Master Thesis

Microstructural characterization of Fe-9\%Cr ODS steel produced via selective laser melting

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Publication Date:
2019-08-20

Permanent Link:
https://doi.org/10.3929/ethz-b-000369648

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ETHZ – EPFL JOINT MASTER IN NUCLEAR ENGINEERING

MASTER THESIS

Microstructural characterization of Fe-9%Cr ODS steel produced via selective laser melting

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AUGUST 20, 2019
ABSTRACT

In this master thesis, the characteristics of reduced-activation ferritic Fe-9%Cr oxide-dispersion-strengthened (ODS) steel, produced via mechanical alloying and laser-based additive manufacturing, are explored, with the main focus on the microstructure and the presence and size of the Y-based nano-oxides. Reference steel samples are also produced with the same processes, in order to characterize the impact of Yttria on the characteristics of the final steel. The study employs metallographic techniques, SEM, TEM, STEM and synchrotron x-ray diffraction to assess the steel properties.

The results show the typical structure and microstructure of metal additive manufacturing. Melt pools and layers are clearly visible. The layer size is on average roughly consistent with the set fabrication parameter, while the melt pools’ size appear to increase with higher energy density. Two types of grains can be identified: elongated columnar grains spanning from the edge towards the centre of the melt pool, and equiaxed grains, mostly localized in the centre. Regions that are expected to have experienced lower thermal gradients during solidification seem to develop larger grains on average. Instances of abnormal grain structure are also highlighted, such as the presence of hourglass-shaped grains. Overall, the samples are clearly fine-grained, with the largest grains still below 2 µm on average.

In some of the samples, a higher degree of porosity than what is expected for this consolidation technique is noticed. Possible explanations are given, such as the large spread in characteristics of the feed powder, possible material stripping during cutting and grinding and volume contraction during the melt pool formation.

Nanoparticles are clearly visible throughout all of the ODS steel samples. They appear larger than expected for high grade ODS, with a large presence of dispersoids above 40 nm in diameter. Their morphology appears to be spherical in most cases and octahedral crystalline in some. There is some evidence supporting the formation of a core-shell structure and heterogeneous composition inside the particles themselves. Possible traces of V presence are also found in some ODS particles. Some dispersoids below 10 nm are also identifiable, but their chemical nature cannot be confirmed due to the limited resolution of EDXS in this study.

ETHZ – Research Collection: DOI: 10.3929/ethz-b-000369648
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<tr>
<td>AM</td>
<td>Additive manufacturing</td>
</tr>
<tr>
<td>APT</td>
<td>Atom probe tomography</td>
</tr>
<tr>
<td>BCC</td>
<td>Body-centered cubic</td>
</tr>
<tr>
<td>CANDU</td>
<td>Canadian deuterium Uranium</td>
</tr>
<tr>
<td>DPA</td>
<td>Displacement per atom</td>
</tr>
<tr>
<td>EDSX</td>
<td>Energy-dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>EMPA</td>
<td>Swiss Federal Laboratories for Materials Science and Technology</td>
</tr>
<tr>
<td>EPFL</td>
<td>École polytechnique fédérale de Lausanne</td>
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<tr>
<td>ETHZ</td>
<td>Swiss Federal Institute of Technology in Zurich</td>
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<tr>
<td>FIB</td>
<td>Focused ion beam</td>
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<tr>
<td>GB</td>
<td>Grain boundary</td>
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<tr>
<td>GFR</td>
<td>Gas-cooled fast reactor</td>
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<tr>
<td>GIF</td>
<td>Generation IV international forum</td>
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<tr>
<td>IASCC</td>
<td>Irradiation-assisted stress corrosion cracking</td>
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<tr>
<td>ICSD</td>
<td>Inorganic crystal structure database</td>
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<tr>
<td>LFR</td>
<td>Lead-cooled fast reactor</td>
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<tr>
<td>LNM</td>
<td>Laboratory for Nuclear Materials</td>
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<tr>
<td>LOM</td>
<td>Light optical microscopy</td>
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<tr>
<td>LWR</td>
<td>Light water reactor</td>
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<tr>
<td>MA</td>
<td>Mechanical alloying</td>
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<tr>
<td>MSR</td>
<td>Molten salt reactor</td>
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<tr>
<td>ODS</td>
<td>Oxide dispersion strengthened</td>
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<tr>
<td>PCA</td>
<td>Process control agent</td>
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<tr>
<td>PSI</td>
<td>Paul Scherrer Institute</td>
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<tr>
<td>RPM</td>
<td>Revolutions per minute</td>
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<tr>
<td>RT</td>
<td>Room temperature</td>
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<tr>
<td>SCHWR</td>
<td>Supercritical heavy water reactor</td>
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<tr>
<td>SE</td>
<td>Secondary electrons</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>SFR</td>
<td>Sodium fast reactor</td>
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<tr>
<td>SLM</td>
<td>Selective laser melting</td>
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<tr>
<td>SLS</td>
<td>Swiss light source</td>
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<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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<tr>
<td>VHTR</td>
<td>Very high temperature reactor</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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I. **Introduction**

