manufacturing process is generally described as a process of joining materials to make objects from 3D model data, usually built layer-by-layer, as opposed to the traditional formative and subtractive manufacturing processes such as forging and machining [5]. Therefore, the benefits of AM technologies mean that AM can potentially complement or replace traditional manufacturing processes. The AM processes allow for the ease and rapid introduction of new designs and customization, and also help to eliminate the need for tooling and fixtures. The technology enables the fabrication of monolithic components thus eliminating the need for assembling and joining and can also be applied to produce complex metallic shapes, which would otherwise be impractical with the use of other manufacturing processes.

Wire-arc additive manufacturing is a directed energy deposition (DED) AM process that uses wire as the feedstock material and an arc as the energy source. The wire-arc additive manufacturing process offers higher deposition rates in comparison to powder-based processes. Furthermore, the relatively inexpensive additive wires, coupled with the utilisation of low-cost, well-established welding technologies make the wire-arc additive manufacturing process more cost competitive [6]. This is a promising AM technique for fabricating large parts with moderate complexity and especially in adding structural details to simple semi-finished forged parts, thus minimising the
amount of machining that may be required. This is particularly attractive for the manufacturing of relatively expensive, difficult-to-machine superalloy components to minimise material waste.

To facilitate the application of this relatively new superalloy, ATI 718Plus, there is the need for a better understanding of the influence of the manufacturing process on its microstructure and properties. To this end, studies over the last few years have been carried out to understand the processing-structure-properties of ATI 718Plus. Manufacturing processes such as forging, welding, rolling, casting, etc. [7–10] that are traditionally used to manufacture Alloy 718 components have been investigated with relative success on ATI 718Plus. However, to the best of my knowledge, few studies are available in the open literature that detail the microstructural development and properties of ATI 718Plus produced by AM processes. To successfully use AM to manufacture ATI 718Plus components, there is the need for a more in-depth understanding of the microstructural changes and microstructural characteristics of the ATI 718Plus deposit. This information is essential for gaining confidence in the use of this material and the evolving manufacturing techniques for critical functional applications, especially in the aerospace industries. Furthermore, the understanding is also crucial for developing material models which will help to optimize and tailor the material properties for intended applications.

Alloy 718 is a good containment material for the hot section of the turbine engine with the capability to safely contain blade fragments, in an unlikely blade-out event. Similar to Alloy 718, ATI 718Plus is also a candidate containment material that is required to sufficiently withstand dynamic impact loading at high strain rates [11]. The use of this superalloy for other stringent applications could also be realized due to its containment ability. However, during AM processes, the repeated solidification and multiple thermal cycles usually lead to a complex microstructure which can adversely affect the mechanical properties of this alloy. Therefore, to successfully adapt
AM technologies for the manufacture of ATI 718Plus components for critical applications, especially under abnormal loading conditions, fundamental knowledge of the relationships among the AM process, microstructure and mechanical properties need to be established. Furthermore, wire-arc additive manufacturing processes are usually used to fabricate near-net shaped components, which typically suffers from poor surface quality. Follow-on machining is a crucial post-deposition part of the process required to ensure the tolerance and surface quality of the deposited components. Since machining is a high strain rate deformation process, understanding the complex material response during this metal removal process is vital for enhancing the machinability of the deposit. However, the deformation behaviour of this deposited alloy at high strain rates has not been studied in the existing literature.

Ni-based superalloys are utilised as structural materials in turbine engines due to their excellent resistance to oxidation and mechanical stability at high-temperatures. Their resistance to oxidation at high-temperatures is attributed to the formation of a dense and stable protective layer of chromia (Cr$_2$O$_3$) or alumina (Al$_2$O$_3$) on the surface. Nevertheless, this protective oxide layer of chromia or alumina can be damaged which would accelerate the degradation of the superalloy components upon exposure to certain types of salts through a process known as hot corrosion [12]. In some certain cost-effective fuels (for example, heavy fuels), the presence of contaminants such as sodium (Na), sulfur (S), and vanadium (V) is sometimes unavoidable and can lead to the formation and deposition of corrosive salts on turbine engine components in high temperatures [13, 14]. Studies have shown that the reaction of the sulphate (Na$_2$SO$_4$) with other salts, such as vanadium pentoxide (V$_2$O$_5$) or sodium chloride (NaCl) can lead to the formation of molten eutectics at low-temperatures and possibly to the accelerated attack of the components [15, 16].
The microstructure generally observed in heavily alloyed materials like ATI 718Plus and Alloy 718, produced by different AM methods, is significantly different from those typically found in their wrought versions. For example, elemental micro-segregation which leads to chemical and microstructural heterogeneities are common features in the Alloy 718 deposit produced by many AM techniques. It is, however, generally known that the corrosion resistance of a material is dependent on its starting microstructure and the processing history, which invariably dictate the microstructure developed and can significantly influence the corrosion characteristics. To this end, efforts have been directed to understand the influence of the microstructure developed during AM and after post-deposition treatment is carried out on the oxidation and aqueous corrosion behaviour of Ni-based superalloys [17–20]. However, to the best of my knowledge, no studies are available in the open literature on the hot corrosion behaviour of Ni-based superalloys produced by any AM technique. Considering that superalloys are subjected to harsh conditions in service, it is important to investigate and understand the hot corrosion characteristics of these alloys produced by AM processes at their service temperatures.

This research is, therefore, initiated to comprehensively characterise the microstructural development and associated properties of ATI 718Plus superalloy produced by using the wire-arc additive manufacturing technique. The following are the objectives to achieve this aim:

1. to produce ATI 718Plus deposits by using the wire-arc additive manufacturing technique and comprehensively characterise the microstructure developed in the as-processed condition. Furthermore, the microstructural changes during post-deposition heat treatment of ATI 718Plus is also investigated;
2. to evaluate the influence of the as-processed microstructure of WAAM ATI 718Plus on its dynamic impact behaviour in comparison to wrought ATI 718Plus and Alloy 718. The influence of the post-deposition heat treatment on the dynamic impact response is also evaluated; and
3. to evaluate the influence of microstructural and chemical inhomogeneities on the low-temperature hot corrosion behaviour of WAAM ATI 718Plus in the as-processed and post-deposition heat treated conditions, in comparison to wrought ATI 718Plus.

1.2 Research Approach

The various tasks necessary to achieve the set objectives are elaborated below:

1. Different layers of WAAM ATI 718Plus deposit are produced by using the Perform Arc robotic welding system. The purpose of this task is to obtain deposition parameters that are capable of building reproducible deposits with minimal macroscopic defects. Temperature measurement is also done with the aid of a thermocouple to monitor the thermal gyration during the deposition.

2. A comprehensive microstructural characterisation of single layer, single-wall/multi-layer, and multi-stringer bead/multi-layer WAAM ATI 718Plus deposits is carried out by scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron probe micro-analysis (EPMA), and electron backscatter diffraction (EBSD).

3. A novel post-deposition heat treatment will be developed to modify the microstructure of the as-processed WAAM ATI 718Plus for improved properties.

4. A variety of different material preparation procedures will be applied, including machining and heat treatment to produce cylindrical samples for high strain rate deformation testing.

5. The dynamic impact deformation of the alloys will be characterised at high strain rates by using a direct Hopkinson pressure bar.

6. To put the dynamic deformation behaviour of ATI 718Plus into perspective, the dynamic impact response of Alloy 718 and ATI 718Plus is comparatively investigated at different temperatures, strain rates, and heat treatment conditions.
7. The dynamic impact behaviour of WAAM ATI 718Plus in the as-processed and post-deposited heat treatment conditions will be examined and documented.

8. A post-deformation microstructural analysis of ATI 718Plus by using SEM and TEM will be carried out.

9. Several material preparation procedures will be used, including machining and heat treatment to produce coupons for hot corrosion testing.

10. The deposition of corrosive salts onto the test coupons will be done by using a salt spray technique and the test coupons will be exposed to temperatures of 650°C and 750°C.

11. The hot corrosion behaviour of WAAM ATI 718Plus will be characterised in the as-processed and post-deposition heat treatment (PDHT) conditions.

1.3 Summary of Major findings

The first phase of this research involves the detailed microstructural characterisation of ATI 718Plus produced by using the wire-arc additive manufacturing process. Extensive formation of eutectic solidification micro-constituents including Laves and MC type carbide phases, induced by micro-segregation are observed in the as-processed ATI 718Plus. Notwithstanding the significant segregation of niobium (Nb), which has been reported to promote the formation of the δ-phase in ATI 718Plus, only η-phase particles are observed in the deposit. A preliminary investigation on the hardness of the build of the alloy, in the as-processed condition, shows a softened zone about 2 mm in width on the deposited metal heat affected zone (DMHAZ) which is potentially damaging to the mechanical properties. Delayed re-precipitation kinetics and the extent of the precipitation of γ' and γ'' in the DMHAZ which is related to the diffusion of segregated solute elements from the interdendritic regions are attributed to this phenomenon. In
addition, an electron backscatter diffraction analysis shows that the deposited ATI 718Plus has a highly textured grain in the <100> direction.

Based on the understanding from the microstructural analysis, a novel post-deposition heat treatment is developed to modify the microstructure of the deposit. The post-deposition heat treatment comprises a homogenisation heat treatment (at 1100°C/2 hrs) and a solution heat treatment (at 954°C/2 hrs) prior to a double aging heat treatment. This treatment is sufficient enough to eliminate the deleterious brittle phase, homogenise the chemistry of the alloy, ensure the precipitation of a moderate amount of η-phase particles along the grain boundaries and homogenously distribute the γ' precipitates within the deposit.

In the second phase, the dynamic impact response of wire-arc deposited ATI 718Plus is characterised by using a direct Hopkinson pressure bar. This is important to determine the resistance of the ATI 718Plus to damage under high strain rate loading. The experimental results show that the impact resistance of the as-processed ATI 718Plus is inferior to both the age-hardened and annealed wrought ATI 718Plus. This is attributed to the presence of eutectic solidification constituents, especially Laves phase particles, in the interdendritic regions and the inhomogeneous distribution of strengthening precipitates in the deposit. In addition, the as-processed alloy shows a moderate directional dependence.

After subjecting the deposits to the newly developed post-deposition heat treatment, the dynamic response and impact resistance are found to be similar and comparable to those of the wrought ATI 718Plus.

Furthermore, based on the experimental result of high strain rate testing, modified Johnson-Cook and Arrhenius-type constitutive material models are established to describe the flow behaviour of
the as-processed ATI 718Plus under high strain rate deformation. This is particularly important for modeling and optimising the required follow-up machining operations for the deposit.

The last phase of this research elaborates on a study of the influence of the compositional and microstructural inhomogeneities on low-temperature hot corrosion behaviour of wire-arc additive manufactured ATI 718Plus. It is found that ATI 718Plus produced by the wire-arc additive manufacturing process, in the as-processed condition, shows significantly less resistance to corrosion in comparison to the wrought alloy. The depletion of Nb and Mo in the dendrite core regions of the deposit reduces resistance to local corrosion and leads to the selective corrosion of these regions. This is attributed to the overall accelerated hot corrosion attacks on the as-processed ATI 718Plus. However, after the application of the newly developed post-deposition heat treatment, significant improvement in the resistance to hot corrosion can be observed. The overall hot corrosion resistance of the deposit after undergoing the newly developed post-deposition heat treatment is lower in comparison to the wrought ATI 718Plus. A significant amount of NbC that is still found along the interdendritic regions which have been shown to be prone to selective accelerated oxidation may be responsible for the reduced resistance.

This study shows that even though the microstructure and properties of ATI 718Plus are inferior to those of its wrought version in the as-processed condition, a tailored post-deposition heat treatment can significantly strengthen the microstructure.
1.4 Thesis Organisation

This thesis consists of the following six chapters.

- **Chapter 1** provides the background information on this research work, rationale for the study, thesis objectives, research approach and a summary of the major findings.

- **Chapter 2** is the literature review and consists of three (3) sections. The first section provides a detailed review of the physical metallurgy of Alloy 718 and ATI 718Plus. The second section reviews the AM processes, with more emphasis on the DED that uses wire as a feedstock material. The third section is a review of two material properties: high strain rate deformation and the hot corrosion of alloys.

- **Chapter 3** provides a detailed description of the experimental methods and equipment used in this research work. Details on wire-arc deposition, heat treatment, high strain rate deformation, and hot corrosion testing are provided in this chapter.

- **Chapter 4** is presented in three parts. The first part presents the microstructure of wrought ATI 718Plus and a detailed microstructural analysis of ATI 718Plus produced by using the wire-arc additive manufacturing technique. In addition, the influence of post-deposition heat treatment on the microstructure of WAAM ATI 718Plus is discussed. In the second and third parts of this chapter, the influence of the microstructure of as-processed WAAM ATI 718Plus on high strain rate deformation and hot corrosion behaviours at low-temperatures, respectively, is presented and discussed. Furthermore, the effectiveness of post-deformation heat treatment of WAAM ATI 718Plus is evaluated by examining these properties.

- **Chapter 5** provides a detailed summary of the major findings of this research work.

- **Chapter 6** provides some insightful recommendations for future work.
CHAPTER TWO

2 LITERATURE REVIEW

This chapter consists of three (3) sections. The first part is a review on the physical metallurgy of Alloy 718 and ATI 718Plus. To gain a better understanding of the microstructure of ATI 718Plus, a review of some of the physical metallurgical characteristics of Alloy 718, the baseline alloy of ATI 718Plus, is provided followed by a review on the development and physical metallurgy of ATI 718Plus.

The second section of this chapter reviews the AM processes, with more emphasis on DED which uses wire as the feedstock material. Also, a review of some of the published literature on the properties and microstructure of additively manufactured Alloy 718 and ATI 718Plus is provided.

The third part of this chapter discusses two of the material properties of the deposited ATI 718Plus that have been investigated in this study - high strain rate deformation and the hot corrosion of alloys in molten salts.

2.1 Physical Metallurgy of Alloy 718 and ATI 718Plus

2.1.1 Physical Metallurgy of Alloy 718

Alloy 718 (also known as Inconel 718) is a nickel-iron (Ni-Fe) based superalloy developed in the 1960s by Herb Eisellstein of Huntington Alloys-INCO [21] to replace the then precipitation strengthening steels which had reached their maximum operating temperature limit for turbine applications. Alloy 718 has been described as one of the most successful superalloys to date [1]. The relatively low cost combined with adequate high-temperature mechanical properties, formability, and weldability are attributed to the success of this alloy. It is extensively used as aircraft jet engine vanes and turbine blade material, and for high-speed airframe parts such as aero-
engine casings, containment structures, spacers, wheels, and high-temperature bolts and fasteners [1]. The typical chemical composition range of wrought Alloy 718 is presented in Table 2.1. These alloying elements are added for specific purposes. Refractory alloy elements with atomic radii and electronic structure comparable to Ni such as chromium (Cr), cobalt (Co), Nb, and Mo are added for solid solution strengthening and stabilising of the γ matrix. Some of the solid solution elements such as Cr also provide resistance to corrosion and high-temperature oxidation. Alloying elements like aluminium (Al), Ti, and Nb promote the precipitation of ordered intermetallic precipitates which provide strengthening to the alloy [22]. The strengthening effect of Alloy 718 is achieved by both solid-solution strengthening and precipitation hardening mechanisms. The main strengthening effect, however, comes from the precipitation of ordered γ' and γ" phases in the matrix of the alloy. While the coherent γ' phase also contributes significantly to the precipitation hardening effect of the alloy, Paulonis et al. [23] showed that the main strengthening effect of Alloy 718 is derived from the metastable γ" phase.

2.1.1.1 Microstructure of Alloy 718

In its standard aged condition, Alloy 718 consists of several phases which can be identified by their characteristic morphology and crystallographic structure. The equilibrium phases found in a homogeneous Alloy 718 are: (a) austenitic solid solution matrix, γ phase, (b) strengthening precipitates, γ' and γ" phases, (c) delta phase (δ) particles, and (d) Nb-rich carbides and Ti-rich carbonitrides. In addition to the phases found in the homogeneous alloy, other phases can be induced during non-equilibrium solidification (Laves phase particles), and phase transformation/precipitation (M₆C carbides and α-Cr phase) after a long exposure time at service temperature. A brief review of the nature and characteristics of the phases in Alloy 718 is presented as follows.
Table 2.1: Limiting chemical composition of IN 718 alloy [24]

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>50.0 – 55.0</td>
</tr>
<tr>
<td>Cr</td>
<td>17.0 – 21.0</td>
</tr>
<tr>
<td>Fe</td>
<td>Balance</td>
</tr>
<tr>
<td>Co</td>
<td>1.0 max</td>
</tr>
<tr>
<td>Nb</td>
<td>5.0 – 5.5</td>
</tr>
<tr>
<td>Ti</td>
<td>0.65 – 1.15</td>
</tr>
<tr>
<td>Al</td>
<td>0.20 – 0.80</td>
</tr>
<tr>
<td>B</td>
<td>0.006 max</td>
</tr>
<tr>
<td>P</td>
<td>0.015 max</td>
</tr>
<tr>
<td>C</td>
<td>0.08 max</td>
</tr>
<tr>
<td>Mo</td>
<td>2.8 – 3.3</td>
</tr>
<tr>
<td>W</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>S</td>
<td>&lt;0.015 max</td>
</tr>
<tr>
<td>Si</td>
<td>0.35 max</td>
</tr>
<tr>
<td>Mn</td>
<td>0.35 max</td>
</tr>
<tr>
<td>Mg</td>
<td>0.0014</td>
</tr>
</tbody>
</table>
a) Austenitic solid solution matrix (γ phase)

Alloy 718 has an austenitic face-centered cubic (FCC) matrix, known as the gamma phase, (γ) which serves as the base for other phases. The γ-matrix contains solid solution elements such as Cr, Fe, Co, Al and Ti. These elements are a substitute for the Ni atoms in the Ni crystal lattice, which distorts the lattice and produces a symmetrical stress field. The stress field induced by the substitutional atoms can interact with the dislocation stress field, thus providing solid solution strengthening effects.

b) Strengthening phase, γ' and γ" phases

As mentioned earlier, the principal strengthening phases of Alloy 718 are the ordered intermetallic γ' and γ" precipitate phases. These precipitates provide strengthening to the alloy through ordered strengthening and coherency strain strengthening [25]. In the fully aged condition, the volume fraction of the γ' precipitates in the matrix is around 4% while that of the γ" precipitates is reported to be about 15% [23].

γ' phase – The γ' phase is an intermetallic ordered FCC (Li2) phase and the secondary strengthening precipitate in Alloy 718 [23]. A schematic diagram of the unit cell is presented in Figure 2.1b. In Alloy 718, the γ' phase is a nanometer-sized spherical particle, uniformly distributed and coherent with the γ matrix. It has a cube-cube orientation relationship with the γ matrix and provides strengthening contribution through both coherency strain and ordered strengthening. The precipitation kinetics of the γ' phase in Alloy 718 are sluggish [23], as opposed to the rapid precipitation kinetics routinely observed in the γ' phase of other Ni-based superalloys (such as Waspaloy). The significant content of Nb in the γ' phase of Alloy 718 has been attributed to this behaviour. Although the γ' phase is a metastable phase and can transform into a hexagonal
close packed $\eta$ phase, this transformation is not commonly reported in Alloy 718 upon exposure to higher temperatures for a long period of time [26].

$\gamma''$ phase – The principal strengthening phase of Alloy 718 is the metastable Ni$_3$Nb $\gamma''$ phase which has a body-centered tetragonal (BCT) D0$_{22}$ ordered crystal structure and the schematic diagram of the unit cell of the $\gamma''$ phase is presented in Figure 2.1(a). The $\gamma''$ phase is precipitated coherently as a nanometer-sized ellipsoidal particle on the $\{100\}$ planes of the $\gamma$ matrix [27]. The orientation relationship between the crystal structure of the $\gamma''$ phase and that of $\gamma$ matrix is $(001)_{\gamma''} \parallel (001)_{\gamma}$ and $<100>_{\gamma''} \parallel <100>_{\gamma}$ [28]. Oblak et al. [25] found that the major contributor to the strength of the $\gamma''$ phase in the fully aged condition is from the coherency strains produced due to the considerable tetragonal distortion of the lattice as a result of the mismatch between the BCT lattice of the $\gamma''$ phase and the FCC lattice of the $\gamma$ matrix. The precipitation kinetics of the $\gamma''$ phase in Alloy 718 is known to be relatively slow; this is the main reason for the good and desirable processability of this alloy. The upper-temperature limit for the application of Alloy 718 is derived from the thermal stability of the $\gamma''$ phase. Since the c-axis of the metastable $\gamma''$ precipitation is a mismatch with the FCC lattice, the $\gamma''$ phase tends to transform to a more thermodynamically stable orthorhombic D0$_3$ Ni$_3$Nb delta ($\delta$) phase at temperatures over 650˚C [29]. The mechanical properties of the alloy at high-temperatures are reduced as a result of this transformation because the stable $\delta$ phase does not significantly contribute to the strength of Alloy 718.
Figure 2.1: Unit cell of (a) BCT structure of $\gamma''$ phase, (b) L1$_2$ ordered FCC structure of $\gamma'$ phase
c) Delta (δ) phase

The δ phase (Ni₃Nb) is an equilibrium intermetallic phase with an orthorhombic (D0₂₁ ordered) crystal structure. The schematic diagram for the unit cell of the δ phase is presented in Figure 2.2. The precipitation of the δ phase in Alloy 718 takes place through solid state diffusion at temperatures between 650°C and 980°C [22], and the orientation relationship with the γ matrix is found to be \( \{111\}_γ \parallel (010)_δ; <1\overline{1}0>γ \parallel [100]_δ \) [27]. The transformation of the δ phase varies depending on the range of the aging temperature. At lower aging temperatures (below 700°C), the δ phase is formed by a cellular reaction, in which nucleation occurs at the grain boundary, followed by growth of thin plates that extend into the grain interior and consumes γ" precipitates [30, 31]. At higher temperatures, the nucleation of the intragranular δ phase is believed to occur at the geometric stacking faults in the γ" precipitates [27]. The solvus temperature of the δ phase is known to be dependent on the composition of Nb and has been found to be between 1005°C and 1015°C in Alloy 718 (with Nb contents of 5.06 to 5.41 wt. %) [32]. The δ phase plates are incoherent with the γ matrix phase and do not contribute to the strengthening of Alloy 718.

d) MC-type Carbides

The most well-known carbides in Alloy 718 are MC-type carbides which have an FCC crystal structure. These carbides are rich in Nb, with some solubility for Ti atoms and are known as niobium carbides (NbCs). Occasionally, metal carbon-nitrides (M(CNs)), which are a Ti-rich variant of the MC-type carbides with some solubility for Nb and nitrogen atoms, are also observed in this alloy [22, 33]. They usually form during the solidification of fusion welds and cast ingot as the primary solidification constituents. When carbides are found as a continuous chain at the grain boundaries, they are detrimental to the ductility and rupture life of the alloy [22].
e) **Laves phase**

The Laves phase is a topologically close-packed (TCP) phase with a hexagonal close-packed structure (HCP). The general formula for the Laves phase is $A_2B$ (C14) with Fe, Ni, and Cr in the A position and Nb, Mo and Si in the B position [34]. It is usually observed in the cast and weld fusion zone of Alloy 718 as a result of the elemental segregation of Nb during solidification. The Laves phase is an intermetallic brittle phase and considered deleterious to the mechanical properties of Alloy 718 [35]. A large amount of Nb is required to form the Laves phase and hence, may reduce the Nb required for the formation of the strengthening phases ($\gamma'$ and $\gamma''$). The Laves phase can be eliminated or reduced by careful thermo-mechanical processing of Alloy 718.
Figure 2.2: Schematic representation of a unit cell of Ni$_3$Nb $\delta$-phase.
2.1.2 Physical Metallurgy of ATI 718Plus

2.1.2.1 Development of ATI 718Plus

In a bid to increase the high-temperature stability of Alloy 718 cost-effectively while maintaining its formability and weldability, the ATI 718Plus superalloy was developed by ATI Allvac Incorporated [4]. Major compositional modifications were made to Alloy 718 which changed the characteristics of its primary strengthening phase and increased the thermal stability of ATI 718Plus to approximately 55°C above that of Alloy 718. Table 2.2 provides the primary compositional changes of ATI 718Plus with respect to its baseline alloy, Alloy 718. It is evident that the Al + Ti content in ATI 718Plus has increased to about 4 wt% while the ratio of Al to Ti is maintained at 4. These modifications have resulted in changing the primary strengthening phase from the metastable γ” phase in Alloy 718 to a more stable γ’ phase in ATI 718Plus [3]. Furthermore, the Fe content is reduced from 18 wt% to 10 wt% and replaced by 9 wt% of Co and 1 wt% of tungsten (W) which contribute to the solid solution strengthening of the γ matrix and increases the stability of the γ’ precipitates [2, 3].

Table compares the high-temperature mechanical properties of Alloy 718 and ATI 718Plus after their composition has been modified. The table shows that ATI 718Plus has superior high-temperature strength, and stress rupture and creep properties to those of its baseline alloy, Alloy 718. ATI 718Plus is now being used for a wide range of static and rotating jet engine applications [36]. It was first applied in a commercial jet engine in 2010 [36] and has now become a significant product within the jet engine supply chain. ATI 718Plus has also been considered by Rolls-Royce and General Electric for the manufacture of the next generation of gas turbine structural components such as combustor plenums, stator, diffuser and turbine cases, turbine frames, etc. [37]. Other potential applications currently being considered include aero and land-based gas turbine disks, forged compressor blades, fasteners, engine shafts and fabricated sheet/plate components [38].
2.1.2.2 Microstructure of ATI 718Plus

The solidification structure, solid-state phase transformation and the structural stability of ATI 718Plus have been investigated by different studies over the last decade [39–41]. The microstructure and solidification characteristics of ATI 718Plus are observed to be similar to those of Alloy 718. However, aside from the modification of the primary strengthening phase due to changes in the composition of Alloy 718, a significant difference has also been reported in the (a) volume fraction and precipitation kinetics of the strengthening precipitates, and (b) the characteristics of the grain boundary phases (δ and η phases) in ATI 718Plus.

2.1.2.2.1 Volume fraction and precipitation kinetics of strengthening phases

The volume fraction of the primary strengthening phase, the γ' phase, in ATI 718Plus, is reported to be about 21 % [39] compared to about 4% reported for Alloy 718 [23]. Also, the presence of the primary strengthening phase in Alloy 718, the γ" phase, has been rarely reported in ATI 718Plus with very few exceptions. Unocic et al. [42] were the first to report the reflection of the γ" phase in the selected area diffraction pattern (SADP) of standard heat treated samples of ATI 718Plus. However, the SADP was taken from the sample after before undergoing a series of combination stress rupture (CSR) tests at 704°C and 620 MPa and the compositional homogeneity before the microstructural analysis was not reported.

Cao [39] showed that ATI 718Plus has faster strengthening kinetics in comparison to Alloy 718. The rate of the precipitation of the γ' phase in ATI 718Plus is much faster than that of the γ" phase in Alloy 718. However, the precipitation kinetics of the γ' phase in ATI 718Plus is much slower than in other γ' strengthened Ni-based superalloys, such as Waspaloy.
Table 2.2: Major compositional difference between ATI 718Plus and Alloy 718

<table>
<thead>
<tr>
<th>Element</th>
<th>ATI 718Plus Composition (wt %)</th>
<th>Alloy 718 Composition (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Balance</td>
<td>54.44</td>
</tr>
<tr>
<td>Cr</td>
<td>17.0 – 21.0</td>
<td>17.94</td>
</tr>
<tr>
<td>Fe</td>
<td>8.0 – 10.0</td>
<td>17.62</td>
</tr>
<tr>
<td>Co</td>
<td>8.0 – 10.0</td>
<td>0.13</td>
</tr>
<tr>
<td>Nb</td>
<td>5.2 – 5.8</td>
<td>5.36</td>
</tr>
<tr>
<td>Ti</td>
<td>0.5 – 1.0</td>
<td>0.94</td>
</tr>
<tr>
<td>Al</td>
<td>1.2 – 1.7</td>
<td>0.46</td>
</tr>
<tr>
<td>B</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>P</td>
<td>0.004</td>
<td>0.007</td>
</tr>
<tr>
<td>C</td>
<td>0.026</td>
<td>0.026</td>
</tr>
<tr>
<td>Mo</td>
<td>2.5 – 3.1</td>
<td>2.93</td>
</tr>
<tr>
<td>W</td>
<td>0.8 – 1.4</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>S</td>
<td>&lt;0.0003</td>
<td>&lt;0.0003</td>
</tr>
<tr>
<td>Si</td>
<td>&lt;0.35</td>
<td>0.05</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;0.35</td>
<td>0.05</td>
</tr>
<tr>
<td>Mg</td>
<td>--</td>
<td>0.0014</td>
</tr>
</tbody>
</table>
Table 2.3: High-temperature mechanical properties and thermal stability of 718Plus in comparison with alloy 718 [39].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>ASTM Grain size No.</th>
<th>Heat treatment</th>
<th>Tensile strength at 704°C</th>
<th>Stress rupture 704°C/552 MPa</th>
<th>Creep 704°C/483 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>UTS MPa</td>
<td>YS MPa</td>
<td>El %</td>
</tr>
<tr>
<td>ATI 718Plus</td>
<td>7</td>
<td>As-HT*</td>
<td>1174</td>
<td>1005</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+ 760°C/350 hrs</td>
<td>1073</td>
<td>874</td>
<td>42.2</td>
</tr>
<tr>
<td>Alloy 718</td>
<td>6</td>
<td>As-HT**</td>
<td>1015</td>
<td>936</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>760°C/350 hrs</td>
<td>762</td>
<td>543</td>
<td>53.8</td>
</tr>
</tbody>
</table>

* Heat treatment – 718Plus: 954°C x 1 hr, AC + 788°C x 2 hrs, FC at 55°C/h to 650°C + 650°C x 8hrs, AC

** Heat treatment – alloy 718: 954°C x 1 hr, AC + 718°C x 8 hrs, FC at 55°C/h to 621°C x 8 hrs, AC
This is attributed to the high concentration of Nb [39] in the γ' precipitates in this alloy, as Nb is known to have a slower diffusion rate in Ni-alloys [40, 43]. In addition, it is shown that the γ' phase in ATI 718Plus has the slowest rate of growth compared to the other strengthening phases in Waspaloy and Alloy 718, which implies that this alloy might have the highest stability in terms of particle growth [39]. The reduced tendency of the coarsening of the γ' phase in ATI 718Plus is believed to be related to the very small misfit between the precipitates and the γ matrix.

