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Abstract
This document is the outcome of a brief literature review into the known properties of metal powder processing via downselected consolidation routes. These are hot isostatic pressing (HIP), additive manufacture (AM) and spark plasma sintering (SPS). Rapid solidification processes (RSP’s) in the manufacture of the powdered raw material link these consolidation routes together. The document thus commences with an introduction to the crystalline states of powdered material where similarities are drawn to AM consolidation since it is also governed by rapid solidification processes. Each consolidation method is taken in turn to describe the material performance rendered by the microstructure, facets and artefacts unique to the process, along with an understanding of the parameters that control the outputs. An overview is then presented of the typical operating conditions in the primary circuit of a nuclear power plant (NPP), so as to develop an understanding of the environment and regulatory scrutiny which will be placed on the manufacture, performance and decommissioning of parts made by powder metallurgical processes. The gaps in knowledge concerning each process as applicable to the intended environment and requirements for nuclear are then listed. Finally the route to code incorporation is examined, and actions are proposed to reach this goal.

Keywords
Powder metallurgy, Primary circuit, PM HIP, AM, SPS, Material properties, Code case incorporation, RCC-M, Testing,
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1. Introduction

Over the past few decades, advances in powder metallurgy have enhanced the outputs of metallic part manufacture, opening doors to a wide variety of applications and industries. There are a host of advantages offered by certain powder metallurgy (PM) consolidation techniques for part manufacture. A few worth mentioning are excellent mechanical properties, isotropic performance, ease of inspectability, low manufacturing footprint, and freeform raw material storage.

Machines performing ‘3D printing’ or Additive Manufacture (AM) are completely automated, often providing a ready to use metallic part with simply an input structured tessellation (STL) model. The conventional routes for metallic part manufacture have involved one or a combination of forging, casting and welding in multiple processes utilizing a variety of skill-sets, materials and equipment. The associated hype is therefore understandable considering the minimal operator input and magnificent structures achievable thanks to the AM route’s degrees of additional manufacturing freedom. There are other PM routes driving the high value technology streams forward: notably hot iso-static pressing (HIP) and spark plasma sintering (SPS). These techniques deliver material properties that often exceed those of conventional routes, all the while delivering levels of consistency and predictability appealing in critical applications where part performance is the key variable of focus.

Use of this technology is widespread, experiencing application in the manufacture of medical & dental implants, electronic components, automotive parts and for the manufacture of high value critical components employed in harsh environments relating to the aerospace and oil & gas sectors, where integrity is the key monitored characteristic. Similar to the high demands on part performance imposed by space craft and deep sea pipelines, certain components in the primary circuit of a nuclear power plant are expected to perform in the face of intense radiation, high operating temperatures and corrosive conditions, and to do so reliably over an expected lifespan ranging between 40-80 years of quasi-continuous operation. The condition of certain components within a primary circuit are therefore regarded as key indicators of plant lifetime, and if require replacement, need to be of the quality required, while additionally being delivered within the time frame for installation. Considering the environmental and financial fallout associated with damage to these
components, it isn’t a wonder that intense scrutiny is placed on their manufacture, maintenance and disposal.

While the aforementioned conventional metallurgical manufacturing routes have evolved considerably over the years, they have retained their advantages and limitations. The design, manufacture, inspection and maintenance of primary circuit components via these routes have been accordingly and extensively standardized, as evident from the governing RCC-M, RSE-M and ASME codes. While limited in the complexity of part manufacturable, the extensive material manipulation during the forging process typically yields a fine microstructure, rendering superior mechanical properties and excellent inspectability using ultrasonic means. This is not to suggest that cast parts are impossible to inspect: grain growth from the solidification mechanism results in larger crystals, which have challenged non-destructive ultrasonic methods to accordingly improve technologically. To counteract the detrimental effects of compositional segregation during solidification, casting enables a more near-net shape route for part manufacture, allowing complex shapes to be achieved without resorting to joining by welds, typically regarded as weak spots in assemblies subjected to high stresses. Where information has been available, a comparison between certain PM techniques and these conventional manufacturing routes are discussed in the succeeding document: D6.2.10 (PM capabilities compared with current processes). In general, the standardization codes account for limitations in each method by imposing restrictions on which components can be manufactured via a particular technique, and by specifying the expectations on composition, mechanical properties and inspection targets accordingly.

While not everything is known about PM to evaluate its superiority over another manufacturing process, it is fair to state that PM techniques in general offer several alternatives in the way metallic parts are manufactured. This can be advantageous when awaiting the manufacture of a safety critical part of a high quality, with a high probability of construction failure for the manufacturer, and with a long associated lead-time for the end user. While progression has been made towards incorporating PM standards in ASME & ASTM (discussed in section 3.1.11), there is no known progress of the same within the RCC-M or RSE-M codes.
1.1. Structure of investigation

The general aims of PowderWay are to develop an understanding of the candidate PM processes and to determine the accordingly constructed candidate replacement parts for application within the primary circuit of a nuclear power plant (NPP). During a road-mapping event, these data were relayed across to participants who represented end users, members of the supply chain and additionally research organisations. The event was a means of verifying the results, and of collecting input from industry regarding their needs and concerns, with a view to also understanding the extent of proprietary data that exists.

This document describes the state of code acceptance of PM parts as applicable to the European nuclear industry. It represents an understanding of the outputs of candidate powder metallurgical processes and their utility in the manufacture of the candidate parts. The strategy and route to code acceptance are presented; based on this and available information, further testing, research and simulations required to achieve the end goal are discussed.

To reiterate, the aims are to present the known capabilities and limitations of each selected PM process, and to propose the steps necessary for incorporation within standards, thus enabling a supply chain to develop and support part manufacture. These capabilities and limitations are determined by examining an accessible and hence finite body of literature concerning a wide range of topics published in the public domain. Considering the wide scope of this study and the short time frame under which it was conducted, it is highly probable that there will be room for improvement. The author has pledged to continue progressing in this aspect and will be available to deliver updates in the future. It is also worth mentioning that the European nuclear industry in general is very conservative with regards to adopting new processes and technologies for reasons that are obvious and mostly related to safety. This is likely to affect the rate of progression towards an end goal of code incorporation, time which will be essential in building a thorough understanding of the processes and thereby a robust case for code amendment. The proposals should reflect an outlook on the culture of safety and recommend a stringent view towards verification before adoption.
1.2. Summary of previous deliverables

As per the down-selection process of the PowderWay project, various PM techniques were evaluated for application within the primary circuit of a nuclear power plant (NPP).

Of course the selection of PM techniques was based on process maturity and output properties, leading to the following downselected methods in decreasing order of priority:

1. Hot iso-static pressing (HIP)
2. Additive manufacture (AM) and
3. Spark plasma sintering (SPS)

Of these, HIP & SPS are solid state consolidation techniques, whereas AM transforms the powdered raw material into a molten state in order to construct the desired part layer by layer.

While the criteria for selection was primarily based around developing ‘high reliability components’, it drew cross cutting relationships with other NUGENIA themes. Namely:

- Improved safety in operation,
- Improved modelling of phenomena in NPP’s,
- Increased public awareness,
- Preparation to avoid technology obsolescence &
- Performance and ageing monitoring of NPP’s for long term operation.

For example, HIPing enables the highly repeatable near net shape (NNS) manufacture of large safety critical parts with isotropic properties and microstructure. This isotropic nature should improve inspectability by ultrasonic means and offer predictable responses to degradation, thus forming a closer match to the outcomes from simulation studies. With the decline of businesses in the European economic area (EEA) capable of manufacturing large forgings, and competition for part manufacture from other industries, PM offers alternatives to mitigate the issue of conventional technology obsolesce within the civil nuclear industry. The identification of candidate processes was determined in D6.2.1 (Candidate processes identified), with a description of their capabilities provided in deliverable D6.2.5 (Process capabilities determined).
Discussion, deliberation and debate with end-users and technology providers revealed several candidate parts for manufacture via PM. The outcomes of this exercise were contributed to in D6.2.3 (End-user requirements defined) and D6.2.11 (Roadmapping), with the parts listed below.

1. Primary circuit pipe elbows
2. Pipe with integrated nozzle
3. Primary pump body
4. Valve units
5. Fuel filter
6. Spacer grid array
7. Compact heat exchanger
8. Dissimilar metal joint (DMJ)
9. Cladding
10. Baffle former bolts (BFB’s)

The detailed material properties of these candidate components, their downselection process and the identification of a supply chain for supporting their manufacture are described in D6.2.6 (Material properties of candidate components determined) & D6.2.8 (Candidate applications and components selected and supply chain identified) respectively.

This document (D6.2.9) will describe the known material properties of the down-selected PM techniques and discuss their suitability for the intended applications by relating to the known damage mechanisms occurring within the target environment. Through this exercise, the limitations in knowledge will be revealed, and thus recommendations can be made for future testing to enhance confidence, as well as the steps to incorporate them within the standardization codes.
2. Process material properties

This section will cover the resultant material properties from the downselected PM processes. These differ widely in the mechanism of consolidation and there exist variations in each technique affecting the variability of the corresponding output. The outcomes might also vary depending on the material being studied. The thorough analysis of a consolidation method as applied to the construction of a part in the required material might not be possible due to limitations in the availability of high quality data. In order to understand the desired properties, parallels would need to be drawn from the available information, enabling an understanding and hypothesis of the underlying microstructure in the intended configuration of application.

The powdered raw material is the single link relating the down-selected PM processes (HIP, SPS & AM) intended for manufacturing the down-selected parts. It is therefore pertinent to start off the discussion with an examination of the same. Of the chosen processes, HIP and SPS can be regarded as volumetric solid state processing, whereas most AM procedures are synonymous with a welding layer-by-layer procedure. It is more likely that in HIP & SPS, the process will retain a microstructure which is an evolution of that within the initial powdered raw material. This means that certain characteristic outputs of the powder manufacture stage are likely to be retained within the final part structure since even though recrystallization, grain growth and diffusion do occur, they are limited and localised. An example of this is shown in Figure 1, where the orthorhombic (Cr,Fe)₂B particles within the face centred cubic (FCC) Fe, Cr, Si solid solution matrix of the particle are retained even after consolidation to 98.5% of the theoretical density by SPS.

![Figure 1: SEM micrographs of Fe-Cr-B alloy following etching showing (a) microstructure of powdered raw material and (b) material consolidated by SPS.](image-url)
A brief overview of powder solidification mechanisms will therefore assist in understanding the structural and compositional states post manufacture, as well as their evolution during consolidation into a part.

In current AM PM practices, certain properties of the initial powder such as phase and grain size are lost in the large melt pool created by the energy source, rendering a microstructure where the grains are oriented according to the build direction and underlying substrate: the profile of thermal dissipation and underlying crystalline face structure respectively. Since these energy sources are highly focussed, of a very high intensity and are scanned at a high rate over what is essentially a growing heat sink, the melt pool will experience rapid solidification similar that observed in powder manufacturing processes such as gas or water atomisation. Understanding the solidification processes during powder manufacture can therefore be beneficial in relating to the outcomes from AM processes.

### 2.1. Rapid solidification processes

In general, the relationship between thermal gradient and velocity of cooling describes the crystalline structures which may form within a metal cooling from the melt. This solidification generally leads to two distinct classes of microstructures: equiaxed and columnar, and in real world processing conditions a variable proportion of the two is generally found in solidified metals. Equiaxed polycrystalline structures typically result in randomly oriented grains grown from multiple nucleation points, implying no directionality in their final structure, whereas columnar structures are characteristically directional and solidify along the thermal gradient between the melt and the solid. Columnar structures are further classified into lamellar, dendritic, cellular and planar according to increasing crystalline growth rate. The thermal gradient also has an effect on these structures, and the terms are related by the following equation:

$$ \frac{d\Delta T}{dt} = -VG $$

- $\Delta T$ = Undercooling
- $t$ = time
- $V$ = crystalline growth rate
- $G$ = thermal gradient at solid-liquid interface

During their production, gas/water atomised powder particles are subjected to rapid solidification processes (RSP) upon exposure to water, argon or nitrogen, resulting in effects
very different from equilibrium conditions. RSP’s can result in metastable phases and amorphous alloys, however the latter is out of the scope of this discussion. As will be discussed in section 2.2 of this document, metastable states can yield mechanical properties far in excess of those expected for a particular alloy during conventional consolidation routes. Metal powder manufacture using material molten via plasma and induction methods followed by rapid quenching in gas or liquid results in a range of solidification mechanisms which depend largely on the method of nucleation and rate of undercooling. With respect to nucleation, certain techniques in gas-atomization maintain a suspension of fine particles in the atomising chamber to initiate solidification and nucleation in the oncoming molten droplets. The rate of undercooling will vary according to particle size and specific heat capacity of the alloy. It is possible to observe both equiaxed and columnar transitions in the rapidly solidified powder particles.

The relationship between G and V resulting in a myriad of structures is represented in the following graph, allowing for microstructural selections to be made depending on the rate of undercooling, and hence the solidification velocity (V) and thermal gradient (G) for that particular alloy.

![Figure 2: Calculated microstructure selection map for superalloy CMSX-4 for use in laser AM repair of single crystal turbine blades.](image)

### 2.1.1. Equiaxed microstructures

There are several instances where equiaxed or grain refined microstructures have been observed in cross sections of powdered material. The suggested theory for the same is based on the remelting of dendrites which partially disperse in the melt to form nucleation points for crystalline growth that extend in all directions. The principles of this technique can be
used to alter the characteristic columnar structures of additively manufactured parts, and the same is discussed in section 2.2.2.

Consider the example where rapid solidification of tool steel powder manufacture results in an equiaxed or compound (equiaxed + dendritic) as shown in the following cross section images. The desirable carbide phases synonymous with this type of steel are observed in the grain boundary or interdendritic regions of the material.

![Figure 3: Equiaxed (left) and compound (right) microstructures of Cr-Mo-V tool steel produced by gas atomisation.](image)

While equiaxed and columnar structures can occur in powder particles of the same size, the reasons for their formation are linked to fragmentation of dendrites during remelting, serving as nucleation points for the former, and directional undercooling during solidification in the latter. Since dendrites typically form nucleation points for the equiaxed structures, and the presence of dendrites is directly linked to the level of undercooling, it is understandable why larger particles exhibit a higher percentage of grain refined structures as collated in the following experimental dataset.

![Figure 4: Analysis of over 200 particles from each size fraction of Cr-Mo-V (Ch12MF4) steel to determine percentage of solidification microstructures present.](image)
The material phase in the dendritic or equiaxed region are different from the underlying area labelled interdendritic in the former. Equiaxed microstructures are highly sought after for their isotropic properties and ease of inspection by ultrasonic probing. Controlling microstructural type, distribution, orientation and size in the part can help improve the material properties, reduce anisotropy, property scatter and ease the process of assurance. Consider the following Bridgmann directional solidification experiment where large lamellar structures are grown at low growth rates, and where variations in elemental concentrations are observed across the distinct boundaries.

In addition to the challenges in examining such as structure ultrasonically, the variations in passivation elements such as Cr could manifest as variations in corrosion performance, which can affect material properties in highly energetic and corrosive environments where structural integrity is desirable, such as the primary circuit of a nuclear power plant (NPP). An example of equiaxed microstructures observed in the gas atomization of copper is shown in the following image.
The precipitates observed accumulating at the grain boundaries are copper oxides. If considered as a candidate for exposure to neutron fluence, the oxides can be particularly problematic due to reduction induced swelling effects by hydrogen bubbles accumulating at the grain boundaries. Section 2.4.5 discusses the presence and detrimental effects of other precipitates in HIPped materials. In general, grain refined structures are desirable in powdered raw material, and especially so for the applications identified by PowderWay where high yield strength materials are desired along with consistent material properties for parts that can be probed with minimal attenuation using ultrasonic waves.

The next set of examples demonstrates the various columnar structures observed in powdered raw material, and these are presented in order of decreasing undercooling rate.