**Concerning nuclear**

In the past two decades, a significant amount of attention has been paid towards the sustainability of the current energy policies worldwide. The prolonged widespread usage of non-renewable sources, in particular fossil fuels, has been linked to a strong increase in CO$_2$ concentration in the atmosphere, up to levels not seen since millions of years ago [1]. The development of modern society cannot prescind from reliable energy sources that can be tuned to match the consumption demands.

*Figure 1: Total world electricity consumption trend between 1990 and 2016, based on IEA data [2].*

*Figure 2: Yearly world CO2 emission trend between 1990 and 2016, based on IEA data [3].*
Since it is extremely unlikely for the trend of growing energy consumption in the world to change, it is necessary to decouple energy production from greenhouse gas emission. This can be achieved by transitioning away from the current widespread use of fossil fuels for our energy needs, towards low-carbon or no-carbon generation methods. Nuclear energy is a strong candidate to fulfil this task, as it shows minimal environmental impact during normal operation while efficiently exploiting a very energy-dense source.

![Electricity generation by fuel, between 1990 and 2016, based on IEA data](image)

Figure 3: Electricity generation by fuel, between 1990 and 2016, based on IEA data [4].

Currently, nuclear energy generation accounts for roughly 10% of the global electricity generation, as shown in Figure 3 [4]. Nevertheless, it is an industry with a long-standing reputation for high safety standards, reliable operation and efficient production.
Current estimates, based solely on the status of mining operations and know uranium deposits, predict that fuel reserves for nuclear power are likely to meet the demands up until year 2100 [6]. This is not including technology developments, discovery of new deposits, fuel reprocessing and nuclear weapon recycling, hence optimistic prospects could see the demand matched even further beyond without significant effort. Nuclear energy also figures very favorably when considering the health impact of normal operation and accidental scenarios combined, with the lowest death rates per TWh of all non-renewable sources of energy [5].

The vast majority of the currently operating nuclear power plants are part of generation II and III/III+. Although significant improvements have been made with respect to safety, there is still considerable potential to improve on efficiency and fuel utilization. Current efficiency of Light Water Reactors (LWR) is around 35%, which is lower than what is currently achieved by conventional thermal power plants. This is mostly a result of the low maximum water temperature achievable in a LWR, which is mostly a result of the performance of current reactor materials. Regarding fuel utilization, the typical operation scheme revolves around a once-through fuel cycle, where the enriched fuel burns in the core over several operation cycles and is then disposed of permanently.
I. Introduction - Concerning nuclear

Concerning nuclear fuel cycle, from mining to final disposal; currently, the possibility to reprocess and reuse nuclear fuel is not exploited to its full potential [7].

This cycle can be improved by reprocessing fuel, a process that has the purpose of extracting the remaining fissile material contained in the spent fuel while separating all the byproducts that are of no further use. However, this is a complicated, expensive and highly controlled process, the latter due to the risk of nuclear weapon proliferation. Other improvements can be made by designing for the possibility of using natural uranium, instead of uranium enriched in fissile content. This is already possible in some currently operating reactors, namely Pressurized Heavy Water Reactors (PHWR) such as the CANadian Deuterium Uranium (CANDU).