The strengthening effect of the γ' phase in ATI 718Plus is found to be related to two (2) major physical phenomena: the coherency strain caused by the γ/γ' lattice misfit, and the formation of an antiphase boundary due to the ordered hardening effect [44–46]. The contribution of the γ' phase in ATI 718Plus to strengthening is found to be more effective than the strengthening effect of the γ' phase in other Ni-based superalloys (such as Waspaloy). However, the strengthening effect of the γ' phase in ATI 718Plus is weaker than that of the γ'' phase in Alloy 718 [39].

The recommended heat treatment for wrought ATI 718Plus [47] to achieve optimum mechanical properties is as follows:

**Solution treatment:** carried out at 954°C /982°C for 1 hr, then air cooled or faster

**Double aging treatment:** carried out at 788°C and held for 8 hrs, cooled at 55°C/s to 704°C held at 704°C for 8 hrs and finally air cooled or faster

The recommended standard heat treatment temperatures for ATI 718Plus is relatively higher than those recommended for Alloy 718.

**2.1.2.2 Characteristics of grain boundary precipitates in ATI 718Plus**

The grain boundary precipitates in ATI 718Plus were initially reported as the orthorhombic δ-phase (Ni3Nb D0₆), conventionally found in Alloy 718 with a slight variation in composition [39,
However, a subsequent microstructural study by Xie et al. [40] reported the presence of a δ-like hexagonal phase in ATI 718Plus which can only be differentiated from the conventional orthorhombic δ-phase by selected electron diffraction patterns. Pickering et al. [49] later concluded that the reported hexagonal phase reported in Xie et al. [40] actually differs from the conventional δ-phase in Alloy 718 in both chemistry and structure. They found the phase to be consistent with the hexagonal $\eta$-Ni$_3$Ti ($D0_{24}$) structure, with a chemistry closed to Ni$_6$AlNb. The likely schematic unit cell structure of the $\eta$-phase postulated by Pickering et al. [40] is presented in Figure 2.3. This $\eta$-like phase was reported to be the dominant precipitated phase at the grain and twin boundaries and within the grains of ATI 718Plus. The change from the δ phase in Alloy 718 to the $\eta$ phase in ATI 718Plus is attributed to the chemical modification especially the increase in the Al content [49]. Further work by Messé et al. [50], who carried out elemental mapping by using high-resolution scanning transmission electron microscopy (HRSTEM) and scanning and transmission analytical electron microscopy (STEM-EDX), showed the presence of a finely layered structure of δ-phase particles that are found together with the $\eta$ phase in ATI 718Plus with a distinct structure and chemistry. They further suggested that the presence/absence of any of the phases in ATI 718Plus may likely be a function of the thermo-mechanical history. A comparison of the chemical composition of the δ and $\eta$ phases in Alloy 718 and ATI 718Plus respectively is provided in Table 2.4
Figure 2.3: The likely structure of $\eta$-Ni$_6$AlNb found in 718Plus [49]

Table 2.4: Chemical composition of phase and phase in Alloy 718 and ATI 718Plus respectively [51]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phase</th>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
<th>Fe</th>
<th>Ti</th>
<th>Al</th>
<th>Nb</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 718</td>
<td>$\delta$ phase</td>
<td>73.0</td>
<td>0.03</td>
<td>0.9</td>
<td>1.6</td>
<td>3.7</td>
<td>0.1</td>
<td>20.1</td>
<td>0.7</td>
</tr>
<tr>
<td>ATI 718Plus</td>
<td>$\eta$ phase</td>
<td>67.2</td>
<td>5.6</td>
<td>1.5</td>
<td>1.5</td>
<td>4.0</td>
<td>6.9</td>
<td>13.0</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Like Alloy 718, the role of these grain boundary precipitates in ATI 718Plus, especially for its mechanical properties, is ambiguous. Viskari et al. [52] showed that the presence of grain boundary precipitates in ATI 718Plus is beneficial in delaying hold-time crack propagation during cyclic loading. Similar studies have also shown that a small amount of homogeneously distributed grain boundary particles in ATI 718Plus is favourable for preventing notch sensitivity and improving resistance to intergranular crack propagation [47, 53]. Peterson et al. [37], also showed that sufficient precipitation of the η phase at the grain boundaries of ATI 718Plus can help to inhibit grain boundary decohesion, thereby improving the creep strength and the ductility balance of the alloy. On the contrary, Wang et al. [51, 54] observed an improvement in the stress rupture life of ATI 718Plus with an increase in the phosphorus content. The improved rupture life was attributed partly to the reduction of the η phase particles at the grain boundaries (which is believed to act as a crack initiator) due to the inhibitory nature of phosphorus on the precipitation of the η phase in ATI 718Plus. Unocic et al. [42] on the other hand observed that the presence of the η phase at the grain boundaries does not have any effect on the environmental cracking resistance of ATI 718Plus. Also, Kearsey et al. [55] observed that the characteristics and volume fraction of the η phase particles along the grain boundaries have no significant effect on the low cycle fatigue life and dwell-fatigue crack nucleation in ATI 718Plus. Wang et al. [51] also showed that the volume of strengthening precipitates in ATI 718Plus is influenced by the volume fraction of the η phase precipitates in the alloy. Since both the η and γ' precipitates compete for similar alloying elements (Nb, Al, and Ti), the formation of the η-phase was observed to moderately reduce the volume fraction of γ' precipitates. There is, however, general consensus that the presence of these grain boundary precipitates in small quantities is beneficial for pinning grain boundaries but excessive precipitation can be detrimental to the properties of ATI 718Plus [49].
Other phases of interest in ATI 718Plus are the MC-type carbides and segregation induced Laves phase which are similar in structure to those in Alloy718 but with a slightly different chemical composition [39]. The formation of Laves eutectics is observed to occur at 1173°C when the Nb content is about 23.6% as shown in the pseudo-binary phase diagram of ATI 718Plus in Figure 2.4. The amount of Laves phase particles formed in ATI 718Plus are found to be slightly less compared to Alloy 718, which could be associated with the lower Fe content in ATI 718Plus [39].

The critical phase transformation temperatures of ATI 718Plus and Alloy 718 obtained through modeling, experimentation and differential thermal analysis (DTA) are summarised in Table 2.5.
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Figure 2.4: Pseudo-Binary Phase Diagram of ATI 718Plus [39]
Table 2.5: Critical Phase Transformation Temperatures of Alloys ATI 718Plus and Alloy 718 [39]

<table>
<thead>
<tr>
<th>Phase Transformation</th>
<th>Modeling</th>
<th>DTA</th>
<th>Metallography</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ATI 718Plus</td>
<td>718</td>
<td>ATI 718Plus</td>
</tr>
<tr>
<td></td>
<td>°C</td>
<td>°C</td>
<td>°C</td>
</tr>
<tr>
<td>Liquidus</td>
<td>1346</td>
<td>1358</td>
<td>1353</td>
</tr>
<tr>
<td>MC Eutectic</td>
<td>1261</td>
<td>1246</td>
<td>1292</td>
</tr>
<tr>
<td>Solidus</td>
<td>1201</td>
<td>1214</td>
<td>1265</td>
</tr>
<tr>
<td>Laves Eutectic</td>
<td>-</td>
<td>-</td>
<td>1173</td>
</tr>
<tr>
<td>δ Solvus</td>
<td>1065</td>
<td>1027</td>
<td>-</td>
</tr>
<tr>
<td>γ' Solvus</td>
<td>995</td>
<td>909</td>
<td>963</td>
</tr>
<tr>
<td>γ' Solvus</td>
<td>968</td>
<td>946</td>
<td>-</td>
</tr>
</tbody>
</table>
2.2 Additive Manufacturing

AM which is synonymous with three-dimensional (3D) printing, is the process of joining materials to build parts layer-by-layer from 3D model data [56]. This technology was initially applied to produce presentation models and prototypes (mainly from wax and polymeric materials) but has been recently extended to fabricating functional complex metallic components for a variety of different applications. Fundamentally, AM systems for fabricating metallic components combine a heat source (which can be laser, electron beam, arc, etc.) with additive feedstocks (powder, wires, and sheets) with a motion system provided either by robotic or gantry systems.

Over the last few decades, research related to AM technologies has received considerable attention both in the academia and the industry, thus prompting the filing of about 3500 AM related patents between 1975 and 2011 [57]. This technology has the potential for reducing component costs by reducing material wastage, especially in fabricating aerospace components which have a high buy-to-fly ratio and shortening the time to market of components. A cost comparative study of AM processes versus traditional machining from solid billets or forging was carried out by Allen [58] who found that the current AM techniques are commercially cost-competitive for aerospace components with a buy: fly ratio of about 12. However, projected future AM systems could be viable for components with a buy to fly ratio as low as 3. Kinsella [59] reported as much as a 30% savings in cost by using a hybrid AM-forging process for the production of Ni-based engine cases compared to only the use of a traditional manufacturing route. In addition, minimising the number of components needed to make a part through AM techniques has the potential for significant savings in costs with the reduction of assembly costs. NASA successfully tested a rocket injector produced by AM with only two parts, as opposed to the 115 parts previously required to make a similar injector [60]. The reduced cost of assembling and joining substantially reduced the cost of
manufacturing the injector. Moreover, the main competitive position of AM processes is in the expeditious and ease in which new designs can be introduced.

2.2.1 Classification of AM processes for metallic components

The AM processes for producing metallic parts can be classified based on three (3) major considerations - the characteristics of the additive material (metal/alloy powder, wire or sheet), the type of energy source applied to joining the additive materials (laser, ultrasonic or electron beam, plasma arc processes) and lastly, how the additive material is fed or supplied (powder-bed based process or direct energy deposition). In this study, the classification will be based on powder-bed AM techniques and DED AM processes.

2.2.1.1 Powder-bed fusion process

The powder-bed AM process is considered to be the most commercially successful AM process for metallic components and the majority of research focuses on this process [6]. It is better developed due to its capability to fabricate parts with high geometrical accuracy and ability to deliver net shaped components. In this process, the additive powder is uniformly spread on the table, or the ‘bed’, and specifically selected regions of the bed are sintered or melted by a thermal energy source (laser or electron beam) to build a single layer of the desired component. Upon the complete melting/sintering of this single layer, the bed is lowered down to the thickness of the single deposited layer, and then a new layer of powder is again spread on the bed with a roller, and the process is repeated. A schematic diagram of the powder-bed AM process with the use of a laser beam is presented in Figure 2.5. The main advantages of this process are that components with high surface quality are produced which might not require post-AM machining. In addition, this process is favourable for the construction of structures with overhanging parts since the powder bed acts as a supporting structure [61]. However, one of the limitations is the extremely
low deposition rate, which is typically around 10 g/min. This has limited the process to the production of small complex metallic parts [6]. Additionally, due to the accumulation of powder around the metallic parts, a de-powdering procedure is usually required after manufacturing which can be a health hazard. Examples of powder-bed fusion processes under different trade names are summarised in Table 2.6 based on the thermal energy utilised and some of their associated companies.
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Figure 2.5: Schematic diagram of a typical powder-bed fusion (DMLS system) [64]
Table 2.6: Classification of Powder-bed fusion AM processes

<table>
<thead>
<tr>
<th>Classification</th>
<th>Process/Trade name</th>
<th>Originally associated organization</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder-bed fusion</td>
<td>Selected Laser Sintering (SLS)</td>
<td>The University of Texas <em>(Licensed to Phoenix System, France)</em></td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td>Selected Laser Melting (SLM)</td>
<td>MTT Tech. Group, Germany <em>(now SLM Solutions)</em></td>
<td>[63]</td>
</tr>
<tr>
<td></td>
<td>Direct Metal Laser Sintering (DMLS)</td>
<td>EOS, Germany</td>
<td>[64]</td>
</tr>
<tr>
<td></td>
<td>Electron Beam Melting (EBM)</td>
<td>ARCAM, Sweden</td>
<td>[55]</td>
</tr>
<tr>
<td></td>
<td>LaserCUSING</td>
<td>Hoffman Innov. Grp, Germany</td>
<td>[66]</td>
</tr>
</tbody>
</table>
2.2.1.2 Directed energy deposition process

In the directed energy deposition (DED) AM process, the additive material is deposited and melted by the thermal source directly on a substrate, layer-by-layer, to produce the required configuration from a model data. This process offers the advantage of producing functionally graded parts with varying materials or alloy compositions since different additive materials can be combined to construct a part [67]. Furthermore, since this process does not depend on a pre-deposited layer of metallic powder, it can be used as a means to repair damaged or worn out parts and also be applied for additional structural details to forged parts [68]. Depending on the nature of the additive material, the DED can be further classified as either DED-powder or DED-wire.

2.2.1.2.1 Directed energy deposition (powder based)

The DED-p process, also known as powder injection AM, is an AM process that combines material/energy delivery for simultaneous depositions. In this technology, the additive material (powder) is injected/propelled through a nozzle by using either an inert gas or gravity into an energy source for melting and then deposited to form the metallic part directly from 3D model data. The schematic diagram for a typical DED-p process is presented in Figure 2.6. Unlike the powder bed processes, the DED-p process does not require post-manufacturing de-powdering. One of the disadvantages of this process however is that the surface quality of the parts is not as good as those produced by the powder-bed AM technique due to the relatively coarser powder size required for this process and the possibility of post-deposition machining [61]. Although the deposition rates of the DED-p are higher than those of the powder-bed process, Choi and Chang [69] observed that the possibility of increased pores may be a limiting factor and concluded that the process window for creating a component with adequate mechanical properties could be narrower. Examples of the different variants of the DED-p presently in use and their associated organisations are summarised in Table 2.7.
Figure 2.6: Schematic diagram showing a typical powder-feed directed energy deposition using laser thermal source [61]
Table 2.7: Classification of Directed Energy Deposition using Powder.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Process/Trade name</th>
<th>Original associated organisation</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Directed Energy deposition (powder)</td>
<td>• Laser Engineering Net Shaping (LENS)</td>
<td>Sandia National Laboratory <em>(Optomec, NM, USA)</em></td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>• Laser Consolidation (LC)</td>
<td>NRC-Canada/GE Global Research <em>(Licensed to Accufusion, Canada)</em></td>
<td>[58]</td>
</tr>
<tr>
<td></td>
<td>• Direct Metal Deposition (DMD)</td>
<td>POM, NM, USA.</td>
<td>[59]</td>
</tr>
<tr>
<td></td>
<td>• Directed light fabrication</td>
<td>Los Alamos, National Laboratory</td>
<td>[60]</td>
</tr>
</tbody>
</table>
2.2.1.2.2 Wire-based AM processes

The wire-based AM process is a form of DED with the use of metal wire as the additive material as opposed to powder. This process offers a higher deposition rate (up to 30-50 g/min) [73], produces components with less porosity and uses the additive material more efficiently in comparison to the powder-based process [74]. Furthermore, the wire-based process eliminates the potential risk associated with inhaling additive powder during the manufacturing process. The availability of low-cost additive wires also makes this process more cost competitive. However, the benefits of high surface quality and precision in the powder-based method are traded in lieu of a high deposition rate with wire-based AM [75].

The wire-based processes can be classified into three main categories depending on the type of the thermal energy utilised; (a) electron-beam based process, also known as electron beam direct manufacturing (EBDM), (b) laser-beam based process also known as wire-laser additive manufacturing (WLAM), and (c) wire-arc additive manufacturing process.

2.2.1.2.2.1 Electron beam direct manufacturing

The EBDM process was developed by Sciaky Inc. based in Chicago, USA. The process was designed to create a near-net-shape component that requires little post-AM machining [76]. In this process, metal wire feedstock is introduced into a molten pool that is created and sustained by a focused electron beam in a high vacuum environment (1.33 x 10^-2 Pascal or lower) [76]. The schematic diagram in Figure 2.7 shows the primary components of the EBDM setup. The EBDM process is also suited for the addition of details onto simplified preforms (from casting or forging). This helps to reduce material wastage especially components that require significant material removal from oversized forgings or material stocks [74]. The mechanical properties and microstructures obtained by using the EBDM process have been reported comparable to those that are wrought. Although there is a trade-off between a high deposition rate and fine-grained
microstructure for some materials (that is, 2219-Al and Ti-6V-4Al), the trade-off does not seem to significantly affect their mechanical properties [74]. Sciaky Inc. in conjunction with the NASA Langley research center has developed a variant of this technology under the tradename of electron beam freeform fabrication (EBF$^3$) [77]. Phinazee [78] showed that the EBF$^3$ has about an 80% higher material efficiency and the cost of fabrication of a component can be reduced by almost 50% in comparison to traditional manufacturing techniques.

2.2.1.2.2 Wire-feed laser deposition

Wire-feed laser deposition (WLD) or WLAM is similar to EBDM but utilises a high-energy laser beam instead of an electron beam to melt the additive wire. Unlike the EBDM, this process does not require a vacuum and is therefore scalable to a wide range of part sizes [6]. The procedure has high precision and provides a better surface quality than the other wire-feed processes, hence it is popular for manufacturing near net shaped metallic parts that require little or no post-deposition machining [79]. In comparing WLD with powder based DED, Syed et al. [80] found that while the deposition freedom of the laser-powder technique is superior to the wire-laser technique, the rate of deposition is much higher and efficiency of raw material usage is much lower in the latter. However, Baufeld and van der Biest [81] observed that the wall thickness in the wire-laser process is restricted by the focused laser beam and found to be narrower compared to the wire-arc based processes which may be disadvantageous when considering the deposition of thick sections [81].
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Electron Beam Additive Manufacturing (EBAM®) Technology | Sciaky:
http://www.sciaky.com/additive-manufacturing/electron-beam-additive-

Figure 2.7: Schematic diagram of an electron beam additive manufacturing process [76]
2.2.1.2.2.3 Wire-arc based additive manufacturing

The wire-arc additive manufacturing technique is a promising wire-feed DED based on conventional arc welding processes. The method utilises arc as the heat source, the feedstock is in the form of a filler wire and the motion system for building the desired configuration is mainly done by robotic systems. The first patent for this AM technique was filed in the 1920s by Baker [82] but only started to gain attention as an AM technique recently due to the advancements in automation technologies and the benefits from this method which excel those of the other AM techniques [6]. That is, this technique has higher deposition rates which makes it suitable for manufacturing components with moderate complexity at a medium to large scale [75]. It has the capacity to produce fully dense metallic components with high material efficiency. Additionally, the energy efficiency of this process is much higher than the energy efficiencies of the wire-laser and electron beam-wire processes [83, 84]. Since the wire-arc based process is an adaptation of the conventional arc welding technique, it utilises a well-established technology with a less complex system and readily available low-cost equipment. The different wire-arc based AM processes that use arc welding technology include: gas metal arc welding (GMAW), gas tungsten arc welding (GTAW), plasma arc welding (PAW), and cold metal transfer (CMT).

GMAW which is also known as metal inert gas (MIG) welding is a process that melts and joins metals by heating them with an arc established between a continuously fed filler wire electrode the metal substrate [85]. The molten pool generated by the arc is shielded from the atmosphere through a blanket of inert gas. Since the wire itself is the electrode, this process has a high deposition rate and is suitable for fabricating large metallic structures. However, the large amount of heat input from the process can lead to large residual stresses and distortion [6].
The CMT process, a modification of the GMAW process, was developed by Fronius International GmbH [86]. In CMT, deposited droplets detach during short-circuiting. In this process, the filler wire is moved forward towards the weld pool and dips into it during the period of arcing. The system detects short-circuiting which causes the welding current to be lowered and the wire starts to retract. The shifting of the wire backwards contributes to the droplet detachment during the short circuiting. The filler wire is moved forward again and the cycle is repeated [86]. The heat input, spatters and distortion level in this process are much lower than those in the conventional GMAW process [87]. Some challenges, such as arc wandering and severe spattering conditions, which are associated with the arc deposition of Ti alloys can be overcome by adopting CMT. In addition, much finer grains are produced in a CMT deposit in comparison to those obtained from GMAW [88].

GTAW and PAW use non-consumable electrodes to produce the arc, while a filler wire is introduced into the molten weld pool separately. The weld is shielded from the atmosphere by using an inert gas that forms an envelope around the weld area. As opposed to the GMAW, where the consumable filler wire is always perpendicular to the substrate, the wire feed orientations for the GTAW and PAW vary, thus allowing more accurate process control [6]. However, the process planning of these welding techniques is more complicated. The major difference between the GTAW and the PAW is in the production of the arc energy itself. While the arc in the GTAW is generated between the non-consumable tungsten electrode and the workpiece itself, an additional nozzle is added in the PAW process where the arc is ‘pre-lit’ between the electrode tip and the water-cooled orifice gas nozzle [89]. The arc is then gradually transferred from between the electrode tip and the orifice gas nozzle to between the electrode and the workpiece. A schematic diagram that shows the difference between the GTAW and PAW is presented in Figure 2.8.
Table 2.8: Comparing the wire-based DED processes

<table>
<thead>
<tr>
<th>Processes</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire-Laser AM</td>
<td>• Good surface finish and precision</td>
<td>• The deposition rate is low</td>
</tr>
<tr>
<td></td>
<td>• Does not require a vacuum</td>
<td>• Poor energy efficiency</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Investment cost is high</td>
</tr>
<tr>
<td>Wire-Electro-beam AM</td>
<td>• Good mechanical properties</td>
<td>• Requires a vacuum</td>
</tr>
<tr>
<td></td>
<td>• Better deposition rates compared to wire-laser based</td>
<td>• Poor surface quality and precision compared to the wire-laser process</td>
</tr>
<tr>
<td></td>
<td>• Relative better energy efficiency compared to the wire-laser process</td>
<td>• High investment cost</td>
</tr>
<tr>
<td>Wire-Arc AM</td>
<td>• The high deposition rate and fast AM process</td>
<td>• Poorer surface quality and precision compared to other wire-fed processes</td>
</tr>
<tr>
<td></td>
<td>• Applied to make large components</td>
<td>• High residual stress and distortion.</td>
</tr>
<tr>
<td></td>
<td>• Possible to produce varieties of superalloys</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Very high energy efficiency</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Low cost of investment</td>
<td></td>
</tr>
</tbody>
</table>
Narrower beads with less distortion can be deposited with the PAW due to the narrow heat impact zones as well as the fine seams [90]. The high plasma arc energy produced in PAW enables a higher deposition rate than with the use of the GTAW[89]. In addition, the PAW process is less sensitive to unintentional arc length variations during deposition, thus producing better builds. However, the plasma arc torches are more complicated and require the correct selection of orifice size and flow rate, and proper electrode configuration. The MER Corporation in Tucson, Arizona has adopted the plasma-arc technology under the trade name of plasma transfer arc-selective freeform fabrication (PTA-SFFF) [91]. They have successfully fabricated turbine disks for aerospace industries and also produced many composite structures for military applications [92].

The GTAW AM process was developed by Rolls-Royce under the trade name of shape metal deposition (SMD) [93]. Initially, the process was not widely adopted for commercial production for many reasons, for e.g., the welding process has to be manually controlled by a skilled technician and there is little understanding of the material properties of parts produced by using this process [94]. Then a EU-funded program called Rapid Production of Large Aerospace Components (ROPOLAC) was licensed to improve the SMD technology to the level where it could be particularly useful for manufacturing large, fully-dense components and also, adding features to already existing forged or cast parts [94]. A test cell, which uses the SMD process, was developed at the end of the project. The GTAW process has the advantage of producing clean high-quality deposits with relatively lower distortion compared to the GMAW AM process. However, the rate of deposition is relatively slow [85]. The rate of deposition with the GTAW process can be increased by preheating the filler metals before feeding them into the arc. The EWI in Ohio, USA [95] developed a hot wire-GTAW process which has been applied to produce parts of various alloys. The increase in the rate of deposition through this process, roughly one order
Figure 2.8: Schematic difference between (a) plasma arc and (b) TIG arc. Note the cylindrical shape of the plasma arc when compared to the conical shape of the TIG arc. Picture (c) & (d) shows the plasma arc and TIG arc respectively [89]

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https://www.pro-fusiononline.com/feedback/tp-aug99.htm
of magnitude, has provided many opportunities for the use of the wire-arc additive manufacturing process, especially in the aerospace industry.

**Challenges of Wire-based AM process**

Notwithstanding the obvious potentials of wire-based AM processes, there are nevertheless some inherent technical challenges. Some of the most significant issues, especially with the wire-arc additive manufacturing process, are the poor quality of the finishing of parts, residual stress and the resultant component distortion, and the lack of a proper understanding of the microstructural development and resultant material properties.

**Accuracy and surface finish of WAAM parts**

One of the major challenges of the wire-based (especially wire-arc) AM is that the accuracy of components and the quality of the surface finishing are particularly poor. Wire-based AM usually produces layers with a greater thickness (1-2 mm) which translates into shorter fabrication time but poor accuracy, which is evidenced in the non-flat layer edges or layer roughness during the deposition process. Singh and Dutta [96] observed that for a given part size, a greater layer thickness during deposition means poorer surface quality which is caused by the ‘stair stepping’ effect. In addition, the ‘hills and valleys’ produced on the surface as a result of overlapping weld beads with the use of wire-based AM usually lead to an uneven surface of the component. The severity of the surface unevenness is influenced by deposition process parameters such as weld bead width, thickness of deposited layers, wire diameter, wire feed rate, travel speed, and weld bead overlap [97]. Consequently, the accuracy of parts produced by a typical wire-based AM process is usually 10 times less than that produced by powder based methods [6]. This has limited the use of wire-based AM processes for the fabrication of near net shapes, which require post-deposition machining as a finishing procedure. Many new wire-based AM systems are now
integrated with machining equipment [79] for a hybrid manufacturing process to produce components with adequate precision and high material efficiency. The idea is for the wire-based process to produce a component to an 80-90% near net shape, and machining is applied to optimize the required tolerance and surface quality of the component.