### 2.1.2. Columnar microstructures

Supercooling or undercooling refers to the high rate of cooling experienced by metal powders during their liquid to crystalline transformation. These crystals grow in planar, cellular and dendritic microstructures according to decreasing cooling rate. The higher the undercooling rate, the lower the chance of dendritic and interdendritic formation and therefore a lower risk of microsegregation as described in Figure 5. Moreover, the faster the crystal growth rate, the slower the nucleation. What this essentially means is that in the absence of external nucleation sources, small rapidly cooled powder particles might have a single point of nucleation and thus contain a primarily planar indiscernible structure within. This is frequently observed in powder manufacturing routes such as plasma rotating electrode process (PREP), which yield a distribution of powder particles varying in size, and also in internal microstructure. This internal microstructure is not immediately evident from surface examination, which appears to be dendritic in all instances. While the internal structure can be revealed through an examination of cross section, an interesting technique to employ is long term etching, revealing two distinct distributions of particles: those with a cube shape indicating a planar microstructure and single point of nucleation, and those with dendritic structures that appear to extend through the part interior as shown in the following images:
The authors observed that the planar growth was more common in smaller particles with a high initial level of undercooling, and proposed that this process was unique to rotating electrode type of powder manufacture since each particle had a unique point for nucleation and hence exhibited planar growth. Of course as the planar solidification increased, the exothermic reaction reduced the level of undercooling, causing the growth to tend towards dendritic like structures. In this study, what the authors refer to as dendrites are in fact an intermediate columnar phase referred to as cellular, and a cross section of the powder particle along with a proposed growth mechanism is provided.

It is suggested that the same planar growth would not be common in gas atomization since the satellite particles suspended in the atomizing chamber to initiate solidification would result in multiple nucleation points and hence a higher probability of equiaxed, cellular or dendritic structures forming.
Evidence of these cellular structures is also observed in instances where gas atomization is employed as shown below for the resultant finer populations of 316L and fully crystalline Fe$_{97}$Si$_3$ particles.

Figure 9: Cross sections of (left) 316L$^7$ and (right) soft magnetic alloy$^8$ demonstrating cellular microstructures.

2.1.3. Phase formation

In order to understand the formation of dendritic structures, the discussion can be supplemented by examining the primary and secondary phase formation in Fe-Cr-Ni alloys, better known as stainless steels. Here, the ratio between austenitic forming elements and ferrite forming elements assists in predicting the primary phase of the solidified material. The formulae$^9$ for calculating this ratio are given as:

\[
Cr_{eq} = (\%Cr) + 1.37(\%Mo) + 1.5(\%Si) + 2(\%Nb) + 3(\%Ti) \tag{2}
\]

\[
Ni_{eq} = (\%Ni) + 22(\%C) + 14.2(\%N) + 0.31(\%Mn) + (\%Cu) \tag{3}
\]

Using the Schaeffler diagram below as a reference, it is observed that a variety of phases are possible depending on these calculated values.

Figure 10: Schaeffler diagram showing phases possible for 316 for a range of Cr and Ni equivalents$^{10}$
However, this is typically the case when equilibrium conditions are allowed to develop during solidification resulting in a particular primary phase with a variation in the interdendritic region. The illustration below shows the difference in location and structure of the ferrite and austenitic phases depending on the Ni content.

![Figure 11: Schematic showing the predominant primary phase transition and location and structure of Ferrite phase in Fe-Cr-Ni alloys according to an increasing Ni content.](image)

When equilibrium conditions are not allowed to develop, in instances where rapid undercooling is present such as in gas atomization or additive manufacture, the presence of metastable phases are possible. In the example presented in Figure 12, a crystalline growth rate of 400 μm/s resulted in a primary ferrite phase forming. As the crystalline growth rate was increased to 1000 μm/s, metastable austenitic dendrites preferentially formed.

![Figure 12: Dendritic structures obtained for Fe-Cr-Ni alloy with varying growth rates (left) 400 μm/s (right) 1000 μm/s.](image)

For a given thermal gradient (G), these metastable phases can be predicted for a particular Cr:Ni ratio and growth velocity by referring to the following microstructure selection map, produced through a design of experiments (DOE) methodology.
The Cr: Ni ratio is an unchangeable parameter in Fe-Cr-Ni alloys, however the growth velocity is related to undercooling rate. Therefore differences in cooling rate would explain the phase differences in the following images of rapidly solidified particles of varying sizes, where the expected primary austenite phase gives way to ferrite in the smaller particles which experience greater undercooling.

Of course, XRay diffraction (XRD) can be used to perform a similar and a more quantitative analysis of crystalline phases in powders for powdered materials, however preparing a solid compact without deforming the powders and thus altering the phase via shear stresses can prove challenging. Not to mention the fact that the results will not necessarily be representative of the part interior.
Finally, powder manufacture also results in featureless interiors, where depending on the composition of the alloy, phase separation can occur at very fast cooling rates. Examples of these are presented for a Cu-Al-Sn alloy where larger particles exhibit a Cu-Al matrix with a Sn dendritic phase. As the particles reduce in size, the dendritic structure is no longer seen, and phase separation of Sn is observed.

![Figure 15: Cross sections of Cu-Al-Sn gas atomised particles showing (left) dendritic Sn microstructure (middle & right) phase separation](image)

2.1.4. Precipitates and inclusions

It is worth noting that oxides exist on the surface of most metals such as stainless steel considered in this study. The smaller the particle size distribution for stainless steel, the larger the surface area in a unit volume of powder, and hence a larger concentration of passivation oxides. These oxides will invariably find themselves within the part interior during consolidation and therefore require consideration on par with any other precipitating phases.

The following images show a dendritic microstructure in gas atomized IN718 particles. Etching and energy dispersive spectroscopy (EDS) was utilized for determining the composition of the precipitates in the interdendritic region, as shown below:
The smaller evenly dispersed precipitates in region 1 are presumed to be intermetallic laves phases, whereas the larger less prevalent laves agglomerates in 2 also have included carbides. It is well regarded that laves phases render uncharacteristic material properties and it is therefore important to know where the exist and how they will change over time under load.

To consider an example where 316LN powders were hot extruded at 900 °C, followed by heat treatment at 1100 °C for 1 h and then aged at 600°C for 1000 h, an increasing number of fine precipitates were observed when compared to the unaged specimen. Cross sections showing these comparisons are provided in the following images.

These precipitates were determined to be nitrides rich in Cr and V. The extruded specimens demonstrated an improvement in yield strength from 250 – 450 MPa as compared to conventional 316L, which the authors attribute to the fine microstructure from rapid solidification powder processes retained in the extruded section. The nitride precipitates from the ageing schedule increase the yield strength to over 600 MPa. Not shown here are the formation of cavities in the unaged specimen, believed to occur in RSP by the
supersaturation of vacancies, which are stabilised by oxygen and which reduce the surface energy through chemisorption. This could be a candidate mechanism for the porosity that accompanies the detrimental impact performance on 316L HIPped parts with increasing oxygen levels at low temperatures, a matter further discussed in section 2.4.7.

An analysis of these precipitates revealed differences in composition across the interface as shown below, which would affect overall part performance.

Figure 18: Atom probe field ion microscopy (APFIM) outputs showing elemental distribution transition from precipitate to matrix of aged 316LN

Inclusions in powdered material can also originate from crucible interactions, which can accumulate within the part interior and function as fracture initiation points. An example of this is discussed in section 2.4.7. It is clear that in addition to the various property developing microstructures produced by rapidly solidified particles, it is worth bearing in mind the various differences in composition and characteristic behaviour that precipitates and inclusions can render within the raw material and hence part, especially since solid state consolidation techniques will not alter their state and presence by very much, and part properties stand to be severely affected by their presence.

In the next section, we will consider how similar RSP’s will be used to construct parts in 3 dimensions via additive manufacture.
2.2. Additive manufacture of candidate components

The term is used to describe a method of manufacture where the desired part is built layer by layer. There are several variations to this technique, each with their own acronym, with electron beam additive manufacture (EBAM), selective laser melting (SLM) and direct energy deposition (DED) being some of the most popular for powder based AM. In general these are distinguished by the energy source and method of powder delivery. While the most popular energy sources in commercially sold machines are lasers and electron beams, there are also reported instances where electric arcs have been used to produce satisfactory results.

Powder delivery routes are typically classified into powder bed or blown powder. In the former, the energy source is scanned over the surface of a powder bed which increases in depth as the part is built up layer by layer, whereas in the latter the powder is blown from a reservoir into the focal point of the energy source. The processes of powder based electron beam and laser cladding are quite similar to blown powder AM with the distinction that cladding is primarily used to develop single or double layer material additions, usually of a differing material onto a metallic substrate.

The literature on this topic is vast and highly fragmented due to the aforementioned variants and materials of interest. Very often, the studies are not systematic enough to draw reliable relationships, and therefore caution must be placed when interpreting their results. As such this review will focus on the more popular materials and methods, centering on the resultant solidification methods and typically associated flaws. For a detailed description on the setup of the various technologies, please refer to deliverable 6.2.5.

Similar to the previously discussed section on powder manufacture, PM based additive manufacturing techniques fall under the classification of rapid solidification processes. The energy source is used to melt a powder fraction as its motion rasterizes the outline of that particular layer in the process. This continuously scanning narrow beam concentrates energy in a particular point, causing the exposed powders to experience temperatures above their melting point, creating a melt pool in a manner very similar to conventional welding. Solidification begins to occur immediately as the beam moves onwards to the next region. The rate at which this occurs is related to the size of the melt pool, exposed energy intensity, speed of beam travel, thermal conductivity of the material and mass of the underlying or surrounding structure, which often functions as a heat sink.
The following sections will examine the microstructures that develop and describe methods to control them. Following this, other process related outcomes unique to this method of consolidation will be described in order to develop a better understanding and hence confidence in the capability of the route.

2.2.1. Epitaxial growth

PM AM is in essence the layering of melt pools that rapidly solidify over each other to form the tracks or building blocks of a part. Each melt pool in successive layers remelts the layer beneath it. This causes the microstructure of the resultant part to adopt a strong directionality. The image below shows the microstructure typically observed in PM AM parts, where the vertical axis indicates the build direction.

Figure 19: Banded microstructure of additively manufactured powderised Ti64 showing epitaxial growth along the build direction (vertical)¹⁶

The bands in the microstructure represent the solidification phases of Ti64, structures which are observed in other alloys too, and are dependent on the solidification mechanism, solidification rate, solute composition. Though the part was built in distinct layers running horizontal to the image, the columnar crystalline growth is oriented along the build direction, indicating that the melt pool representing the active build region rapidly solidifies in a conformation that matches the underlying structure. While the artefact appears unique to the additive method of manufacture, similar epitaxial growth is seen in related manufacturing processes such as cladding and welding, and also the bridgmann solidification technique shown in 2.1.1. The grains are dendritic and oriented parallel to the thermal gradient i.e. direction of thermal dissipation, causing the molten material to crystallise according to the crystalline face of the solid substrate. In addition to powder based AM
techniques and as seen in the following SEM micrographs, similar effects are observed while using wire as the source material.

![SEM micrographs](image)

**Figure 20:** Cross section of IN718 wire AM using an arc energy source showing epitaxial growth aligned with the build direction.

For a nuclear application, these long grains scatter ultrasonic waves, and hence hinder ideal methods for through life inspection. There are methods to disrupt it and evidence and theories for the same will be discussed in the following subsection. The orientation of grains can also increase the anisotropy of part properties, rendering characteristics that differ depending on the direction of load. In addition to the epitaxial effect, RSP’s resulting from the rapid scanning of high energy density processes using lasers and electron beams show a crystalline dependence on the direction of beam travel, which can affect the angle of grain growth. This manifests as a zig-zag crystalline pattern, when the direction of beam travel alternates in successive layers. Shown below, the underlying substrate which includes the active layer functions as a heat sink, causing the resultant dendrites to solidify at an angle acute to the direction of beam travel.

![Diagram](image)

**Figure 21:** (a) Schematic showing zig-zag grain growth across layers, elaborated when beam travel direction alternates in successive layers and (b) evidence of this in a cross section of a Ti alloy wall constructed using PM.
Such a dependence on scan path would indicate that the directionality in terms of materials properties is affected by the choice of construction methodology. This is especially important to consider in instances such as the repair of a single crystal part where accurate grain matching is required between the parent material and deposited layers, and where the epitaxial effect would aid in this faculty. Since the relatively cooler substrate forms a heat sink, causing the heat to dissipate into the structure which includes the recently solidified part of the active layer, the output structure will be skewed with respect to the path of beam travel. There have been attempts to control the dendrite orientation using directional cooling as shown in this study concerning the PM AM manufacture of walls from a superalloy material.

![Schematic showing proposed method of controlling dendrite orientation during AM using base cooling.](image1)

(Diagram: Schematic showing proposed method of controlling dendrite orientation during AM using base cooling.)

By water cooling the substrate, it is possible to render a thermal gradient where the heat dissipation from the melt resists the urge to follow the melt pool and instead follows a direction parallel to the induced cold spot, thus orienting the solidifying structures accordingly. The authors suggest that the cooling effect reduces the grain boundary misorientation, allowing for more ordered structures to be grown in each successive layer.

The epitaxial growth in a PM AM part can also lead to variations in the mode of crack propagation depending on the orientation of the grains. Shown in the schematic below derived from experimental analysis, the fatigue crack growth behaviour varies according to its propagation with respect to the build direction.
The authors note that when tested normal to the build direction, the growth rate was restricted when the grains were more closely spaced, resulting in transgranular propagation. In contrast, there appeared to be no resistance to propagation for cracks parallel to the build direction resulting in a shorter fatigue life. HIP improved on this behaviour considerably by removing some of the directionality in the part, tending to a more equiaxed distribution at the cost of grain growth.

### 2.2.2. Columnar to equiaxed transitions (CET)

Epitaxial effects result in compositional variations within the part and render anisotropic mechanical performance as previously discussed. CET is therefore desirable for reasons related to achieving isotropic material properties, enhanced inspectability via ultrasonic means and finally for improving the profile of the consolidation route as a robust process for a nuclear application.

While a columnar epitaxial microstructure is typically expected via the additive manufacture route, there are methods for altering this to equiaxed and this is referred to as CET. This discussion excludes the aforementioned HIP processing from the remit. It is observed that when constructing a part by AM, the microstructure in the remelted zone from the underlying layer or substrate frequently adopts a columnar structure, where as the zone on the uppermost section tends to present an equiaxed structure. Shown below is a cross section from laser melting (cladding) of Titanium alloy powders showing these variations.
across the melt zone, where an equiaxed grain zone (EGZ) sits atop the underlying layer composed of both the heat affected zone (HAZ) and coarse grain zones (CGZ).

![Figure 24: Image showing variation in microstructure across a Ti alloy cladding illustrating the locations of heat affected zone (HAZ), coarse grain region (CGZ) and equiaxed grain region (EGZ).](image)

These microstructural variations are not just limited to cladding, and similar patterns are observed in additively manufactured parts. Consider a single wall superalloy structure built in 4 successive additive passes:

![Figure 25: (Left) Epitaxial columnar growth observed in the cross section of a Ni superalloy wall formed by 4 passes of blown powder laser melting. (Right) EBSD imaging showing increasing misorientation of the columnar grains and a finite proportion of equiaxed structures at the top.](image)

EBSD imaging shows that the grain misorientation increases with successive layers and is especially high in the uppermost layer. This is to be expected since as discussed, the growth orientation aligns ever so slightly with the direction of travel, which appears to be the same for all 4 layers in this study resulting in steady misorientation in the cross section of the beam path. In order to understand the origin of the equiaxed grains we must refer to the general theory of CET, where the diffusion of dendrites from the regions surrounding an undercooled melt zone can result in nucleation points for equiaxed grains. This would explain the conditions under which the equiaxed grains form at the uppermost surface of the layer under typical conditions. This same phenomenon has been demonstrated in the deposition of a weld on a Mg alloy work piece. Arc based energy inputs were used in this
study, and supplemented by an ultrasonic probe to agitate the weld pool shown below. Tungsten was chosen as the probe material since it had a higher melting point than the work piece material.

![Figure 26](image)

Figure 26: (a & b) Schematics showing the setup for ultrasonic agitation of a weld pool. (c) Mechanism for grain refining of the weld pool using dendrites from the mushy zone as nuclei for equiaxed grain growth.  

By comparing the EBSD maps of the cross section, it is possible to observe the effects with and without ultrasonic agitation.

![Figure 27](image)

Figure 27: Polarised light micrographs of arc weld paths on a Mg alloy workpiece showing (left) columnar grain growth following the thermal gradient and (right) equiaxed structures achieved by ultrasonic stirring of the weld pool.