In order to overcome these challenges, the IV generation of nuclear reactor is in development. Whereas the III generation of nuclear reactors consists mainly on substantial improvements on the performance and safety of II generation reactors, IV generation reactors are transformative both in design and in concept. There are six reactor technologies that have been selected by the Generation IV International Forum (GIF) [8] for further development and research:

- The Gas-cooled Fast Reactor (GFR);
• The Lead-cooled Fast Reactor (LFR);
• The Molten Salt Reactor (MSR);
• The Supercritical Water-cooled Reactor (SWCR);
• The Sodium-cooled Fast Reactor (SFR);
• The Very High Temperature Reactor (VHTR).

![Figure 6: Irradiation damage and temperatures for current and planned nuclear energy systems. [9]](image)

Among the goals of these new reactor designs there are an increase in the lifetime of the installation, excellence of safety and reliability and more efficient fuel utilization. An increase in coolant temperature would certainly benefit the thermal efficiency of the cycle, but it is not possible for the present nuclear reactors. There is a hard limit to the maximum achievable temperature to prevent core damage, mainly because of cladding oxidation, which releases hydrogen in LWR systems. Future reactors employ different materials and coolants to reach noticeably higher temperatures, without risk of hydrogen production. This clearly represents also an enhancement of the inherent safety of the system.

From the perspective of reactor physics, all of the existing reactors make use of the thermal neutron spectrum (neutron energy ~0.0253 eV), whereas several of these reactors plan to use the fast neutron spectrum (neutron energy >1 MeV). This has the advantage of allowing improving fuel utilization by allowing to burn fissionable material (i.e. material that can only undergo fission if the impacting neutron has sufficient energy), such as Uranium-238, the most abundant of Uranium isotopes. It also allows to burn minor actinides more efficiently,
which is very relevant for the stated goal of reducing the long-lived radioactive waste, of which they make up the largest portion.

Nuclear fusion reactors also utilize neutrons, as they are produced in fusion reactions. Typically, the most common reaction in this system is the Deuterium-Tritium fusion reaction:

\[
\frac{2}{1}D + \frac{3}{1}T \rightarrow \frac{4}{2}He (3.5 \text{ MeV}) + \frac{1}{0}n (14.1 \text{ MeV})
\]

Neutrons produced in this reaction are also fast neutrons, with even higher energy compared to fission neutrons; it is worth mentioning that since the energy liberated is divided between two products, the distribution is simply based on their masses, which results in monoenergetic neutrons being generated. Here they are used specifically as a carrier of the energy generated by fusion itself, which can then be extracted and used in a conventional steam cycle. This is possible since neutrons, especially fast neutrons, do not interact strongly with matter, meaning that they tend to have a longer mean free path, and they carry most of the energy produced in a fusion reaction.

However, both IV generation reactors and fusion reactors also suffer from the downsides of higher temperature and faster neutrons. It is known that displacement damage from neutron irradiation scales with the energy of the neutrons, as more energetic primary knock-on atoms will be produced by them, which in turn produce more cascades. Furthermore, high temperatures induce creep, thermally induced plastic deformation of materials under stress, in structural materials, which reduces the lifetime of the power plant. Furthermore, the simultaneous effects of high dose on materials and high temperature give rise to radiation induced creep effects, which can significantly degrade the performance of materials.

**Steels for nuclear applications**

The materials requirements for future nuclear installations present a challenge. First, good to excellent mechanical properties are required, as the cladding, the reactor pressure vessel (RPV) and the other structural components are subject to considerable mechanical stress during operation. The RPV specifically is also considered the most critical component, as it is deemed “irreplaceable”, thus the limiting factor for the lifetime of the whole power plant. Secondly, good thermal conductivity is required, especially for the cladding, as otherwise the peak temperature in the fuel pellets themselves would increase up to dangerous levels, which could threaten its integrity. High thermal stability, no phase transitions and high melting point are also desirable characteristics. Thirdly, as already mentioned, all of these materials are exposed to high fluence of fast neutrons, hence two more requirements arise: they must be especially impervious to irradiation damage and they must not undergo strong activation under neutron irradiation. Because of the latter, special care must be paid especially to the alloying elements, as common ones such as Molybdenum or Niobium need
to be avoided. Other consequences of high dose environment such as growth and swelling must also be avoided, as they contribute to the degradation of mechanical properties while simultaneously disrupting the planned geometry of the systems, which is especially dangerous for fuel rod cladding. Finally, several of these systems include chemically aggressive environments (e.g. SCWR, MSR), thus good corrosion resistance is mandatory; nuclear installations present the problem of Irradiation Assisted Stress Corrosion Cracking (IASCC) as well, which is a severe and unpredictable interaction, which represents a serious threat integrity of the system.