**Residual stress and distortion**

Due to the significant heat input during wire-feed processes, high residual stresses are produced in the component after deposition especially with the use of an arc as the energy source. The residual stresses are due to thermally induced strain which results with shrinkage of the material during cooling [98] and reported to be highest along the deposition direction. These residual stresses can then cause the distortion of the component and possibly the premature failure of the part in service [99]. Although residual stresses may be alleviated by post-deposition treatment, the induced distortion is permanent and can only be reduced by minimizing and controlling the developed residual thermal stresses during deposition. A number of investigations have been ongoing that seek to build strategies that minimize and control thermal stresses during deposition. They mainly focus on varying the scanning pattern of the deposition, pre-substrate heating temperature, and inter-layer deposition treatment such as inter-pass rolling [6, 75]. Nickel et al. [101] and Nickel [102] examined the thermal stress produced during shape deposition manufacturing (SDM), by using both experimental and finite element (FE) analyses. They found that distortion can be significantly minimised by using the right scanning pattern to configure a substrate: a short raster pattern is favoured on beam substrates, while spiral scanning patterns are preferred on plates. Colegrove et al. [102] also found that high-pressure inter-pass rolling can help to minimise the residual stress and distortion in wire-arc manufactured components. Furthermore, preheating the substrate uniformly before deposition has also been reported in [92] to minimize the residual thermal stress during SMD.
2.2.2 Previous studies: AM of Alloy 718-type alloys

There has been considerable work conducted on the feasibility of using AM techniques to produce functional superalloy components for the aerospace industry. Among the different types of Ni-based superalloys, Alloy 718 has gained special attention because of its significant use in aero-engines [104]. Several studies have been carried out to understand the microstructural changes and properties of Alloy 718 components produced by using the various AM techniques. In many of these earlier publications, there is consensus that the microstructural changes of additively manufactured Alloy 718 deposits are dependent on the AM technique deposition parameters used, and the scanning patterns during the component build-up [6, 68, 75, 99, 105–108]. Sadowski et al. [109] observed that the deposition power and quality of additive powder have the greatest effects on the quality of Alloy 718. An excessively low/high deposition power can lead to the formation of voids, porosity and humps, as well as bead detachment of the deposit. The grain structure and texture of additively manufactured Alloy 718 deposits have been found to be dependent on the scanning pattern during deposition. Dinda et al. [110] and Wei et al. [111] used experimental testing and numerical modeling respectively, to show the possibility of controlling the texture of additively manufactured deposits by modifying the scanning pattern for deposition. Similarly, Dehoff et al. [108] showed that the crystallographic texture of electron beam deposited Alloy 718 can be controlled by varying the processing parameters and scan strategy. Furthermore, Liu et al. [112] investigated the effect of laser scanning path on the microstructure and mechanical properties of as-deposited Alloy 718. They observed that deposits subjected to single direction raster scanning (SDRS) exhibited columnar dendrites that grow epitaxially along the deposition direction. However, such continuous epitaxial growth is inhibited in deposits subjected to cross direction raster scanning (CDRS), thus increasing the orientation deviation of dendrites and enhancing ductility [112].
The local formation of deleterious phases attributed to chemical segregation during solidification is often reported in Alloy 718 produced by using AM techniques [113–117]. A fraction of these deleterious phases in the deposit is found to depend on the cooling rate during deposition which is in turn influenced by the deposition parameters [118]. During the laser deposition of Alloy 718, Ma et al. [119] observed that the size and volume fraction of the Laves phase particles in the interdendritic regions of the deposit increase with laser energy. The liqiation and re-solidification of the Laves phase particles along the interdendritic regions of Alloy 718 welds and deposits have been reported to promote the initiation and propagation of liqiation cracking [61, 120]. In the laser AM of Alloy 718 in Chen et al. [121], liqiation cracking along the interdendritic regions of the deposit was observed and found to be initiated at the weak site in the deposit near the fusion line in the pre-deposited layer, and mainly attributed to the liqiation of the Laves phase particles. Similarly, the formation of deleterious oxide films such as Al₂O₃ and Cr₂O₃ have also been reported [122] in laser additively manufactured Alloy 718. Zhang et al. [122] observed that the oxides films act as preferential sites for the nucleation for intermetallic compounds (such as NbC and TiN) and also serve as sites of crack initiation.

Due to the repeated deposition during component build up, complex thermal cycles occur within the deposit build. These thermal cycles, coupled with elemental micro-segregation during deposition, have also been shown to promote non-uniform solid-state transformations across the deposit build in Alloy 718. Tian et al. [123] and Sames et al. [124] observed heterogeneity in the microstructural and mechanical properties of additively manufactured Alloy 718 with the use of laser and electron beam AM techniques, respectively. This heterogeneity is attributed to the solid-state precipitation of the primary strengthening phase in the local regions due to the thermal gyrations during deposition along with elemental micro-segregation in the alloy. This microstructure heterogeneity can create weak local regions in the deposit, which would result in
stress concentration in those regions and therefore compromise the integrity of the deposit during service.

Clark et al. [125] and Baufeld et al. [126] examined the feasibility of applying a wire-arc based process to manufacture Alloy 718 superalloy components. In performing the manufacturing trials on a combustion outer casing through a hybrid manufacturing route with an SMD-forging process, Clark et al. [125] concluded that SMD is a viable method of fabricating complex Alloy 718 components and can serve as a process for adding details to pre-formed parts. Further investigation of the microstructural and mechanical properties of SMD deposited Alloy 718 was performed by Baufeld et al. [126]. It was observed that the tensile properties of deposits manufactured by using SMD are superior to their cast versions and these properties can be further enhanced by using a tailored heat treatment procedure. In a recent study of WAAM Alloy 718 by Xu et al. [127, 128], it was observed that the additively manufactured alloy showed a significantly low strength as compared to the wrought alloy after the recommended post-deposition heat-treatment. The lower strength was attributed to the large columnar grain structure and the formation of numerous less-desirable precipitates in the wire-arc manufactured Alloy 718. However, in-process thermomechanical processing was observed to significantly improve the strength of the additively manufactured alloy deposits after post-deposition heat treatment.

Idell et al. [129, 130] pioneered a study on the AM of ATI 718Plus superalloy. Their work centered on a microstructural study of as-deposited ATI 718Plus produced through direct metal laser sintering. The as-deposited microstructure showed columnar dendritic solidification along the build direction, with highly textured grains in the <100> direction. Their X-ray diffraction (XRD) analysis suggested that $\gamma'$ precipitates are present in the $\gamma$ matrix; however, their distribution in the deposit and their effects on the properties were not reported. Surprisingly, no HCP ($\eta$) phase
particles were observed in the deposit even though an increase in Al in ATI 718Plus has been shown to promote the formation of the η phase. Its absence was attributed to the abnormal increase of Nb in the inter-dendritic regions which promotes the formation of the orthorhombic δ phase particles in place of the η-phase particles. The presence of Laves phase particles, which are caused by the micro-segregation of Nb commonly observed in additively manufactured Alloy 718, and the welded microstructure of ATI 718Plus have not been discussed in these studies. Also, there is no discussion on the inhomogeneity of the microstructure or mechanical properties, which been observed earlier for Alloy 718 in [117].

2.3 High strain rate deformation

It is well established that the deformation behaviour of materials is significantly influenced by the loading conditions. The influence of the rate of loading on material properties, as reported by Hopkinson [131] is one of the more notable work. The deformation response of metals and alloys under a quasi-static condition (strain rate between $10^{-3}$ s$^{-1}$ to 1 s$^{-1}$) typically differs from those deformed at high strain rates (usually $>10^3$ s$^{-1}$). This difference in the deformation response is attributed to the change in the rate-controlling mechanism of the dislocation motion at different loading rates [132]. The thermal activation process, in which dislocation tends to overcome obstacles through the thermal vibration of the lattice atoms, governs the plastic deformation in quasi-static loading conditions up to $10^2$ s$^{-1}$. The deformation at high strain rates is controlled by phonon viscous drag, in which the motion of dislocations through the lattice is slowed down by viscous drag.

High strain rate deformation occurs in numerous applications, and some typical examples are impacted deformation in containment systems, metal cutting operations, automobile crashes, explosive fasteners for space shuttles, and military applications such as in penetrations and
explosions. Thus, the dynamic response of materials at high strain rates is now included as a critical design criterion for some of these applications.

Under these impact loading and high strain rate applications, localised heating usually emerges as a result of the rapid deformation which can lead to the localisation of plastic flow [133]. Intense localisation of plastic flow in a narrow band, called the adiabatic shear band (ASB), is a major precursor to catastrophic brittle failure. The formation of ASBs in materials has been studied by several authors and numerous factors such as the loading conditions, material properties (hardness, thermal conductivity and heat capacity), and material microstructure have been observed to significantly influence the propensity to form ASBs [133]. Materials with low thermal conductivity, high hardness, and low strain hardening have been found to be more prone to form ASBs [133].

The microstructure of precipitation strengthened alloys, in particular, are found to have a disparate effect on high strain rate deformation depending on the presence of precipitates, the precipitate size and strengthening mechanism in the alloy [134–136]. Several studies have been carried out on various Ni-based superalloys to understand the influence of high strain rates on the microstructure in dynamic responses for machining and containment applications. Ugodilinwa [137] observed that the presence and size of the strengthening precipitates in the matrix of the Haynes 282 alloy have a profound influence on the formation of ASBs. The aging of Haynes 282 was observed to increase its susceptibility to impact failure compared to solution heat treatment, which is attributed to the lower strain hardening capability of aged Haynes 282. DeMange et al. [138, 139] found that solution heat treated Alloy 718 can more readily absorb impact loading and resists strain localisation under ballistic impact to a higher extent than the precipitate-bearing microstructure in comparison. Similarly, a recent shear localisation study of Alloy 718 by
Johansson et al. [140] showed that although precipitation hardening increases the flow stress of the alloy, strain localisation which leads to the formation of deleterious shear bands is promoted.

2.3.1 Studies on high strain rate of additively manufactured alloys

Most studies on the mechanical behaviour of additively processed alloys have so far been limited to carrying out tests under quasi-static loading conditions with only a few who have sought to understand dynamic response under high strain rates. There have been some impact studies on additively manufactured alloys that use different techniques such as electron beam melting (EBM) -Ti-6Al-4V [141], laser engineered net shaping (LENS) 304L [142], 316L [143] and direct metal laser sintered (DMLS) Al alloys [144, 145]. These studies have shown that additively manufactured alloys are promising candidates for ballistic impact and high strain rate applications. However, there are few works in the open literature on the high strain deformation of additively manufactured Ni-based superalloys. An impact study was carried out on the additive friction stir manufactured IN 625 by Rivera et al. [146] who showed that this additively manufactured alloy has comparative properties to both its cast and wrought equivalent. In a similar study by Puppala et al. [147] it was observed that IN 625 produced by using laser rapid manufacturing showed a moderately lower impact toughness in comparison to its wrought version. However, they also observed that post-deposition stress relief marginally increased the impact toughness.

2.3.2 Material constitutive models for numerical simulation

Wire-arc based AM is a near-net shaped manufacturing process which usually requires follow-up machining to optimize the surface quality and tolerance of the parts. Finite element (FE) modeling of the machining processes has been found to be a beneficial and efficient tool in evaluating the machinability of metals and alloys. It is also used to optimise machining process conditions while reducing the number of costly experimental trials needed [148]. It is, however, worth noting that
a reliable material model which describes the dynamic flow behaviour of a workpiece that is comparable to that which occurs during cutting operations, is the key to constructing an accurate and reliable machining model [149].

Presently, there are several models used to describe the dynamic flow stress of materials under high strain rates and temperatures. The two most popular models are the Johnson-Cook (J-C) and the Arrhenius-type (AT) models.

2.3.2.1 Johnson-Cook model

The J-C model has been extensively applied in simulating machining processes and modeling impact loading in structural components. The original model is:

\[ \sigma = (A + B\varepsilon^n)(1 + Cln\dot{\varepsilon}^*)(1 - T^m) \]  

(2.1)

where \(A, B, n, m,\) and \(C\) are the material constants, \(\varepsilon\) is the plastic strain, \(\dot{\varepsilon}^* = \dot{\varepsilon}/\dot{\varepsilon}_0\) is the dimensionless strain rate (\(\dot{\varepsilon}\) is the strain rate, while \(\dot{\varepsilon}_0\) is the reference strain rate), \(T^*\) is the homologous temperature \((T^* = \frac{T - T_r}{T_m - T_r})\) where \(T_m\) = melting temperature of the material and \(T_r\), reference temperature, 298 K) and \(\sigma\) is the flow stress. This model assumes that the effects of strain hardening, strain rate hardening and thermal softening on the flow stress of materials are mutually independent and the coupled effects of these factors are therefore ignored. In most materials, however, the coupled effects of temperature, strain rate and strain on the flow stress are usually observed. Owing to this deficiency, modifications to the J-C model have been made by different authors to capture these coupled effects [150–154]. Lin et al. [155] introduced some material constants \((\lambda_1 and \lambda_2)\) to take the coupled effects of temperature and strain rates into consideration for predicting the flow stress of high strength steel and the results obtained showed that the modified version significantly improves the accuracy of the predicted material behaviour.
2.3.2.2 **Arrhenius-type model**

The AT model is another common phenomenological based model used to describe the plastic flow behaviour of materials at high temperatures and strain rates. Sellar and McTegart [156] showed that the relationships among the flow stress, strain rates, and temperature can be expressed by using an AT equation:

$$\dot{\varepsilon} = AF(\sigma) \exp \left( \frac{-Q}{RT} \right)$$  \hspace{1cm} (2.2)

where $F(\sigma) = \begin{cases} 
\sigma^{n'} & \alpha \sigma < 0.8 \\
\exp(\beta \sigma) & \alpha \sigma > 1.2 \\
\sinh(\alpha \sigma)^n & \text{for all } \sigma 
\end{cases}$

where $\dot{\varepsilon}$ is the strain rate (s$^{-1}$), $Q$ is the activation energy in (kJ/mole), $R$ is a gas constant (8.314 J/mol$^{-1}$K$^{-1}$) and $T$ is the temperature (Kelvin). $\sigma$ is the flow stress (MPa) for a given strain, and $A$, $\beta$, $n'$ and $\alpha$ are the material constants, $\alpha=\beta/n$. The AT model has also undergone several modifications over the years, including the introduction of the Zener-Hollomon parameter (Z) [157] and a strain-dependent parameter [158, 159] to improve the ability of the model to predict for different materials. Recently, a compensation of strain for the material constants in the AT model was proposed by Lin et al. [160]. This strain compensated Arrhenius type (ATC) model has been successfully applied to predict, with improved accuracy, the flow stress of metals and alloys over a wide range of temperatures and strain rates.
2.4 Hot corrosion

Hot corrosion is the salt-induced accelerated oxidation of metals and alloys, which takes place at a rate significantly higher than that typically associated with high-temperature oxidation. This phenomenon is the most common attack observed on high-temperature components used in gas-turbines, industrial boilers, waste incinerators and power generating systems. The attack is the result of the deposition of different salts on the structural parts from impurities, such as sulphur (S), sodium (Na), vanadium (V), potassium (K), chlorine (Cl), lead (Pb), etc., which are present in fuel. In the earliest studies on hot corrosion, a significant amount of sodium sulphate salt was observed and generally believed to be responsible for accelerated corrosion [161]. However, over the years, other salt deposits such as V₂O₅, potassium sulphate (K₂SO₄), lead (II) sulphate (PbSO₄), and NaCl were also reported for their role in the accelerated degradation of metals and alloys [162, 163]. Failure and maintenance related to hot corrosion are reported to account for about 5-10% of the total operating cost of components in power generating systems [164]. As a result of their economic impact, more studies have been carried out over the years to understand the source of the salt deposits and the mechanism of hot corrosion to mitigate its occurrence. The two likely sources of the salt deposition on turbine components, as reported by Bornstein and Allen [165], are through the condensation of salt from the gas phase in the turbine environment and the direct impaction of large salt particles on the structural components. It has been observed that for condensation to occur, it is essential that the surface temperature of the component is below the dew point of the salt. The characteristics and the amount of condensed salt deposits depend on the composition and concentration of impurities in the turbine environment. In the case of direct impaction of salt particles, the liquid or solid salt found in the environment upon impact adhere to the hot surface of the components. For the attack to progress, it is generally expected that the
deposited salt on the surface of the alloy is in a molten state, although it has been reported that only a thick and dense solid salt deposit is required for corrosion to proceed [166].

Hot corrosion is generally classified based on temperature and mechanism; that is, Type I or high-temperature hot corrosion or Type II or low-temperature hot corrosion. Type I corrosion is mainly observed at temperatures between 800ºC - 950ºC, which are usually above the melting temperature of Na₂SO₄ salts (melting temperature = 884ºC). There have been several mechanisms proposed that could be responsible for the occurrence of Type I corrosion when exposed to Na₂SO₄, but salt-fluxing (basic-acid fluxing) [167] is the most commonly accepted one. Salt-fluxing, which involves the dissolution of the protective oxide layer on the surface of the alloy, can be categorised as either basic or acidic fluxing. Basic fluxing is the dissolution of the protective oxide scale caused by a highly basic melt (with high 𝑎_{Na₂O}) [168]. Acidic fluxing on the other hand is the dissolution of the protective oxide layer caused by a highly acidic melt (with high 𝑝_{SO₃}) [169].

The characteristics of salt-fluxing that are predominant during the hot corrosion process when exposed to Na₂SO₄ have been observed to be largely influenced by the composition of the alloy. Alloys with elements like Al and Cr tend towards basic fluxing while alloys with elements such as W, Mo and V tend towards acidic fluxing [170]. A feature common to Na₂SO₄ hot corrosion regardless of the mechanism is that the onset of accelerated corrosion (also known as the propagation stage) is usually preceded by an incubation period (initiation stage) [171]. In the initiation stage, the alloy shows little or no weight loss/gain, which is the same as if the salt is not present. During this stage, the reaction between the alloy and molten salt result in the depletion of the elements needed to form the protective scale followed by the incorporation of an element such as sulfur or oxygen from the molten salt into the alloy, and then the dissolution of oxides or development of cracks in the scale occur. These changes which occur in the initiation stage, render the alloy susceptible to accelerated corrosion attacks in the propagation stage.
Type II corrosion usually occurs at temperatures between 600°C and 750°C, which are substantially below the melting temperatures of alkali sulphate. In the past, it was generally assumed that severe hot corrosion problems are not expected to occur at temperatures below the melting point of Na₂SO₄ (884°C) since molten salts are important for hot corrosion to proceed. However, this assumption was later challenged when turbine engine components operating at much lower temperature (between 600°C -750 ºC) in marine environments were severely attacked by hot corrosion [172]. For example, hot corrosion induced pitting was observed by Conde and Wareham [173] on a Nimonic 105 blade after operating in a marine environment at an approximate temperature of 750°C. The most widely acknowledged process for accelerated degradation due to Type II hot corrosion is the formation of salts with low melting point eutectics which degrade the component. Chiang et al. [174], and Luthra [172] showed that low melting eutectics are possible through the reaction of Na₂SO₄-MSO₄ (where M is either Ni or Co). Since (MSO₄) is formed due to the sulphation of metal oxides (NiO or CoO), a minimum sulfur trioxide (SO₃) partial pressure is generally required for the corrosion to proceed [172].

The formation of low-temperature eutectic salts can also occur due to the reaction of Na₂SO₄ with salts formed by other impurities such as V, Cl, Pb, etc., which are found in the turbine environment and can lead to the degradation of the structural components at moderate temperatures [16, 175–178]. Certain cost-effective fuels (e.g. heavy fuels) can contain up to 4% sulphur, 500 ppm of vanadium and several tens of ppm of sodium. After combustion, this can lead to the formation of a mixture of salt deposits on the components [179]. Luthra [180] carried out a thermochemical analysis of impurity deposits on gas turbines that use liquid fuels which contain Na, S, and V at different impurity concentrations and temperatures. It was observed that fuel which contained 1 wt % of S, 2 ppm of Na, and 30 ppm of V, a mixture of rich salt deposits of Na₂SO₄, V₂O₅, and NaVO₃ are expected to form between temperatures of 600º C and 1000ºC. A mixture of the
deposited salts such as Na$_2$SO$_4$ and V$_2$O$_5$ can lead to the formation to low melting eutectics even at temperatures as low as 500ºC, as seen in the phase diagram in Figure 2.9. Numerous hot corrosion studies have been carried out on Ni-based alloys for mixtures of Na$_2$SO$_4$ and V$_2$O$_5$ at temperatures between 550ºC – 900ºC to examine the corrosion mechanism. One important mechanism proposed by Davin et al. [181] is that accelerated corrosion in mixtures of Na$_2$SO$_4$ and V$_2$O$_4$ is due to the formation of low-melting vanadates which serve as both a fast diffusion path to allow the rapid transport of oxygen to the metal surface and a fluxing agent for the dissolution of the protective oxide scale. Cr$_2$O$_3$ which normally protects the surface of Cr containing superalloys was found to be ineffective in V$_2$O$_5$ containing salts.

Several factors are known to influence the hot corrosion resistance of alloys which include the chemical composition, temperature, characteristics of the salt deposit and more importantly, the microstructure of the attacked material. The microstructure of metal and alloys is typically determined by the processing history. The process by which the material is produced, i.e. casting, wrought, welding or additively manufacturing can very much affect the hot corrosion properties. For instance, the chemical inhomogeneity in Ni-based superalloy components produced by casting as a result of elemental segregation during solidification can cause local Cr or Al depleted zones, thus resulting in an overall reduction of corrosion resistance.
Figure 2.9: The phase diagram of the Na$_2$SO$_4$ – V$_2$O$_5$ system [182].
2.5 Literature summary and research scope

From the literature review in this chapter, it is evident that ATI 718Plus which is a recently developed Ni-based superalloy, can be a low-cost higher temperature replacement for its baseline alloy, Alloy 718. This is due to its better formability, weldability, and high-temperature stability compared to Alloy 718. As a result, ATI 718Plus is starting to be used in some of the static and rotary aero-engines.

The AM process is a viable manufacturing route for producing complex monolithic aerospace components. The WAAM process can improve the cost competitiveness of the AM process due to its high rates of deposition and higher material and energy efficiencies. This AM process is suitable for producing near-net-shape aero-engine components with moderate complexities at a medium to large scale. Alloy 718 produced by different AM processes has been found to contain significant elemental segregation which induces the formation of brittle intermetallic phase particles that are known to be detrimental to the mechanical properties of the alloy. In addition, this elemental segregation along with thermal gyration during deposition results in the non-uniform precipitation of the strengthening precipitates in the deposit thus leading to heterogeneous properties of the deposit. Furthermore, highly textured columnar grains are routinely observed in Alloy 718 deposits which may have an important impact on the high-temperature mechanical properties of the component in service.

Although elemental segregation in ATI 718Plus produced by DMLS has been shown to change the characteristics of the grain boundary phase formed, there is no study in the open literature that elaborates on the microstructural development and associated properties of ATI 718Plus produced by an AM process. This alloy is applied in critical areas where it is required to withstand dynamic impact loading, as well as resist highly corrosive environments at high operating temperatures.
However, the processing of the alloy can significantly affect its microstructure and affect its intended properties. In order to apply AM processes to manufacture ATI 718Plus aero-engine components, an in-depth understanding of the microstructure developed during the AM process and fundamental knowledge of the corresponding properties are essential for successful commercial applications of ATI 718Plus.

This research is, therefore, carried out to comprehensively characterise the microstructural development and associated properties of ATI 718Plus superalloy produced by using WAAM. The materials and methods will be discussed in the following chapter.
CHAPTER THREE

3 MATERIALS AND METHODS

3.1 Introduction

This chapter consists of three sections which provide an overview of the experimental techniques used in the thesis. The first section provides the experimental procedures used for the wire-arc deposition, microstructural characterisation, and post-deposition heat treatment. The second section explains the procedures for obtaining the high strain rate deformation behaviour of the alloys by using the direct Hopkinson pressure bar (DIHPB) technique. Lastly, the experimental procedures used to characterise the hot corrosion behaviour of WAAM ATI 718Plus and wrought ATI 718Plus are presented in the third section.

3.2 Materials

The wrought alloys used in this study are hot rolled Alloy 718 and ATI 718Plus. Their chemical composition is presented in Table 3.1. The alloys were supplied by ATI Specialty Materials. The ATI 718Plus additive wire, which is about 1.6 mm in diameter, was supplied by Tricor Alloys, Ohio, USA. The chemical composition of the wire is also provided in Table 3.1.

3.3 Wire-Arc Additive Manufacturing of ATI 718Plus

A Perform Arc robotic welding system integrated with a 6 DOF Panasonic VR-004 robot was used to fabricate the deposits with the use of WAAM. The robotic arm is fitted with a tungsten inert gas (TIG) welder, wire-feeder, and all other associated peripherals (see Figure 3.1). In addition, a cylinder of argon gas which was used to shield the molten pool from the atmosphere was installed into the system. The substrate material, on which deposition was made, was attached firmly to the table with a mechanical vice capable of X-Y movement. The programming of the robot and the control of the wire-arc deposition was done by using a teach pendant.
Figure 3.1: TIG Welder fitted with 6 DOF PANASONIC VR-004 Robot
3.3.1 WAAM ATI 718Plus deposit

The hot rolled ATI 718Plus plate with dimensions of 12.5 mm x 110 mm x 45 mm was used as the substrate material for all of the depositions. The surface oxide on the plate from previous processing activities was removed by grinding (see Figure 3.1) and wire-arc depositions were made on the wrought alloy in the mill annealed condition. Based on the deposition parameter established with the use of the same robotic welding system in Thukaram [183] for some of the Ni-alloys, considerable trials of deposition were carried out to obtain a smooth and reproducible deposit with fewer visual defects. Since the scope of this study is focused on the investigation of the nature of phases produced during the wire-arc AM process, a single process parameter capable of producing defect free deposits is selected for study. After this was achieved, a series single-wall of 1-10-layer deposits was laid on the substrate with the use of the deposition parameters in Table 3.2. The scanning and build directions applied during the single-wall deposition are presented schematically in Figure 3.2a. The total length of all the deposits is about 70 mm, and no time delays were allowed between the deposition scans.

Using the deposition parameters for single wall deposition, a multilayer block was produced for extracting samples for the high strain rate deformation tests and hot corrosion experiments. In producing the block material, a number of single layers were deposited adjacent to each other with an overlap between the weld beads. To obtain a reasonable microstructurally flat overlapping surface with few valleys, an overlap distance of $d = 0.75 \times W_d$ was used for the deposition; where $W_d$ is the width of a single bead and d is the overlap distance as seen in the schematic diagram in Figure 3.2b. After depositing a single layer, the process was then repeated with another layer stacked on top of the previous layer to produce the block material (see Figure 3.4).
Table 3.1: Composition of wrought Alloy 718, ATI 718Plus, and ATI 718Plus filler wire in wt.%

<table>
<thead>
<tr>
<th>Concentration (wt%)</th>
<th>Materials</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Wrought 718</td>
</tr>
<tr>
<td>Nb</td>
<td>5.4</td>
</tr>
<tr>
<td>Fe</td>
<td>17.6</td>
</tr>
<tr>
<td>Cr</td>
<td>17.9</td>
</tr>
<tr>
<td>W</td>
<td>0.01</td>
</tr>
<tr>
<td>Ti</td>
<td>0.94</td>
</tr>
<tr>
<td>Al</td>
<td>0.46</td>
</tr>
<tr>
<td>Mo</td>
<td>2.9</td>
</tr>
<tr>
<td>Co</td>
<td>0.13</td>
</tr>
<tr>
<td>C (ppm)</td>
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</tr>
<tr>
<td>B (ppm)</td>
<td>40</td>
</tr>
<tr>
<td>Si</td>
<td>0.05</td>
</tr>
<tr>
<td>P (ppm)</td>
<td>70</td>
</tr>
<tr>
<td>Mn</td>
<td>0.05</td>
</tr>
</tbody>
</table>
3.3.2 Temperature Measurement

To monitor the thermal cycle during the deposition scans, a K-type thermocouple was resistance spot welded to the substrate before the deposition. The thermocouple was protected from the arc with tantalum foil with a thickness of 0.12 mm that was spot welded over the thermocouple. The influence of the tantalum foil on the thermocouple response time was accessed by using different foil dimensions (30mm$^2$ and 100 mm$^2$). A single-wall, 10-layer deposit was placed over the tantalum plate and the temperature cycle during deposition was monitored and recorded by using the control display.

3.4 Material Characterisation

The samples that were subjected to optical microscopy (OM) and SEM were sectioned and then mounted in conductive Bakelite. They were subsequently grounded and polished by using standard metallographic techniques and further polished chemically in a colloidal silica suspension with a Vibromet polisher. After polishing, the samples were either etched with Kalling’s #2 reagent by swabbing or electro-etched in 170 ml of phosphoric acid (H$_3$PO$_4$) +10 mL of sulfuric acid (H$_2$SO$_4$) + 15 g of chromium trioxide (CrO$_3$) at 5 V for 20 seconds depending on the desired microstructure.

The OM analysis was performed by using a Axio Vert inverted optical microscope (Carl Zeiss). The SEM analysis was performed with a JEOL 5900 scanning electron microscope (Oxford Instruments) with an ultra-thin window energy dispersive spectrometer (EDS) and an FEI Nova NanoSEM 450 with a high-resolution field emission gun (FEG). EBSD was conducted by using a Philips LX30 scanning electron microscope, equipped with an EDS (Oxford Instruments) and EBSD detector and analysis system. The electron microprobe analysis was conducted by using a Cameca SX100 electron microprobe equipped with Princeton Gamma Tech (PGT) Prism 2000 detector.
Thin foils used for carrying out TEM were also sectioned from some of the selected regions of the deposit, grounded to about 100 µm by using 400 grit silicon carbide paper and punched out into 3 mm coupons before subjected to dimpling and electro-polishing. The electro-polishing of the foils was carried out with a twin-jet polisher in a solution of 10% chloric acid + 90% methyl alcohol at around 233 K (-40°C).

TEM was performed on a FEI Talos F200X transmission electron microscope equipped with a Super-X EDS system with 4 silicon drift detectors (SDDs).

The hardness profile across the WAAM ATI 718Plus deposit was obtained with a Buehler micro-hardness tester under a load of 300-g by using the same sample as that for the SEM.