The extent of grain refinement is directly dependent on the amplitude of the oscillation, and additionally follows an optimum dependence on the offset distance between the arc and ultrasonic probe. It should be feasible to install a similar setup on a powder based AM platform. Grain refinement in an AM part does not always require physical agitation to achieve and convective flows in the melt pool could be responsible for a similar outcome. As the study below shows, it is possible to cross over in terms of these microstructures by simply increasing the energy level of the incident beam for a particular melting strategy.
Figure 28: Optical images of uppermost surface (top row) and EBSD maps (bottom row) of cross section of cubic microstructures fabricated in IN718 in a powder bed configuration for electron beam currents (a) 10mA and (b) 20mA for a beam ON time of 0.25ms.

The melting strategy in this case was spot based as opposed to the continuous rasterising scanning strategy typically used in additive manufacture. Shown below, the spot scanning strategy adopted ensures an even preheating of the layer during build.

Figure 29: (Left) Rasterising continuous scanning strategy for layer manufacture (Right) Spot scanning strategy where focus is moved to consecutive point before beam is switched on for a predetermined time.

In addition to the microstructural differences observed within the cross section, it is possible to distinguish the individual melt pools in the sample constructed via the lower power beam current. This suggests that the preheating temperature is below the solidus temperature of the material, a factor the authors suggest is crucial to the differences in microstructure observed. The preheat temperature would enable the convective flows in the melt pool to
circulate fine dendrite fragments from the layer below to serve as nucleation points fuelling the observed equiaxed growth.

### 2.2.3. Grain size control

In section 2.2.1, the effect of the thermal gradient in the melt pool was responsible for a range of solidification processes, which exhibit variations in phase and composition. According to the general solidification theory discussed previously, crystallisation in columnar mode will yield microstructures with successively finer spacing in between dendrites for increasing cooling rate. For additively manufactured parts, this is cooling rate is controlled by the scanning speed of the energy source shown in the following image

![Figure 30: Influence of cooling rates in the microstructure of additively manufactured parts brought on by increasing the travel speed of the energy source, resulting in finer dendrite arm spacings.](image)

Of course, these cooling rates will vary on the mass and composition of the surrounding solid structure such as when comparing larger bulk samples to thin layers where the rate of heat dissipation is much higher. An example is shown in the following images:

![Figure 31: (Left) Bulk microstructure of EBM manufactured Ti64 vs the same for a 1.1mm thin wall (right). Note magnifications are equal in both instances.](image)

In the bulk microstructure, α phase grains are surrounded by a small β phase region, and in the thin wall structure of the same material prepared by the same method and where
thermal dissipation rates are more rapid, $\alpha'$ martensite platelets are observed within a $\alpha$ matrix. The difference is more apparent when you consider the hardness measurements between the two, which demonstrate an increase from 3.5GPa to 4.8GPa for the thin wall structure due to the martensitic phase. It is therefore worth noting the effect that cooling rate can have on microstructural phases and hence material properties. This is generally of concern only when constructing parts with wide variations in volume thickness over critical features where inhomogenous variations in microstructure could occur. The part downselection process during the PowderWay project has selected fuel filters and heat exchangers as candidate AM components, with the former fall under the areas of concern. The cooling rate and hence resultant structures are not only affected by energy source travel speed, but also the energy source itself. Similar variations in microstructure can be observed by simply changing the energy source. The differences in structures obtained for EBAM and SLM for comparable conditions are shown below.

![Figure 32: Optimised Ti64 walls prepared by EBAM (left) and SLM (right)](image)

The arrows indicate the columnar grains, oriented in the aforementioned zig-zag conformation mentioned, and tending to align according to the thermal gradient described in 2.2.1. The mode of energy transfer in EBAM is conduction, whereas convection is the predominant mode in SLM. In general, EBAM has a higher energy density and therefore slower cooling rates, leading to $\alpha$ phase grains surrounded by a $\beta$ phase region. In SLM, $\alpha'$ martensite platelets preferentially form indicating relatively rapid solidification rates.

Of course if scanning speed and energy source type result in variations in microstructure, the same must be true for the intensity of the energy source. Increases in laser power within blown powder 316 AM for constant travel speed, spot size and powder delivery rate result in successively larger dendrites forming as shown in Figure 33.
This is to be expected since increasing power results in larger energy and hence slower crystalline growth rate leading to larger dendrite arm spacings. The cooling rates of 310\textsuperscript{25} and 316\textsuperscript{36} stainless steels can be determined using an empirical empirical relationships by measuring the dendrite arm spacings:

\[
\lambda_1 = 80 \varepsilon^{-0.33} \quad (3)
\]
\[
\lambda_2 = 25 \varepsilon^{-0.28} \quad (4)
\]

- $\lambda_1$ = primary dendrite arm spacing in microns
- $\lambda_2$ = secondary dendrite arm spacing in microns
- $\varepsilon$ = cooling rate in K/s

The performance impacts on increasing beam energy are typically decreasing trends in hardness, yield strength and tensile strength as shown in the following graphs.

Of course this is dependent on the grain size, and similar and distinct decreases in tensile and yield strength through the part have been observed in laser metal deposition of 304L as shown below:
The higher yield strength and tensile strength values for the low power structure results from the relatively faster cooling rate and hence finer grain sizes. The decreasing trend in these values as the distance from the substrate increases is due to the substrate being water cooled. The thermal gradient will change with increasing distance from the block, resulting in grain size increases.

This correlation between grain size and yield strength is typical for metallic crystals and is expressed by the Hall-Petch relationship shown below:

\[
\sigma_y = \sigma_0 + \frac{k}{\sqrt{d}}
\]  

- \(\sigma_y\) is the yield strength
- \(d\) = average grain diameter
- \(\sigma_0\) & \(k\) are material constants

The single general observation from the equation is that the yield strength is inversely proportional to grain size diameter. The same trends in mechanical performance are observed as the scanning speed is steadily increased, resulting in lower beam interaction and hence faster cooling rates.

Figure 35: SLM AM of 304L showing variations in mechanical properties at low power (2300W) and high power (4000W).

Figure 36: Improved mechanical properties of 316L test specimens for increasing laser scanning speeds.

Note the increase in hardness, which generally and directly accompanies yield strength.
2.2.4. Build variations

The aforementioned relationship between cooling rate and construction parameters would suggest that reduced interaction with the powder through increased scanning speeds or decreased beam energy would render a continually increased improvement in mechanical performance. There are limitations to this since optimum levels exist for these parameters when manufacturing via AM. Varying the interaction between the energy sources and powder can result in a range of effects. This is observed when constructing a single track at constant scan speed for decreasing beam energies. At the high end of the spectrum, distortion is observed on the track, leading to a desirable continuous track at intermediate energies, and finally resulting in a discontinuous track below this value as shown in the following sets of images:

![Continuous with distortion](image)
![Continuous smooth track](image)
![Large semicircle droplets](image)

Figure 37: 316L powder deposited onto a 316L substrate with constant scanning rate 2.4m/min and decreasing beam energy values (top) 200W (middle) 150W & (bottom) 100W

The discontinuous track i.e. droplets as is referred to in the study are an artefact known as balling, where the instability of the melt pool from low energy input results in solidification reactions that manifest as droplets in order to conserve free energy. This phenomenon can lead to discontinuous tracks and hence porosity within the part. Balling is not only related to insufficient heat input or rapid scanning speeds. It can also be observed in instances where
impurities are present, resulting in disturbances in the melt pool as shown in the following high speed photographic images showing spattering occurring.

![High speed photographic data of the melt pool in an AM part being constructed on a 17-4 PH stainless steel powder bed](image)

Figure 38: High speed photographic data of the melt pool in an AM part being constructed on a 17-4 PH stainless steel powder bed.

It is also worth mentioning that since AM parts are built layer by layer, the material properties will be expected to vary along and across the build direction as introduced in section 2.2.1. A study examining the stress vs strain curves for walls built using a high (4000W) vs low (2300W) energy source suggest that the parts can generally tolerate a higher maximum stress along the longitudinal build axis.

![Blown powder laser AM of a 304L wall showing locations of test bars and (right) stress vs strain curves for the same](image)

Figure 39: (Left) Blown powder laser AM of a 304L wall showing locations of test bars and (right) stress vs strain curves for the same.

As discussed in 2.2.3, the differences between the low and high power curves are presumably due to the resultant grain size differences. A study of SLM construction of a thin walled part yielded significant differences in mechanical properties depending on the orientation of the test specimen to the build direction as shown in the following table.
<table>
<thead>
<tr>
<th>Material</th>
<th>Yield strength (MPa)</th>
<th>Fracture strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited part (parallel)</td>
<td>558</td>
<td>639</td>
<td>21</td>
</tr>
<tr>
<td>As deposited part (vertical)</td>
<td>352</td>
<td>536</td>
<td>46</td>
</tr>
</tbody>
</table>

Table 1: Differences in strength and ductility for identical 316L test parts built parallel to and vertical from the substrate layer.\textsuperscript{24}

As expected, the yield strength in the direction parallel to the substrate is higher than in the direction normal to it. This is due to the relatively lower inter layer bonding between adjacent layers lowering the tensile strength of the part under load. Increasing the extent of overlapping between successive layers and a post construction annealing schedule should help improve these properties. Similar results have been observed in powder bed laser melting of 316L powders, where the reported as built yield strength values were much higher across the build plate (662 – 678 MPa) than along the build direction (527 – 557 MPa)\textsuperscript{29}. The elongation values seem to follow a similar trend where they are higher along the vertical axis as compared to the horizontal, attributed to the epitaxial growth.

### 2.2.5. Porosity

Increasing the beam energy for a particular focus diameter or reducing the scanning speed will increase the interaction time with the powder and substrate. As described in figure 37, track distortion is a likely and significant issue of excessive exposure. Additionally, increased interaction times can result in a phenomenon called keyholing, which can increase structural porosity. Under ideal conditions in laser melting based additive manufacture, the incident energy is sufficient to create a melt pool from the exposed powder and this melt pool has sufficient enthalpy to form a metallurgically solid bond with the underlying structure. If the incident energy exceeds a threshold value, there might occur thermal penetration along the exposed axis causing evaporation and plasma formation within the melt pool. The resultant vapour cavity within the melt increases energy absorption, resulting in a deeper than normal penetration. This is the mechanism of keyholing, and the differences compared to the optimal condition are presented in the following cross sectional images.
Cross sectional tomography of a single track better illustrates the porosity that develops from the keyholing phenomenon along a track.

Essentially, the longer the laser interaction time, the greater the chance of keyhole defects being generated. It is helpful in this instance to evaluate the outcomes with the help of more appropriate parameters: energy density and laser interaction time. The formulae for the same are given by:

\[
\text{Energy Density} = \frac{P}{vLh} \quad \text{(7)}
\]

\[
\text{Interaction time} = \frac{d}{v} \quad \text{(8)}
\]
Using these equations, it is possible to account for the effect of multiple parameters when determining the optimum conditions for constructing a part in a particular material. The linear relationship between interaction time, energy density and penetration depth for increasing beam power can be determined for any materials as demonstrated in the following graphs.

It is possible to observe that increasing energy densities and interaction times can lead to increased penetration depths and thus a greater chance of keyholing. These experimental data can be used to construct simulations for estimating the threshold of keyholing for a particular material.

Porosity can be related to keyholing and/or balling effects. It can also be formed as a result of the choice of scanning methodology and active melt pool penetration into adjacent layers. The images below show this porosity developing between adjacent tracks, and also evidence of unmelted powders.
While briefly touched upon in section 2.2.2 for CET, evaluating complex scanning methodologies for porosity reduction are out of the scope of this discussion. Manufacturers of commercial equipment have invested heavily in understanding this aspect thoroughly, and can now consistently achieve full theoretical density parts under preprogrammed subroutines, where the opportunity to control grain structure and size might be restricted. From the perspective of this study, it is important to consider the impact of porosity on material properties. Porosity ranks fairly high on the list of undesirables in AM for parts in critical applications. The image below shows the evolution and increase in porosity fraction from 0.1 – 0.18% of an annealed SS specimen subjected to tensile loading towards catastrophic failure.
As is to be expected, an increase in porosity will cause the a part to fail under comparatively lower tensile loads. An example of this is shown from the same study, where an increase in porosity was induced by increasing the beam travel speed from 222 mm/s to 400 mm/s., resulting in lowered interaction time and hence insufficient melting resulting in porosity. Shown below, crack initiation is visible at 400MPa, followed by catastrophic failure shortly above this value.

![Figure 45: (a) Tomographic renderings and (b) cross sections showing damage evolution in a high porosity AM test specimen subject to tensile loading](image)

The part porosity and hence density was altered by simply changing the travel speed. Beam energy also contributes to this value since increasing energies result in increasing interaction times, and hence a reduction in issues where incomplete melting of the powdered material has occurred. The following plot shows how these parameters are related to each other.

![Figure 46: Relative density measurement of 48 additively manufactured 316L pillars showing dependence on laser energy and beam scanning speed](image)

While the effect of porosity on yield strength and ductility have been discussed, it is also possible to observe a decreasing trend in hardness values as shown below.
While the hardness measurements are likely to be affected by surface breaking porosity affecting the indentation, it is also likely that there are internal pores collapsing under load. In addition to porosity from unmelted particles, the large surface area of the powdered particles is prone to environmental interactions, resulting in inclusions that find their way into the part interior. An example of these inclusions are oxides which originate from passivation films that develop on the surface of stainless steels. When constructing a part via blown powder AM, the powder particles are introduced to the focal plane of the energy source under a shielding gas to limit exposure to atmosphere. It is likely that the turbulence from the process and the rapidly changing viscosity of the melt pool can result in gaseous entrapment. While examining the fracture surfaces of blown powder austenitic steel tensile specimens, it is possible to observe unmelted particles, oxide inclusions, entrapped gas as seen from the following fractographs.

2.2.6. Segregation and stresses

In addition to keyhole porosity being generated by excessive energy input, solute segregation can be a related artefact. Here, the incident electron beam energy is above the optimum level for the Ti alloy, resulting in a banded microstructure across the part. On closer examination, these bands were observed to be microstructural variations, with the dark characteristic lamellar structures sandwiched in between light irregular γ and α2
phases. EDX analysis shows a variation in the enrichment of the key elements across these bands.

![Figure 49: Cross section of a part built via electron beam melting of a Niobium rich Titanium Aluminide with a beam current of 12mA and a preheating temperature of 1100C showing (left) distinct bands (right) EDX analysis of these bands.](image)

Depending on the material composition and choice of processing parameters, other forms of segregation may occur. The distinct melt pools observed in the cross section of a laser melted Ni superalloy reveal a precipitate phase manifesting within the typically expected columnar grains.

![Figure 50: Cross sectional images of structure built using powder bed laser AM of IN718 showing (left) distinct melt pools and (right) γ phase grains growing across the melt pools and γ' precipitates manifesting as circular and cuboidal features within these grains.](image)

The authors suggest that the dark areas at the edges of the melt pools are typically due to particle sintering as opposed to melting, and often there appear pores in between these pools, which is related to insufficient interaction energy.
Finally, consideration is given to the manner in which residual stress develops in the part during construction. Post consolidation heat treatments generally aid in relieving these stresses, however the stresses can cause distortions or cracking during the build process and are therefore desirable to control. Certain stainless steels can precipitate ferrite phases during rapid solidification, which can aid in a resistance to cracking. The schematic below shows the types of residual stresses that develop within a track upon exposure to an energy source.

Figure 51: Components of stress in an AM track during (Left) heating and (Right) cooling

During this exposure, the track and underlying layers/substrate expand, followed by localised compression once the beam has been moved/scanned away. This results in development of a tensile stress state on the uppermost layer, which sits within a region of compressive stress. The radius and depth of these layers are dependent on energy density, material composition and beam interaction time. Briefly discussed previously, the accumulation of these stresses are known to result in a range of defects such as delamination, distortion and cracking. Increased part distortion is observed between the addition of a successive layer, as shown in the graph:

Figure 52: Trend in distortion related to residual stress development in an IN625 structure. Note (ii) indicates deposition passes for the construction of a single layer

Increasing the dwell times will therefore result in increased part distortion. Additionally the ability of the part to respond to incident thermal energy will result in increased distortion during additive manufacture. This correlation is predictable and observable from the results
shown below where the material with the higher CTE (IN625) has a much higher residual stress than the Ti64.

![Graph showing residual stress comparisons between additively manufactured Titanium and Nickel alloy parts.](image)

Figure 53: Comparisons between residual stresses between additively manufactured Titanium and Nickel alloy parts.\textsuperscript{16}

These data also suggest that the amount of stress is directly related to the energy density of the process. The studies into residual stress development are limited, and they do not account for the stresses developed by phase transformation during cool down. For austenitic stainless steels, heat treatment is regarded as essential for developing material properties, and in particular for normalizing residual stresses. A study of stainless steel 316L test specimens manufactured through the powder bed laser fusion method show a dramatic drop in ultimate tensile strength and yield strength following annealing.

<table>
<thead>
<tr>
<th>AM SS condition</th>
<th>UTS (MPa)</th>
<th>YS(MPa)</th>
<th>Elongation(%)</th>
<th>RA(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As built</td>
<td>705 ± 15</td>
<td>590 ± 17</td>
<td>44 ± 7</td>
<td>53 ± 10</td>
</tr>
<tr>
<td>Annealed</td>
<td>635 ± 17</td>
<td>375 ± 11</td>
<td>51 ± 3</td>
<td>57 ± 8</td>
</tr>
</tbody>
</table>

Table 2: Change in mechanical properties following annealing for additively manufactured 316L test specimens machined from a bulk structure prepared via laser based powder bed fusion.\textsuperscript{12}
2.3. Spark Plasma Sintering of metals

There are several acronyms used to describe this method of powder consolidation. In addition to SPS, pulsed electric current sintering (PECS), field assisted sintering technique (FAST), direct current sintering (DCS) and electric field assisted sintering (EFAS) are synonyms and subtle variations in what is essentially the same underlying technique. Described in deliverable 6.2.5 and hence forth referred to as SPS to maintain continuity, a combination of uniaxial pressure and a pulsed DC current are employed to consolidate a metallic powder compact within a conductive die.

2.3.1. Mechanism of consolidation

The term plasma and spark have been under dispute by researchers who have claimed not to observe either through visual means, or by detecting fast fourier transforms of the voltage or electromagnetic emissions typically produced by the presence of plasma and/or sparks\(^{36}\), which would explain some of the differences in acronyms. On the opposition camp, studies examining the development of porous materials have unearthed evidence of bridging between particle necks, which draws focus into the various mechanisms contributing to consolidation.

The following equation illustrates the sintering model proposed by Kuczynski, used to derive the diffusion coefficient for a particular sintering hold time and temperature of spherical particles.

\[
    t = \frac{R^3 \xi^5 K T}{80 \sigma \delta^3 D}
\]  

- \(t\) = holding time
- \(R\) = radius of particle
- \(\xi\) = relative sintering neck (x/R)
- \(D\) = diffusion coefficient
- \(\sigma\) = surface tension coefficient
- \(\delta = 3.6E-10 \text{ m}\)
- \(K = \text{boltzmanns constant}\)
- \(T = \text{sintering temperature}\)

For SPS, this results in a coefficient to 9.24E-8 m\(^2\)/s for a sintering temperature rise to 1100 °C with a hold time of 300s. By comparison, hot pressing at the same temperature and with much longer hold times (2700s) results in a diffusion coefficient of just 2.1E-8 m\(^2\)/s. Considering the rapid grain growth and described in section 2.3.6 showing evidence of pore
boundary diffusion, the enhanced diffusion coefficients do not come as a big surprise. The study also noted evidence of fine bridging structures at the necks and in between adjacent particles shown in the next set of images. The high diffusion rates could manifest as a physical effect, which could provide as an interesting explanation for the bridging structures.

Figure 54: Bridging structures in between particles and at the necks between stainless steel particles in contact after consolidation via SPS. The authors attribute these structures to the formation of plasma during the sintering process, but this remains to be confirmed. It is also possible that these are the result of electro-transport phenomenon characteristic of field sintering. A reason for the same could be the Branly effect, where the material transitions from an insulator to a conductor in the presence of an electric field. Shown below is evidence from the early stages of consolidation, with evidence of molten material at the interparticle contacts that match effects observed in a control study attempting to replicate the coherer (Branly) effect.

Figure 55: SEM micrograph of copper powder particles early in a typical consolidation cycle, showing evidence of microwelding occurring in the region surrounding interparticle contacts.

The offered theory is that most surface-active metallic powders are available in a pre-oxidised state due to their inevitable exposure to atmosphere following atomisation and during sieving and blending. When these are exposed to a low voltage high current electric field, a spark can be generated as the material transitions from an insulator to a conductor, inducing an electromagnetic field that develops in the inter particle microwelds observed.
2.3.2. Oxide removal

The advantage of using SPS when compared to other powder metallurgical consolidation techniques is additionally the removal of surface oxide layers on the powder particles by the electrical discharge. A study into the consolidation of Al based bulk metallic glasses (BMG) showed that this removal was related to the heating rate, with more effective removal observed for higher ramp up rates as shown in the images below.

![Figure 56: (Left column) Bright field TEM imaging and (Right column) electron diffraction patterns for an Al based metallic glass powder consolidated via SPS to 248.5 °C at 600MPa for 10m at heating rates of (Top row) 5 °C/min & (Bottom row) 10 °C/min.](image)

The bright field TEM imaging shows that the selected area electron diffraction (SAED) at the interface for the sample sintered at the higher heating rates i.e. 40 °C/min is amorphous, and does not show the diffraction patterns synonymous with oxides as observed at the interparticle interface where a relatively lower heating rate was employed. EDX analysis additionally confirmed that oxygen was absent at the interface. The rapid heating rate also resulted in a slight improvement in compact density. Not all field-sintering techniques yield the same results. When comparing resistance sintering to SPS, the constant application of current by the former only leads to oxides at the powder surfaces to form grain boundary structures. The authors argue that with pulsed SPS, the theoretical generation and sustenance of plasma causes disruption of the oxide film through heating, ionization and electron bombardment. This yields a cleaning effect, allowing adjacent grains to make contact with each other. Varying results are experienced for the success in oxide disruption, with pulse frequency and ramp up rate hypothesized as being the key variables.
A conflicting study\(^5\) suggested that, it is in fact the slow heating rate which is responsible for the particle oxide cleaning effect. As part of a series of studies conducted by Olevsky et al\(^{41}\), which argue that consolidation in SPS is a result of thermal and athermal parameters and phenomena. Heating rate, thermal gradients driving thermal diffusion, interparticle melting caused by non uniform temperature profiles and thermal stresses driving dislocation creep are examples of thermal phenomena. The athermal parameters are governed by the flow of electrons through electromigration, electroplasticity, ponderomotive forces, the electromagnetic pinch effect and finally the removal of oxide films through dielectric breakdown and defect generation at grain boundaries. Their investigation into modelling thermal diffusion assumed that the oxide films on the surface of metallic powders would restrict the thermal conductivity of the compact. The conclusions were that high frequency pulses would increase the thermal diffusion of atoms and vacancies in the material, that this diffusion was inversely proportional to particle size. This would initially be seen as contributing to sintering by the development of interparticle necks, but the resultant pores would attract vacancies during the final stages, impeding densification. This highlights the caveats of employing high frequency pulses during sintering.

### 2.3.3. Joining via SPS

In comparison to powders utilised by HIP and AM, those utilized in SPS have a much finer PSD, of the order of tens of nanometers to a several microns in critical dimension. This distribution is typically achieved by mechanical milling. Since its inception, SPS has been used in the consolidation and forming of ceramic, metallic and intermetallic parts. The key advantages are the lower apparent sintering temperatures and shorter processing times, making it highly viable from an industrial processing stand point. In addition, functional grading between dissimilar materials is made possible through SPS, where a high strength interface between 316L and MoSi\(_2\) was achieved as shown in the following images.

![Figure 57: (Left) Schematic and (Right) optical micrograph showing a graded dissimilar metal joint between 316L and MoSi2 using SPS as the method of consolidation.](image-url)
This type of joint is desirable for connecting Molybdenum based components utilised in high temperature environments to systems composed of conventional ferrous based alloys. The obstacle frequently encountered is one of microcracks and high residual stresses due to differences in the coefficient of thermal expansion (CTE) between these materials. While the outcomes were not without evidence of cracking, these were fewer in number and found to originate from the MoSi$_2$ surface, presumed to occur due to the lower material susceptibility to tension stress. To demonstrate another capability of employing SPS, consider the following image, which shows a joint between two pieces of stainless steel bar, interfaced by a what was initially a thin powder layer with matching composition.

![Figure 58: Joint created by interfacing two pieces of stainless steel bar with a thin layer of 316L powder and subjected to a pressure of 38.2MPa during field assisted consolidation.](image)

What is especially interesting is the absence of a heat affected zone (HAZ) revealing a very clean interface across the joint. Comparing the strength of the joint to that of the parent material shows a drop in ultimate tensile stress and strain, however the reported values of the joint appear to be quite interesting considering the thickness of the joint and minimal dilution into the end pieces.

![Figure 59: UTS and maximum strain values for SPS consolidated joints at pressures (P1) 38.2MPa and (P2) 63.7MPa in comparison to (AR) the wrought bar.](image)
However this is not to suggest that HAZ does not occur via SPS. The images below show this, evidenced by the discoloration and the microstructural analysis which reveal a high delta ferrite content within the joint.

Figure 60: Cross section of SPS consolidated 316L powder joint between two pieces of stainless steel showing evidence of a head affected zone and microstructure enriched in delta ferrite.

The deformation of the joint reveals one of the issues with this mode of consolidation, where the electric current can travel inhomogenously through a powder compact, choosing to follow the path of least resistance, and thus leading to the irregularity observed. Factors such as imposed pressure, powder quantity, die contact area, heating power and holding time can all have an effect on the homogeneity of sintering. It is suggested that the resistance of the interlayer is affected by the oxide layer on the particle surface and the constriction imposed by interconnected powder particles. Joint temperatures of upto 1152°C were measured after heating for just 2s, and this has been attributed to the joule heating, which is directly proportional to the resistivity of the material and square of current density. The authors experienced challenges in maintaining the heat within the powder compact due to the adjacent areas functioning as heat sinks.

2.3.4. Die interactions and stresses

When consolidating a part via SPS, welding can occur between the compact and punch if precautions are not taken. This leads to difficulties in extracting the sample from the die, and in the introduction of stresses that may lead to failure of the compact and/or die during removal. A common work around is to use a graphite foil interface. It is observed that when
compacting austenitic materials using this interface material, carbon from the foil diffuses into the powder compact, resulting in chromium carbide formation at the grain boundaries. Depending on the process parameters, this can result in an interaction depth of upto 200 μm as shown in the following SEM micrographs:

![Figure 61: SEM micrographs of the (Left) face of a 316L part consolidated via SPS showing the presence of intergranular Chromium carbides and (Right) cross section of the same sample illustrating the depth of this layer from the face on the right (Note observations have been made after grinding and electropolishing to a depth of 100μm below original face)](image)

The authors note the absence of these intergranular carbides when using a boron nitride (BN) spray in addition to the graphite foil, where an apparent increase in porosity is observed. However the exact interfacial location or method of application to the die is not described. The authors were able to achieve a relative density of just 95% using the BN spray technique.

Uniaxial compression yields different effects in temperature and stress homogeneity within materials varying in electrical conductivity. In a study comparing experimentally verified FEM simulations between alumina and copper, the authors note large radial thermal gradients evolving within the alumina sample, whereas a very low inhomogeneity was observed in the copper sample presented in the successive schematics.

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Figure 62: Simulations showing the development of hydrostatic stresses between the compact and die during consolidation depending on whether the sample is (Left column) alumina i.e. non-conductive or (Right column) copper i.e. conductive

This is to be expected since sintering in ceramics is driven by the heat radiating from the interface with the graphite die into the sample. Interestingly, when attempting to compare the stresses between the two, the differences in CTE between the alumina and graphite die were much less than the copper sample, leading to lower hydrostatic stress gradients on the axial direction. These stresses can extend to the die wall and cause premature failure. Differences in thermal conductivity between the sample and die can induce sample failure during cool down, a matter of special concern in alumina.

Hybrid SPS furnaces are considered to be the solution for the stress generation and employ heating elements to control the chamber temperature, offering a higher degree of control during ramp down conditions.

2.3.5. Process control parameters

Considering the microwelds observed on some particle surfaces after just 2s of sintering, it is fair to assume that there is the potential to overshoot the sintering temperature set point. Feedback loops employed by SPS furnaces are generally a pyrometer examining black body radiation or a thermocouple inserted into the die. Depending on the bit rate of these sensors, controlling such a high diffusion process will prove challenging without some overshoot occurring and affecting consolidation, microstructure and therefore part properties. Since the temperature and pressure profiles are the main parameters for
controlling consolidation, they need to be better understood and this section will attempt to do just that.

Differing onset points of the temperature and pressure cycle have determined that there isn’t a large difference in final density or average grain size as shown in the following data:

![Figure 63: Temperature and pressure profiles showing compaction cycles with (a) simultaneous application of temperature and pressure (b) delayed onset of pressure (c) delayed onset of temperature. The table below shows the set points and differences in relative density and average grain size for the three profile variations.](image)

<table>
<thead>
<tr>
<th>Holding time (s)</th>
<th>Dwell temperature (K)</th>
<th>Max pressure (MPa)</th>
<th>Temperature/pressure profile</th>
<th>Relative densities (%)</th>
<th>Average grain size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1323</td>
<td>50</td>
<td>A</td>
<td>93.7</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B</td>
<td>94.4</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>93.9</td>
<td>0.46</td>
</tr>
</tbody>
</table>

By examining the outputs of the study into consolidation of 316L powders in the following graph, it is possible to draw a conclusion regarding the effect of sintering pressure on relative density, which does not appear to be quite so significant, however the hold times do weigh heavily on the outcome.

![Figure 64: Effect of sintering temperature (T), hold time (t) and pressure (P) on the relative density of a 316L powder compact consolidated via SPS.](image)
An inverse relationship was observed between increasing temperature and yield strength. Grain growth is expected to increase at higher sintering temperatures, and when considering the Hall & Petch relationship, the decrease in strength is relatable. Increasing pressure impacts the yield strength in a similar trend, but to a lesser extent as shown in the table below.

<table>
<thead>
<tr>
<th>SPS Processing parameters (yield strength / ductility)</th>
<th>700 °C</th>
<th>850 °C</th>
<th>1000 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 MPa</td>
<td>278 MPa/43%</td>
<td>154 MPa/59%</td>
<td>134 MPa/67%</td>
</tr>
<tr>
<td>65 MPa</td>
<td>265 MPa/49%</td>
<td>158 MPa/56%</td>
<td>130 MPa/65%</td>
</tr>
<tr>
<td>80 MPa</td>
<td>253 MPa/50%</td>
<td>166 MPa/59%</td>
<td>150 MPa/58%</td>
</tr>
</tbody>
</table>

Table 3: Table showing yield strength and ductile performance for SPS compacts of Nickel powder subjected to varying sintering temperatures and punch pressures

Achieving near theoretical density is a desirable factor in field assisted consolidation. With regards to achieving this, the maximum sintering temperature was found to have the greatest influence over the outcome. The table below shows the temperature induced densification effect on two distinct ferrous alloys.

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>316L</td>
</tr>
<tr>
<td>750</td>
<td>85.4</td>
</tr>
<tr>
<td>850</td>
<td>93</td>
</tr>
<tr>
<td>950</td>
<td>93.9</td>
</tr>
<tr>
<td>1050</td>
<td>93.3</td>
</tr>
</tbody>
</table>

Table 4: Effect of sintering temperature on relative densities of 316L and Fe14Cr1W

A study characterising the mechanical properties of nitrogen containing nickel free austenitic stainless steels arrives at similar conclusions regarding the relationship between compact density and temperature. An inverse relationship was drawn between achieved part density and average particle size, and this is to be expected since the increased surface area of the smaller particles function as a driving force for necking.
Starting material powder

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>800</th>
<th>900</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g cm(^{-3}))</td>
<td>6.25</td>
<td>7.27</td>
<td>7.70</td>
<td>6.77</td>
<td>7.48</td>
<td>7.77</td>
</tr>
<tr>
<td>Relative density (%)</td>
<td>80.27</td>
<td>93.43</td>
<td>98.99</td>
<td>87.24</td>
<td>96.12</td>
<td>99.78</td>
</tr>
<tr>
<td>Apparent porosity (%)</td>
<td>16.67</td>
<td>4.81</td>
<td>0.78</td>
<td>10.65</td>
<td>2.93</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Table 5: Outputs of density in respect to varying particle sizes and sintering temperatures for nitrogen stabilised stainless steels\(^{49}\)

To understand the dependence of final density with particle size, consider a water atomised 90 μm particles of a FeMo alloy, consolidated as is and after being subjected to ball milling for 20h. While the distinct particle sizes themselves do not increase due to welding of Fe from the milling process, the grain boundary area and dislocation density did increase, resulting in a higher driving force during sintering. Discussed in section 2.1, larger particles during the atomisation process cool relatively slower than smaller ones in the same material, resulting in larger grain formation within the former. Shown below the punch displacement curves for the two compacts are identical, just shifted on the x axis, with the onset of densification being at a lower apparent sintering temperature for the milled powders due to the high concentrations of dislocations.