### 3.5 Heat treatment procedures

The recommended heat treatment procedures for wrought Alloy 718 and ATI 718Plus are summarised in Table 3.3. The heat treatment consisted of a solution heat treatment at 954°C-982°C to precipitate the δ and η-phases, respectively. This was followed by a two-step ageing treatment for the optimum precipitation of the strengthening precipitates in the alloys. PDHTs were also conducted on the WAAM ATI 718Plus, and the procedure and microstructural changes during the heat treatments are discussed in detail in Section 4.3.8.2.
Table 3.2: Deposition parameters for the deposits

<table>
<thead>
<tr>
<th>Deposition Parameters</th>
<th></th>
</tr>
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<tbody>
<tr>
<td>Arc current (A)</td>
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</tr>
<tr>
<td>Travel speed (m/min)</td>
<td>0.1</td>
</tr>
<tr>
<td>Wire feed speed (m/min)</td>
<td>0.4</td>
</tr>
<tr>
<td>Arc length (mm)</td>
<td>3 - 4</td>
</tr>
<tr>
<td>Gas Flow Rate (l/min)</td>
<td>15</td>
</tr>
</tbody>
</table>

Figure 3.2: (a) Schematic diagram of deposition showing (a) the scanning and building directions of the single wall deposit, (b) overlapping layer of multiple stringer depositions.
Figure 3.3: Typical WAAM ATI 718Plus multiple-stringer/multiple-layer deposits.
3.6 Mechanical Deformation under Quasi-static and High Strain Rates

To characterise the deformation behaviour of the alloys under quasi-static and high strain rate conditions, cylindrical test samples were machined from the alloys by using an electric discharge machine (EDM).

3.6.1 Quasi-static compression test

A United Hydraulic testing machine with a maximum load carrying capacity of 600 kN was used to investigate the deformation behaviour of the wrought alloys under quasi-static compressive loading. The ends of the cylindrical samples were polished and lubricated with molybdenum disulfide grease to minimise the effect of friction between the ends during deformation.

3.6.2 High strain rate deformation experiment

The dynamic properties of the alloys at high strain rates were characterised by using DIHPB. The DIHPB was developed at the University of Manitoba and has been used to characterise different materials at very high strain rates and large strains [184–188]. The schematic diagram of the DIHPB and a photograph of the installed pressure bar are shown in Figure 3.4 and Figure 3.5, respectively. The equipment consists of a transmission bar and a projectile, which are both 38 mm in diameter and constructed from AISI 4340 steel, along with a gas gun to fire the projectile. The length of the projectile and the transmission bar is 225 mm and 1.5 m respectively and the impact ends are hardened and have hardness values of approximately 53 HRC. A strain gage is attached to the transmitter bar which is connected to a differential amplifier and a digital oscilloscope to monitor the strain history during impact testing. The deformation test procedures with the use of this equipment has been discussed in detail in [184].
Table 3.3: Recommended standard heat treatment procedures for ATI 718Plus® and Alloy 718.

<table>
<thead>
<tr>
<th>Heat treatment designation</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Recommended heat treatment ATI 718Plus</strong></td>
<td><strong>Solution heat treated (SHT) at 982/954 °C (for 1 hr) then, water quenching (WQ)</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Aged at 788 °C for 8 hrs, cool at 55°C/hr to 704 °C,</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Hold at 704 °C for 8 hrs + air cool</strong></td>
</tr>
<tr>
<td><strong>Recommended heat treatment Alloy 718</strong></td>
<td><strong>Solution heat treated (SHT) at 954 °C (for 1 hr) then, water quenching (WQ)</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Aged at 718 °C for 8 hrs, cool at 55°C/hr to 620°C,</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Hold at 620 °C for 8 hrs + air cool</strong></td>
</tr>
</tbody>
</table>
For the high-temperature tests, a fixture was attached to the equipment (see Figure 3.6) which allowed for ease of transfer of the sample from the furnace to the impact site in a safe and repeatable manner. A dummy sample equipped with a thermocouple was used to estimate the heating and cooling times. A soaking time of 10 min was observed to be adequate for the heating and homogenisation of the sample at the desired temperature. The average time for the sample to leave the furnace until impact was between 4-6 seconds. At 800°C, the temperature drop was estimated to be approximately 14°C after 10 seconds of removing the sample from the furnace. This is accounted for by super-heating the sample at 10°C above the testing temperature.

The elastic wave signals recorded and stored by the oscilloscope were used to plot the dynamic stress-strain graphs. The true strain ($\varepsilon_t$) can be plotted by using the following relation:

$$\varepsilon_t = \ln \frac{l(t)}{l_o}$$

(3.1)

where $l_0$ is the initial sample length and $l(t)$ is the instantaneous change in length which can be obtained directly from a known function of force, $f(t)$:[189]:

$$l(t) = l_0 - v_0 t + \frac{2}{ZA} \int_0^t f(t') dt'$$

(3.2)

where $v_0$ is the impact velocity, Z is the mechanical impedance of the bar and $A$ is the cross-section area of the bar.

The equivalent true stress ($\sigma$) is obtained by [184]:

$$\sigma = \sigma_t - \sigma_r$$

(3.3)

where $\sigma_t$ is the experimental stress obtained by:

$$\sigma_t = \frac{F(t)}{A(t)}$$

(3.4)
Figure 3.4: The schematic diagram of the direct impact Hopkinson pressure bar (DIHPB) system.
Figure 3.5: Photograph of the direct impact pressure bar in University of Manitoba.

Figure 3.6: Fixture for specimen transfer during the high-temperature test.
where \( F(t) \) is the load pulse that corresponds to time \( t \) and \( A \) is the instantaneous cross-section area, and the radial stress \( \sigma_r \) due to inertia during impact deformation is estimated with:

\[
\sigma_r = \frac{3\rho}{8}\left(\frac{a_0}{l_0}\right)^2v_0\left(1 - \epsilon(t)\right)^3
\]  

(3.5)

where \( a_o \) is the initial radius of the sample, \( \rho \) is the density of the bar and \( \epsilon(t) \) is the engineering strain.

### 3.7 Hot Corrosion Experiment

Hot corrosion test samples with dimensions of 12 x 10 x 4mm were sectioned from both the deposited material and the wrought ATI 718Plus with the EDM. The wrought ATI 718Plus samples were subjected to the recommended standard heat treatment as summarised in Table 3.3.

The test coupons for the hot corrosion testing were first grounded by using silicon-carbide paper down to 600 grit and then cleaned in acetone to remove any grease. A saturated solution was prepared by dissolving laboratory grade \( \text{Na}_2\text{SO}_4 \) and \( \text{V}_2\text{O}_5 \) in distilled water at a ratio of 40:60, respectively, to produce sodium vanadate eutectics at low melting temperatures as low as 500\(^\circ\)C.

The coupons were heated on a hot plate to approximately 160\(^\circ\)C while a salt mixture was simultaneously sprayed onto their surface with a spray gun. During the salt application, the test coupons were constantly weighed to ensure that the proper quantity of salt was deposited onto them. Approximately 5.0\( \pm \) 0.2 mg of the salt mixture was deposited on each of the test samples.

The coated samples were then placed into an alumina crucible and isothermally oxidized at 650\(^\circ\)C and 705\(^\circ\)C in air for 0.5, 1, 2, 4, 10, 20,40,60,80 and 100 hrs. To obtain the changes in weight, the salt-coated samples were weighed before and after they were oxidized by using a Sartorius Entris64-1S laboratory balance with an accuracy of 0.1 mg.
CHAPTER FOUR

4 RESULTS AND DISCUSSION

4.1 Introduction

The results of the experimental work and discussion in this chapter are presented in three parts. The first part discusses the microstructure of the wrought ATI 718Plus and details of the microstructural analysis of ATI 718Plus produced by the wire-arc additive manufacturing process. In addition, the influence of PDHTs on the microstructure of WAAM ATI 718Plus is also discussed. In the second and third parts of this chapter, the influence of the as-processed WAAM ATI 718Plus microstructure on high strain rate deformation and hot corrosion behaviour at low-temperatures, respectively, is presented and discussed. Furthermore, the effectiveness of the post-deformation heat treatments on WAAM ATI 718Plus is assessed.

4.2 Microstructure of wrought ATI 718Plus

The microstructure of wrought ATI 718Plus after the recommended standard heat treatment is presented in Figure 4.1 and Figure 4.2. The wrought alloy was used as the substrate material during deposition and as the reference alloy when evaluating the properties of the WAAM ATI 718Plus.

The OM image and the EBSD inverse pole figure (IPF) map of the wrought ATI 718Plus are presented in Figure 4.1. The wrought ATI 718Plus shows an equiaxed and random grain structure, with an approximate grain size of 20 µm (Figure 4.1a and 41b). A higher magnification SEM micrograph image (Figure 4.2a) reveals the presence of grain boundary precipitates which have been generally identified as η phase particles [49, 50]. In addition, blocky discrete intragranular particles are distributed in the wrought alloy. The SEM/EDS analysis of the intragranular particles shows that they are based on Nb and Ti-rich primary carbides (MC carbides).
Figure 4.1: Microstructure of wrought ATI 718Plus (a) the optical micrograph and (b) the EBSD inverse pole figure.
Figure 4.2: (a) SEM image showing the η-phase precipitates and MC carbides, and (b) TEM micrographs showing dark-field image of γ' in ATI 718Plus
The TEM analysis was used to analyse the crystallographic characteristics of the nano-sized precipitates in the wrought alloy. Figure 4.2b presents the dark-field (DF) image of the \( \gamma' \) precipitates in ATI 718Plus. The superlattice reflection in the inset confirms that only \( \gamma' \) strengthening precipitates are found in the matrix of the alloy. The \( \gamma' \) precipitates have a spherical morphology and the estimated average diameter of the precipitates is about 20-30 nm in size.

4.3 Microstructural Analyses of ATI 718Plus Produced by WAAM

This section provides details on the solidification characteristics and solid-state microstructural transformations during the single-layer, single-wall/multiple-layer and multi-stringer bead/multiple-layer deposition of WAAM ATI 718Plus.

4.3.1 Macrostructure and Morphology of Single Wall Deposition

The initial deposition trials showed that the morphology of the deposit is largely affected by the arc current when the wire feed rates, arc length and travel speed are held constant. Figure 4.3(a) and 4.3(b) show flatter and wider deposits with increased arc current, respectively. The optical micrograph image of a two-layer single wall deposit is shown in Figure 4.4a. The dotted white line shows the fusion line between the first deposition and the subsequent deposition scan. After the second deposition scan, the thickness of the first layer is reduced. This is attributed to the re-melting of the top portion of the previous deposit that was in direct contact with the molten metal, thus becoming part of the new solidifying layer. This phenomenon is also found in all of the multilayer deposits, as the thickness of the final deposition scan is always the greatest. After these initial trials, single wall deposits with 5 and 10 layers of WAAM ATI 718Plus were made on the substrate for both hardness measurements and microstructural analysis. The fusion lines that can be seen in the X-Z direction in Figure 4.4b, and rippled surface on the exterior of the wall (see Figure 3.3) indicate the deposition scans. Previous studies have reported that the extent of the rippled surface is based on some of the deposition parameters and feedstock dimensions [6, 75].
In this study, the diameter of the filler wire is about 1.6 mm, which is relatively wide and hence results in an obvious rippled surface. Other than the rippled surface, there are no cracks, improperly fused areas or pores observed in any of the deposits.

4.3.2 Hardness profile of deposit

Figure 4.5 shows the hardness profiles of the 1, 5 and 10-layer deposits after carrying out the Vickers micro-indentation test. An average of 20 hardness measurements were made for each point and the standard deviation for each point is plotted in the shaded region. The profiles were measured along the centre line of the transverse section of the build-up. There is no significant variation in the hardness of the deposits measured in the transverse (X – Z) direction and that measured along the longitudinal (Y - Z) direction. It can be observed in the figure that the hardness values for the as-solidified single-layer deposit (as-solidified zone (ASZ) henceforth) and those for the final layer of the 5 and 10-layer depositions are comparable (about 270 HV). The similarity in the hardness of these regions can be attributed to the similar solidification characteristics and the fact that they are not subjected to further thermal cycles after solidification. The bottom-middle region (denoted as the hardened zone (HZ) henceforth) has the highest hardness value (average value about 330 HV) of the deposit. In general, the size of the hardened region of the deposit from the substrate increases with deposition scans. Surprisingly, the region below the ASZ which spans about 2 mm (denoted as the DMHAZ henceforth) was observed to have the least amount of hardness (about 230 HV) in the deposit. This soft zone was also found to be transient and moves with each subsequent deposition scan as seen in the hardness profile of the HZ in Figure 4.5.
Figure 4.3: Optical image showing the effect on arc current on the macrostructure of 1-layer deposits (a) 130A (b) 100A

Figure 4.4: Macrostructure of ATI 718Plus deposit showing (a) a 2-layer deposit (a) a 10-layer deposit, on ATI 718Plus substrate.
It is worth noting that even though previous studies have indicated that there is a hardness gradient and mechanical heterogeneity in additively manufactured deposits \cite{117, 124}, the observed softening behavior in this study has not been reported in additively manufactured Alloy 718 or ATI 718Plus. A similar softening behavior, with deleterious effects on the mechanical properties, has been reported in the HAZ of dual-phase steel \cite{190}. The phenomenon which is known as HAZ softening was first identified when dual-phase steels were flash butt welded for wheel rim use \cite{191}. It was found that failure consistently occurs at the previously softened HAZ, which is caused by the tempering of martensite in the HAZ during the welding process. The softening behaviour observed in this work, if neglected during processing, could have detrimental effects on the integrity of the finished deposit in service. It is thus imperative to have a proper understanding of the developed microstructure and the underlying mechanism of the observed softening of the WAAM ATI 718Plus.

### 4.3.3 Temperature evaluation during 10-layer deposition

To analyse the phase transformation in WAAM ATI 718Plus, the thermal profile during deposition scans is an important factor which needs to be taken into consideration. To do so, the temperature measurement method in Segerstark \cite{192} is modified for use in this study, as discussed in the experiment and method (section 3.3.2). The solid black line in Figure 4.6 shows the temperature measured by the thermocouple at the bottom of the 10-layer deposit. During the first deposition scan, the temperature initially increases from room temperature to around 1230°C. This recorded peak temperature measured by the thermocouple is believed to be significantly lower than the actual temperature required to melt ATI 718Plus superalloy. The discrepancy can be attributed to the time needed to conduct heat through the shielding foil (tantalum) to the thermocouple along with the fact that the substrate material is a heat sink and dissipates heat rapidly.
Figure 4.5: Hardness profile of the 1, 5 and 10-layer depositions
So, the measured temperature of the first layer will depend on the type and thickness of the protective material and the dimensions of the substrate material. However, as the temperature of the thermocouple equilibrates with the deposit and substrate, the measured temperature for the subsequent deposition provided a better idea of the actual temperature found at the bottom of the deposit during scans. The temperature measured at the bottom of the deposit during the first three (3) deposition scans exceeds 1000°C but remained below that subsequently. Also, due to the size of the substrate material which serves as a heat sink, the temperature after the first layer is deposited decreases to 400°C and then increases afterward. Aside from these exceptions, the temperature at the bottom of the deposit during the deposition of 10 layers of the alloy gyrated approximately between 700°C - 900°C (cooling approximately 5°C/s within each cycle) and subsequently cooled down to room temperature at a rate of 5°C/s after deposition.

The insertion of a thermocouple in the build to monitor the thermal cycles during scans is not feasible in this study. Therefore, thermal values in the build were estimated by using the thermal history from the bottom of the build. The estimated temperature for the 6th layer (middle of the deposit) and the 9th layer of the deposit (the DMHAZ) are also presented as a dotted line in Figure 4.6a. The blue dotted line denotes the approximate range of the ageing temperature for the precipitation of \( \gamma'/\gamma'' \) phase [39]. The estimated temperature frequency distribution of the three zones of the deposit is plotted in Figure 4.6b. The middle and bottom zones of the deposit are observed to have spent considerable time in the ageing temperature range of the alloying during the deposition scan, hence significant precipitation and strengthening are expected in these two zones. In addition, the temperature at the DMHAZ (or 9th layer) during the final deposition scan is over 1373 K (1100°C) which exceeds the solvus temperature of the strengthening precipitates (\( \gamma'/\gamma'' \) precipitates). Therefore, if any strengthening precipitates form during the solidification of this zone, they are anticipated to have completely dissolved during the final deposition scan.
Figure 4.6: (a) Temperature profile of the deposit at different locations in the build (b) Estimated frequency distribution of temperature of 1st, 6th and 9th layer depositions.
4.3.4 Microstructural Characterisation of Single-layer WAAM ATI 718Plus

An essential prerequisite to determining the fundamental reason for softening behavior is a proper understanding of the solidification characteristics and solid-state transformation during the single-layer deposition of ATI 718Plus. Low magnified optical and SEM micrograph images of a single layer deposit are shown in Figure 4.7. The OM micrograph image shows a with columnar and equiaxed dendritic solidified structure, in which the columnar structure is at the bottom in the direction of the heat extraction, while the equiaxed structure is at the top. The fine equiaxed structure at the top may be due to the considerable cooling effect from the shielding gas. An examination of the deposit by using a scanning electron microscope at higher magnification shows that there are some secondary phase particles in the inter-dendritic regions, see Figure 4.8a. Most of the second phase particles are irregular in shape and distributed discretely along the interdendritic regions. Also associated with these irregularly shaped particles are some blocky-shaped particles. A preliminary SEM/EDS analysis on these secondary constituents showed they are enriched with Nb. A similar microstructure was reported in the solidified fusion zone of the ATI 718Plus weld [193–195] and in the AM of Alloy 718 [125]. The morphology of these particles, their location and composition suggest that they are based on the Laves phase and MC type of carbides.

Furthermore, the SEM backscatter image in Figure 4.8b shows a bright compositionally contrasting ring around these interdendritic particles, which suggests that these bright regions contain higher atomic elements.
Figure 4.7: Optical and SEM micrographs showing the solidification microstructure of a single layer deposit
A high-resolution scanning electron microscope with an FEG was used to examine the microstructure of these bright regions (see Figure 4.8c). A dense population of nano-sized precipitates was observed around the secondary phase constituents and in other areas of the interdendritic regions. These precipitates are, however, fine and their details cannot be resolved with the SEM. They are believed to be the strengthening precipitates in ATI 718Plus which could be any of γ' and γ" precipitates or a combination of both. Although thermodynamic calculations showed that the precipitation of γ" is expected in ATI 718Plus [39], the presence of γ" precipitates in this alloy are not usually observed with only a few exceptions [42]. Besides the strengthening precipitates, plate-like particles were also observed in the interdendritic regions. The morphology of these particles suggests that they are either the δ or η phase particles often reported in the grain boundaries of ATI 718Plus but in this case, precipitated along the interdendritic regions.

TEM was carried out to examine the structure and composition of the secondary constituents in the interdendritic regions and resolve and verify the characteristics of the associated precipitates. Figure 4.9 shows a TEM bright field (BF) image and the selected area diffraction patterns (SADPs) of the blocky-shaped particles observed in the interdendritic regions. Details of the TEM/EDS analysis are summarised in Table 4.1, which shows that the particles have a high Nb content with a significant amount of Ti. The SADP of the [001], [110] and [130] zone axes presented in Figure 4.9(b-d), respectively, indicates that the crystal structure is a cubic NaCl-type structure with a lattice parameter a=0.45 nm. From the EDS analysis and the SADP, it can be concluded that these particles are composed of Nb, or Ti-rich carbides (NbC). Similarly, a TEM BF image of the other irregular shape particles in the interdendritic region and the SADP of the [1\overline{1}00], [10\overline{1}0] and [2\overline{2}03] zone axes are shown in Figure 4.10.
Figure 4.8: SEM micrographs of single layer deposited ATI 718Plus showing (a) eutectic solidification micro-constituents in the interdendritic regions, (b) bright contrast rings along the interdendritic regions, and (c) high magnification image of nano-scale interdendritic particles.
The TEM/EDS carried out on these particles shows that they contain a relatively large amount of Nb, Cr, Ni, Fe and other minor elements that have a composition close to \((\text{Ni,Cr,Fe})_2(\text{Nb,Mo,Ti})\) at% as shown in Table 4.1. Also, the SADPs in Figure 4.10(b) to 4.10(d) show that these particles have a hexagonal crystal structure with a lattice parameter \(a=0.48\) nm and \(c=0.78\) nm. The TEM analysis confirmed that these irregular particles are based on the Laves phase. The presence of Laves phase particles has not been previously reported in ATI 718Plus produced by using the AM process[129, 130]. It is generally known that the presence of Laves phase particles in ATI 718Plus is detrimental to its mechanical properties. The need for post-deposition treatment to eliminate or reduce the content of Laves phase particles in the deposit is essential for wire-based AM processes.

To analyse the strengthening precipitates observed in the interdendritic region, TEM analysis was performed on the deposit. The TEM/SADP from the \([100]\) zone axis of the \(\gamma\) matrix is presented in Figure 4.11a. Super-lattice reflections that correspond to \(\gamma'\) and \(\gamma''\) can be observed in the interdendritic regions with proximity to the secondary phase constituents. The BF image of the interdendritic region in Figure 4.11c shows the strengthening precipitates but due to the high coherency with the matrix, the \(\gamma'\) precipitates are barely visible. A DF image of the \(\gamma''\) precipitates in Figure 4.11d shows that the average length and width of the \(\gamma''\) precipitates along the interdendritic region is about 20 nm and 5 nm respectively. Also, the DF image of the \((001)\) reflection in Figure 4.11f shows the average size of the \(\gamma'\) precipitates to be about 10 nm. White streaks can be observed to be associated with the \(\gamma'\) precipitates, which could have been from the \(\gamma''\) reflections, thus suggesting that there could be associated precipitation of the \(\gamma'\) and \(\gamma''\) precipitates. Xie et al. [43] and Cozar [196] reported similarly associated precipitation of \(\gamma'\) and \(\gamma''\) precipitates in modified Alloy 718. They attributed the precipitation behaviour to the content and ratio of Nb, Ti, and Al in the Ni alloy.
Table 4.1: EPMA/WDS point analysis of interdendritic regions of the deposit, and TEM/EDS of Laves phase and MC carbide particles.

<table>
<thead>
<tr>
<th>Elements</th>
<th>As-solidified interdendritic</th>
<th>DMHAZ interdendritic</th>
<th>Laves phase</th>
<th>MC carbide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%</td>
<td>at%</td>
<td>wt%</td>
<td>at%</td>
</tr>
<tr>
<td>1. Ni</td>
<td>50.5</td>
<td>51.0</td>
<td>51.2</td>
<td>51.2</td>
</tr>
<tr>
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<td>1.3</td>
<td>2.9</td>
<td>1.4</td>
<td>3.0</td>
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</tr>
<tr>
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</tr>
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<td>9.1</td>
<td>9.5</td>
</tr>
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<td>6. Mo</td>
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<td>2.0</td>
<td>3.0</td>
<td>1.8</td>
</tr>
<tr>
<td>7. Nb</td>
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<td>5.8</td>
<td>7.2</td>
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</tr>
<tr>
<td>8. Ti</td>
<td>1.1</td>
<td>1.3</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>9. W</td>
<td>0.8</td>
<td>0.3</td>
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<td>0.3</td>
</tr>
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</table>
Figure 4.9: TEM analysis of single layer deposited ATI 718Plus showing (a) bright field (BF) image of NbC, and the selected area diffraction pattern (SADPs) from (b) [001] (c) [110] and (d) [130] zone axis of the carbide.
Figure 4.10: TEM analysis of single layer deposited ATI 718Plus showing (a) BF image of Laves phase, and the SADPs from (b) [11\overline{1}00], (c) [2\overline{1}10] and [2\overline{2}03] zone axis of the Laves particle.
Figure 4.11: TEM analysis of single layer deposited ATI 718Plus (a) SADP from the interdendritic region showing the super-lattice reflection from $\gamma'$ and $\gamma''$ precipitates (b) SAD pattern from the interdendritic/dendritic core boundary showing the reflections from only $\gamma'$ precipitates (c) BF image of strengthen precipitates in the interdendritic regions (d) dark-field (DF) image of $\gamma''$ taken from the encircled diffraction spots in (a), and (e) dark-field image of $\gamma'$ and $\gamma''$ precipitates taken from the (001) reflection in (a).
Elemental micro-segregation during solidification may have influenced the concentration of these elements in the interdendritic regions, thus prompting the formation of the observed associated precipitates. Furthermore, most of the strengthening precipitates are concentrated along the interdendritic regions. The concentration of the precipitates reduces with increasing distance from the interdendritic regions. Inside the dendrites, only $\gamma'$ precipitates formed in the regions close to the interdendritic regions without $\gamma''$ precipitates as seen in the SADP in Figure 4.11b, while no evidence of either $\gamma'$ or $\gamma''$ precipitates was observed within the dendrite core. The observed strengthening precipitates in the interdendritic regions of the as-solidified deposit could have somewhat strengthened the deposit.

4.3.4.1 Solidification characteristics and elemental micro-segregation

To explain the non-uniform accelerated precipitation and the formation of secondary constituents along the interdendritic regions, the solidification characteristics of ATI 718Plus need to be well understood. The distribution of elements in WAAM ATI 718Plus, measured by the partition coefficient $k$ is given in Table 4.2. The elemental distribution/partition coefficient $k$, which is the ratio of the concentration of the solute in the solid to that in the liquid at equilibrium, was calculated by using the EPMA/ wavelength-dispersive spectroscopy (WDS) data obtained from the dendrite core regions. According to Bower et al. [197], solute re-distribution can be described by using the following equation under equilibrium conditions and the assumption of complete mixing in the liquid and no diffusion in the solid:

$$C_s = kC_0[1 - f_s]^{(k-1)} \quad (4.1)$$

where $C_s$ is the composition of the solid at the liquid/solid interface, $C_0$ the nominal composition and $f_s$ is the volume fraction of the solid. At the start of the solidification, $f_s=0$, and the first solid to form the liquid (dendrite core) will have a composition of $kC_0$. Therefore, the ratio between the dendrite core composition and the nominal composition of ATI 718Plus will yield the partition
Table 4.2: EPMA/WDS elemental distribution within the dendritic core regions and the partition coefficient of the WAAM 718Plus

<table>
<thead>
<tr>
<th>Element (wt%)</th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Nb</th>
<th>Mo</th>
<th>Ti</th>
<th>Fe</th>
<th>Al</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrite core</td>
<td>51.8</td>
<td>19.3</td>
<td>9.1</td>
<td>3.1</td>
<td>2.5</td>
<td>0.6</td>
<td>10.6</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Partition coefficient, $k$</td>
<td>1.00</td>
<td>1.09</td>
<td>1.01</td>
<td>0.56</td>
<td>0.81</td>
<td>0.75</td>
<td>1.16</td>
<td>1.00</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Figure 4.12: JMatPro simulation showing the partitioning of alloying elements at the liquid-solid interface
coefficient, \( k \) at the beginning of solidification. Alloying elements with \( k < 1 \) tend to partition to the interdendritic liquid while elements with \( k > 1 \) partition to the dendritic core regions. It is seen in Table 4.2, that while Nb, Mo, and Ti significantly partition to the interdendritic regions, Cr, Ni, Co, and Fe moderately partition to the dendrite core. The selective partitioning of Nb, Ti, and C to the interdendritic regions is known to be responsible for the formation of Laves phase particles and MC-type carbides during the solidification of the ATI 718Plus and Alloy 718 [41], which is consistent with the observations in this study. In comparing the partition coefficient, \( k \), calculated in this work with that reported in a previous study on the fusion zone of EBW ATI 718Plus by Vishwakarma [195], it is observed that the elemental segregation in both systems follows a similar pattern. However, there is a significant increase in the segregation of Nb and Ti to the interdendritic liquid during solidification in wire-arc deposition as shown by the lower partition coefficient values. This may be attributed to the higher heat input in arc-based systems (estimated heat input in this study \( \sim 1200\text{J/mm} \)) which enhances micro-segregation [11]. Moreover, this study shows that \( \gamma'' \) precipitates, which have been rarely reported to be observed in ATI 718Plus, can indeed form due to elemental micro-segregation.

The solidification behaviour of cast ATI 718Plus and the weld fusion zone of ATI 718Plus has been previously investigated [see 7,9,27]. During the solidification of ATI 718Plus, the primary \( \gamma \)-dendrite is the first solid to appear. As this dendrite grows, solute elements such as Nb and Ti with a partition coefficient \( k < 1 \) [194, 195] are injected into the interdendritic liquid, which is the reason for their increased concentration in the interdendritic liquid. After a while, the concentration of these solute element in the interdendritic liquid is increased with the increasing growth of the \( \gamma \)-dendrites, thus promoting the onset of the formation of secondary phase constituents. Due to the enrichment of the interdendritic liquid with Nb and Ti which are strong carbide forming elements, MC-type carbides eventually form through a non-variant eutectic reaction at about 1565 K
(1292°C) [39, 195]. The formation of MC-type carbides depletes the interdendritic liquid with most of its carbon content [21]; however, the liquid continues to be enriched with Nb with further growth of the γ-dendrites. In the final stage of the solidification, the Nb content in the interdendritic liquid would have increased to about 19.7 wt% (as shown in Figure 4.12) which exceeds the supersaturation limit of Nb in the liquid [39], thus triggering the formation of Laves phase particles at the end of the solidification through a non-variant eutectic reaction reported to occur at about 1446 K (1173°C) [39].

### 4.3.4.2 Accelerated precipitation of strengthening phase

As discussed earlier, the segregation of Nb takes place in the interdendritic liquid during solidification thus leading to the formation of secondary phase constituents. The γ-matrix around the interdendritic regions is expected to be enriched with Nb compared to the γ-matrix in the dendrite core, and this can be observed in the SEM backscatter image in Figure 4.8b. The EPMA/WDS analysis presented in Table 4.1 and shows the composition of γ-matrix in the interdendritic regions and the dendrite core regions, respectively. The interdendritic regions have a significantly higher content of Nb of about 9.2 wt% which is in agreement with the solubility limit of Nb in the γ-matrix [at 1446 K (1173°C)] as shown in the pseudo-binary phase diagram of ATI 718Plus developed by Cao et al. [39]. The accelerated precipitation of the strengthening precipitates observed in the interdendritic regions can be attributed to the increased Nb content which contributes to their formation. To validate this assertion, a TTT-diagram of an Nb-enriched γ-matrix is constructed by using a Java-based material property software (JMatPro) and compared with that constructed from a nominal ATI 718Plus as presented in Figure 4.13. It is apparent from the plot that the kinetics of the precipitation of the γ'/γ" precipitates is faster with a higher Nb content.
Figure 4.13: Calculated TTT curve for $\gamma'$, $\gamma''$ and $\delta$-phase precipitates of ATI 718Plus and modified ATI 718Plus (from the interdendritic regions) using JMatPro software
Also, contrary to the precipitation characteristics of ATI 718Plus [39], the kinetics of $\gamma''$ seems to be faster than that of $\gamma'$ in the interdendritic region as presented in the constructed TTT plot in Figure 4.13. The higher content of Nb which significantly changes the chemistry of the interdendritic regions due to segregation may be responsible for this seemingly change in the precipitation order of the strengthening precipitates. In previous studies, Cozar and Pineau [196] and Xie et al. [43] reported that when the ratio of Al + Ti at% to Nb at% is greater than 0.8, the precipitation of $\gamma'$ precedes that of $\gamma''$ in Ni-based superalloys. Sundararaman et al. [27] concluded that the precipitation of $\gamma'$ does not seem to precede that of $\gamma''$ in Alloy 718 superalloys (with Al + Ti/Nb ~ 0.6). A more recent study by Alam et al. [198] on the early stages of the ageing of Alloy 718 (with Al + Ti/Nb ~ 0.7) found out that the precipitation of $\gamma''$ precedes that of $\gamma'$ during the early ageing of the superalloy. In this study, Al + Ti/Nb at the interdendritic region is estimated to be around 0.71, which is obviously less than the 0.8 recommended by Cozar and Pineau [196] as the point of reference for changes in the precipitation order and may be the reason for the observed change in the calculated precipitation order at the interdendritic regions.

Similar results, in term of the microstructure of the first layer, are obtained in the TIG welds of ATI 718Plus [194] which were investigated as a preliminary study of the wire-arc additive manufacturing deposition. Since the influence of arc process on the microstructure of ATI 718Plus was not available in open literature, the study allows the comprehensive understanding of the influence of the process on the microstructure of the alloy.
4.3.5 Microstructural Characterisation of Single Wall/Multi-layer WAAM ATI 718Plus

4.3.5.1 Liquation and re-solidification of $\gamma$/Laves eutectics

Typical solidification microstructures and solid-state transformations of a single deposited layer of ATI 718Plus during WAAM were discussed in the previous section (which is comparable to the solidification microstructure of every subsequently deposited layer). Upon subsequent deposition scans, the previous layer acts as the substrate for the succeeding layer and is affected by the heat from the molten pool of the new deposition. The top part of the earlier deposit which is in contact with the molten pool is re-melted and becomes part of the new deposit as described earlier. The regions below the top layers with temperatures that are not high enough to melt the bulk alloy but enough to liquefy the low melting eutectics (such as the $\gamma$/Laves eutectics) cause some of the eutectic particles to dissolve into the surrounding $\gamma$-matrix and the most of the particles liquefy as shown in Figure 4.14a. The liquid Laves phase changes to continuous long chain particles and, in some cases, along the grain boundaries of the deposit as shown in Figure 4.14b. With a similar microstructure as Alloy 718 after selective laser melting (SLM) [121, 199] the HAZ of ATI 718Plus [193, 195] shows that these metallurgical features promote the initiation and propagation of liquation cracking. In this study, notwithstanding the presence of these metallurgical features in the DMHAZ, no cracks are observed in the deposit. This could be due to the amount of induced strain that acts on the liquated Laves phase during re-solidification. It has been suggested [200] that there is relatively less thermal stress generated in the HAZ during high heat input welding- like the modified TIG system used in this study. Induced thermal stress in the HAZ has been recognised [193, 201] as a key factor that influences liquation cracking in the welding of ATI 718Plus and cracking can be minimised by utilising a high heat input deposition process.
Figure 4.14: (a) SEM micrograph showing the re-solidification of continuous Laves phase in the deposit after subsequent deposition scan (b) OM micrograph showing some re-solidified Laves phase along the grain boundaries.
4.3.5.2 Grain morphology and textural characteristics of deposit

An EBSD analysis was carried out to examine the grain morphology and the texture of the single wall WAAM ATI 718Plus deposit due to the re-melting that took place during the deposition scans. The inverse pole figure (IPF) of the top and bottom/substrate in the transverse cross-section (X-Z direction) of the deposit is presented in Figure 4.15a and 4.15b respectively. It can be observed in Figure 4.15b that fine equiaxed grains with a thickness of a few microns form around the substrate/deposit interface. The observed fine grains could be attributed to the rapid cooling rate of the first deposit on the substrate. However, further up into the build, the grains are much coarser and columnar, and oriented in the direction of the heat flow. These grains are observed to grow across the layers of the deposited scans, which may be due to the epitaxial growth that took place in the preferred growth direction. A high thermal gradient at the liquid/solid interface at low solidification velocity is recognised [110, 202] as the necessary conditions for the observed epitaxial growth and these conditions have been likely achieved during the single-wall WAAM ATI 718Plus. Moreover, it is well established that FCC crystals have the fastest growth during solidification in the <100> directions. As a result, it can be observed from the IPF that even though the grains at the bottom of the build around the substrate-deposit interface are randomly oriented, only grains with their <100> direction nearly parallel to the build direction are favoured to grow rapidly, while the growth of the other grains, that are not favourably oriented is truncated. This may explain why most of the grains in single-wall WAAM ATI 718Plus are highly textured in the <100> directions as seen in the IPF in Figure 4.15. Furthermore, in the substrate (as shown in Figure 4.15b), about 250 µm below the substrate/deposit interface, there is significant grain growth. The grains in this region have grown from < 20 µm to about 50-70 µm in size. This may be attributed to the dissolution of the grain boundary pinning particles during the deposition scans,
Figure 4.15: IPF based orientation maps obtained from the 10-layer deposited ATI 718Plus showing (a) few misoriented grains at the top of the deposit (b) highly textured grains at the bottom of the deposit with only fine misoriented grains at the deposit/substrate.
as described in the work of Ding et al. [202]. The temperature measured on the substrate during the first scan in this work was observed to be above the solvus of the δ/η particles in ATI 718Plus [39]. This likely caused the grain boundary particles close to the substrate to dissolve during the first few deposition scans thus allowing for grain growth.

The EBSD analysis provided in Figure 4.15 shows that single-wall WAAM ATI 718Plus have highly textured grains in the build direction. This microstructure may also carry a potentially detrimental effect due to the possibility of anisotropy of the mechanical properties.

4.3.5.3 Analysis of strengthening precipitates in the single-wall/multi-layer deposit

The solid-state transformation and formation of strengthening phases in the hardened-zone (HZ) and softening of the DMHAZ due to the thermal gyrations during deposition scans are discussed in this section. High-resolution SEM micrograph images from the interdendritic region of the DMHAZ are shown in Figure 4.16a. Although not evident from the micrograph images, the white contrasting regions around the Laves phase particles suggest that small precipitates are likely to be found along the interdendritic region of the DMHAZ. A TEM analysis was carried out to verify the presence and characteristics of these precipitates. The SADP obtained through the TEM image of the [100] zone axis of the γ-matrix taken from the white contrasting regions around the Laves phase particles is presented in Figure 4.16c. The diffraction shows the superlattice reflections of both the γ' and γ" precipitates which confirms their presence close to the secondary constituents along the interdendritic regions of the DMHAZ. However, moving away from these secondary constituents towards the dendrite interior, only weak γ' superlattice reflections are found at the dendrite boundary, and within the dendrite core itself, no γ'/γ" reflections are observed. Based on the DF image obtained by TEM in Figure 4.16d, the average length of the γ" precipitates in the
Figure 4.16: (a) High-resolution SEM micrograph from the DMHAZ showing fine strengthening precipitates around the Laves phase particles. TEM analysis from the interdendritic region around the Laves phase particles in the DMHAZ showing (b) BF image of strengthening precipitates (c) SADP showing the superlattice reflections from γ' and γ'' precipitates (d) DF image of γ'' precipitates from the encircled diffraction spots in (c), and (f) DF image of γ' precipitates using (001) reflections.
Figure 4.17: (a) High resolution SEM micrograph of the HZ (bottom region) of the deposit. TEM micrographs showing (b) DF image of finer γ’ precipitates in the dendrite core and, (c) BF image showing larger γ’ precipitates in the interdendritic regions.
interdendritic region of the DMHAZ is about 5-7 nm. The DF image in Figure 4.16e shows that the average diameter of the γ' precipitates is <5 nm. The estimated precipitate size in the DMHAZ is significantly smaller than the average size of the γ'/γ'' precipitates observed earlier in the ASZ.

A typical high-resolution SEM micrograph image of the bottom of the deposit is presented in Figure 4.17a. As discussed earlier, this area of the deposit is exposed for a considerable amount of time to the ageing temperature range of ATI 718Plus, which promotes the nucleation and growth of precipitates. The spherical morphology of the precipitates in the micrograph indicates that the γ' precipitates are the dominant strengthening phase. Larger precipitates are found at the interdendritic regions near the secondary constituents which become smaller in size towards the dendrite core regions. Although strengthening phases are also expected within the dendrite core due to the longer ageing time, the details of the precipitates are not clear in the SEM image, likely due to their small size. The SADP obtained by carrying out TEM of the [100] zone axis of the γ-matrix in the interdendritic regions of the deposit showed superlattice reflections from both the γ' and γ'' precipitates. However, there is only the reflection of the γ' precipitates in the dendrite core. The γ' precipitates along the interdendritic region are 25-30 nm in size, and those in the dendrite cores are estimated to be around 5 nm as seen in Figure 4.17b and 4.17c respectively. This spatial variation of the precipitates across the deposit can be attributed to the different concentrations of Nb in the deposit, which likely affected the precipitation kinetics of the precipitates.
Table 4.3: Estimated area fraction of three zones of the deposit.

<table>
<thead>
<tr>
<th>ZONE</th>
<th>REGION</th>
<th>% area fraction</th>
<th>Total % area fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Site of precipitate concentration (%)</td>
<td>Strengthening precipitates from the site (%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BOTTOM ZONE</td>
<td>Interdendritic regions</td>
<td>44.8</td>
<td>22.2</td>
</tr>
<tr>
<td></td>
<td>Dendrite core</td>
<td>55.2</td>
<td>15.1</td>
</tr>
<tr>
<td>DMHAZ</td>
<td>Interdendritic regions</td>
<td>32</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>Dendrite core</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>AS-ZONE</td>
<td>Interdendritic regions</td>
<td>31.0</td>
<td>21.1</td>
</tr>
<tr>
<td></td>
<td>Dendrite core</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
4.3.5.4 Quantification of strengthening precipitates

Due to the spatial variations of the strengthening precipitates within the build, a two-step analysis was carried out to estimate the precipitation in the different zones: (i) the area fraction of the regions where there is likely to be precipitation is first estimated by using a low magnification SEM micrograph image, and then (ii) the area fraction of the nano-precipitates in these regions is then determined from high-resolution SEM and TEM micrograph images. A similar method was used by Makiewicz [203] who examined solid-state transformation of Alloy 718. The longitudinal sections of the deposit from the ASZ, DMHAZ and the HZ were utilised for quantification purposes. Table 4.3 summarises the estimated area fractions of the precipitates from the different zones of the deposit. It is evident that the overall area fraction of the strengthening precipitates in the DMHAZ, which is about 3.4%, is the smallest of all three zones analysed. The ASZ which has an estimated area fraction of 6.5% is almost twice that estimated from the DMHAZ. The bottom of the deposit gives the highest estimated area fraction of the precipitates in the deposit of about 18.2%. It is known that the overall strengthening achieved in ATI 718Plus, is influenced by the size and volume fraction of the strengthening precipitates, $\gamma'/\gamma''$. Therefore, it can be inferred that the softening behavior observed in the DMHAZ is attributed to the small size and low fraction of strengthening precipitates. The next step is to verify the uniqueness of this softening behaviour to the DMHAZ.

4.3.5.5 Rationalisation of softening behavior in DMHAZ

4.3.5.5.1 Diffusion of segregated solute elements in DMHAZ

Changes in the local concentration of segregated solute elements in the DMHAZ as a result of each subsequent scan is evaluated with an EPMA. Elemental mapping of the Nb distribution, in the ASZ and the DMHAZ (from the X-Y direction) of the deposit, is presented in Figure 4.18(a)
and 4.18(b), respectively. Also, the data from the quantitative point analysis carried out by WDS are provided in Table 4.1 for their respective interdendritic regions.

It is evident from the elemental mapping in Figure 4.18b that there is a significant reduction in the concentration of Nb along the interdendritic region of the DMHAZ compared to that obtained after solidification in Figure 4.18a. This could be due to the diffusion of Nb away from the interdendritic region to the dendrite core as a result of the high concentration gradient of the Nb in the deposit. Moreover, it is reported that the diffusion of Nb in highly alloyed Ni-based superalloys is temperature dependent. Nb diffuses much faster in Ni-based superalloys at temperatures above 1373 K (1100°C) [204, 205] which is the temperature that the DMHAZ likely experienced during the subsequent deposition scan. These could be the reasons for the significant reduction in the concentration of Nb in the interdendritic region of the DMHAZ.

4.3.5.5.2 Delayed re-precipitation of \(\gamma'/\gamma^{''}\) in DMHAZ

The strengthening precipitates formed in the DMHAZ during solidification presumably dissolved during the subsequent scan, as discussed earlier. Following the slow rate of cooling [about 278 K/s (5°C/s)], these strengthening precipitates are re-formed, albeit with a different precipitation kinetics. JMatPro simulation was carried out to understand the effect of the changes to the composition on the precipitation behaviour in the interdendritic region, for both the ASZ and DMHAZ of the deposit. Using the compositional data from the EPMA/WDS summarised in Table 4.1 and assuming similar cooling rates under thermodynamic conditions, the calculated result obtained is presented in Figure 4.19.
Figure 4.18: EMPA/WDS elemental mapping showing the concentration of Nb in the (a) ASZ (b) DMHAZ.
Figure 4.19: JMatPro calculation of the strengthening precipitates in the ASZ and the DMAZ showing (a) precipitates sizes (b) volume fractions of precipitates
Although the simulation showed only the precipitation of the $\gamma''$ precipitates under equilibrium conditions, the obtained result is in good agreement with the experimental observations. As seen in Figure 4.19a, the average size of the strengthening precipitates formed in the interdendritic region of the ASZ (~27 nm), is almost 3-4 times that in the interdendritic region of the DMHAZ (~8 nm). This is attributed to the high Nb content in this zone as discussed earlier, and diffusion induced reduction in Nb content was observed to significantly reduce the precipitation kinetics in the DMHAZ.

Similarly, the simulated result in Figure 4.19b shows that the volume fraction of the precipitates formed in the ASZ is more than twice that of the precipitates formed in the DMHAZ. It is seen that the diffusion of Nb away from the interdendritic regions not only affects the kinetics of the reformed precipitates, but also the extent of their formation. It is thus important to note that, the different thermal and cooling cycles during WAAM can significantly influence the local composition and sequence of microstructural changes in ATI 718Plus.

### 4.3.6 Characterisation of plate-like particles in WAAM ATI 718Plus

Plate-like particles are found to be distributed along the interdendritic regions of the deposit, and more of these particles were observed at the bottom than the top area of the single wall deposit. A previous study of DMLS ATI 718Plus by Idell et al. [129] reported the unexpected formation of $\delta$ phase instead $\eta$-phase particles. This unexpected formation of the $\delta$-phase is attributed to the elemental segregation of Nb which changes the chemistry of the deposit. To validate this claim, a TEM analysis was carried out on these particles in the as-deposited condition. Although the particles are too small to conduct a conclusive analysis, the observed diffraction pattern does not seem to match the orthorhombic crystal structure and not likely to be $\delta$ phase particles as reported
Figure 4.20: TEM analysis of the deposit showing (a) the BF image of η- phase particles (b) SADP at $[110]_\gamma([112\bar{0}]\eta)$ zone axis, and (c) SADP $[112]_\gamma([11\bar{0}0]\eta)$ at zone axis
Figure 4.21: TEM/EDS mapping showing the composition of the η-phase particles (b) TEM/EDS line scan showing the composition profile of the η phase.
in Idell et al. [129]. To increase the size of these particles for proper analysis, the deposit was subjected to ageing at 1123 K (850°C) for 48 hours which is believed to be less than the solvus temperature of both the δ and η phases. The SADPs obtained by TEM from the aged deposit by using the zone axes parallel to $[110]_\gamma([1\bar{1}20]_\eta)$ and $[112]_\gamma([1\bar{1}00]_\eta)$ are presented in Figure 4.20b and 4.20c, respectively. The diffraction patterns show that the particles are consistent with the ordered η- hexagonal (D0$_{24}$) structure reported in the grain boundaries of ATI 718Plus by Pickering et al. [49]. Also, the TEM/EDS mapping in Figure 4.21 shows that the chemical composition of this phase includes Ni, Nb, Ti and small amounts of Al which is also consistent with the composition of the η Ni$_3$Ti phase reported in ATI 718Plus [51].

From the TEM/SADP and the TEM/EDS analysis, the plate-like phase formed along the interdendritic region of the deposit is believed to belong to the hexagonal η Ni$_3$Ti phase and these η phase particles are presumed to be the dominant plate-like precipitates in the deposit.

4.3.7 Multi-Stringer Bead/Multi-layer WAAM ATI 718Plus

A low-magnification OM image of the microstructure of multi-stringer bead/multi-layer WAAM ATI 718Plus in the transverse (X-Z) direction is presented in Figure 4.22. The interface between the overlapping hatches and alternating layers of the build material can be observed from the micrograph image. As well, coarse columnar grains that are oriented in the direction of the build and appear across the clad tracks can be seen in the deposit. A higher magnified OM micrograph image shows that there is a network of dendritic solidification structures that are also oriented in the build direction (Figure 4.22b). The fusion line between the hatches shows evidence of the re-melting of the previous layer during deposition. Furthermore, similar to the observed grain orientation in the single wall deposit, the EBSD inverse pole figure of the multi-stringer bead deposits suggests that the grains are strongly textured in the <001> direction; see Figure 4.23.
The SEM micrograph images in Figure 4.24, show the presence of the Laves phase and MC-type carbides particles along the interdendritic spaces of the multi-stringer bead deposits produced by WAAM. A significantly higher fraction of the η phase particles in comparison to the single-wall deposit is formed along with the Laves phase particles. Furthermore, the non-uniform distribution of the strengthening precipitates are also observed in the deposit. The TEM/SADP images from the interdendritic regions shows the superlattice reflection of both the γ' and γ'' precipitates which confirms their precipitation in the interdendritic regions during deposition; see Figure 4.24c. In the dendrite core, however, only the superlattice reflection from the γ' precipitates is observed in the SADP in Figure 4.24d, which suggests only the presence of fine γ' precipitates. The differences in the characteristics and distribution of the strengthening particles which have been discussed earlier are due to the enrichment and depletion of Nb and Ti in the interdendritic and dendrite core regions, respectively.
Figure 4.22: As-deposited multilayer stringent WAAM ATI 718Plus microstructure (a) Low-magnification OM image of the deposit showing the clad tracks (b) A higher magnified OM image showing re-melting in the fusion boundary
Figure 4.23: EBSD inverse pole figure showing the orientation of the Multiple stringer/multiple layer WAAM ATI 718Plus

Figure 4.24: Multiple stringer WAAM ATI 718Plus microstructure (a),(b) SEM micrographs showing Laves phase, MC-carbide, η-phase and strengthening precipitates along the interdendritic regions, (c) and (d) TEM/SADP (from [100] zone axis) showing the reflections from both γ'∕γ'' precipitates in the interdendritic region and only γ' precipitates in the dendrite core, respectively.
4.3.8 Post-deposition heat treatment of WAAM ATI 718Plus

Although the presence of strengthening precipitates are seen in the as-processed alloy, they do not form uniformly across the build. In addition, the AM processes, especially the wire-based technique, have internal stress levels that need to be alleviated by post deposition heat treatment. Therefore, there is a need for PDHTs to produce uniform precipitation of the strengthening phase and alleviate the internal stress of the deposited material.

4.3.8.1 Recommended standard heat treatment

For PDHTs to produce uniform precipitation of the strengthening phase and alleviate the internal stress of the deposited material, the WAAM ATI 718Plus was subjected to the recommended standard heat treatment (STA) for wrought ATI 718Plus [47], which involves a solution heat treatment (SHT) prior to a two step aging process as shown in Table 3.3.

The optical micrograph image after standard heat treatment shows that the dendritic structure of the deposit is still maintained without any indication of recrystallization of the columnar grains in the as-processed condition (Figure 4.25). A more magnified SEM micrograph image (Figure 4.26) shows that the partial dissolution of the interdendritic Laves phase particles is associated with excessive η-phase lamellar particles that form simultaneously with the dissolution of the Laves phase. It is worth mentioning that these η-phase particles are primarily distributed along the interdendritic region and not the grain boundaries as normally desired.

The SEM/EDS elemental line scan across the interdendritic region of the WAAM ATI 718Plus + STA (Figure 4.27) shows limited compositional homogenisation as the interdendritic regions of the deposit is still relatively enriched in Nb as observed in Figure 4.27b. The large quantity and distribution of η-phase particles along the interdendritic region can be attributed to the high concentration of Nb released from the dissolving Laves phase.
Figure 4.25: WAAM ATI 718Plus +STA optical image showing the solidification and grain structure.

Figure 4.26: SEM image showing lamellar η-phase particles associated with partially dissolved Laves phase (inert: presence of γ' strengthening precipitates distributed uniformly within the deposit).
Figure 4.27: SEM/EDS scan across the interdendritic regions enrich in Nb.
Furthermore, the SEM micrograph image also shows the uniform precipitation of the strengthening precipitates in the deposit after the recommended heat treatment. The spherical morphology of the precipitates suggests that they belong to the $\gamma'$ phase. TEM analysis was performed to ascertain the characteristics of the strengthening precipitates, especially to confirm the likely presence of $\gamma''$ precipitates in the deposit after the standard heat treatment. The diffraction pattern of the [112] zone axis in Figure 4.28b confirms the presence of only $\gamma'$ precipitates in the deposit with no observed superlattice reflections from the $\gamma''$ phase. It is possible that all of the $\gamma''$ precipitates formed during deposition completely dissolved during the solution heat treatment and could not re-form during the subsequent ageing treatment.

No cracks were observed in the WAAM ATI 718Plus deposit after the application of the recommended standard heat treatment for ATI 718Plus. Similar result was observed in the fusion zone and heat affected zone (HAZ) of TIG welded ATI 718Plus [201]. This is in contrary to previously reported case in low-heat input electron beam welding (EBW) of ATI 718Plus [206]. The cracks in the EBW ATI 718Plus were largely attributed to prior embrittlement of HAZ grain boundaries by Laves and $\delta$ phase particles formed during the welding process. The preclusion of PWHT cracking in the TIG welded ATI 718Plus is attributed to the shallower thermal gradient experienced in the HAZ during a typical high heat input TIG welding. The shallow thermal gradient induces lower residual stresses in the HAZ, after welding, compared to lower heat input welds produced by EBW. It was observed from the study that the formation of brittle HAZ intergranular microconstituents may not be a sufficient factor to determine cracking propensity, the extent of heat input during welding may be another major factor that influences HAZ cracking during PWHT in ATI 718Plus.

Similar to the effect of the $\delta$-phase in Alloy 718, small amount of $\eta$-phase particles that are precipitated discontinuously along the grain boundaries of ATI 718Plus is desirable for improving
notch sensitivity, increasing resistance to grain boundary creep fracture and inhibiting grain growth [39, 52, 54]. However, excessive amounts of these grain boundary precipitates have been shown to have a detrimental effect on the mechanical properties, notably the loss in ductility with increased η-phase precipitation [207, 208]. Moreover, since the η-phase competes with γ' for similar elements, excessive precipitation of the η-phase has been reported to affect the volume fraction of the primary strengthening phase in ATI 718Plus [51]. Furthermore, Krakow et al. [209] observed that topologically close-packed (TCP) phases are preferentially nucleated at η-phase particles during long time exposure of ATI 718Plus at service temperature. Thus, many η-phases will likely increase the volume fraction of the nucleated TCP phases. It is also important to note that the η-phase particles in the deposit are preferentially precipitates along the interdendritic regions rather than along the grain boundaries where they are beneficial to the mechanical properties. Kuo et al. [210, 211], studied the effect of similar interdendritic δ-phase on the mechanical properties of additively manufactured Alloy 718. It was observed that the precipitation of the δ-phase particles along the interdendritic regions of the deposit significantly decreases the creep life and ductility of the alloy. Based on these previous studies, the observed microstructure of the deposit in the STA condition, is not desirable and will likely compromise the mechanical integrity of the alloy during service. Therefore, there is a need for a new heat treatment procedure that will eliminate the detrimental Laves phase particles, remove the chemical inhomogeneity, produce moderate fraction of η-phase particles along the grain boundaries and uniformly distributes strengthening precipitates.
Figure 4.28: TEM SADP of the WAAM deposit showing only γ' reflections after PDHT
4.3.8.2 Development of Improved Heat Treatment Procedure for WAAM ATI 718Plus

To further strengthen the microstructure of the WAAM ATI 718Plus, this section will provide a discussion on the development of a new post-deposition heat treatment that will dissolve the detrimental Laves phase, homogenise the chemistry, moderately precipitate the η-phase at the grain boundaries, and produce uniformly distributed γ’ precipitates to strengthen the deposit. The post-deposition heat treatment procedure involves a homogenisation heat treatment followed by solution heat treatment and two step ageing process.

4.3.8.2.1 Homogenisation heat treatment

Homogenisation heat treatment (HHT) was performed to eliminate the Laves phase particles in the deposit, prior to the implementation of the solution heat treatment and ageing of WAAM ATI 718Plus. Although no previous studies in the extant literature have discussed the homogenisation of additively manufactured ATI 718Plus, earlier work on cast ATI 718Plus conducted by Andersson et al. [212] showed that the dissolution of second phase particles can only be achieved at temperatures over 1075°C (1348 K) and obvious dissolution begins to occur at 1100°C (1373 K) [213]. In this study, a homogenisation temperature of 1100°C (1373 K) is used with a dwell time of 30 mins to 4 hrs to ensure the complete dissolution of the interdendritic Laves phase and minimise the growth of grains in the deposit.

The OM micrograph images of the deposit after homogenisation for different dwell times are presented in Figure 4.29. The micrograph images show that the dendritic structure of the deposit is still maintained after 30 mins of dwell time with a little indication of any recrystallisation of the columnar grains in the as-processed condition. After 1 hr of dwell time, both the dendritic microstructure and recrystallized grains can be observed, and a more recrystallized structure is observed in the sample held at 1100°C (1373 K) for 2 and 4 hrs of dwell time. The degree of
Figure 4.29: Optical microstructure of wire-arc deposited ATI 718Plus® homogenised at 1100 °C for a different holding time
homogenisation, in this study, is assessed based on the remaining Laves phase particles after the selected holding time. The SEM micrograph images after homogenisation show that the Laves phase particles are eliminated only after 2 hrs of dwell time; see Figure 4.30. In addition, SEM/EDS linescan was used to assess the degree of elemental redistribution across the prior interdendritic regions. A greater chemical homogenisation in the deposit is observed as shown in Figure 4.31b. Since the detrimental Laves phase particles dissolved after 2 hrs of holding time, a homogenisation temperature of 1100°C (1373 K) and soaking time of 2 hrs were selected for WAAM ATI 718Plus.

MC-type carbide particles were found to be distributed along the prior interdendritic regions of the WAAM ATI 718Plus, after the homogenisation treatment; see Figure 4.31. While the selected the homogenisation heat treatment temperature is adequate to eliminate the deleterious Laves phase particles, it is, however, insufficient to dissolve the carbides found in the deposit.