The drive to eliminate Nickel in stainless steels is based on the high elemental cost. Powders with a high value of nitrogen are therefore employed to stabilise and enhance the austenitic character of the resultant part. It is expected that during the process of sintering, the
nitrogen level will decrease, and analysis shows that this does occur at a level proportional to sintering temperature, however this value is fractional and not highly significant. The properties for the resultant SPS compacts far exceed the norm for this material type, and are given in the table below.

<table>
<thead>
<tr>
<th>Starting material powder</th>
<th>Powder A (55μm)</th>
<th>Powder B (27μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sintering temperature (°C)</strong></td>
<td>800</td>
<td>900</td>
</tr>
<tr>
<td>UTS Rm (MPa)</td>
<td>210</td>
<td>650</td>
</tr>
<tr>
<td>YS Rp0.2 (MPa)</td>
<td>-</td>
<td>595</td>
</tr>
</tbody>
</table>

Table 6: Outputs of material strength in respect to varying particle sizes and sintering temperatures for nitrogen stabilised stainless steels

It is important to remember that while the UTS and yield strength increases are related to the improved density at higher temperatures, the parts could be affected by the reduction in nitrogen from the sintering process. This could explain the slight dip in properties at higher sintering temperatures. Of course the property improvements in the compacts containing smaller particles could be due to the increased surface area, finer grain size and the general strengthening effect of nitrogen at the grain boundaries.

In a study describing the consolidation of stainless steel powders, it was observed that the apparent porosity of the compact was inversely proportional to the initial mean powder particle size and as discussed previously, inversely related to the holding time as shown in the graph below.

![Figure 66: Apparent porosity of stainless steel SPS compacts as a function of mean particle diameter, sintering temperature and sintering hold times at a pressure of 48 kPa](image-url)
2.3.6. Grain growth

Baseline determination in a study concerning the formulation of steel composites using SPS reveals as expected, a direct correlation between sintering temperature and density, and also an improvement in Young’s modulus.

<table>
<thead>
<tr>
<th>Sintering conditions</th>
<th>Time (min)</th>
<th>Apparent density ( \rho_0 ) (g cm(^{-3} ))</th>
<th>( \rho_0/\rho_{\text{theoretical}} ) (%)</th>
<th>Porosity (%)</th>
<th>Youngs modulus ( E ) (GPa)</th>
<th>( E/E_{\text{theoretical}} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>5</td>
<td>6.73 ± 0.03</td>
<td>83 ± 0.3</td>
<td>15.32</td>
<td>165 ± 3</td>
<td>79 ± 1</td>
</tr>
<tr>
<td>1100</td>
<td>5</td>
<td>7.75 ± 0.01</td>
<td>97 ± 0.3</td>
<td>0.92</td>
<td>196 ± 5</td>
<td>94 ± 2</td>
</tr>
<tr>
<td>1000</td>
<td>30</td>
<td>6.87 ± 0.02</td>
<td>86 ± 0.3</td>
<td>11.65</td>
<td>176 ± 3</td>
<td>84 ± 1</td>
</tr>
<tr>
<td>1100</td>
<td>30</td>
<td>7.82 ± 0.02</td>
<td>98 ± 0.3</td>
<td>0.89</td>
<td>208 ± 4</td>
<td>99 ± 1</td>
</tr>
</tbody>
</table>

Table 7: Analysis results of 316L particles compacted by SPS under varying temperatures and hold times, showing the impact on Young’s modulus.51

In a study examining the influence of temperature and pressure on the microstructure of Nickel compacts, it was noted that temperature had the greatest effect on increasing outputs such as compact density.

Table 8: SEM micrographs of cross sections of pure Nickel compacts showing grain size variations at constant SPS pressure and hold time with increasing sintering temperature.47

The caveat of resorting to long hold times or high sintering temperatures to improve part density is the risk of grain growth as noted from the example above, which would negate some of the advantages of this consolidation technique. Shown below is the effect of grain
growth of Tungsten where the sintering temperature is varied, while the remaining parameters are kept constant.

Figure 67: Porosity reduction in a Tungsten compact illustrating the trade off in terms of grain growth for increasing sintering temperatures (a) 1600 °C (b) 1700 °C (c) 1800 °C for a hold time of 5 minutes each.

It is interesting to observe that the grain growth is so rapid that the interparticle pores have migrated towards the grain interior. The location of these pores is regarded as unfavorable from the perspective of general sintering theory since their removal is dependent on lattice diffusion of material, and hence relatively slow as compared to the majority of diffusional mechanisms which favour the interparticle neck region. This effect can be controlled through a step wise heating cycle, where the first step and hold profile before ramp up to sintering temperature favours interfacial atomic diffusion at particle necks. Grain growth factors as high as 5 were observed in the study, and this was reduced to below 2 using the step wise heating routine. Inevitably, densification occurred at the cost of grain growth, and the authors argue this could be avoided by correct choice of PSD and by ensuring homogenous distribution of these powder variations within the presintered compact.

Evidence of this pore migration towards the grain interior is also seen in compacts of pure Nickel where heating rates of 100 °C/minute were employed.

Figure 68: SEM micrographs of cross sections of pure Nickel compacts showing pore boundary migration which accompanies rapid grain growth when the sintering temperature is increased.
The structures appear equiaxed and show low directionality/ anisotropy compared to the AM counterparts. Presented in section 2.2.3, the Hall and Petch relationship suggests that the mechanical properties of a material can be improved by a reduction in grain size. There is an enormous drive to develop materials processing techniques that assist in achieving this goal. Shown in the following image is the microstructural characterisation of a consolidated compact of 316L having achieved near theoretical density, showing a distribution of fine equiaxed grains.

![EBSD imaging and size distribution of grains of a compact of 316L powder consolidated to 99.6% RD via SPS at 1373K at a pressure of 50MPa.](image)

Since hardness is directly related to yield stress, it is possible to draw relations with the reduction in grain size to improvements. This is observed when drawing comparisons to cast equivalents, where the effect of reducing grain size can be observed in terms of Vickers hardness.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean grain size (μm)</th>
<th>Relative densities (%)</th>
<th>Hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast + annealed (1175 °C – 12h - vacuum)</td>
<td>49 ± 50</td>
<td>100</td>
<td>111 ± 3</td>
</tr>
<tr>
<td>Cast + annealed (1050 °C – 10h – vacuum)</td>
<td>16.2 ± 13.6</td>
<td>100</td>
<td>145 ± 4</td>
</tr>
<tr>
<td>SPS density: 99.6 %</td>
<td>2.65 ± 1.82</td>
<td>99.6 ± 0.3</td>
<td>209 ± 3</td>
</tr>
<tr>
<td>SPS density: 97.5%</td>
<td>1.27 ± 0.62</td>
<td>97.5 ± 0.1</td>
<td>237 ± 4</td>
</tr>
</tbody>
</table>

Table 9: Comparison between powder consolidated compacts of different densities and cast and annealed variants in the same composition showing correlation between hardness values and grain sizes.
Similar values of density could be achieved at lower temperatures if the holding times were increased. However this comes at the cost of increasing grain size. The improvement in measured hardness of the SPS samples reached nearly double the value. The lower density compact exhibited a much higher hardness, and these improvements could simply be attributed to the reduced grain size in each case.

2.3.7. Corrosion performance

The data to compare the corrosion resistance of SPS stainless steels was available. Potentiodynamic polarisation tests were carried out to evaluate the corrosion resistance and the curves below suggest a direct relationship between performance and compact porosity i.e. part density.

![Figure 70: Potentiodynamic polarisation curves showing comparisons between cast and field sintered parts composed of 316L](image)

The corrosion potential \(E_{corr}\) of the cast piece falls in between that of the low and high density SPS compacts. Both SPS samples demonstrate a much larger passivation region as compared to the cast part, which is explained as being due to the comparatively finer grain sizes. It is also important to note that the pitting potential \(E_p\) of the high density sintered compact occurs at a much more anodic value indicating that it is more resistant to pit initiation. The graph below describes a similar behaviour for SPS’d 316L powders which have been ball milled and then subjected to polarisation tests under similar conditions.
Here, the cast reference sample shows a much larger passivation region at low current densities when compared to the previous study, which suggests a good stability of the layer. The high density compact from sintering as received powder denoted P1 has a lower corrosion potential, but a wide passive region as previously described. Both ball milled and consolidated samples (P2) do not demonstrate a distinct passive region, and the reason for this could be related to the relatively lower density. The reason for resorting to ball milling was to increase the grain boundary region as a means of creating irradiation damage sinks for a nuclear application. In a study employing mechanical alloying (ball milling) and SPS, comparing the effect of nitrogen content and nitride precipitates on ultrafine stainless steel powders, large scale increases in Vickers hardness and tensile strength were observed for increasing Nitrogen content. The study observed a gradual decrease in corrosion current and current density for increasing values of N in the solution, thus improving the corrosion performance of the material.

<table>
<thead>
<tr>
<th>Nitrogen content (wt%)</th>
<th>Free corrosion current ($I_{corr}$/A)</th>
<th>Corrosion current density (A cm$^{-2}$)</th>
<th>Corrosion rate (g m$^{-2}$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No nitride addition</td>
<td>$1.63 \times 10^{-4}$</td>
<td>$6.52 \times 10^{-4}$</td>
<td>4.53</td>
</tr>
<tr>
<td>1.01</td>
<td>$7.49 \times 10^{-5}$</td>
<td>$2.996 \times 10^{-4}$</td>
<td>2.08</td>
</tr>
<tr>
<td>1.19</td>
<td>$6.98 \times 10^{-5}$</td>
<td>$2.792 \times 10^{-4}$</td>
<td>1.936</td>
</tr>
<tr>
<td>1.32</td>
<td>$1.09 \times 10^{-6}$</td>
<td>$4.36 \times 10^{-5}$</td>
<td>0.3</td>
</tr>
<tr>
<td>1.33</td>
<td>$6.96 \times 10^{-6}$</td>
<td>$2.784 \times 10^{-5}$</td>
<td>0.1932</td>
</tr>
</tbody>
</table>

Table 10: Corrosion performance concerning nitrogen additions to 304 grade stainless steel via ball milling.
2.4. Hot isostatic pressing material properties

This is the most mature PM method under consideration for developing primary circuit parts. An introduction to hot isostatic pressing (HIP) is described in deliverable 6.2.5. To recap, it can be regarded as a mode of solid casting where the powdered raw material is loaded within a hollow canister and then consolidated to a near net shape. The canister represents the form of the final intended part and is exaggerated in dimension to account for shrinkage during consolidation. During loading, the canister is tapped to achieve a prerequisite density, better known known as the tap density, and this is ideally 65-70% of the value desired in the final part. It is then vacuum outgassed at an elevated temperature before being sealed. The canister is loaded within a HIP furnace and subjected to a consolidation cycle at high temperature and pressure. Following this, the canister is subjected to heat treatment if required to develop material properties before the canister is removed by etching or machining to the required dimensions. Recent modules added to HIP furnaces allow the cooling rate to be controlled quite accurately and rapidly, suggested as minimizing residual stresses and developing material properties, thus allowing the customer to forego the subsequent heat treatment stage. The maximum cycle temperature is always below the melting point of the powder, and the subjected pressure is held above the yield point of the metal for that particular temperature. The yield point of metals reduce at elevated temperatures, making it possible for isostatically applied pressures to remove any internal porosity through plastic deformation, creep and diffusion. Using this principle, HIP furnaces can be used to eliminate internal porosity from parts manufactured via other consolidation processes such as castings, additive manufacture, field assisted sintering and forging.

This section will attempt to present and understanding into the key processing parameters and resultant material properties specific to the PM HIP manufacturing process. The reader is guided to the section on further testing and research to better understand the gaps in this study as applicable to the downselected parts.

2.4.1. Initial powder density effects

The powder particle distribution employed in PM HIP is typically larger than than in AM or SPS, and falls between the range of 45-150 μm. While loading into the canister, the structure is subjected to a tapping motion to achieve the required initial density. In production runs,
this tapping is controlled in terms of part orientation, vibrational amplitude, frequency and exposure time to minimise variability between batches. Research carried out into understanding the impact of this processing stage has shown that the tapping motion can induce a convection like flow of the powder as shown in the following schematic derived from an experiment using a transparent mock up canister and employing powders of different colours.

![Schematic showing results of an experiment into powder rearrangement during tapping where (Left) convection like flows occur & (Right) top view of canister showing cross sections under consideration.](image)

This motion is driven by gravity and the force of axial acceleration. The authors assume that for a cylindrical canister stood on the short axis and subjected to tapping by a RETSCH Vibro device at a frequency of 40 Hz for 5 minutes, the powder contained is distributed symmetrically across the central cross section (denoted 2 in the schematic above). Extending this study to the analysis of 316L powders (PSD = 3-500 μm), freezing this cross section of choice in an epoxy resin, it was possible to quantify the differences in relative density for variations in tapping frequency and orientation as shown below:

![Relative density distribution maps for canisters tapped under varying conditions of vibration (f), time (t), refill cycles (r), & inclination (I) for (a) f = 40 Hz, t = 5 min, r = 2, I = vertical (b) f = 75 Hz, t = 5 min, r = 2, I = vertical (c) f = 75 Hz,](image)
The tapping methodology can therefore induce a gradient in the particle size distribution in localised regions within the part. In order to consider the impact on the final part, consider the following images which show the comparisons between simulation and real world experiments, which appear to agree quite well with each other. These differences manifest themselves as variations in deformation within the final product as shown below.

Note the difference between deformation and distortion here. Canister ‘a’ shows the largest deformation but minimal distortion since the initial tapping density was quite uniform across the volume of the cross section analysed. In contrast, canister ‘d’ shows extreme distortion, presumably due to the density gradient that developed when tapping in the horizontal plane. Regions of low initial density appear to have experienced a high degree of distortion during shrinkage. The simulation employs the macroscopic approach to tracking shrinkage derived from a well known viscoplastic densification model developed by Abouaf et al\textsuperscript{59}. More on this will be discussed in section 2.4.2.

The volume of thicker sections of parts can create complications during shrinkage as shown in this example for the development of a plasma shield blanket in the international
thermonuclear experimental reactor (ITER), where tubes for cooling channels are installed within grooves machined into a solid substrate, coated with powder and then encapsulated within a thin shell before being HIPped. This study illustrates the versatility of PM HIP as a technique for interfacing with existing structures.

The study shows that the embedding of these tubes in a complex conformation and to a high standard is indeed possible. The authors indicate the distortion was comparable to simulations showing acceptable outcomes, carried out in advance. In addition to local deformation being within expected ranges, an indicator of success was the cross section of the embedded tubing retaining its circular shape following consolidation. Prior to this, validation experiments were carried out to refine the model and predict differences in canister sagging normal to the machined groove, depending on differences in the volume of powder above.
The simulation model used here is again a variation in the viscoplastic model. It suggests that the larger the volume of powder relative to the surrounding area, the more likely there is to be severe deformation in the axes normal to the gradient of porosity, resulting in distortion to the entire structure, including the pipe cross section which appears elliptical before optimisation. Deformation occurs in the direction normal to the midplane of the face, and proportional to the thickness of the compact in that direction. By predicting this, workarounds were explored to minimise distortion and achieve the previously described desirable outcome. This can be achieved though iterative simulation practises described in section 2.4.2.

Discussed earlier, consolidation within hot isostatic processing involves subjecting the canister to a pressure above the yield stress of the material for that particular temperature. The yield stress decreases with increasing temperature, resulting in three distinct mechanisms that lead to full consolidation as described in the example below.