The EBSD IPF of the WAAM ATI 718Plus, after the homogenisation heat treatment, is presented in Figure 4.32. The IPF shows a significant number of annealing twins in addition to crystallised grains. Furthermore, a significant reduction in the texture of the grains is observed in WAAM ATI 718Plus after the homogenisation heat treatment. As previously mentioned, considerable residual stresses are generated due to the thermal gyration during deposition owing to the high heat input in carrying out WAAM. The deformation induced by the residual stresses serve as a driving force for recrystallisation during homogenisation. Dinda et al. [214] reported significant recrystallisation in DMLS IN 625 after a post-deposition homogenisation treatment at 1200°C. The recrystallisation was attributed to the residual stress generated by the DMLS process. Thus, the considerable recrystallisation observed in this study is believed to be driven by to the residual
Figure 4.30: SEM microstructure of wire-arc deposited ATI 718Plus® homogenised at 1100 °C for a different holding time.
Figure 4.31: (a) SEM image showing MC-type carbides alloy the interdendritic region of the deposit after homogenisation, (b) corresponding SEM/EDS scan plot across the interdendritic regions showing relative redistribution of alloying element in the deposit.
stress induced during deposition. Moreover, the formation of significant annealing twins in the deposit after homogenisation showed that the WAAM ATI 718Plus, in the as-processed condition, contains a considerable amount of residual stress which is alleviated by the formation of annealing twins.

4.3.8.2.2 Solution heat treatment and ageing

Solution heat treatment (SHT) was applied to the deposit at 954°C for 1 hour, after the homogenisation heat treatment, as recommended for η-phase precipitation in ATI 718Plus. The SEM micrograph images of the deposit show little precipitation of the η-phase particles along the grain boundaries of the deposit, see Figure 4.33a. After holding for 2 hrs at 954°C, a moderate amount of grain boundary η-phase particles is found in the deposit as seen in Figure 4.33b. This indicates that the precipitation of the η-phase in ATI 718Plus may likely be delayed by prior super-solvus homogenisation solution heat treatments and a longer time will be required to precipitate the same volume fraction as in the wrought alloy.

After the SHT, two-step aging process as recommended (see Table 3.3) for ATI 718Plus was applied to the WAAM ATI 718Plus. The TEM/SADP and the DF image of the deposit after homogenisation (1100°C/2 hrs), solution heat treatment (954°C/2 hrs) and double ageing processes (WAAM ATI 718Plus +HHT+STA) are shown in Figure 4.34. The diffraction pattern shows that the γ' precipitates are the only strengthening second phase precipitates in the WAAM ATI 718Plus +HHT+STA (Figure 4.34). The DF image of the precipitates taken from the (001γ) reflection shows that the precipitates are uniformly distributed and range in size between 20-30 nm as seen in Figure 4.34b. No Laves phase particles were observed under the SEM and TEM analysis, which indicates that these Nb-rich particles have been eliminated during the homogenisation treatment.
Figure 4.32: EBSD inverse pole figure showing the grain orientation and structure after homogenisation heat treatment.
Figure 4.33: SEM micrograph of WAAM ATI 718Plus subjected to (a) SHT 954 °C for 1 hr and, (b) SHT at 954 °C for 2 hr + ageing, after homogenisation heat treatment.
Figure 4.34: (a) TEM/SADP from [100] zone axis showing the reflection of only γ' precipitates in the deposit. (b) Dark-field image of γ' precipitates taking from the (001) reflection showing a spherical morphology and sizes ranging from 20-30 nm
4.4 Characterisation of dynamic impact behaviour of WAAM ATI 718Plus

In this section, the influence of the developed microstructure in the as-processed WAAM ATI 718Plus on the mechanical properties is presented and discussed in comparison with the wrought alloy. The mechanical properties of WAAM ATI 718Plus were assessed by using dynamic impact deformation at high strain rates. Dynamic deformation was selected as a mechanical property because it provides not only the ballistic impact response of the WAAM ATI 718Plus, which is crucial for containment applications, vital flow behaviour essential for machining can also be extracted. The wire-arc additive manufacturing technique, like other wire-based DED processes, is utilised to fabricate near-net shaped components which often require follow-up machining. During machining, metals and alloys experience high strain rates and large strains. Therefore, a proper understanding of the complex deformation that occurs during this metal cutting operation is vital for improving and optimising the machinability of the deposit. A constitutive material model, which is a vital input for FE simulation and modeling of machining processes, is developed for the as-processed WAAM ATI 718Plus.

4.4.1 High strain rate deformation of wire-arc additively manufactured ATI 718Plus

This section presents and discusses the dynamic impact response of WAAM ATI 718Plus. The impact behaviour in the as-processed condition is first investigated and compared with wrought ATI 718Plus. Thereafter, the dynamic behaviour of the deposit subject to the newly developed heat treatment for WAAM ATI 718Plus is investigated. Details on the study of the microstructural changes of the alloy after deformation are provided.
4.4.1.1 Sample preparation and deformation conditions of WAAM ATI 718Plus

To produce the WAAM ATI 718Plus test samples, cylindrical test samples with a diameter of 9.5 mm were machined from the deposited material by using EDM. The machined samples were then separated from the substrate and cut so that they have a length of 9.0 mm; see Figure 4.35. To investigate the effect of the directional dependence on the dynamic behaviour of the deposits, the test samples were extracted in the transverse (X) and longitudinal (Y) directions. Furthermore, to compare the impact properties with those of the wrought alloy, test samples with the same dimensions as those of the deposits were machined from the ATI 718Plus plate.

Some of the WAAM ATI 718Plus test samples were subjected to the post-deposition heat treatment developed in this work prior to impact. The microstructure of wrought ATI 718Plus and multi-stringer bead/multi-layer WAAM ATI 718Plus, from which the test samples were extracted, are provided in section 4.2 and section 4.3.7, respectively. The deformation tests were carried out with different projectile impact momentums, ranging from 20 to 35 kg.m/s which resulted in strain rates between 1500 s⁻¹ to 3500 s⁻¹ (see Table 4.4). The elastic wave signals recorded and stored by the oscilloscope from the transmission bar were then used to generate the dynamic stress-strain plots as shown in Section 3.6.2.
Figure 4.35: Preparation of Impacted ATI 718Plus samples produced by wire-arc AM process
4.4.1.2 Dynamic impact behaviour of as-processed WAAM ATI 718Plus

The as-processed WAAM ATI 718Plus samples were deformed at different impact momentums and along the X, Y, and Z directions. Sample low-magnification OM images of WAAM ATI 718Plus deformed in the 3 directions are presented in Figure 4.37. The various impact momentums that are applied in this study along with their estimated corresponding strain rates and the condition of the impacted samples are summarised in Table 4.4

The compressive impact behaviour of the as-processed WAAM ATI 718Plus, deformed at room temperature and at different impact momentums along the build direction (Z), is presented in Figure 4.36a. The deposit shows an increasing peak flow stress with an increase in the impact momentum. A similar positive strain rate sensitivity was observed for wrought ATI 718Plus which was deformed in both the annealed and aged conditions.

Figure 4.36b shows the stress-strain plots of the as-processed WAAM ATI 718Plus subjected to an impact momentum of 28.5 kg m/s, in the X, Y and Z directions. It is observed that flow stress of the deposits which are deformed along the build and the longitudinal directions are comparable but slightly higher than that of the deposit which is deformed along the transverse direction. The differences in the impact behaviour along the different directions could be due to the inhomogeneity of the strengthening precipitates and the textural properties of the as-processed WAAM ATI 718Plus which promotes anisotropy.

To compare the dynamic behaviour of WAAM ATI 718Plus with that of their wrought versions, impact tests were carried out on the wrought alloy in both the solution heat treated and aged conditions, as well as under an impact momentum of 28.5 kg m/s.
Figure 4.36: Dynamic compressive stress-strain plots of as-deposited ATI 718Plus® (a) deformed in the build direction at different impact momentum. (b) deformed, at 28.5 kgm/s impact momentum, in the X, Y and Z directions.
Figure 4.37: Low magnification OM images showing deformed WAAM ATI 718Plus along (a) build direction, (b) transverse, and (c) longitudinal directions.
Table 4.4: Impact momentum applied during deformation with the corresponding strain rates and specimens’ condition after impact

<table>
<thead>
<tr>
<th>Alloy Type</th>
<th>Alloy Condition</th>
<th>Impact Momentum (kgm/s)</th>
<th>Average strain rate (s⁻¹)</th>
<th>Specimen condition after impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAAM ATI 718Plus</td>
<td>As-processed</td>
<td>20.4</td>
<td>1586</td>
<td>Safe</td>
</tr>
<tr>
<td></td>
<td>(along Z-direction)</td>
<td>28.5</td>
<td>2907</td>
<td>Failed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35.6</td>
<td>3422</td>
<td>Failed</td>
</tr>
<tr>
<td></td>
<td>HHT (2hrs) + SHT (2hrs) + Aged</td>
<td>28.5</td>
<td>2811</td>
<td>Safe</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35.6</td>
<td>3465</td>
<td>Failed</td>
</tr>
<tr>
<td>Wrought ATI 718Plus</td>
<td>SHT</td>
<td>28.5</td>
<td>3011</td>
<td>Safe</td>
</tr>
<tr>
<td></td>
<td>STA</td>
<td>28.5</td>
<td>2801</td>
<td>Safe</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35.6</td>
<td>3500</td>
<td>Failed</td>
</tr>
</tbody>
</table>

*STA = Recommended heat treatment for ATI 718Plus (SHT + Aging)
The as-processed WAAM ATI 718Plus shows a lower flow stress in comparison to the wrought alloy in the aged condition, but higher flow stress than the wrought alloy in the solution heat treatment condition; see Figure 4.38a. In contrast, the as-processed sample shows a lower work hardening rate compared to the solution heat treated wrought alloy but moderately higher work hardening rate than the wrought alloy in the age-hardened condition, as shown in Figure 4.38b.

The presence of strengthening precipitates has been observed to significantly reduce the strain hardening tendency of alloys [215, 216]. This explains for the lower strain hardening rate of both the as-deposited and age-hardened wrought alloys in comparison to the solutionised wrought alloy. However, most of the precipitates in the as-deposited alloy are still not sufficiently aged and easily shearable by dislocation which explains for their moderately higher strain hardening rate compared to the wrought alloy in the fully aged condition.

A visual inspection of the as-processed WAAM ATI 718Plus after deformation showed that there is bulk inhomogeneous deformation during impact loading. An example of the deformed WAAM ATI 718Plus and wrought ATI 718Plus samples is presented in Figure 4.39. It can be observed that the former shows substantial surface roughness compared to the latter, which is more homogeneously deformed. The surface roughness could be due to the microstructural inhomogeneity in the as-processed WAAM ATI 718Plus.

Lower resistance to impact damage was observed in the as-processed WAAM ATI 718Plus in comparison to the wrought alloy in both the solutionised and age-hardened conditions; see Table 4.4.
Figure 4.38: Impact test results of as-deposited and wrought ATI 718Plus®, comparing (a) the true stress vs true strain, and (b) the strain hardening rate as a function of true strain (deformed at 28.5 kg.m/s impact momentum)
Under a similar loading condition, the wrought alloy showed no signs of failure while the as-processed WAAM ATI 718Plus showed some signs of cracking at an impact momentum of 28.5 kg m/s.

The OM micrograph image of deformed WAAM ATI 718Plus in Figure 4.40a show an inhomogeneous microstructure, with localised deformation in the dendrite core regions of the deposit. The inhomogeneous distribution of the strengthening precipitates in the as-processed alloy leads to the development of local soft dendritic cores and harder interdendritic regions. This may promote the preferential concentration of deformation in the soft regions during impact. Also, cracks are observed to be preferentially initiated at the layer interface/fusion boundaries as seen in the OM image in Figure 4.40b. The initiation of cracks in the as-deposited alloy is believed to be induced by deleterious second phase particles in the interdendritic regions, as shown by the red arrows in the SEM micrograph image in Figure 4.41a. Significantly more of these brittle phases are found around the fusion boundary, where re-melting has occurred, which is likely the reason for the preferential initiation of cracking in this region. In addition, it is presumed that second phase particles contributed to the propagation of the cracks through the alloy, which led to failure. In the cracked WAAM ATI 718Plus sample, the solidification constituents can be seen to decorate the fractured surface of the alloy, as shown in Figure 4.41b.

It is therefore observed that the as-processed WAAM ATI 718Plus has lower impact resistance in comparison to the wrought alloy. The failure of the deposit is promoted by the non-uniform distribution of strengthening precipitates and the presence of brittle second phase particles in the interdendritic regions. Therefore, post-deposition heat treatment will be required to strengthen the microstructure for ballistic impact applications.
Figure 4.39: Representative impacted specimen showing (a) wrought ATI 718Plus® (SHT and STA) and (b) as-deposited ATI 718Plus® with significant surface roughness.

Figure 4.40: Optical images of deformed deposit showing (a) inhomogeneous deformation confined within dendrite cores, and (b) cracks initiated at fusion boundaries.
Figure 4.41: SEM micrographs of deformed deposit showing (a) crack initiation at second phase particles (b) eutectic particles decorating the crack surface
4.4.1.3 Dynamic impact behaviour of WAAM ATI 718Plus+HHT+STA

After applying the new heat treatment developed to strengthen the microstructure of WAAM ATI 718Plus (discussed in Section 4.3.8.2), the dynamic impact deformation behaviour of the deposit is discussed in this section.

The dynamic response of the WAAM ATI 718Plus+HHT+STA deformed in the X, Y and Z directions at an impact momentum of 28.5 kg m/s is presented in Figure 4.42a. In contrast to the observed deformation behaviour of the as-processed WAAM ATI 718Plus, the flow stress of the WAAM ATI 718Plus+HHT+STA shows a similar deformation behaviour when deformed along the three different directions. The similarity in the impact properties may be attributed to a more uniform grain structure and the homogenous distribution of the strengthening precipitates. Furthermore, in comparison to the wrought alloy in the aged condition, the WAAM ATI 718Plus+HHT+STA shows similar dynamic behaviour and impact resistance as shown in Figure 4.42b.

4.4.1.4 Microstructural Changes of Aged ATI 718Plus after Deformation

At an impact momentum of 35.6 kg m/s, the wrought and the WAAM ATI 718Plus+HHT+STA cracked due to adiabatic shear failure. Samples of SEM micrograph images of the failed samples, which are sectioned and prepared after impact deformation, are presented in Figure 4.43. It can be observed that the WAAM ATI 718Plus+HHT+STA shows moderately higher global deformation and a relatively wider shear band in comparison to the wrought alloy. The higher global deformation may also be related to the larger grain size which suggests that a coarser grain size is beneficial to inhibit strain localisation during impact loading.
Figure 4.42: Compressive stress-strain plot of alloys deformed at 28.5 kg.m/s, comparing (a) WAAM ATI 718Plus+HHT+STA deformed in X, Y and Z directions, (b) the WAAM ATI 718Plus+HHT+STA and wrought ATI 718Plus.
Figure 4.43: SEM micrographs of deformed samples (a) aged wrought ATI 718Plus (b) WAAM ATI 718Plus + HHT+STA showing relatively wider shear band.
A representative sample for TEM analysis was extracted across the shear band to investigate the microstructural changes in and around the shear band during impact loading. Due to the brittle characteristics of the band, several cracks emerged in the shear band region after sample preparation which restricted the analysis of the shear band. However, the BF image of the regions close to the cracks obtained by TEM shows the presence of nano-sized grains, see Figure 4.44. The corresponding SADPs taken from this region, as shown in the inset, show uniform rings, which confirm the presence and existence of a large number of fine grains in this region. Some of the grains are as small as 20 nm, which suggests that dynamic recrystallization (DRx) occurred during impact loading. This region of recrystallized grains is most likely a part of the shear band as a similar microstructure is typically observed within the ASBs in alloys under impact loading [217, 218]. In addition to the grain refinement in the ASB, no γ' precipitates, which were observed in the non-deformed sample, could not be found, which suggests the dissolution of the strengthening precipitates in the ASB during dynamic impact loading. The temperature increase in the ASB can be estimated with:

\[
\Delta T = \frac{\beta}{\rho C_v} \int_0^{\varepsilon_f} \sigma d\varepsilon
\]

where β is a Taylor–Quinney coefficient which is the fraction of the plastic work converted into heat (usually taken as 0.9), ρ is the density of the material (8.24 g/cc for ATI 718 Plus) and C_v is the specific heat capacity of the material (in this case, 0.44 J g\(^{-1}\) C\(^{-1}\)[219]). The true strain within the shear band has been roughly estimated in Alloy 718 to reach 4.5 in the top-hat sample, however, in this study, the strain is conservatively taken to be between 1.5 and 2.5. Applying this strain to Eq. (4.2), the estimated adiabatic temperature in the shear band is between 800˚C and 1200˚C.
Figure 4.44: TEM image of the region near the crack tip (believed to be within the shear band) showing small DRx grains. The corresponding diffraction pattern is inserted in the image.
Figure 4.45: TEM micrographs of the region adjacent to the shear band showing, (a) bright-field image of heavily deformed microstructure with dislocation cells/sub-grains and some nano-twins, and (b) dark-field image of nano-twins (the image was taken from the \(\overline{111}\) \(_{\text{twin}}\) diffract spot in the insert)
Figure 4.46: TEM selected area diffraction pattern taken from the [112] zone axis showing no reflections from \( \gamma' \) precipitates
This high temperature contributes to the dynamic recrystallisation of the shear band and possibly the dissolution of the strengthening precipitates in the band as the upper end of the temperature is above the solvus temperature of the $\gamma'$ precipitates.

Adjacent to the recrystallized region is a heavily deformed microstructure with elongated dislocation cells/sub-grains in the BF image obtained by TEM, see Figure 4.45a. In addition, a significant number of nano-twins are observed in this region as shown in the DF image in Figure 4.45b. The DF image is taken from the $(\bar{1}1\bar{1})_{\text{twin}}$ diffraction spot in the inset. Surprisingly, the SADP taken from this region of the deposit shows no reflection from the ordered phase (Figure 4.46) which also suggests the dissolution of the strengthening precipitates in this region during impact deformation. The adiabatic temperature increase during the impact loading is mostly confined within the shear band, with the highest point in the middle of the band, and then dropping significantly moving into the bulk material. The temperature increases in the regions adjacent to the shear band is believed to be significantly lower than the estimated temperature and will likely be less than the solvus temperature of the $\gamma'$ precipitates. The observed dissolution of the strengthening precipitates may be due to other mechanisms aside from temperature increase. For instance, Cohen [220] showed that strain-enhanced diffusivity through dislocation-assisted diffusion along moving dislocations with short-circuiting paths can become significant with deformation at high strain rates and low temperatures. Similarly, Lojkowski et al. [221] also observed that high dislocation density during high strain rate deformation provides the driving force for the dissolution of carbides in steels. Although dislocation-assisted diffusion has been used to explain for the instantaneous dissolution of precipitates in the shear bands of Al and Mg alloys [222, 223], this diffusion may also be attributed to the dissolution of strengthening precipitates outside the core of the ASB. The high density of dislocation in the adjacent region
of the ASB, which contributes to diffusion during dynamic loading coupled with increased temperature in the region, may be attributed to the observed dissolution of the $\gamma'$ precipitates.

4.4.2 Comparative Study of Dynamic Impact Behaviour of Wrought Alloy 718 and ATI 718Plus

4.4.2.1 Introduction

To put the dynamic behaviour of WAAM ATI 718Plus into perspective, it is necessary to compare the deformation behaviour of ATI 718Plus with some comparable materials with similar applications. Alloy 718 is a choice material for ballistic impact applications, especially as a containment material in the hot-section of jet-engines. Therefore, a comparative deformation study of wrought Alloy 718 and ATI 718Plus at a high strain rate is first carried out in different heat treatment conditions, and with different strain rates and temperatures. Subsequently, the high strain rate deformation behaviour of WAAM ATI 718Plus was investigated.

4.4.2.2 Microstructure of wrought Alloy 718 and ATI Plus before deformation

Test samples machined from both wrought Alloy 718 and ATI 718Plus were subjected to annealing and aging heat treatments. The heat treatments were designed to produce two different material microstructures – precipitate-free and precipitate-bearing microstructures. The heat treatment procedures for both alloys and their corresponding Vickers’s micro-hardness values are summarised in Table 4.5. The annealing temperature for the alloys was chosen to ensure the dissolution of their strengthening precipitates without significantly increasing their grain size. The microstructure of standard aged ATI 718Plus has been presented in detailed earlier in section 4.2.
Table 4.5: Heat treatment procedures for ATI 718Plus and Alloy 718 and their corresponding hardness values

<table>
<thead>
<tr>
<th>Heat treatment Condition</th>
<th>Alloy</th>
<th>Procedure</th>
<th>Hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealing heat treated</td>
<td>ATI 718Plus</td>
<td>Solution heat treated at 1000 °C for 1hr + water quenching (WQ)</td>
<td>245</td>
</tr>
<tr>
<td></td>
<td>Alloy 718</td>
<td>Solution heat treated at 1000 °C for 1hr + water quenching (WQ)</td>
<td>250</td>
</tr>
<tr>
<td>Aged</td>
<td>ATI 718Plus</td>
<td>Solution heat treated at 982 °C for 1hr + WQ, then Aged at 788 °C for 8 hrs, cool at 55°C/hr to 704 °C, Hold at 704 °C for 8 hrs + WQ</td>
<td>478</td>
</tr>
<tr>
<td></td>
<td>Alloy 718</td>
<td>Solution heat treated at 954 °C for 1hr + WQ, then Aged at 718 °C for 8 hrs, cool at 55°C/hr to 621°C, Hold at 621 °C for 8 hrs + WQ</td>
<td>484</td>
</tr>
</tbody>
</table>
Figure 4.47: Microstructure of wrought Alloy 718 (a) the optical micrograph and (b) the EBSD inverse pole figure.
Figure 4.48: SEM image showing the δ-phase precipitates and MC carbides, and (b) TEM micrographs showing bright-field image of γ" in Alloy 718.
The microstructure of Alloy 718 after the implementation of the recommended aging heat treatment is presented in Figure 4.47 and Figure 4.48. The grain size for Alloy 718 after the heat treatments is estimated to be about 15 µm (see Figure 4.47a). In addition, the alloy exhibits an equiaxed and randomised grain structure as shown in the EBSD IPF micrograph image in Figure 4.47b. The SEM micrograph image of Alloy 718 in Figure 4.48 shows the presence of δ-phase particles along the grain boundaries of the alloy. MC carbides are also observed to be randomly distributed in the matrix of the alloy.

TEM analysis of the fully aged Alloy 718 before deformation is presented in Figure 4.48b. The micrograph image is the BF image of γ" precipitates in the matrix of Alloy 718, detailed by the coherency strain contrast. The SADP in the inset shows some secondary reflections that correspond to the γ" and γ' precipitates, which indicate the presence of these precipitates in Alloy 718. The γ" precipitates have an ellipsoidal and disc-shaped morphology and the diameter of the major axis is estimated to be about 35-40 nm with a minor thickness of 5-10 nm.

4.4.2.1 Quasi-static compressive behaviour of Alloy 718 and ATI 718Plus

The alloys were first deformed under quasi-static loading to determine their behaviour under this loading condition. The strain rate used was approximately 3 x 10⁻³ s⁻¹.

The quasi-static compression results of Alloy 718 and ATI 718Plus are presented in Figure 4.49a. The plots show that the flow stress of both alloys when fully aged is significantly greater than those that are solution heat treated. Furthermore, the flow stress of both alloys is observed to increase with increasing strain, without flow stress saturation. The strain hardening rate of the alloys under quasi-static loading, which is the slope of the true stress-true strain curve, \( \frac{d\sigma}{d\varepsilon} \), is presented in Figure 4.49b. It can be observed that the annealed alloys show a higher strain hardening rate compared to those that are age-hardened, before saturation occurs at about a strain
of 0.45. Although the yield stress of Alloy 718 is slightly higher than that of ATI 718Plus in both heat-treated conditions, the latter shows a higher strain hardening rate. The deformation of both alloys is dominated by strain hardening and no softening behavior is observed under a quasi-static loading condition.

Both age-hardened alloys showed cracks that originate from their edges after deformation. The initiation of the cracking was observed as a sharp decline in the strain rate hardening curves of both alloys (Figure 4.49b) but Alloy 718 started to crack (at about a strain of 0.59) before ATI 718Plus (at about a strain of 0.65) which may indicate that the latter has higher ductility. However, no cracking was observed in the annealed alloys.
Figure 4.49: Quasi-static compression test results of IN 718 and ATI 718Plus® showing (a) the true stress vs true strain plot, and (b) the strain hardening rate plot as a function of true strain.
4.4.2.2 Dynamic impact behaviour of wrought Alloy 718 and ATI 718Plus

Dynamic stress-strain curves

To obtain the dynamic test results for the alloys, the average of three individual tests were taken for each condition to ensure the repeatability of the results. Figure 4.50 is a sample plot of three individual tests and the calculated mean curve. Following a similar procedure, the dynamic impact test results for both Alloy 718 and ATI 718Plus are presented in Figure 4.51a after undergoing solution heat treatment and deformed at room temperature. In addition, the strain rate plots as a function of the impact momentum and deformation time for typical impact tests are also presented in Figure 4.51b. The average strain rates that correspond to each impact momentum are estimated and summarised in Table 4.6. The stress-strain plots show that there is an increase in the flow stress of both alloys with increasing impact momentum. Similar to the observation in the quasi-static test, ATI 718Plus shows a significantly higher strain hardening response compared to Alloy 718. The strain hardening response of ATI 718Plus also appears to increase with increasing impact momentum. Contrary to their behaviour under quasi-static loading in which deformation is dominated by strain hardening, thermal softening quickly affects the strain hardening response of the alloys under dynamic loading. Thermal softening begins to dominate the deformation when the work hardening rate of the alloys is less than zero. The plotted work hardening rate for both alloys after they are solution heat treated and deform at an approximate strain rate of 2500s⁻¹ is shown in Figure 4.52. It can be observed that even though the strain hardening rate of ATI 718Plus is significantly higher than that of Alloy 718, thermal softening dominates both alloys at a strain of about 0.4.

The true stress-true strain test results under dynamic loading for the age-hardened Alloy 718 and ATI 718Plus at room temperature are shown in Figure 4.53a. Compared to quasi-static loading,
Figure 4.50: A representative plot of three individual tests and the calculated mean curve of ATI 718Plus deformed at 500°C and at 28.5 kg m/s.
Figure 4.51: Dynamic test results of solution heat treated Alloy 718 and ATI 718Plus® showing the true stress vs true strain plots, and (b) Typical strain rates as a function of impact momentum for annealed Alloy 718 samples.
Figure 4.52: A representative strain hardening rate plots of IN 718 and ATI 718Plus®, deformed at 28.5 kgm/s, as a function of true strain.
the flow stress of the aged hardened alloys is significantly higher than the solution heat treated alloys. For the impact momentum applied in this study, the aged Alloy 718 shows a higher flow stress compared to ATI 718Plus; however, the strain hardening response of the latter is slightly higher than that of the former. Figure 4.53b is a sample plot of the strain hardening rate of the age hardened alloys, in which ATI 718Plus shows a moderately higher critical strain (at a strain of about 0.25), at which the thermal softening begins to govern the strain hardening more so than Alloy 718 (at a strain of about 0.15). This shows that the age-hardened Alloy 718 is more susceptible to strain localisation and adiabatic shear failure.

Furthermore, the strain-hardening rate of the age-hardened alloys which is plotted in Figure 4.53b is compared with that of the solution heat treated samples in Figure 4.52. A significantly lower strain hardening rate is observed for the age-hardened alloys. Also, a significantly higher critical strain (at a strain of about 0.4) is observed in the solution heat treated alloys, which shows that the annealed alloys can inhibit strain localisation during dynamic impact loading. The conditions of the alloys after deformation with their corresponding impact momentum are summarised in Table 4.6. In the solution heat treated condition, both alloys showed a similar tendency to fail based on the appearance of the adiabatic shear band and cracking initiates at the highest impact momentum applied in this study. After age hardening, both alloys fragmented at approximately 3500s\(^{-1}\), but Alloy 718 seems to tend more to adiabatic shear failure. Localised shear bands and cracking are found in the Alloy 718 sample deformed at 2500 s\(^{-1}\) which is not the case for ATI 718Plus.
Figure 4.53: Dynamic test of age-hardened Alloy 718 and ATI 718Plus showing (a) the true stress vs true strain plot, and (b) the strain hardening rate plot as a function of true strain (deformed at approximately at 3500 s$^{-1}$).
Table 4.6: Impact responses of IN 718 and ATI 718Plus under different heat treatment conditions.

<table>
<thead>
<tr>
<th>Heat treatment Condition</th>
<th>Alloy</th>
<th>Impact Momentum (kgm/s)</th>
<th>Average strain rate (s⁻¹)</th>
<th>Specimen condition after impact</th>
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<td>20.4</td>
<td>1255</td>
<td>Safe</td>
</tr>
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<td>28.5</td>
<td>2567</td>
<td>Safe</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35.6</td>
<td>3627</td>
<td>Safe</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45.0</td>
<td>4624</td>
<td>ASB and crack</td>
</tr>
<tr>
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<td>Alloy 718</td>
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<td>1501</td>
<td>Safe</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.5</td>
<td>2633</td>
<td>Safe</td>
</tr>
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<td></td>
<td></td>
<td>45.0</td>
<td>4711</td>
<td>ASB and crack</td>
</tr>
<tr>
<td>Aged</td>
<td>ATI 718Plus®</td>
<td>20.4</td>
<td>1201</td>
<td>Safe</td>
</tr>
<tr>
<td></td>
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<td></td>
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<td>3500</td>
<td>Fragmented</td>
</tr>
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<td>Alloy 718</td>
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<td>Safe</td>
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<td></td>
<td></td>
<td>28.5</td>
<td>2386</td>
<td>ASB and crack</td>
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<tr>
<td></td>
<td></td>
<td>35.6</td>
<td>3337</td>
<td>Fragmented</td>
</tr>
</tbody>
</table>
(a) Strain rate and temperature effects

The dependence of the flow stress (at 0.1 strain) on the average strain rate of Alloy 718 and ATI 718Plus is shown in Figure 4.54. It is seen that both alloys, in the different heat treatment conditions considered, show a positive strain rate sensitivity. The strain rate sensitivity of the solution heat treated alloys is, however, significantly higher than that of the age hardened alloys. Similarly, the plotted post-deformation hardness of the alloys also shows that the annealed alloys have a higher strain hardening response; see in Figure 4.55. Furthermore, while the strain rate sensitivity and strain hardening response of the age hardened Alloy 718 sample begin to peak above 2500 s\(^{-1}\), the age hardened ATI 718Plus sample continue to show a moderate strain rate sensitivity and strain hardening for all the strain rates applied.

Figure 4.56a and 4.44b are the true stress-strain plots of the annealed and age hardened ATI 718Plus samples respectively (at an approximate strain rate of 2500 s\(^{-1}\)), shown as a function of the deformation temperature. It can be observed that the flow stress of ATI 718Plus in the different heat treatment conditions decreases with increasing temperature. Also, the stress-strain of the age-hardened Alloy 718 sample plotted as a function of the deformation temperature shows a similar trend in Figure 4.57. The flow stress of both alloys (at a strain of 0.1) as a function of temperature is shown in Figure 4.58. It can be observed that while the flow stress of the age hardened Alloy 718 sample decreases from about 1966 MPa at room temperature to 1064 MPa at 800°C (~ 46% reduction in flow stress), the flow stress of the age hardened ATI 718Plus sample on the other hand is only reduced by approximately ~ 29% (from 1761 MPa at room temperature to 1252 MPa at 800°C). This shows that Alloy 718 is significantly susceptible to softening with temperature after age hardening compared to ATI 718Plus.
Figure 4.54: Flow stress (at 0.1 strain) versus strain rates in compression for Alloy 718 and ATI 718Plus in both solution heat treated and age-hardened conditions.

Figure 4.55: Post-deformation hardness vs strain rate for Alloy 718 and ATI 718Plus in both solution heat treated and age-hardened conditions.
Figure 4.56: True stress-true strain of ATI 718Plus®, deformed at 28.5 kgm/s, versus temperature (a) in solution heat treated condition, and (b) in the age-hardened condition.
Figure 4.57: True stress -true strain of age-hardened IN 718, deformed at 28.5 kgm/s, verse temperature.

Figure 4.58: Flow stress (at 0.1 strain) as a function of temperature of IN 718 and ATI 718Plus® deformed at 28.5 kgm/s.
(a) Microstructural observation of deformed samples

The sample micrograph images of Alloy 718 and ATI 718Plus when deformed at room temperature and strain rates at which the samples start to fail, are shown in Figure 4.59. From the micrograph images, it can be observed that the alloys in the different heat treatment conditions fail due to strain localisation which leads to the formation of ASBs. For the solution heat treated alloys, it can be observed in Figure 4.59a and 4.47b that the formation of ASBs is preceded by the bulk deformation of the alloys and extensive deformation in the grains adjacent to the ASB. No difference in the sample deformation can be observed between the solution heat treated alloys, aside from their initial grain size.

For the age-hardened alloys which are shown in Figure 4.60c and 4.48d, minimal bulk deformation is observed with little or no deformation of the grains along the ASB. In comparing the bulk deformation of both alloys in the age-hardened condition, slightly more deformation is observed in ATI 718Plus, which can be due to its slightly higher strain hardening response.

4.4.2.3 Influence of compositional and microstructural modifications on deformation behaviours

The differences in the chemical composition and the primary strengthening precipitates of Alloy 718 and ATI 718Plus have a significant effect on their deformation behaviour and tendency to form ASBs under dynamic impact loading. ATI 718Plus was observed to show a relatively higher strain hardening behavior and strain rate sensitivity under similar loading conditions. Furthermore, similar to observations in earlier studies [138, 224], the microstructure of the alloys has an important influence on their dynamic behaviour under high strain rate loading.
Figure 4.59: SEM micrographs of solution heat treated (a) Alloy 718 and (b) ATI 718Plus, deformed at 45 kgm/s, showing extensive deformation of grains along the ASB.
Figure 4.60: SEM images of age-hardened (a) Alloy 718 deformed at 28.5 kgm/s and (b) ATI 718Plus deformed at 35.6 kgm/s, both showing a narrow-localised shear band with limited grain deformed grains.
The solution heat treated alloys clearly show a greater strain hardening tendency which inhibits strain localisation in comparison to the aged alloys.

The overall strength contribution of the crystal structure of a precipitation hardened alloy can be expressed as a combination of different strengthening effects as follows [225]:

$$\sigma_{oy} = \sigma_{gb} + \sigma_{ss} + \sigma_{pt}$$

(4.3)

where $\sigma_{oy}$ is the overall yield strength of the alloy, $\sigma_{gb}$ is the contribution from grain boundary strengthening, $\sigma_{ss}$ from solid-solution strengthening and $\sigma_{pt}$ from precipitation strengthening. It is worth mentioning that Eq. (4.3) is used mainly for quasi-static loading conditions but can however be qualitatively applied to understand the deformation response of alloys under dynamic conditions.

4.4.2.3.1 Influence of compositional modification on dynamic response

In the solution heat treated conditions, most of the strengthening precipitates are dissolved in the matrix of the alloy so that the precipitation strengthening component in Eq. (4.3) is assumed to be zero (i.e $\sigma_{pt} = 0$). This implies that the overall strengthening of the solution heat treated alloy is derived mainly from the grain boundaries and solid solution strengthening effects. However, considering that the grain size of Alloy 718 and ATI 718Plus used here is comparable, the changes in the dynamic behaviour between the two alloys cannot be attributed to the difference in the grain boundary strengthening effects. In terms of solid-solution strengthening, the significant increase in the strain hardening and strain rate sensitivity observed in ATI 718Plus may be related to its composition modification. Alloying elements in Ni-based superalloys are known to influence their stacking fault energy (SFE) and as result, influence the deformation process of the alloys. Shang et al. [226] found that alloying additions such as Mo, Nb, tungsten (W) and technetium (Tc) have the greatest effect in reducing the SFE of Ni. In a similar study by
Gallagher [227], the addition of Co to Ni alloys also significantly reduces the SFE of Ni. A lower SFE increases the spacing between partial dislocations and inhibits dislocation mobility and dislocation cross-slip during plastic deformation, and therefore increases the tendency of the material to deform by twinning. Deformation twinning is known to significantly increase the work hardening rate of a material during deformation [228]. Rohatgi et al. [229] observed an increase in the tendency for deformation twinning in Cu alloys as the SFE decreases due to the addition of Al. The abrupt increase in the work hardening rate, with decreasing SFE, was attributed to the transition from the dislocation generation mechanism to deformation twinning. Furthermore, during the shock loading of Ni alloys, Millet et al. [230] reported a shift from dislocation generation to twin dominated plasticity as the SFE of Ni is reduced due to the addition of Co. In summary, it can be concluded that in the development of ATI 718Plus, the addition of alloying elements such as Co and W to partially replace Fe will reduce the SFE of the new alloy. In a comparative study on the hot deformation behaviour of Alloy 718 and ATI 718Plus, Momeni et al. [231] observed a greater yield drop in ATI 718Plus which was attributed to the effect of the alloying modification which reduced the SFE of the alloy. Therefore, it can be inferred that the observed difference in the deformation behaviour of both alloys in the solution heat treated condition can be attributed to the reduction of SFE as a result of the compositional modification. The reduction of the SFE increases the tendency of deformation twinning and the strain hardening rate of the alloys.

4.4.2.3.2 Influence of changes in primary strengthening phase on dynamic response

In the age-hardened condition, the strength of Alloy 718 and ATI 718Plus depends primarily on the precipitation strengthening component of Eq. (4.3). Furthermore, earlier studies on Alloy 718 have demonstrated that the presence of strengthening precipitates in the alloy has the greatest influence on its dynamic shear localisation [215]. It is therefore proposed that the observed
difference in the deformation behaviour of Alloy 718 and ATI 718Plus, in the aged condition, is directly related to the characteristics of the strengthening phase found in the alloys. It is widely known that the primary strengthening precipitates in Alloy 718 and ATI 718Plus are the γ" and γ' precipitates respectively. In Alloy 718, Oblak et al. [25] observed that while the ordered particles ensure the pairwise motion of dislocation, the strength of the alloy comes predominately from the coherency strain hardening created by the γ"- γ mismatch. Similarly, Chaturvedi and Han [232] estimated the mismatch between γ" and the matrix, γ, to be about 2.86% and concluded that the strength of Alloy 718 can be adequately accounted for by the coherent strain hardening produced by γ". However in many γ' strengthened Ni-based superalloys, the ordered strengthening effect is considered to mainly increase the strength of the alloys [233–236] although the effect of the coherency strain on the strength of the alloys is believed to be in some cases substantial. In ATI 718Plus, a γ' phase strengthened alloy, the misfit between the γ' phase and the matrix, γ, has been estimated to be between 0.3 - 0.4% and a combination of both coherency strain and ordered hardening effects are considered to contribute to the strength of ATI 718Plus. These changes in the principal strengthening phase and consequently the strengthening mechanism, may influence variations in the deformation behaviour of the alloys as observed in the deformation test results.

Furthermore, the changes in the principal strengthening phase of ATI 718Plus are considered to reduce the contribution from coherency hardening compared to Alloy 718. The considerable temperature-softening characteristics of the age-hardened Alloy 718 may be attributed to the higher strengthening effect of coherency hardening, as its influence has been shown to be reduced with an increase in temperature [25, 237]. Moreover, it is commonly accepted that ordered strengthening, which is assumed to contribute more to the strength of ATI 718Plus, has a superior strengthening effect at high temperatures (>800˚C) compared to coherency strain hardening [28].
Pursche and Meyer [238] found that the temperature-softening characteristic of materials is a crucial property for determining their tendency to adiabatic shear failure. It was found that a greater decline in the flow stress with temperature results in a greater tendency of a material to shear localisation. Therefore, it is possible that the high-stress decline in age-hardened Alloy 718 with temperature along with lower strain hardening tendency and high strength at room temperature may be attributed to the greater tendency of the alloy to form ASB compared to ATI 718Plus.

This study shows that ATI 718Plus is a more resistant material to damage during dynamic impact deformation at high strain rates compared to the most commonly used Fe-Ni based superalloy Alloy 718. ATI 718Plus shows both a higher strain hardening and strain rate sensitivity in heat treatment conditions than Alloy 718, for all the strain rates applied. The difference in the deformation behaviour of the solution heat treated alloys is attributed to the reduced SFE in ATI 718Plus due to the compositional modification. The difference in the age-hardened alloys, however, is considered to be as the result of the disparity in the strengthening mechanisms of the alloys. Alloy 718 showed the lowest critical strain and a higher susceptibility to shear localisation. This behaviour is attributed to the observed stronger temperature-softening characteristic of Alloy 718 along with the limited strain hardening response of the alloy under impact loading.

The results from this study provide vital information that has not been reported in the literature in that ATI 718Plus is more resistant to damage during ballistic impact deformation at high strain rates compared to the most widely used Fe-Ni based superalloy, Alloy 718.
4.4.2.4 Constitutive models for flow stress of WAAM ATI 718Plus

The constitutive material models based on the modified J-C model and strain compensated AT model are established for the as-processed alloy in this section. These models are selected because they are reliable and extensively used to describe the flow behaviour of materials in the modeling and simulating of machining operations as well as in containment applications.

To obtain the constitutive material models for the as-processed WAAM ATI 718Plus, samples were deformed at different average strain rates between 1 s\(^{-1}\) to 3500 s\(^{-1}\) and over a range of deformation temperatures (from 25°C to 800°C). The true stress-true strain plots of WAAM ATI 718Plus deformed at room temperature, under different strain rates are presented in Figure 4.61a. In addition, a sample stress-strain plot of the deposit deformed at approximately 3000s\(^{-1}\) under different temperatures is shown in Figure 4.61b. It can be seen that the flow stress of the deposit is sensitive to both temperature and strain rate.

4.4.2.4.1 Arrhenius-type model with compensated strain

It has been shown that the relationships among temperature, flow stress, and strain rate can be expressed by using an AT equation [156]:

\[
\dot{\varepsilon} = AF(\sigma) \exp\left(\frac{-Q}{RT}\right)
\]  

(4.4)

where \(F(\sigma) = \begin{cases} \sigma^n & \text{if } \alpha \sigma < 0.8 \\ \exp(\beta \sigma) & \text{if } \alpha \sigma > 1.2 \\ \sinh(\alpha \sigma)^n & \text{for all } \sigma \end{cases}\)
Figure 4.61: True stress-true strain of wire-arc deposited ATI 718Plus (a) deformed under various strain rate at room temperature, (b) deformed at 3000s$^{-1}$ at various temperatures
where $\dot{\varepsilon}$ is the strain rate ($s^{-1}$), $R$ is a gas constant (8.314 J/mol·K⁻¹), $Q$ is the activation energy in (kJ/mole), and $T$ is the temperature (Kelvin). $\sigma$ is the flow stress (MPa) for a given strain, and $A$, $\beta$, $n'$ and $\alpha$ are the material constants, $\alpha=\beta/n$.

The Zener-Hollomon parameter ($Z$) [157] can be used to express the effect of strain rate and temperature on the deformation behaviour of metals and alloys:

$$Z = \dot{\varepsilon} \exp\left(\frac{Q}{RT}\right)$$ \hspace{1cm} (4.5)

The influence of strain on the flow stress of the material is not considered in Eqs. (4.4) and (4.5). In this work, a strain-compensated Arrhenius model is used as proposed by Lin et al. [160], in which the influence of strain on the material constants is considered. To account for the linear elastic strain, an offset of 0.05 strain is used for the alloys. This is used to compensate for the overestimation of the elastic strain during high strain rate experiments, as seen in Figure 4.61a.

To illustrate the solution procedure for determining the material constants of the AT model with compensated strain, a plastic strain value of 0.075 is used as an example.

*Estimation of material constants in Arrhenius-type model*

Substituting the power and exponential laws of $F(\sigma)$ into Eq. (4.4) for low-stress level ($\alpha\sigma<0.8$) and high-stress level ($\alpha\sigma>1.2$), respectively, will yield:

$$\dot{\varepsilon} = B\sigma^{n'}$$ \hspace{1cm} (4.6)

$$\dot{\varepsilon} = B' \exp(\beta\sigma)$$ \hspace{1cm} (4.7)

where the $B$ and $B'$ are material constants.
Figure 4.62: Plots of (a) \( \ln(\sigma) \) vs. \( \ln(\dot{\varepsilon}) \) and (b) \( \sigma \) vs. \( \ln(\dot{\varepsilon}) \) at 0.075 strain.
Taking the logarithm of Eqs. (4.6) and (4.7) yields:

\[
\ln(\sigma) = \frac{1}{n'} \ln(\dot{\varepsilon}) - \frac{1}{n'} \ln(B) \tag{4.8}
\]

\[
\sigma = \frac{1}{\beta} \ln(\dot{\varepsilon}) - \frac{1}{\beta} \ln(B') \tag{4.9}
\]

The flow stress values that correspond to the strain rates from the experiment performed in this work are substituted into Eqs. (4.8) and (4.9) to give the relationship between the flow stress and strain rate as presented in Figure 4.62. The value of \( n' \) and \( \beta \) can be obtained from the slope of the plots of \( \ln(\sigma) \) vs \( \ln(\dot{\varepsilon}) \) and \( \sigma \) vs \( \ln(\dot{\varepsilon}) \) respectively.

The average value of the slopes at different deformation temperatures are used to obtain the \( n' \) and \( \beta \) values, which are subsequently used to calculate \( \alpha = \beta/n' \). The mean value of \( n' \) and \( \beta \) obtained from the plots at 0.075 are 4.43826 and 0.005089 respectively, and \( \alpha \) is calculated as 0.001146638.

For all stress levels, Eq. (4.4) can be written as:

\[
\dot{\varepsilon} = A(\sinh(\alpha \sigma))^n \exp \left( \frac{-Q}{RT} \right) \tag{4.10}
\]

By taking the logarithm of Eq. (4.10) and rearranging the result yields:

\[
\ln[\sinh(\alpha \sigma)] = \frac{1}{n} \ln\dot{\varepsilon} + \frac{Q}{nRT} - \frac{\ln A}{n} \tag{4.11}
\]

By substituting the values of the strain rate and the corresponding flow stress (at a strain of 0.075) for all of the test temperatures into Eq. (4.11), the relationship between \( \ln[\sinh(\alpha \sigma)] \) and \( \ln\dot{\varepsilon} \) is plotted in Figure 4.63a. The value of \( n \) can be obtained from the mean of the slope values from these plots. The differentiation of Eq. (4.10), at a constant strain rate, gives:
\[ Q = Rn \frac{d[\ln(\sinh(\alpha \sigma))]}{d \left( \frac{1}{T} \right)} \]  

(4.12)

The plot of \( \ln[\sinh(\alpha \sigma)] \) vs \( \frac{1000}{T} \), presented in Figure 4.63b, is applied to calculate the activation energy, \( Q \), by using the average of the slope values of the plot at different strain rates. Hence, the value of \( A \) can be calculated by using Eq (4.11) from the intercept of \( \ln[\sinh(\alpha \sigma)] \) vs \( \ln(\dot{\varepsilon}) \).

To compensate for the influence of strain on the flow stress, the values of the material constants (\( Q, A, n, \) and \( \alpha \)) for the constitutive equation are calculated under different strain levels (from 0.005 to 0.125). To express the effect of strain on material constants, a 4\textsuperscript{th} order polynomial is used to fit each constant as presented in Eq. (4.13) and Figure 4.64. The coefficients of these polynomials are given in Table 4.7

\[
\begin{align*}
\alpha &= \alpha_0 + \alpha_1 \varepsilon^1 + \alpha_2 \varepsilon^2 + \alpha_3 \varepsilon^3 + \alpha_4 \varepsilon^4 \\
n &= n_0 + n_1 \varepsilon^1 + n_2 \varepsilon^2 + n_3 \varepsilon^3 + n_4 \varepsilon^4 \\
Q &= Q_0 + Q_1 \varepsilon^1 + Q_2 \varepsilon^2 + Q_3 \varepsilon^3 + Q_4 \varepsilon^4 \\
\ln A &= D_0 + D_1 \varepsilon^1 + D_2 \varepsilon^2 + D_3 \varepsilon^3 + D_4 \varepsilon^4
\end{align*}
\]  

(4.13)

By applying the hyperbolic sine function, the flow stress can be expressed as a function of the Zener-Hollomon parameter, \( Z \) (by combining Eqs. (4.5) and (4.10)), as presented in Eq. (4.14):

\[
\sigma = \frac{1}{\alpha} \ln \left\{ \left( \frac{Z}{\bar{A}} \right)^{1/\bar{n}} + \left[ \left( \frac{Z}{\bar{A}} \right)^{2/\bar{n}} + 1 \right]^{1/2} \right\}
\]  

(4.14)

Using the strain compensated Arrhenius equation, a comparison between the predicted flow stress and the experimental data obtained at various strain rates and temperatures are presented in Figure 4.65.
Figure 4.63: Plots of (a) $\ln[\sinh(\alpha\sigma)]$ vs. $\ln(\dot{\varepsilon})$ (b)$\ln\left[\sinh(\alpha\sigma) vs \frac{1000}{T}\right]$
Figure 4.64: Variation of material constant (a)$\alpha$, (b)$n$, (c)$Q$ and (d)$\ln A$
Table 4.7: Polynomial function coefficient of material constants $\alpha$, $n$, $Q$ and $\ln A$.

<table>
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<tr>
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<th>$n$</th>
<th>$Q$</th>
<th>$\ln A$</th>
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<td>$\alpha_2$</td>
<td>-0.0203</td>
<td>$n_2$</td>
<td>-120.78</td>
<td>$Q_2$</td>
</tr>
<tr>
<td>$\alpha_3$</td>
<td>0.9784</td>
<td>$n_3$</td>
<td>10520</td>
<td>$Q_3$</td>
</tr>
<tr>
<td>$\alpha_4$</td>
<td>-4.4803</td>
<td>$n_4$</td>
<td>-53164</td>
<td>$Q_4$</td>
</tr>
</tbody>
</table>

(a)

![Graph showing true stress vs. true strain for different temperatures.](image)
Figure 4.65: A plot comparing the experimental flow stress with the predicted values at different strain rate (a) 1500s$^{-1}$ (b) 3000s$^{-1}$ and (c) 3500s$^{-1}$, using the strain-compensated Arrhenius-type model.
4.4.2.4.2 Modified Johnson-Cook Model

In this work, a modified J-C model which considers the strain hardening parts of the original J-C model and the coupled effects of temperature and the strain rate on the flow stress as proposed by Lin et al. [155] is applied. The modified J-C expression is presented in Eq. (4.15):

\[
\sigma = (A + B\varepsilon^n)(1 + C_1\ln \dot{\varepsilon}^*) \exp[(\lambda_1 + \lambda_2\ln \dot{\varepsilon}^*)(T - T_r)]
\]  
\[(4.15)\]

where \(A, B, n, C_1, \lambda_1, \) and \(\lambda_2\) are the material constants, \(\varepsilon\) is the plastic strain, \(\dot{\varepsilon}^* = \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0}\) is a dimensionless strain rate (\(\dot{\varepsilon}\) is the strain rate, while \(\dot{\varepsilon}_0\) is the reference strain rate (1s\(^{-1}\)), \(T\) is the absolute temperature, \(T_r\) (298 K) is the reference temperature and \(\sigma\) is the flow stress.

**Estimation of material constants**

At the reference temperature (298 K) and strain rate (1s\(^{-1}\)), Eq. (4.15) is reduced to:

\[
\sigma = A + B\varepsilon^n
\]  
\[(4.16)\]

The values of the \(A, B, n\) can be obtained by a non-linear curve fitting and optimisation of the quasi-static experimental \(\sigma\) vs \(\varepsilon\) data.

Eq. (4.15), at the reference temperature, can be expressed as:

\[
\frac{\sigma}{A + B\varepsilon^n} = (1 + C_1\ln \dot{\varepsilon}^*)
\]  
\[(4.17)\]

By substituting the different strain rates and their corresponding flow stress at various strain values into Eq. (4.17), \(C_1\) can be obtained from the slope of the linear fit of \(\frac{\sigma}{A + B\varepsilon^n}\) against \(\ln \dot{\varepsilon}^*\) as shown in Figure 4.66.

Introducing a new parameter \(\lambda\), where \(\lambda = (\lambda_1 + \lambda_2\ln \dot{\varepsilon}^*)\), Eq. (4.15) can be expressed as:

\[
\frac{\sigma}{[(A + B\varepsilon^n)(1 + C_1\ln \dot{\varepsilon}^*)]} = e^{\lambda(T - T_r)}
\]  
\[(4.18)\]
Figure 4.66: Plot of $\frac{\sigma}{A + B \dot{\varepsilon}^n}$ against $ln\dot{\varepsilon}^*$ at reference the temperature (293 K)

Table 4.8: Evaluated Johnson-Cook Material constant

<table>
<thead>
<tr>
<th>J-C materials constant</th>
<th>$A$</th>
<th>$B$</th>
<th>$n$</th>
<th>$C_1$</th>
<th>$\lambda_1$</th>
<th>$\lambda_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>632.5</td>
<td>1721.31</td>
<td>0.655</td>
<td>0.0658</td>
<td>-0.00191</td>
<td>1.6173 × 10^{-4}</td>
</tr>
</tbody>
</table>
Taking the logarithm of both sides of Eq. 4.18 yields:

\[
\ln\left\{\frac{\sigma}{[(A + B\varepsilon^n)(1 + C_1\ln\dot{\varepsilon}^*)]}\right\} = \lambda(T - T_r) \tag{4.19}
\]

\[
\ln\left\{\frac{\sigma}{[(A + B\varepsilon^n)(1 + C_1\ln\dot{\varepsilon}^*)]}\right\} \text{ vs } (T - T_r) \text{ is plotted for different strains and temperatures at different strain rates as presented in Figure 4.67. From these plots, the } \lambda \text{ values are obtained at different strain rates from the slope. The values of } \lambda \text{ are plotted against } \ln\dot{\varepsilon}^*, \text{ and the slope and the intercept give } \lambda_2 \text{ and } \lambda_1 \text{ respectively (seen Figure 4.68). The material constants of the modified J-C model are summarised in Table 4.8.}

Thus, the relationship among the flow stress } \sigma, \text{ strain } \varepsilon, \text{ strain rate } \dot{\varepsilon} \text{ and temperature } T \text{ is expressed based on the modified J-C model in Eq. (4.15); The plots of flow stress vs true strain which use the modified J-C model are presented in Figure 4.69.}

\[
\sigma = (632.5 + 1721.31\varepsilon^{0.655})(1 + 0.0658\ln\dot{\varepsilon}^*) \times \\
\exp[(-0.00191 + 1.6173E^{-4}\ln\dot{\varepsilon}^*)(T - T_r)]
\]
Figure 4.67: Plots of $\ln\left\{\frac{\sigma}{[(A+B\varepsilon^n)(1+C_1ln\varepsilon^*)]}\right\}$ vs. $(T - T_r)$ at the various strain rates: (a) $1500s^{-1}$ (b) $3000s^{-1}$ and (c) $3500s^{-1}$

Figure 4.68: The plot of and $\lambda$ against $ln\dot{\varepsilon}^*$. 
Figure 4.69: Plots comparing the flow stress from experimental data and predicted values using modified Johnson-Cook model at various strain rates (a) 1500s\(^{-1}\) (b)3000s\(^{-1}\) and (c)3500s\(^{-1}\)
4.4.2.4.3 Verification of constitutive models

The reliability of the constitutive models, the strain compensated AT and the modified J-C models, to predict the flow stress of as-deposited ATI 718Plus was accessed by using two standard statistical parameters. The correlation coefficient (R) and the average absolute relative error (AARE) are the two statistical parameters selected and presented in Eqs. (4.20) and (4.21) respectively.

\[
R = \frac{\sum_{i=1}^{N} (E_i - \bar{E})(P_i - \bar{P})}{\sqrt{\sum_{i=1}^{N} (E_i - \bar{E})^2 \sum_{i=1}^{N} (P_i - \bar{P})^2}}
\]  

(4.20)

\[
AARE \, (\%) = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{E_i - P_i}{E_i} \right| \times 100
\]

(4.21)

where \(E_i\) is the experimental data, \(P_i\) is the predicted values derived from the constitutive models, and \(\bar{E}\) and \(\bar{P}\) are the mean values of \(E\) and \(P\), respectively. \(N\) is the total number of data points used for the analysis. When the value of \(R=1\) and the value of AARE=0, the experimental flow stress is perfectly equal to the predicted values of the flow stress by the model. The correlation coefficient usually gives the linear relationship between the obtained experimental data and the predicted values, which can sometimes be prone to bias [239]. In contrast, the average absolute relative error is a less biased statistical parameter for determining the reliability of a model, as it is based on a term by term correlation of the relative error between the predicated value and the experimental data.

The correlation plots of the experimental data and predicted values are presented in Figure 4.70. In addition, the values of R and AARE calculated from the data by using both the strain compensated AT model and the modified JC model are inputted into the respective correlation plots.
Figure 4.70: Correlation between experimental data and the predicted flow stress using (a) strain compensated Arrhenius-type model, and (b) modified Johnson-Cook model
The modified J-C model produces a higher correlation coefficient and a lower value for the AARE in comparison to the strain compensated AT model. This shows that the modified J-C model is a more suitable constitutive model to predict the flow stress of as-deposited ATI 718Plus superalloy under high strain rate deformation.