![HIP densification map of a superalloy powder showing curves corresponding to the contributing mechanisms at a constant temperature of 1200 °C with a particle diameter of 50 μm](image)

At low densities, nearly instantaneous plastic yield is responsible for significant densification. This is followed by power law creep, which is related to the exponential pressure component, which is also linearly related to the applied pressure. Finally at very high densities, pore closure is facilitated by diffusion at the grain boundaries at the necks created by inter particle contact. In practice this does not occur uniformly within the part interior, since these densification mechanisms are reliant on temperature which propagates from the exterior inwards leading to a corresponding densification front. This densification front has a higher thermal conductivity as compared to the less dense powder interior leading to
irregular deformation. Studies have shown that this can be worked around by modifying the thermal and pressure cycles as shown below.

![Thermal and pressure cycles](image)

**Figure 77:** Impact of (Bottom row) the onset points of thermal and pressing cycle with regards to (Top row) images showing the resultant distortion of identical canisters containing tool steel powder for variations in onset time.

Here, the early onset of temperature is used to lightly sinter the interparticle contacts within the canister improving thermal conductivity into the part interior and hence resulting in improved deformation during consolidation. The caveat of resorting to this approach is the likelihood of grain growth or compositional segregation occurring from the sintering process, a matter elaborated on in sections 2.4.4 & 2.3.6.

Recent studies have shown that the position of the canisters and overall material mass in respect to the heating elements within the HIP furnace can have an impact on the distortion. For a homogenous initial particle distribution, there is a variation in deformation for canisters exposed an asymmetrical the thermal gradient within the furnace as illustrated by the schematic and image below.

![Thermal gradient within furnace](image)

**Figure 78:** Canister containing homogenous initial density of 3-500um 316L powder HIPped (Left) in close proximity to the furnace heating element showing (Right) distortion in the facing direction.
This is to be expected since the development of a densification front drives consolidation, and the proximity of the part to a heating element is going to enhance consolidation in a localised region resulting in a finite amount of distortion. When HIPing a porous billet, the shape deformation along the radial direction is much more severe when compared to the axial. Additionally, there appears to be a dependence between the thickness of the canister wall and the respective deformation in that direction as shown in the following experimental and simulation results.

![Figure 79: Image showing simulation and experimental outcomes for 316L powder HIPped under identical conditions, showing the impact of canister thickness on distortion along the normal axis.](image)

This suggests that shrinkage and deformation is affected by canister stiffness. It is for this reason that the introduction of welds during canister construction creates complications in shrinkage. What is quite clear is that deformation is affected by several variables, and that this needs to be predictable.

2.4.2. Simulation approaches

When considering HIPing for large parts such as those identified in this study, consideration should be given to the high associated raw material costs and the complexities where initial density variations or proximity to heating elements can result in local distortion, risking manufacturing failure. Rather than resort to the costly trial and error route, simulation offers several advantages for minimising risk. There are three schools of thought when attempting to model the removal of porosity via HIPing

1. The microscopic approach
This route is derived from sintering technology and assumes a single particle and its surroundings to obtain rate equations for the creep and diffusion densification mechanisms, which describe the transitions in relative density of an encapsulated compact in response to temperature and pressure. These equations take into account parameters such as particle size, distribution, shape, grain size, molecular volume, surface energy, temperature gradients, non steady state pressure, temperature and yield stress when calculating how the compaction might take place\(^53\). The criticism of this approach is that it does not relate the dynamic strain component to density, reducing the ability to predict deformation, especially in instances where the stress contains a deviatoric component.

2. The macroscopic approach

This approach assumes the powder compact as a continuous medium containing porosity. The model is derived from the plastic theory of solid materials. The coefficients used in the descriptive equations have to be obtained experimentally and are unique to a particular set of HIP parameters due to variable dominance by the aforementioned mechanisms of consolidation. In contrast to the microscopic approach, it is possible to account for shape deformation in complex geometries, and refinements to the Abouaf viscoplastic equation\(^59\) have yielded satisfactory results to date\(^61,66\).

3. The combined approach

Also known as the constitutive equation, the macro and microscopic approach have been united to account for interparticle densification and continuous plasticity of a porous material.\(^67\) Here, the canister stiffness and thickness can impose a variable density within the part, where thicker sections deform less, reducing the density of the powder within. This approach has been demonstrated by Wei et al\(^68\), when they attempted to use Perzyna’s constitutive relation to model consolidation in an IN625 turbine disc shown in the following image.
The approach clearly needs refinement, and the authors attribute the discrepancy in results to uncompensated powder rearrangements during the early stages of HIP consolidation. Whatever the method of modelling the shrinkage, the end goal is to account for the shrinkage mechanism and design the canister accordingly. A good example of this has been presented in the iterative determination of an optimum canister by simply considering the contribution of plastic deformation since it accounts for 90% of the initial and major shrinkage which manifest as either deformation or distortion. The authors optimise the canister through an interative process of FEM, and then validate the same through a demonstrator model, which shows good agreement with the results as shown below:

The authors report that this optimization was carried out on an affordable computing setup over a span of just 5 hours. Another example of iterative modeling is demonstrated using the concept of invert optimisation, which states that regions experiencing higher deformation should be rendered with a larger initial dimension. A computational loop based on the viscoplastic equation is applied and the results sent to comparator (optimizer), which
modifies an initially selected canister design until desired values for the final part are reached.

This approach is especially interesting since it accounts for the stiffness introduced by weldments, initial density gradients, temperature gradients within the furnace and container stiffness within the iterative process.

### 2.4.3. Variations in final density

Aside from deformation, porosity is the next most concerning factor when employing HIPing since it is affected by several parameters such as cycle time, temperature, pressure and particle size distribution in addition to the aforementioned deformation affecting parameters.

Final density is one of the most sought after characteristics when resorting to HIPing. In general it is assumed that consolidation will yield a fully dense part. However this is not always the case, and a previously discussed study into the consolidation of a turbine disc form shows variations in density through the part.
Cross sectional analysis confirms the difference in porosity for the less dense regions in A when compared to other regions. As mentioned before, the authors concluded that the differences in final density could also be attributed to powder movement and rearrangement during initial HIP. They also hypothesize that considering the spherical shape of the pores, it is likely that the degassing stage did not remove the gases within the compact. The high HIP temperatures and pressures would cause these gases to dissolve into the matrix, only to re-emerge during the depressurisation cycle. It is also possible that the gases originate from the atomisation cycle. A final consideration is that of a canister leak during HIPing resulting in Argon ingress.

In addition to the irregular deformation discussed earlier, the effect of a densification front during HIPing would lead to differences in density within the part interior, and this is shown below.

As expected, the measured density is much higher at the part surface than within the centre. In general, overall density is affected by the cycle parameters such as temperature, pressure and hold time. The outputs from a study into consolidation of tool steel (melting point of 1650°C) shows this dependence.
<table>
<thead>
<tr>
<th>Pressure (MN/m²)</th>
<th>Temperature (°C)</th>
<th>Dwell time (hours)</th>
<th>Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1000</td>
<td>1</td>
<td>96.6</td>
</tr>
<tr>
<td>100</td>
<td>1000</td>
<td>2</td>
<td>98.2</td>
</tr>
<tr>
<td>100</td>
<td>1050</td>
<td>1</td>
<td>99.6</td>
</tr>
<tr>
<td>100</td>
<td>1100</td>
<td>1</td>
<td>99.7</td>
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<tr>
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<td>2</td>
<td>99.8</td>
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<td>1150</td>
<td>1</td>
<td>99.8</td>
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<td>1</td>
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</tr>
<tr>
<td>150</td>
<td>1200</td>
<td>1</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 11: Variations in relative density for variations in set points of temperature, pressure and hold time for tool steel.

For a constant pressure, a steady increase in density is observed for increasing temperatures. Additionally at lower densities, longer hold times show increases in density, however this appears to be become saturated at higher values which is expected since boundary diffusion is dominant at higher densities, and occurs at a much slower rate than the faster power law creep and instantaneous plastic deformation at successively lower densities. Increases in pressure at a constant temperature also show subtle density increases. Additional experimental data to support change in density is shown in the image below describing the consolidation of IN718.

![Figure 85: Graph superimposing the heating cycle on the relative density outputs of simulation and experimental results for a demonstrator model composed of IN718 powder](image_url)

Here, the high predicted rate change at approximately 200 minutes into the cycle illustrates the dramatic effect of the plastic deformation and power law creep components on densification. The authors were focusing purely on shape deformation and thus eliminated...
the impact of diffusion into their modeling. In general, densification maps shown below can be constructed for most materials, and used as guides for relating porosity to cycle specific parameters such as hold times, homologous temperature and normalized pressure.

![Densification Maps](image1)

Figure 86 (Left) Density-temperature diagram and (Right) density-normalised pressure diagram for HIPing of tool steel. These account for particle size distribution, but appear to make no considerations for canister complexity or container stiffness.

### 2.4.4. Grain growth

High temperatures and long hold times to improve density are not without detrimental effects since these can come at the cost of grain growth. Shown below, increases in HIPing temperature of IN718 powders manifest as steady increases in grain size:

![EBSD Maps](image2)

Figure 87: EBSD maps showing grain size increases for IN718 powder compacts HIPped at (Left) 1180°C (Middle) 1210°C (Right) 1260°C at ~ 160MPa for 4 h

Similar grain growth has been observed when another nickel superalloy was hipped at temperatures above and below the gamma prime solvus temperature (1160°C) for that particular alloy.
Grain growth can be limited by methods such as precipitate pinning and solute drag. While considering the effects of grain growth, it is important to also discuss an artefact specific to solid state consolidation techniques such as PM HIP: namely prior particle boundaries (PPB’s).

### 2.4.5. Prior particle boundaries and other inclusions

The formation of PPB’s is frequently related to powder contamination by oxygen, carbon or nitrogen leading to oxides, carbides or carbonitride networks decorating the inter particle contact regions, in a shape reminiscent of the initial powder particles. These PPB’s can have detrimental effects on ductility at high temperatures. It can also dramatically increase fatigue at low cyclic stresses and thus reduce the stresses at which rupture occurs. Shown below, these are presented as clear indications of powder particle boundaries in cross sections of the HIPped sample.
The images show outlines of what once were powder particles. Recrystallisation can be regarded as having occurred since there is evidence that the grain growth has crossed the PPB’s. Also evident from the above image is the presence of precipitates within the powders and at the PPB’s. These gradually diminish by increasing the HIPing temperature, however this can come at the cost of melting at the interparticle contacts as shown below.

The grains in this instance are significantly larger than those obtained at lower temperatures, and the melting risks compositional segregation. Discussed previously in rapid solidification processes, these PPB precipitates are similar to laves phases. For the example under discussion, their structure and composition are described below, which confirms the presence of MC carbides.
Increasing temperatures result in finer precipitates within the particles, and a more disordered precipitate network at the PPB’s, restraining their pinning effect on grain growth. This has an effect of initiating fractures from regions where they accumulate, a matter discussed in section 2.4.5

Most of the parts of priority interest in PowderWay are composed of stainless steels and will require heat treatment/solution annealing to develop the required properties. As such, this will result in modifying the phase of the precipitates. While the required data set has not been found for a stainless steel, consider the precipitate change within a Nickel based superalloy, showing that the carbide precipitates dominate at the PPB, whereas needle shaped δ precipitates manifest within a certain window of solution annealing temperatures.

![Figure 92: SEM micrographs of IN718 powders HIPped at 1210°C at ~160 MPa for 4h followed by ageing at 720°C for 8h, 620°C for 8h and then air cooled following the following solution annealing regimes (a) no SA (b) SA at 940°C for 1h (c) SA at 980°C for 1h (d) SA at 1050°C for 1h](image)

The location of these precipitates is not specifically linked to the ageing process but linked more to the solution annealing stage since similar δ phase precipitates and MC carbides have been confirmed in study on similar materials following solution annealing.
The impact of PPB’s is seen in the mode of fracture shown below, where the fracture surface at elevated temperatures (650°C) is inter particle at low temperatures, transitioning to ductile at higher temperatures.

### 2.4.6. Effect of temperature and heat treatment

The HIPping temperature is primarily explored with a view to achieving a required density, to achieve recrystallisation and growth across the PPB’s. As observed, the dwell temperature from the process is directly proportional to the grain growth. This has an impact on the mechanical properties as shown in the graph below:

![Graph showing mechanical properties](image)

**Figure 94:** Mechanical properties obtained from tensile testing at 650 °C for IN718 powders HIPped at various temperatures at ~ 160MPa for 4h.
The steady decrease in yield strength is to be expected due to the hall-petch relationship described previously, where the material hardness is expected to follow a similar trend. The sharp increases in elongation and fracture stress are indications of improved ductility. This transition occurs between the temperature range of 1140 – 1180 °C, which are below and above the incipient melting point of the laves phase in cast IN718. In addition to the density improvement which is assumed and not indicated in this study, this dissolution of laves could be a prerequisite for an improvement in the mechanical properties of solid state consolidation processes. Another factor worth considering is that the sample HIPped at 1140 °C did not result in complete recrystallisation. The impact of these transitions are better understood when considering the fracture surfaces of the test specimens shown in the image below:

Figure 95: Elevated temperature fracture testing showing the fracture surface of IN718 powders HIPped at ~160MPa for 4 hours at temperatures (a) 1140 °C (b) 1180 °C (c) 1210 °C & (d) 1260 °C.

The sample HIPped at 1140 °C shows an interparticle fracture mode evident from the crater like morphology indicating regions where individual particles appear to have been pulled out. As the HIPing temperature transitions to above the melting point of the laves phase, the interparticle fracture mode is reduced, giving way to a dimpled surface indicative of ductile fracture. At higher temperatures, the dimpled surface is predominant indicating transgranular fracture. Cracks observed at higher temperatures were shown to be rich in MC
carbides and laves phases. This transition between interparticle separation and transgranular modes of fracture has been observed in other materials as shown for maraging steel in the following images.

Figure 96: Tensile fracture surfaces of maraging steel powder HIPped at (Left) 1012°C and (Right) 1262°C at 103 MPa.

The corresponding impact of increasing HIPing temperature on mechanical properties is given below and correlates well with the improved fracture toughness and ductility as grain growth occurs and the density is certainly improved.

Figure 97: Mechanical properties of maraging steel powder HIPped at various temperatures at 103Mpa for 3h.
Here, the detrimental properties at the lowest temperatures are due to retained porosity. Here too, PPB’s are noted within the interior. The properties continue to improve dramatically following complete consolidation at intermediate temperatures, and continue to do so as recrystallisation and grain growth occurs past the PPB’s, which no longer decorate their boundaries. Note a slight decrease in yield strength at high temperatures to indicate the dependence on grain size which has surely increased by this point. Solution treatment is widely regarded as a mode of improving material properties and in this study, its effect can be observed in the mode of fracture following thermal ageing when compared to a control sample without solution annealing. The differences in mode of fracture between transgranular ductile and intergranular brittle shown below:

![Figure 98: SEM images showing differences in mode of fracture between two aged specimens of IN718 subjected to (Left) solution treatment (Right) without solution annealing.](image)

The mode of fracture is evidenced as occurring along the prior particle boundaries, suggesting that the HIP temperature (1200 °C @ 120 Mpa for 3h) was not enough to disrupt the oxides and MC carbide network at the prior particle boundaries, which appear to be markedly reduced following solution annealing as demonstrated in the images below:

![Figure 99: SEM micrographs of etched cross sections of IN718 HIPped specimens subjected to (Left) solution annealing at 980 °C for 1h and (Right) no solution annealing.](image)
2.4.7. Effect of oxides

Quite often, interactions with the crucible during atomization can result in inclusions within the powder particle which eventually find themselves within the part interior. These are typically clusters of HfO$_2$, ZrO$_2$ and Al$_2$O$_3$. During tension testing, these clusters were found to be predictably responsible for crack initiation as shown below.

![Figure 100: SEM micrographs of fracture surface of nickel superalloy HIPped, aged and then subjected to tension-tension fatigues testing to failure at 9.2189E6 cycles.](image)

The propensity to fail at lower cycles depends on the proximity of the cluster to edge of the sample surface. EDX analysis reveals their composition is Hafnium as shown below.

![Figure 101: (Left) SEM fractograph of an aged HIPped nickel superalloy showing the presence of non metallic inclusions, and (Right) EDX analysis of the same](image)

The authors also note evidence of smaller more compact alumina clusters at initiation sites and suggest that in comparison to Hafnia, they result in a longer low cycle fatigue life. When compared to the effect of PPB precipitates, it is indicated that inclusion clusters are more concerning for the final part properties.

An equally concerning effect when it comes to PM HIPing is the amount of oxygen introduced by way of the passivation films on the surface of the powdered raw material. The smaller the particles, the larger the surface area, and hence the larger content of oxygen that could find itself within a volume fraction of the product. A recent study has elucidated the detrimental effects of this oxygen content on the final part through investigations into
absorbed impact energy. A strong correlation between lowered impact toughness and increased oxygen content in 316L is evident from the graph given below:

![Charpy impact toughness versus oxygen content](image)

*Figure 102: Results from charpy impact tests correlating absorbed energy with oxygen content in the composition of a HIPped 316L material at varying test temperatures.*

The increased oxygen content results in an increased number of inclusions and pores as shown in the images below:

![Optical images](image)

*Figure 103: Optical images showing cross sectional differences in apparent porosity for as polished 316L parts HIPped at 1150 °C and 105 MPa for 3.5 h with varying oxygen contents of (Left) 100ppm and (Right) 190ppm.*

Similar and detrimental relationships between increased oxygen content and decreased impact toughness have been observed in the testing of a magnesium alloy formulated from powdered state, shown in the next graph.
Figure 104: Results from charpy impact tests showing the correlation between absorbed energy and oxygen content for a Mg-3Al-Zn alloy part hot extruded from a powdered state.\textsuperscript{76}

The authors attribute this as occurring due to the increased presence of MgO and Mg(OH)\textsubscript{2} inclusions pinning dislocations, resulting in lowered plastic deformation and hence lower absorbed impact energy.
3. Testing and Simulation specified

In the previous section, certain key process material properties of the downselected PM parts were examined. Before specifying the avenues for further research, testing and simulation, an examination of the intended application environment would be in order. The following subsection represents an adaptation from an excellent review into the material challenges in nuclear energy\textsuperscript{77}. The reader is referred to this document for a more detailed description.

When considering the operation of a nuclear reactor, it is important to recognise that there are two types of scenarios: normal and emergency operating conditions. Normal operation of reactors include activities ranging from commissioning, start up, inspection, maintenance such as fuel replacement etc., whereas emergency operations involve abnormal events which could arise from pressurised thermal shock, resulting in large thermal stresses capable of critically propagating existing cracks. These abnormal events are typically classified under reactivity initiated accidents (RIA) and loss of cooling accidents (LOCA). The subunits of the NPP and the materials they are composed of are required to cope with these scenarios effectively to maintain safe and reliable operation, and are classified accordingly. The reactor environment is highly energetic, irradiating the surrounding environment with neutrons, gamma radiation and heat, steadily causing damage to the parts and materials in this environment and a knock on effect for connected systems. When designing a new or modified part for the primary circuit of the nuclear power plant, it is important to compensate for the environmental degradation phenomena in addition to typical materials design criteria such as tensile properties, hardness, cyclic fatigue, creep fatigue and thermal creep.

The two types of degradation are attributed to either radiation damage or chemical compatibility, and a bit of background on both is presented before observing the application. The primary circuits of light water reactors such as the PWR function at temperatures ranging between 290 and 320°C. The coolant operates at a very low electrochemical potential (<500mV relative to standard hydrogen electrode) for controlling corrosion, and has added hydrogen (3ppm), boric acid (1000ppm) and LiOH (2-4ppm) for respectively scavenging radiolysis products, controlling reactivity, and controlling pH. The boron is responsible for controlling solid corrosion products, corrosion of the fuel cladding, and
general reactivity. In comparison the BWR has lower operating temperatures (275-288°C), and a higher ECP (150mV) due a combination of boiling and radiolysis.

3.1. Radiation damage sources

There are three main sources of radiation damage: fission products, neutrons and gamma rays.

1. High energy fission products:

The fission products are generally confined to the fuel, and comprise of high energy elements between 90-150 atomic mass units (amu). The products that are ejected from the surface of the fuel pellets have a maximum interaction range of 10 μm.

2. Neutrons

For materials within the RPV, the exposure to neutron bombardment results in a quantifiable damage of displacements per atom (dpa), an internationally standardised parameter. A displacement damage of 1 indicates an average of the number of times all atoms in the material have been displaced from their initial lattice sites. The fission reaction generates neutrons with energies of 2MeV. This energy is absorbed by the coolant and surrounding structures which experience displacement damage. This damage reaches values of 15dpa for the fuel cladding, and drops off exponentially from this first barrier to the fuel. In contrast, the damage in the RPV wall for a PWR can reach 0.05dpa over 40 years of operation. The displacement damage causes significant changes to the microstructure of exposed materials, weighing heavily on mechanical properties such as strength, hardness, ductility, fracture toughness, creep, embrittlement and fatigue. Elevated temperatures within the operating environment aggravate these damages in the form of failure modes such as

- Fracture toughness degradation (due to environmental conditions)
- Irradiation-assisted stress corrosion cracking (IASCC),
- Corrosion fatigue

3. Gamma rays
Like neutrons, these rays affect the surrounding material through a mechanism of atomic displacement. The localised heating caused by exposure to gamma rays in a phenomenon called gamma heating can exert a large influence on the temperatures within the material, elevating them to more than 50 °C above the temperature of the coolant. Furthermore, the radiolysis interaction with the coolant yields free radicals, increasing the corrosion potential: the governing factor in high temperature stress corrosion cracking.

3.2. Radiation damage mechanisms

Having identified the sources of radiation damage, the mechanisms by which they affect exposed parts are considered to understand the modes of failure.

1. Low temperature hardening and embrittlement

At low to intermediate operating temperatures, increases are observed in the number of defect clusters such as dislocation loops and helium bubbles. Upon increasing in density, they serve as obstacles to dislocation motion, resulting in hardness increases and corresponding decreases in fracture toughness and tensile elongation. These effects appear pronounced above damage levels of 0.1 dpa. Irradiated materials experiencing reductions in elongation and strain hardening can trace these issues back to strain hardening exhaustion and flow localisation mechanisms.

It is well known that the ductile to brittle transition temperature is strongly related to operational fracture toughness, and is more pronounced in body centred cubic materials such as ferritic or martensitic steel. Irradiation damage causes this transition temperature to be shifted and in some cases increase above the plants normal standby temperatures. When compared to the core internals, the irradiation damage to the stainless steel cladding on the reactor pressure vessel (RPV) is 3-4 orders of magnitude lower than the core internals. This still subjects the RPV to radiation hardening and fracture toughness embrittlement.

2. Radiation induced and modified solute segregation and phase instability

The materials subjected to neutron radiation undergo microstructural evolutions, among which is solute segregation or precipitation, which in the short term is observed at elevated temperatures (> 400°C), and an in the long term at lower temperatures (~300°C) which fall in the realm of typical PWR operating conditions.
3. Irradiation creep

This mechanism of damage can be specific to hexagonal close packed materials. The nucleation and presence of dislocation loop clusters can cause preferential expansion in one plane, whereas contraction and shrinkage in another, all the while conserving volume. This effect is termed as irradiation creep, and is observed in anisotropic materials such as graphite and alloys of zirconium and beryllium. This damage is directly proportional to the applied stresses and exposure with radiation. This irradiation creep can induce stress relaxation of bolts and springs.

4. Void swelling

This type of damage takes place through a nucleation growth mechanism. Irradiation over time causes a supersaturation of vacancies, resulting in an initial growth phase, leading onto a steady state swell. Undesirable and unacceptable volumetric steady state swelling rates of 0.2-1% are observed per dpa for components exposed to high neutron radiation. Initially, it was thought that this mode of degradation was limited to higher temperature cores with ranges between 400-650 °C. However long term experiments have confirmed that this issue also occurs at lower temperatures such as within typical PWR’s. The aforementioned gamma heating exacerbates this mechanism of void swelling. Bolts and plates experiencing void swelling would create stresses in the regions of contact, giving rise to irradiation assisted stress corrosion cracking (IASCC).

Research is underway to extend the duration of the transient region, delaying the steady state swell. When coupled with irradiation creep, the deformation can appear amplified.

5. High temperature Helium embrittlement

At high temperature operation, reactions within exposed materials can produce and eject bubbles of Helium, which inevitably migrate towards the grain boundaries, causing dramatic reductions in strength and reductions in total elongation. This effect is typically observed at elevated temperatures of about 0.5-0.6 TM (melting point of the metal). The annealing effect on the lattice at these temperatures has the effect of recovery from radiation damage.
3.3. Mechanisms of chemical incompatibility

As mentioned previously, gamma irradiation can cause modifications to the coolant potential through the production of free radicals. These modifications to coolant chemistry would affect parts of the primary circuit such as the piping, elbows, pressuriser, steam generator, pump casing and impeller for the same.

The various forms of corrosion degradation are

- Stress corrosion cracking
- Flow assisted corrosion
- Nodular corrosion
- Shadow corrosion
- CRUD induced localised corrosion
- Fretting of ZrO₂ fuel cladding

Of these, stress corrosion cracking (SCC) is the most well known of all corrosion damage mechanisms, and has been the most dominant mode of failure over the past 25 years. SCC of nickel alloys is highly dependent on the composition and state of the coolant. The mode of construction also has an effect on cracking since a single cold rolling operation can increase the growth rate by two orders of magnitude. Irradiation has an effect on the SCC process in a process known as irradiation assisted stress corrosion cracking (IASCC). Some of the resultant key mechanisms are localised deformation, solute segregation of minor elements, hardening and grain boundary chromium depletion where there is an increased susceptibility to IASCC under oxidising conditions.

The forms of corrosion cracking can either be trans or intergranular SCC. In the more common form i.e. intergranular stress corrosion cracking (IGSCC), the mechanism of cracking occurs along the interdendritic path in materials subjected to tensile stresses. In an example where sensitization is observed within an austenitic stainless steel, the depletion of chromium from the faces of grains forms chromium carbide networks in the interdendritic region. These network are anodic compared to the surrounding grains, resulting in a preferential pathway for corrosion attack and crack propagation when under tensile stress.
The source of this tensile stress could be welded joints and residual stresses within the component. As a solution, low carbon alloys are used.

### 3.4. Primary pipework fatigue failure

This is one of the most significant damage mechanisms in components experiencing cycling loading. There are three stages of onset: crack initiation, crack growth and failure. The microstructure of the material in question governs the fatigue life of the component. While fine grained microstructures offer good resistance to crack initiation, the stress intensity factor threshold \((\Delta K_{th})\) was found to increase with grain size, suggesting that coarse grained materials are more resistant to fatigue crack initiation and propagation. This is used as the basis of the Paris law, a widely used methodology for quantifying the growth rate of cracks with high stress intensity factors. However this model does not account for the micron sized fatigue cracks that grow at stress intensities lower than the threshold, and at rates higher than those predicted by the Paris law, hypothesized as being due to the lack of fully developed closure.

For parts manufactured via conventional techniques such as casting, the mechanical response of neighbouring grains is typically anisotropic, leading to plastic deformation at low stresses. Cyclic loads warrant defect accumulation, which leads to fatigue crack initiation at sites such as persistent slip bands and twin boundaries or grain boundaries, and inclusions, which appear to be the main sites of crack formation when under a high number of cyclic loads.

### 3.5. Requirements imposed on PM parts

Of the downselected parts, the fuel filter, baffle bolts and spacer grid assembly sit within the RPV and would therefore be exposed to neutron irradiation and gamma radiation over their operational lifetime. There is a risk in the event of fretting wear of the fuel cladding for the spacer grid to experience additional damage by high energy fission products radiating from the fuel pellets. The response of these parts to fracture toughness embrittlement by radiation needs to be within the acceptable limits for their lifetime. The large surface area associated with the finer powders employed in AM and SPS used for manufacturing these parts suggests that the levels of oxides and oxide networks within these parts will be much higher than conventional counterpart. Changes in segregation and phase instability in
response to radiation need to be verified for these parts. Additionally, these novel routes of manufacture might yield variations in vacancy defects due to the method of consolidation, affecting their performance in respect to void swelling. This needs to be verified as acceptable and within limits.

All the parts selected invariably form some part of the primary circuit. They are therefore all exposed to the coolant during their operational lifetime. While additives to the coolant reduce its corrosion potential, the ability of the part to withstand stress corrosion cracking (SCC) is a key indicator of its suitability for a primary circuit application. Discussed in section 2.4.1, the oxygen content of a PM part is inversely proportional to its fracture toughness, especially at low temperatures. Embrittlement by exposure to neutron fluence or ductile-brittle transitions by thermal fatigue can contribute to the critical propagation of corrosion induced cracks under stress.

Cobalt is a trace element in stainless steel parts, generally present as an impurity in Fe ores. Transmutation of Cobalt results in activated corrosion products flowing through the coolant, and in addition to the impact it has on the structural materials it flows past, it also introduces risks to occupational health and disposal\textsuperscript{78}. The mechanism of activation for PM parts in the primary circuit needs to be measured and checked for conformance.

The components of the primary circuit would need to demonstrate the ability to maintain integrity in the face of pressurised thermal shock resulting from a reactor shut down under abnormal conditions. While this typically related to the reactor pressure vessel structure, any cladding employed on the RPV via a PM route would need to be verified for compliance. Parts such as elbows and integrated nozzles in the primary circuit and welds connecting PM parts also need to be considered for their ability to safely withstand thermal shock following ageing experiments and simulations representative of their installation period.

**3.6. Opportunities for powder metallurgy**

The role of material performance and integrity is especially critical when making decisions concerning power uprates, plant life extension, as well as when considering new reactor technologies. Briefly discussed below, these pose opportunities for powder metallurgical processes where alternatives to conventional manufacturing processes can be offered.
1. Power uprates:

Increasing the output of the reactor core has a direct increase in the damage levels experienced by parts. In order to justify such a decision, a thorough risk analysis must be conducted. Parts demonstrating isotropic material properties, with low scatter in their performance data, and retaining the ability to track sub critical flaws non destructively and with minimal occupational exposure to radiation will assist in the assurance process. These are all benefits purported to be offered by solid state consolidation processes such as SPS and HIP due to a fine and consistent grain size, and with high process repeatability.

2. Plant life extension:

When considering whether a plant can operate safely past its design lifetime, the condition of irreparable parts is the key indicator, and similar to the situation concerning power uprates, the knowledge and predictability of degradation mechanisms in all key parts is essential for assurance. With regards to the replaceable items such as piping and heat exchangers, the predictability offered by PM parts and the removal of welds through near net shape manufacture such as in PM HIP would improve the economics and safety of replacement and assurance. Fine grain sizes would theoretically scatter ultrasonic waves less and potentially offer deeper penetration into the material thickness. Moreover, techniques such as directed energy deposition (DED) type PM would offer the ability to carry out on site repairs to large parts without the need for decommissioning and costly replacement.

3. New reactor technologies

There are a number of fission technologies on the horizon as shown in the list below and not all structural components are proposed for manufacture via metals.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Concept</th>
<th>Pressure (MPa)</th>
<th>Temp (°C)</th>
<th>Fuel</th>
<th>Coolant</th>
<th>Packaging</th>
<th>Reactor type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>Liquid</td>
<td>10-30</td>
<td>450-550</td>
<td>UO₂</td>
<td>H₂O</td>
<td>Integral</td>
<td>Boiling</td>
</tr>
<tr>
<td>Molten</td>
<td>Salt</td>
<td>15-20</td>
<td>200-300</td>
<td>UO₂</td>
<td>H₂O</td>
<td>Integral</td>
<td>Boiling</td>
</tr>
<tr>
<td>Gas</td>
<td>Fission</td>
<td>5-10</td>
<td>800-900</td>
<td>UO₂</td>
<td>H₂O</td>
<td>Integral</td>
<td>Boiling</td>
</tr>
<tr>
<td>Gas</td>
<td>Fast</td>
<td>10-15</td>
<td>1500-1800</td>
<td>UO₂</td>
<td>H₂O</td>
<td>Boiling</td>
<td>Boiling</td>
</tr>
<tr>
<td>Gas</td>
<td>Inert</td>
<td>10-15</td>
<td>1500-1800</td>
<td>UO₂</td>
<td>H₂O</td>
<td>Boiling</td>
<td>Boiling</td>
</tr>
</tbody>
</table>

Table 12: Current and future generation fission reactor technologies listing the operating environments and materials used and proposed for use.77
Powder consolidation processes could hold the key to determining how these parts are constructed. Of course, it would involve extensive testing and acceptance by the regulatory code in order to develop the supply chain. This document presents the method for code case incorporation of a PM part within a PWR, and this is discussed in section 3.1.11.