The better predictability of the modified J-C model may be attributed to its ability to better model the coupled effects of temperature and strain rate on the flow stress of the deposit. The $\lambda_1$ and $\lambda_2$ in the term $\exp[(\lambda_1 + \lambda_2 \ln \dot{\varepsilon}^*)(T - T_r)]$ of the modified J-C model represent the coupled effect of temperature and strain rate and thus have better predictability. In the strain compensated AT model, however, the coupled effects of temperature and strain rate are represented by a material constant $Q$. To obtain $Q$, a linear fit is assumed for the plot of $\ln \left[ \sinh (\alpha \sigma) \right] vs \frac{1000}{T}$ at a given strain. However, it can be observed in Figure 4.63b that the linear fit provides a poor fit for the plot for all strain rates. The linear fit underestimates the stress at 473 K and 673 K but overestimates the stress at high temperatures (1073 K) as seen in Figure 4.63b. The temperature dependence of deposited ATI 718Plus on the flow stress is predominately governed by the intermetallic strengthening precipitates, $\gamma'$. In this alloy, the strengthening effect of the $\gamma'$ precipitates are robust up to moderately high temperatures, $\sim 973$ K [38], accompanied with a minimal reduction in strength. At higher temperatures, however, a sharp decline in strength is usually observed as evident at 1073 K in Figure 4.63b, and the non-linearity of $\ln \left[ \sinh (\alpha \sigma) \right] vs \frac{1000}{T}$ (from 298 K to 1073 K) may be attributed to this phenomenon. As a result of the inaccuracy from the estimation of the material constant $Q$, the predictability of the strain compensated Arrhenius model is negatively affected at those temperatures (as seen in the AARE vs deformation temperature plots in Figure 4.71). It can be observed that at the reference temperature (298 K), the strain compensated Arrhenius model shows a low value of the AARE,
however, the error increases significantly at high deformation temperatures. The error in the modified JC model remains low and moderately varies over all the deformation temperatures.
Figure 4.71: AARE plot against the deformation temperature for the modified J-C and ATC model
4.5 Characterisation of hot corrosion behaviour of WAAM ATI 718Plus

4.5.1 Introduction

The hot corrosion behaviour of as-processed WAAM ATI 718Plus in comparison with wrought ATI 718Plus at 650°C and 705°C is presented and discussed in this section. The investigation aims to provide insight into the influence of microstructural and chemical inhomogeneities produced in WAAM ATI 718Plus on the hot corrosion properties. Furthermore, the effectiveness of the PDHTs on the hot corrosion resistance of WAAM ATI 718Plus is also evaluated and discussed.

Prior to the corrosion experiment, some of the WAAM ATI 718Plus test samples were subjected to two PDHTs – the recommended standard heat treatment for ATI 718Plus (WAAM ATI 718Plus+STA) and the new post-deposition heat treatment developed to strengthen the microstructure of the WAAM ATI 718Plus (WAAM ATI 718Plus+HHT+STA). The microstructure of the WAAM ATI 718Plus+STA and WAAM ATI 718Plus+HHT+STA is discussed in Sections 4.3.8.1 and 4.3.8.2, respectively.

After the corrosion tests, the oxides on the samples were characterised by using a Bruker D5000 X-ray diffractometer with Cu Kα radiation at a step size of 0.01° over 2θ which ranged from 4° to 90° and a step time of 4 s. The surface and cross-section of the corroded samples were also analysed by using SEM to study the morphology and the chemical composition of the corrosion products.

4.5.2 Development of Oxide Scale after Hot Corrosion

The SEM/backscattered electron (BSE) micrograph images of the surface of salt coated coupons that are exposed to a temperature of 705 °C for 1 h and 10 h are presented in Figure 4.72a and 4.72b, respectively. The formation of sodium vanadate salt can be observed between the Na₂SO₄
salt on the surface of the alloy (Figure 4.72a). The formation of sodium vanadate may be attributed to the reaction between the Na$_2$SO$_4$ and V$_2$O$_5$ salt at the test temperature. After 10 hrs of exposure to a temperature of 705 ºC, Ni-V-O rich crystals can be seen precipitating on the surface of the salt (see Figure 4.72a).

The SEM micrograph images of the exposed surface after washing in hot distilled water for w-ATI 718Plus and WAAM ATI 718Plus subjected to corrosion at 705ºC for 30 mins are presented in Figure 4.73a and 4.73b, respectively. Besides selective attacks on the grain boundaries and preferential oxidation of the carbides, the overall corrosion of the exposed surface of wrought ATI 718Plus appears to be considerably uniform (Figure 4.73a). In contrast, preferential attacks on the dendritic core regions are found in WAAM ATI 718Plus (Figure 4.73b). The dendritic core regions which have been selectively attacked by the molten salt appear to have valleys while the interdendritic regions decorated with Laves phase particles stand in relief. Oxides formed on the surface of the alloys, after 100 hrs of exposure to a temperature of 705ºC, are found in the SEM images in Figure 4.73c and 4.73d. The semi-quantitative SEM/EDS analysis shows a similar composition of the oxide on the surface of the alloy in both conditions. The composition is mixed and rich in Ni, Cr, V, Nb, Fe, and Co. It is also observed that certain parts of the oxide layer appear brighter when observed in the backscattered mode of the scanning electron microscope. The SEM/EDS analysis shows that these bright particles are rich in Nb. It was observed that there are moderately more brighter regions in the WAAM ATI 718Plus compared to the wrought alloy, which can be attributed to the oxidation of the solidification microconstituents that are rich in Nb. Furthermore, an XRD analysis was performed to identify the types of oxides formed on the surface of the alloys and the results are presented in Figure 4.74.
Figure 4.72: SEM/BSE micrographs of the surface of the hot corroded specimens of (a) 1 hr and (b) 10hrs at 705 °C
Figure 4.73: (a) and (b) SEM micrograph of the exposed surface of the wrought ATI 718Plus and WAAM ATI 718Plus, respectively after 30mins at 705 °C, (c) and (d) SEM micrograph of the oxide scale formed on the surface of wrought ATI 718Plus and WAAM ATI 718Plus, respectively after 100 hrs at 705 °C.
The XRD peaks obtained for both wrought ATI 718Plus and WAAM ATI 718 are similar, which suggests that the alloy in both conditions contain the same type of oxides. Although it is somewhat difficult to precisely identify the phases present due to the complexity and similarity of the crystal structure of the oxides, the X-ray diffraction data along with the SEM/EDS analysis indicate that the possible oxides are Ni₃(VO₄)₂, NiFe₂O₄, NiO, CoO, NiCr₂O₄, FeVO₄, Cr₂O₃, CrVO₄, and FeNb₂O₆.

Micrograph images of the cross-sections of wrought ATI 718Plus and WAAM ATI 718Plus (after 100 hrs of exposure to a temperature of 705°C), along with their corresponding EDS elemental mapping results are shown in Figure 4.75 and Figure 4.77, respectively. The total thickness of the scale formed varies depending on the processing method used to produce the alloy and the WAAM ATI 718Plus shows a higher scale thickness for the two conditions. It is also observed that the scale thickness of the WAAM ATI 718Plus varies significantly along the different directions. The total thickness of the oxide scale on the surface perpendicular to the build direction of the WAAM ATI 718Plus is appreciably greater than that along the build direction (see Figure 4.77a and 4.77b). Furthermore, as observed from the exposed surface of the WAAM ATI 718Plus (see Figure 4.73b), selective corrosion of the dendritic core regions can also be observed in the cross-section of the WAAM ATI 718Plus, which is not obvious in the wrought ATI 718Plus.

Notwithstanding the processing means, the oxide scale on the ATI 718Plus alloy in the two conditions is essentially similar. The scale consists of two different oxide layers – the outer oxide and the inner oxide layers, separated by a thin layer of semi-continuous Nb-rich oxide, as shown in the EDS elemental maps in Figure 4.75b and Figure 4.77c.
Figure 4.74: X-ray diffraction results of the surface scale of wrought ATI 718Plus and WAAM ATI 718Plus after 100 h of hot corrosion experiment at 705 °C
The sandwiched Nb-rich oxide between the two scales is occasionally observed to result in the delamination of the external oxide layer from the inner oxide layer (see Figure 4.75a). The results of the SEM/EDS point analysis (wt %) across the external oxide scale of wrought ATI 718Plus and WAAM ATI 718Plus are provided in Figure 4.76 and Figure 4.78, respectively. The results show that the outer scale is mainly rich in Ni, V, and O with small amounts of Cr, Co, and Fe. A higher magnified image of the outer scale, (see inset in Figure 4.75a) shows discrete oxides (rich in Cr, Co, and Fe) embedded in the matrix of the Ni-V-O-rich oxide (darker regions). The inner oxide layer, on the other hand, consists of a mix of different oxides rich in Cr, Ni, Nb and smaller amounts of Co, Fe, and V. Seiersten and Kofstad [240] studied the hot corrosion mechanism of Ni-based alloys in sodium vanadate salt at temperatures between 650ºC - 800ºC. An outer oxide layer, rich in Ni, V, and O identified as Ni₃(VO₄)₂ was reported to form above an inner oxide layer that contained a mix of NiO, Cr₂O₃, and Al₂O₃. The formation of the Ni₃(VO₄)₂ was attributed to the fluxing of the molten vanadate on the earlier oxide scale formed beneath the molten salt, especially the NiO.

A similar fluxing action on the NiO scale in the NaVO₃-V₂O₅ melt was also reported by Porcayo-Calderon et al. [241]. The EDS and X-ray diffraction results suggest that the outer oxide layer observed in this study consists mainly of Ni₃(VO₄)₂. The inner layer oxide layer, however, likely comprises a mix of NiO, CoO, Cr₂O₃, NiCr₂O₄, NiFe₂O₄, FeVO₄, CrVO₄, and Nb₂O₅. Furthermore, EDS scans across the alloys (Figure 4.76 and Figure 4.78) also show depletion of Cr, Nb, and Fe in addition to the enrichment of Ni in the region adjacent to the inner oxide layer thus suggesting that these elements are actively participating in the oxidation process. Within the depleted region, randomly distributed pits which contain small amounts of S (EDS elemental map in Figure 4.76), are observed.
Figure 4.75: (a) SEM image of the scale on wrought ATI 718Plus after 100 h exposure at 705 °C and (b) the corresponding EDS maps for O, V, Cr, Nb, Ni, S, and Co. The white dotted line indicates the region between the outer and the inner scale.
Figure 4.76: SEM/EDS composition plots of wrought ATI 718Plus across the scale for (a) Ni, Cr, Co, Fe and Nb (b) O, V, and S, versus distance after 100 h of exposure at 705 ºC. The scan starts from the surface of the corroded specimen (zero) moving into the substrate
Figure 4.77: SEM image of the scale on WAAM ATI 718Plus after 100 h exposure at 705 °C (a) perpendicular to the build direction, (b) parallel to the build direction, and (c) the corresponding EDS maps for O, V, Cr, Nb, Ni, S, and Co. The white dotted line indicates the region between the outer and the inner scale.
Figure 4.78: SEM/EDS composition plots of w-ATI 718Plus across the scale for (a) Ni, Cr, Co, Fe and Nb (b) O, V, and S, versus distance after 100 h of exposure at 705 °C. The scan starts from the surface of the corroded specimen (zero) moving into the substrate.
Based on the analysis, it is proposed that the hot corrosion of the alloys occurs in two stages - the oxidation of alloying elements followed by the fluxing of the oxides by the molten salt.

4.5.3 Hot Corrosion Kinetics of Wrought and WAAM ATI 718Plus

The mass-gain after isothermal exposure of ATI 718Plus in the two conditions at 650°C and 705°C is presented in Figure 4.79a. Using the parabolic rate expression in Eq. (4.22), a straight line fit of the \((m/A)^2\) against \(t\) is obtained from the corrosion data as shown in Figure 4.79b and the parabolic rate constants \(k_p\) obtained from the alloys are summarised in Table 4.9.

\[
\left( \frac{\Delta m}{A} \right)^2 = k_p t
\]  

(4.22)

where \(\Delta m/A\) (mg/cm\(^2\)) is the mass-gain, \(k_p\) (mg\(^2\)/cm\(^4\)/h) is a parabolic rate constant and \(t\) (h) is the oxidation time. Based on the \(k_p\) obtained from the fitting, a modelled mass-gain is obtained and plotted as the solid line in Figure 4.79a. This shows that the mass-gain of the alloy, in all of the conditions tested, follows approximately the parabolic kinetics at 650°C and 705°C. This suggests that the corrosion kinetics of these alloys are controlled by the diffusion of reactive species through the oxide scales. Generally, larger mass-gain and parabolic rate constants \(s(k_p)\) are observed for alloys exposed to a temperature of 705°C in comparison to those exposed to a temperature of 650°C, which indicates an increase in the corrosion rate with increasing temperature. Increasing the test temperature reduces the viscosity of the melt, thereby increasing the fluxing ability of the molten salt and the rate of hot corrosion attacks. Sidky and Hocking [14] reported a similar accelerated attack of Ni-based alloys with increasing temperatures in \(\text{Na}_2\text{SO}_4+\text{NaVO}_3\) which was attributed to the increasing fluxing ability. It is obvious from the plots that the WAAM ATI 718Plus shows higher mass-gain and corrosion rates than the wrought alloy, which can be attributed to the different microstructures in the two conditions.
Figure 4.79: The mass gain per unit area plotted as a function of time, and (b) (mass gain per unit area)$^2$ plotted as a function of time, for w-ATI 718Plus and WAAM ATI 718Plus, exposed at 650 °C and 705 °C.
Table 4.9: Parabolic rate constant ($K_p$) obtained from fitting the hot corrosion data of w-ATI 718Plus and WAAM ATI 718Plus up to 100 hours at 650 ºC and 705 ºC

<table>
<thead>
<tr>
<th>Alloy type</th>
<th>Parabolic rate constant ($K_p$) from the line fit (mg²/cm⁴/h)</th>
<th>Parabolic rate constant ($K_p$) from the line fit (mg²/cm⁴/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>650 ºC</td>
<td>705 ºC</td>
</tr>
<tr>
<td>w-ATI 718Plus</td>
<td>$1.172 \times 10^{-2}$</td>
<td>$2.215 \times 10^{-2}$</td>
</tr>
<tr>
<td>WAAM 718Plus</td>
<td>$1.969 \times 10^{-2}$</td>
<td>$4.898 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
The experimental results show that WAAM ATI 718Plus has a lower resistance to corrosion than the wrought ATI 718Plus between 650°C – 700°C up to 100 hours. Notwithstanding the minimal variation in the content of Cr within the deposit, as seen in the EPMA/WDS analysis, selective corrosion of the dendritic cores can be observed. Although Cr is usually added to Ni-based superalloys to improve oxidation resistance, the dendrite core regions in this study, with moderately higher Cr, are the preferential region for hot corrosion attacks (see Figure 4.77a). This shows that the Cr in the presence of the molten salt used in this study has limited influence on corrosion resistance. This is in agreement with the observations of Sidky and Hocking [14] who found that the beneficial influence of Cr in Ni-based alloys significantly diminishes as the amount of NaVO₃ added to Na₂SO₄ is increased, and a harmful effect was observed in pure NaVO₃ as a result of the formation of non-protective CrVO₄.

Alloy 625 weld-clad onto a coal-fired boiler tube was observed by Luer et al. [242] to show preferential corrosion attacks that eventually caused localised crack initiation. The preferential attacks occurred within the dendritic core regions of the weld-clad depleted of Mo and Nb. They proposed that the depletion of Mo and Nb in the dendrite core regions of the clad due to elemental segregation, locally reduces its corrosion resistance and leads to preferential attacks. Similarly, Kalivodová et al. [243] also observed a localised and enhanced corrosion in an IN 625 weld exposed to a flue gas environment which was also attributed to the segregation of Mo and Nb within the weld. The beneficial influence of Nb on high-temperature oxidation and hot corrosion of Ni-based alloys has been investigated by several authors. He et al. [244] reported increased corrosion resistance in a mixed oxidising environment when the amount of Nb is increased. In addition, Weng et al. [245] reported a notably higher hot corrosion resistance of Ni-based superalloys, with increased Nb addition which was attributed to a more compact and protective formed scale. It can therefore be proposed in this study that the selective attacks and the
accelerated attacks on the WAAM ATI 718Plus in comparison to wrought ATI 718Plus are related to the segregation of Nb and Mo in the deposit. In contrast to the chemically homogeneous wrought ATI 718Plus, a significantly lower concentration of Nb and Mo are observed in the dendrite core regions of WAAM ATI 718Plus based on the WDS data and the partition coefficient in Table 4.2. These may be responsible for the lower resistance of these regions and consequently the enhanced corrosion attacks on the WAAM ATI 718Plus.

The significantly thicker oxide scale formed on the surface perpendicular to the build direction (Figure 4.77a) in comparison to other directions (Figure 4.77b) may also be in part related to the increased selective attacks of the dendritic core regions of the WAAM ATI 718Plus that are oriented perpendicular to the salt. The preferential attack of the dendritic core regions which leads to the formation of a thicker oxide scale along to the build direction is schematically shown in Figure 4.80. The depleted dendrite core regions along the build direction could favour a rapid attack that leads to a thicker oxide scale on the surface perpendicular to this direction. The enriched interdendritic regions, which have relatively higher resistance to corrosion, however, can reduce the attack on the surface parallel to the build direction as shown in Figure 4.80. In addition, variation in oxide scale thickness was also observed on the surface of additively manufactured Alloy 718 exposed to air at 800˚C in Sadeghimeresht et al [246]. The variation in thickness is attributed to the varied grain texture in the different directions of the deposited alloy. In this study, a significant texture can be observed in the IPF image of the WAAM ATI 718Plus (Figure 4.23b), which suggests that the effect of orientation may also have a notable role on the variation of the thickness in the different directions of the build.
Figure 4.80: Schematic diagram showing the plausible preferential attack of the dendritic core regions of the deposit.
From the foregoing discussion, it is obvious that the chemical inhomogeneities that lead to microstructural heterogeneities in the WAAM ATI 718Plus have a profound influence on reducing the hot corrosion resistance of the alloy in comparison to the wrought ATI 718Plus. Therefore, to improve the hot corrosion resistance of the deposit, a post-deposition heat treatment is necessary to homogenise the chemical and microstructural inhomogeneities in the WAAM ATI 718Plus.

4.5.4 Hot Corrosion Kinetics of Post-deposition Heat Treated WAAM ATI 718Plus

The WAAM ATI 718Plus was subjected to two PDHTs that comprised the recommended standard heat treatment for ATI 718Plus (WAAM 718Plus+STA) and the new post-deposition heat treatment developed in this study (WAAM ATI 718Plus+HHT+STA) to improve the corrosion resistance of the deposit.

The mass gain of WAAM ATI 718Plus+STA and WAAM ATI 718Plus+HHT+STA, in addition to that of wrought ATI 718Plus and as-processed WAAM ATI 718Plus after exposure to hot corrosion at a temperature of 705 °C, against the holding time is plotted in Figure 4.81. It is observed that the post-deposition heat treatment generally increases the hot corrosion resistance of WAAM 718Plus. A moderately higher increase can be observed for the WAAM ATI 718Plus+HHT+STA \([with k_p = 2.84 \times 10^{-2} mg^2/cm^4/h]\) as opposed to the WAAM ATI 718Plus+STA \([with k_p = (3.32 \times 10^{-2}) m g^2/cm^4/h]\). The enhanced resistance to hot corrosion can be attributed to the greater homogenisation of the microstructure and the redistribution of the segregated elements, especially Nb. Significantly greater elemental redistribution and enhanced homogenisation of the microstructure, including the recrystallisation and reduction of texture, are achieved in WAAM ATI 718Plus+HHT+STA.
Figure 4.81: The mass gain per unit area plotted as a function of time for WAAM ATI 718Plus+STA and WAAM ATI 718Plus+HHT+STA exposed at 705 °C (in solid line), together with the reference WAAM ATI 718Plus and the wrought ATI 718Plus in dotted lines.

Figure 4.82: SEM image of the scale on WAAM ATI 718Plus+HHT+STA after 100 h exposure at 705 °C
In addition, the microstructure of the oxide scale on WAAM ATI 718Plus+HHT+STA, in Figure 17, is similar to that observed on the wrought alloy with no selective oxidation. The influence of the build orientation on corrosion behaviour, observed in the WAAM ATI 718Plus, is minimised after the homogenisation heat treatment.

Although there is enhanced corrosion resistance after post-deposition treatment is carried out, the resistance is still lower in comparison to the wrought ATI 718Plus. This lower resistance may be attributed to the large amounts of NbC along the prior interdendritic regions in the WAAM ATI 718Plus+HHT+STA, which were not eliminated by the post-deposition treatment. Preferential accelerated oxidation of NbC, which is known to occur in Ni-alloys [247], may negatively influence the hot corrosion of WAAM ATI 718Plus+HHT+STA.
CHAPTER FIVE

5 SUMMARY AND CONCLUSION

5.1 Summary

The outcome of this research work can be summarised into the following findings:

5.1.1 Microstructural Analyses of ATI 718Plus Produced by WAAM

1. Extensive segregation of alloying elements is observed in ATI 718Plus produced by using WAAM. Alloying elements like Nb, Ti and Mo segregated extensively into the interdendritic liquid.

2. The elemental micro-segregation to the interdendritic liquid results in the formation of detrimental secondary phase particles, which are found to be Laves phase particles and MC-type carbides. In addition, the non-homogenous accelerated precipitation of the $\gamma'$ and $\gamma''$ phases enhanced by the micro-segregation and lower cooling rate is observed along the interdendritic regions of the deposit.

3. Notwithstanding the extensive segregation of Nb in the deposit, the crystallographic structure of the plate-like particles formed in the interdendritic regions is found to be consistent with the $\eta$-Ni$_3$Ti D0$_{24}$ phase, in contrast to the $\delta$-phase that is generally reported in Alloy 718.

4. As shown by the EBSD analysis of the multilayer deposition, the build has a highly textured microstructure with only a few misorientations at the substrate-deposit boundary and the surface of the deposit.

5. In this study, notwithstanding the presence of the metallurgical features which are believed to promote liquation cracking in the deposited metal heat affected zone, no cracks are
observed in the deposit. Low residual stresses that act on the liquated Laves phase during re-solidification, due to the high heat input of the TIG system, may be responsible for the preclusion of cracking in the deposit.

6. A potentially detrimental softening zone is found at the DMHAZ. Theoretical calculations and experimental observations reveal that the softening is the result of the diffusion-induced reduction of Nb content in the interdendritic region of the DMHAZ, which reduces both the extent and the kinetics of the precipitation of the strengthening phase.

7. From the microstructural study, all the as-processed ATI 718Plus samples are observed to be free from internal cracks and the layer dimensions are stable during the entire deposition process despite the extensive segregation of alloying elements and repeated thermal cycles. This shows that the wire-arc additive manufacturing process can be used to produce structurally sound, large near-net shaped components.

8. Excessive precipitation of interdendritic η-phase particles that are associated with the undissolved Laves phase is observed after subjecting the WAAM ATI 718Plus deposit to the recommended standard heat treatment for ATI 718Plus. This type of microstructure is known to be deleterious to the mechanical properties of ATI 718Plus, and thus requires the design of new heat treatment procedures for ATI 718Plus produced by using the AM process.

9. A novel heat treatment that comprises a homogenisation heat treatment (at 1100°C/2 hrs) + solution heat treatment (at 954°C/2 hrs) prior to the double aging heat treatment is sufficient to eliminate the deleterious brittle phase, ensure the precipitation of a moderate amount of η-phase particles along the grain boundaries and homogenously distribute the γ' precipitates within the deposit.
10. Considerable recrystallisation is observed in the WAAM ATI 718Plus after the new post-deposition heat treatment is carried out. The recrystallisation is believed to be driven by the residual stress induced during the WAAM deposition. In addition, a significant number of annealing twins are also observed in the deposit after the heat treatment.

5.1.2 Characterisation of dynamic impact behaviour of WAAM ATI 718Plus

1. The high strain rate deformation of WAAM ATI 718Plus in the as-processed condition shows an increase in the peak flow stress under greater impact momentum. Furthermore, the as-deposited alloy shows a moderate dependence on the direction with the highest strength along the build direction.

2. The WAAM ATI 718Plus in the as-deposited condition shows less impact resistance compared to the wrought ATI 718Plus in both the age-hardened and solutionised conditions. This is attributed to the presence of eutectic solidification constituents, especially Laves phase particles, in the interdendritic regions of the deposit.

3. After subjecting the WAAM ATI 718Plus deposits to the newly developed post-deposition heat treatment procedure, the dynamic response and impact resistance is found to be similar and comparable to those of the wrought alloy.

4. At an impact momentum of 38.5 kg m/s, both the wrought alloy and the deposit fail due to the formation of ASBs. Nano-sized grains and a heavily deformed microstructure with some nano-twins are observed in the shear band and the adjacent regions to the shear band, respectively.

5. Interestingly, the dissolution of the $\gamma'$ precipitates in the ASB and the regions adjacent to the ASB is observed in the age-hardened WAAM ATI 718Plus deposit after impact. The
dissolution of the strengthening precipitates is attributed to the coupled effect of dislocation
assisted diffusion and temperature increase due to severe plastic deformation in the ASB during
impact loading.

6. High strain rate study in this work provides vital and previously unreported information in that
ATI 718Plus has higher resistance to damage during ballistic impact deformation at high strain
rates compared to the most widely used Fe-Ni based superalloy, Alloy 718. ATI 718Plus shows
higher strain hardening and strain rate sensitivity in two heat treatment conditions and inhibits
the formation of ASBs.

5.1.3 Characterisation of hot corrosion behaviour of WAAM ATI 718Plus

1. The WAAM ATI 718Plus in the as-deposited condition shows a significantly lower resistance
to hot corrosion in comparison to the wrought version.

2. The depletion of Nb and Mo in the dendrite core regions reduces local corrosion resistance
and facilitates selective hot corrosion attacks on these regions. These result in overall
accelerated hot corrosion attacks on the WAAM 718Plus compared to the wrought
ATI 718Plus.

3. PDHTs which comprise the recommended standard heat treatment for ATI 718Plus and the
newly developed post-deposition heat treatment are applied to the WAAM ATI 718Plus to
improve the corrosion resistance.

4. The WAAM ATI 718Plus subjected to the newly developed post-deposition treatment shows
higher resistance to hot corrosion in comparison to the standard heat-treated deposits. This
is attributed to the enhanced chemical and microstructural homogenisation in the latter.
5. The overall hot corrosion resistance of the post-deposition heat treated alloy is, however, still lower in comparison to the wrought ATI 718Plus. A significantly larger amount of NbC is still found along the interdendritic regions, which has been shown to be prone to selective accelerated oxidation and may be responsible for the reduced resistance.

6. The probable hot corrosion mechanism found in this study is first the oxidation of the alloying elements in the ATI 718Plus by the inward diffusion of oxygen through the molten salt to form oxides, then fluxing of these oxide scales subsequently takes place.

5.2 Conclusions

The following major conclusions are drawn from this research work:

1. Extensive formation of eutectic solidification micro-constituents including Laves and MC-type carbide phases, induced by micro-segregation, are produced by in ATI 718Plus superalloy in the as-deposited condition by the WAAM process. In addition, heterogeneous distribution of the key strengthening phase precipitates occurred in the as-processed alloy. These necessitated the development of a novel heat treatment procedure to modify the microstructure for enhanced properties.

2. The mechanical property, in term of the ballistic impact resistance of wire-arc additive manufactured ATI 718Plus, in the as-processed condition, is inferior to that of the wrought alloy. The lower impact resistance is associated with the presence of eutectic solidification constituents in the interdendritic regions and to the inhomogeneous distribution of the strengthening precipitates in the deposit. However, after the application of a novel post-deposition heat treatment to strengthen the microstructure, the wire-arc additive manufactured alloy exhibits a dynamic response and impact resistance comparable to those of the wrought alloy.
3. The hot corrosion resistance of ATI 718Plus produced by the wire-arc additive manufacturing process, in the as-deposited condition, is significantly lower than that of the wrought alloy. The poor hot corrosion resistance is associated with the chemical inhomogeneity, especially the depletion of Nb and Mo within the dendrite core regions of the deposit. The application of post-deposition heat treatment substantially improves the corrosion resistance.

4. This research work shows that notwithstanding the inferior microstructure and properties obtained in as-processed wire-arc additive manufactured ATI 718Plus, a tailored post-deposition heat treatment, achieved through detailed microstructural study, can significantly strengthen the microstructure and improve the properties to levels comparable to those of the wrought alloy.
6 RECOMMENDATIONS FOR FUTURE WORK

1. The post-deposition heat treatment developed for WAAM ATI 718Plus is observed to significantly increase the resistance to dynamic impacts and hot corrosion of the deposit. Further studies on other mechanical properties such as notch sensitivity, high and low cycle fatigue, high-temperature and low-temperature tensile tests and stress rupture test should be explored.

2. The approach used in this study to improve the dynamic impact resistance and hot corrosion characteristics of WAAM ATI 718Plus should also be explored for other Ni-based superalloys produced by wire-based additive manufacturing techniques. Furthermore, similar approach used in this work should also be explored for other additive manufacturing techniques.

3. A significant amount of NbC particles are observed in the as-processed alloy which are still found along the interdendritic region after the application of the homogenization heat treatment. The carbides are observed to be prone to accelerated selective oxidation which can adversely influence the high-temperature or hot corrosion properties of the deposit. The influence of the starting additive wire composition on the formation of the carbides should be investigated.
RESEARCH CONTRIBUTIONS FROM THIS WORK

Peer-reviewed Journal Publications:


Conference proceeding:


Conference Poster presentations:


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