3.7. General comments on further testing

The PowderWay project has set out to achieve a task which involved interaction with the end users concerning requirements, determination and down selection of candidate parts, evaluation of most mature PM processes and down slection of the same, and finally a roadmapping event where members on the supply chain could determine the route forward based on the information available. To reiterate the notice served in the introduction, the information presented in this document is by no means a complete picture of the state of art. It is meant to be a first step. Through the process, it has been determined that much of the information required with regards to the material of choice may not be available in the public domain, and large fractions of these data could be held by members of the service industry, manufacturing parts for various industries such as aerospace, automotive, defense and medicine. It is refreshing to note from the roadmapping exercise that much of the information concerning material performance are processing conditions is expected to be available when required. Of course these data constitute intellectual property and exposing the information would require assurances from the end user and regulatory body to indicate the likelihood for development of a new industry for members on the PM supply chain.

As we have seen from the previous subsection, the requirements and damages occurring within a nuclear power plant (NPP) are unique to this industry. As such, the body of available PM knowledge (both public domain and proprietary) may not have the overlapping information (for example response to neutron irradiation) necessary for demonstrating a complete case for regulatory code amendment. Therefore if progress is to be made towards an end goal, due care must be placed on the investigations and their methodologies. The following are are some general considerations to be made during researching and when planning new experiments.

For stainless steel parts which constitute the majority of downselected parts under consideration, a passivation layer develops on the surface of each particle. Powder manufacturers have managed to keep the thickness of this layer fairly thin at between 20 &
The particle size distribution is chosen primarily to achieve the required tap density before HIPing, which lies between 65-70% of the theoretical density. The particle size dictates the available surface area and hence the oxygen content within the part. For large high quality HIPped parts, it is currently possible to achieve an average oxygen content between 100-150 ppm. Obviously this value will increase for consolidation processes such as AM and SPS, which employ a finer distribution of particles for manufacture. To supplement the study into the effect of oxygen on the fracture toughness of HIPped parts, it would be desirable to obtain similar information for AM & SPS. Additionally, when considering the manufacture of PM parts in low alloy steels (LAS) for dissimilar joints, the powders produced will not have the advantage of a passivation layer developing, and are thus expected to absorb oxygen steadily over time if not hermetically sealed.

It has been presented in this document that the distribution of initial powder density had a noticeable effect on distortion during consolidation, and much of the research available does not take this into consideration. Considering that the price of powdered raw material can rise to about 5x in comparison to conventional processes, and that several of the downselected parts are complex in dimension and weigh in between 5-10 thousand kilogrammes, it becomes especially important to get the simulation as accurate as possible. Additionally from the perspective of reproducibility, methods such as tapping frequency, amplitude, orientation need to be strictly controlled.

Very few of the studies reported for the study into AM actually report if the reseachers employed virgin powder for the construction of the part. Depending on the mode of construction i.e. powder bed or blown powder, the low yield in both processes may express a matter of concern from a nuclear perspective. For example the powder bed process constantly loads the chamber with a volume of powder that is as high as that of the structure being built. To improve the density of the final part and to prevent powder fly off when the beam is being scanned over the surface, a common technique utilised is to lightly sinter each layer or increase the powder bed temperature. When this is not employed, it is worth noting that the incident energy from the beam has a gaussian like profile. This results in a range of effects from melting to light sintering at the edges of the track. These sintering effects result in a change in particle morphology, which alter the particle size distribution, and additionally increase the concentration of contaminants. To keep the process cost
effective, equipment manufacturers integrate collection, sieving and powder reuse mechanisms within their equipment. However the impact of this on final part properties in the materials of choice are unknown.

There has been much discussion concerning the advantages of powder metallurgy in comparison to conventional processes. Reduced scattering by ultrasonic waves and hence improved resolution is commonly referred to. However there is little information available regarding how this compares to conventional methods.

New manufacturing processes bring with them their own distinct modes of failure. For example, the directionality introduced by epitaxial effects and layer by layer build process would suggest compromising modes of loading for AM parts. The relatively smaller PSD employed by AM would result in a larger oxygen and contaminant content within the part, and the mixing effects in the resultant melt pool could result in an accumulation of oxides which might function as crack initiation sites.

The surface oxides from the powder particles would suggest the development of oxide networks within the interior of solid state consolidation techniques, and this has been proven to affect the fracture toughness of PM HIPped parts. The atomising process could introduce entrapped gases, voids and non metallic inclusions from the crucibles as is shown before. Under load such as described in the LCF tests from section 2.4.7, these inclusions have been determined to function as initiators of failure through cracking. The rate of propagation would depend on the loads, size of inclusion, location on part and material performance specific for that manufacturing route. For the downselected parts it is possible to determine the loads and required material performance.

3.8. List of AM specific further testing, research and simulation

The intention is to improve the understanding of AM technology so that the intended parts may be built. As the technology matures and acceptance is approved, robust AM processes can be explored for manufacturing parts and for autonomous and high quality repair of high value components within NPP’s. PM AM technology may also be used to construct elaborate HIP canisters in a shorter time, and with a greater complexity than what is presently achievable. The following represents a list of queries based on the discussions in this document, directing future efforts in order to meet the requirements for application
consideration. The materials of interest are 304LN, 316LN, 308L, 309L, IN82, IN182 and Titanium alloys.

1. How does the directionality arising from columnar growth affect fracture mode (initiation and propagation)?
2. CET experiments need to be carried out a used to determine the finest average grain size achievable.
3. What are the optimum build parameters for the selected parts, minimising effects such as keyholing, solute segregation, porosity and anisotropy while achieving the required material performance.
4. How to overcome the intrinsic surface roughness in order to inspect a complex part ultrasonically?
5. How to equiaxed AM parts compare in mechanical properties and inspectability to equivalent forged, HIP and SPS parts?
6. How can surface roughness be eliminated in machine inaccessible regions of a constructed part?
7. How can the incremental distortion and residual stress during the build process be minimised?
8. What are the impacts of shielding i.e. how do atmospheric interactions affect final part properties?
9. Determine impact of mechanical properties on contaminant/oxide pickup due to the high surface area of employed powders.
10. Simulate the process parameters to achieve the desired microstructure from the process.
11. Develop feedback loops to ensure that the part being built is of the correct dimension to what is required.
12. Conduct corrosion testing, thermal fatigue testing and irradiation response (where required) to the application conditions.
13. What is the route for decommissioning these parts, especially if containing radioisotopes?
3.9. List of SPS specific further testing, research and simulation

A brief review of the mechanisms that may be responsible for diffusion and consolidation have been discussed. There is still a long way to go before a part can be constructed or evaluated for application within a NPP. To accelerate the process, it is worth focussing on the aspects that set it apart from the other consolidation processes: rapid consolidation, functional grading and the potential to remove oxide networks. The materials under consideration are 304, 316 and LAS.

1. Are the oxide layers on the surface of particles retained as networks in the consolidated part? or are they disrupted by the consolidation method?
2. If oxide layers are indeed being disrupted, where do they diffuse to?
3. Can ageing experiments reveal their location and distribution via precipitation mechanisms?
4. How do the material properties change following annealing and heat treatment?
5. How does the corrosion performance compare to forged and HIPped parts with similar microstructures and grain sizes.
6. How do sintering hold times affect material performance?
7. Is there conclusive proof that hybrid furnaces assist in mitigating residual stresses?
8. What is the consolidation performance of powders with varying thicknesses of passivation layers?
9. How do these materials respond to ultrasonic testing?
10. Compare the corrosion response to forged and HIPped parts.
11. How do these parts withstand thermal fatigue?
12. What is their response to neutron irradiation?
13. What is the methodology for using the technique to manufacture dissimilar metal safe ends?
14. Model the diffusion process during consolidation.
15. Determine method for decommissioning.

3.10. List of HIP specific further testing, research and simulation

The state of knowledge in HIPing is very advanced and as such there does not appear to be any obstacle in knowledge (other than long term irradiation response) that would affect their consideration for application in the primary circuit away from the extent of neutron
fluence. Ideal parts in this instance would be the valves, elbows and pipes with integrated nozzles. As the technology stands, it is a robust alternative to large scale forgings. The following list concerns the fine tuning of predictability during the stages of processing. The materials under consideration are 304L & 316L.

1. Study to iteratively simulate optimum initial densities for complex canister shapes and the processing stages to achieve this outcome.
2. Study to check if the densification front in HIPped parts can lead to variable grain growth through the part thickness.
3. What is the method for detecting the presence of argon in the powder or canister post degassing?
4. Iterative simulation to determine the local distortion impact of asymmetric thermal gradients experienced by that part within the furnace, and the amendments to the canister design to respond to this.
5. How repeatable can the process be made? What is the property scatter between two identically processed canisters? How might the variability be affected by differing service providers with the same statement of work (SOW)?
6. Does the densification front yield variations in porosity across thicker sections of a part?
7. Develop / obtain densification maps for the candidate material composition.
8. What is the mechanism for oxygen induced lowering of fracture toughness?
9. How will the part integrity respond to neutron damage?
10. Are there retained oxide networks and how are they affected by PSD?
11. What is the joining performance of HIPped parts?
12. How does ultrasonic evaluation of HIPped parts compare to forged equivalents in terms of signal to noise ratio and penetration depth?
13. Experimental investigation into precipitate and residual stress development during cooling including impact of the same under accelerated conditions.
14. Will there be a risk in the level of activated Co and Nb generated via HIPped parts?
15. What is the procedure for decommissioning?
3.11. Status of code acceptance

At this moment, there are no clauses in the European nuclear standards (RCC-M or RSE-M) permitting the manufacture of primary circuit parts via powder metallurgy. Since their inception, these codes have catered to the conventional routes for part manufacture, where the product forms are well known and embedded accordingly. It is expected that the powdered raw material might pose some obstacles in relating to perceptions of the product form. Therefore our focus at this stage is on the most mature technology: HIP, to demonstrate the best case for consideration. Recent ASTM standards A988 and A989 describe the specification for HIPping stainless and alloy steel parts for high temperature service. This has been used as the justification for a code case into ASME, an effort championed by a task group led by the electric power research institute (EPRI). The goal is to incorporate a standard within ASME-III. Shown below is a technology roadmap published by EPRI, describing their route to standardisation for HIP technologies with a primary circuit nuclear application.

![Technology roadmap describing the plan and progress made by the EPRI in developing standards for ASTM and ASME concerning the implementation and use of HIPped parts in NPP's.](image-url)
RCC-M references several internationally recognised standards including ASTM and it is therefore not improbable that the specifications for A988 & A989 would be accessible when interacting with the regulator. The nuclear regulator is the key focus in this venture and their requirements and approval will dictate whether a part is considered for evaluation or application within a primary circuit. As such the methods of approach are unique depending on the application and therefore not generally published. The following schematic describes a consultation with the end user to better understand the pathway of obtaining approval for the installation of a PM part within the primary circuit of an existing or new NPP:

![Qualification Stages Diagram]

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**Figure 106: General pathway for incorporating a new part or manufacturing process within a European NPP.**

It is advisable to approach the regulator fairly early on to indicate intentions. Any candidate part needs to be qualified according to the stages listed in the red box above and in a manner that is specific to the intended application. The matter is simplified if the part sits outside the zone of neutron irradiation as is the case for the elbows, or is isolable like certain valves units. An intention to amend the specification is submitted to the standardisation body (AFCEN) as a modification request (MR). Once the qualification package is complete, it is submitted to the regulator, who if satisfied that the information is of the format and quality required for the application, will commission a demonstrator piece to be manufactured. This will be sectioned and examined for compliance with the claims in the qualification package related to manufacturing quality, measurable properties, joining and
inspection performance. Any discrepancies might result in a referral back to the qualification stage to gather more information. The process is repeated until an acceptable match is obtained. Once approved, a second part will be commissioned, which following acceptable non destructive evaluation results may be installed in the target location within an existing reactor for a finite period in order to subject it to environment specific ageing. At the end of this predetermined period, the part will be decommissioned and spliced to check for conformance with the predicted ageing response. Through these stages, the data generated will be examined by the regulator and the standardisation body who will respond accordingly. The route to standard amendment can be described in the following flow chart:

![Flow chart describing the various stages of examination and evaluation of a modification request (MR) within AFCEN, with the aim of an amendment being issued within the target specification.](image)

While this procedure may appear daunting, it ensures that the focus is placed on verification before application. A strategy therefore needs to be adopted to approach this task, and this in essence is the roadmap for the future. The plan should be to start with a part, process and material to demonstrate the case for powder metallurgy, with the intention of eventually introducing a range of other parts, processes and materials through their paces.

- The parts listed in this document, should be debated in terms of what appeals to the end user in terms of requirement, risk and urgency. This debate should be led by the end-user to ensure that obstacles accessing required data are minimised.
• A neutral organisation should be tasked with attending to subsequent matters such as investigations and liaising with the regulatory officials.

• This task group will commission a study examining the cost and procedure to take at least two priority parts down the code case route.
  - This will first require obtaining and examining the detailed design specifications for the parts under examination.
  - The regulator will be approached to indicate intentions and to confirm the various stages of approval including the details of a typical data package for the amendment of the sections in RCC-M & RSE-M that the parts in question pertain to. Feedback concerning risk and unknowns will be factored into the results.
  - A literature review will then be conducted into all available data concerning the modes of failure typical to these parts and the performance exhibited by the conventional method of manufacture. The literature review will also extend to the processing method in question, and will evaluate all related data so as to develop an exhaustive list of capabilities and flaws.
  - Concurrently, interaction with the supply chain will assist in determining the cost of raw material and processing required to facilitate the amendment. During this interaction, the extent and quality of proprietary data, and finally the capabilities from a volume production perspective will be considered.
  - The available data will be compared with the required data set to determine the extent and hence cost of analysis required.
  - The total cost breakdown will be presented to the task group along with a projected spending time frame, risk and alternative pathways to the goal.

• The task group will seek funding for the venture and proceed to follow the path set out.
4. Concluding remarks

This document represents a first step in understanding the state of several powder metallurgical processes, with the aim of utilising these techniques to construct high reliability parts for new and existing nuclear power plants. Considering the critical nature of the intended application, no stone of knowledge should be left unturned, and the considered scope should therefore extend from the raw material right through the target environment to the decommissioning stage. As such, the narrative began with an overview of rapid solidification processes leading to the microstructures and phases developing within the powdered material. These RSP’s can be applied to the understanding of additive manufacture, where they provide an additional insight into the structures that develop, and how they may be controlled in order to raise the profile of the resultant parts for a nuclear application. The examination into field assisted sintering revealed several extremely desirable outputs from an industrial processing perspective such as rapid consolidation while retaining a fine grain size. It also revealed areas of unknowns such as an agreeable mechanism driving mass transport and diffusional flows. Both AM and SPS parts can be improved by HIPing, but it is unknown how a procedure like that would affect properties such as grain size. From the outcomes of the roadmapping event, and by briefly examining the progress made in technology incorporation within ASTM and to a lesser degree ASME, it is quite likely that PM HIP will be the PM method that leads the way. This is primarily due to its maturity as a process, while being equally due to the material properties obtained; properties which consistently meet or exceed those of wrought counterparts. The technique has found utility in critical applications within the aerospace, automotive and oil and gas sectors and the wealth of information suggests that it should have no issues with meeting the high integrity demands of a nuclear application. Recently reported effects on toughness degradation in response to increasing oxide levels appear concerning, but the lowest toughness value measured is still in excess of the minimum stipulated in the specifications for wrought material. While on this topic, the ingress of adsorbate material (passivation layers or inclusions) from the powder surface into the part interior is inevitable in all these methods due to the very state of the raw material. Gaining an understanding on the impact it has on part properties, especially in response to degradation mechanisms and perturbations will be extremely valuable. A brief overview of the procedures to seek code acceptance within Europe are presented. Following down this route would require the
formation of a dedicated workgroup supported by industry, with the financial resources required to field the queries and demands of the European nuclear regulator while progressing towards the goal of code acceptance.


    


    

71. Chang, L., Sun, W., Cui, Y. & Yang, R. Influences of hot-isostatic-pressing temperature on microstructure, tensile properties and tensile fracture mode of Inconel 718 powder compact.
    

    

    


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