For the role of structural materials, austenitic stainless steels have typically been employed. They have good to excellent mechanical properties. The Young’s modulus at room temperature for series 300 stainless steels is usually around 200 GPa, whereas the yield strength can reach up to 300 MPa. Cold working can increase the latter even up to even 700 MPa, at the cost of a significantly reduced ductility. Increasing operation temperature above 500 °C produces a significant reduction of the mechanical properties and exposes the material to creep. High chromium allows for good corrosion in aqueous environments, but only at temperatures lower than 300 °C, otherwise strong oxidation of the metal occurs. Under irradiation, austenitic stainless steel experience substantial hardening, with a subsequent strong decrease in ductility, and non-negligible amounts of Helium production, which damage the material and form bubbles. At temperatures below 300 °C, interstitial defects tend to migrate towards sinks and vacancies and bubbles remain largely stationary. Increasing the temperature further induces vacancy agglomeration into cavities and helium bubbles coalescence, which is cause for dramatic swelling [10]. This phenomenon happens at a rate of ~1% per dpa [11] and it is severely impacting the performance of such steels in high-displacement-per-atom and temperature reactors, which include many of the IV generation and fusion designs.

A prominent candidate that has been considered for these applications is ferritic-martensitic steel. This material has several advantages over austenitic stainless steel, in particular in high-temperature and high-dose scenarios. Mechanically, it has high fracture toughness and ductility, but with respect to yield strength and hardness, it generally scores lower than its austenitic counterparts. Thermally, it presents very good properties, with a good thermal conductance and a smaller thermal expansion coefficient. These properties also lead to a decrease in the development of thermal stresses, low susceptibility to thermal shock and better thermal fatigue response. Irradiation still induces a degradation of the mechanical properties, namely reduced ductility and fracture toughness and ductile to brittle transmission temperature (DBTT) increase, but the level of hardening experienced is low and the irradiation creep susceptibility appears to be lower than in austenitic steels. Point-defect and helium production under irradiation still constitutes a grave threat to the properties of the materials, but compared to austenitic stainless steel, ferritic steel experiences considerably less swelling, with a swelling rate of ~0.012% per dpa [11] [12]. To further improve properties under irradiation, Reduced Activation Ferritic Martensitic (RAFM) are
being developed, with the intent of removing common, but easily activated by neutrons, alloying elements and impurities (such as Co, Cu, Ni, Mo and Nb) to replace them with low-activation alternatives (such as W, Mn, V, Ti and Ta) [13].

Both austenitic and ferritic stainless steel appear to be suitable candidates for II and III generation nuclear power plants as structural materials. However, an increase in operational temperature induces a decrease in performance in terms of mechanical properties (mainly due to creep) corrosion resistance. An improvement of the response to high-irradiation systems is also required to ensure the longest lifetime possible for the installation.

A promising candidate exists in oxide dispersion strengthened (ODS) ferritic steel. This material employs a form of precipitation-strengthening, induced by oxide nanoparticles finely dispersed with high density through the metal. The precipitates interact specifically with the dislocations, acting as barriers to their movement [14], which results in significantly increased resistance to creep. Generally, the tensile strength and the hardness also improve as a consequence of the presence of precipitates, with stronger improvements the higher the density of precipitates; there are results showing ductility being negatively impacted compared to conventional ferritic steel in samples produced by hot extrusion [15]. Among the excellent properties of this material there is also an improved resistance to irradiation, as the nanoparticles act as sinks for the irradiation defects and He produced. This property can be characterized with the sink-strength, which is an index of the global tendency for irradiation defects to be trapped into sinks. It is shown that the addition of ODS particles in the matrix significantly improves the sink-strength [12]. Overall, this results in an outstanding stability and retention of the properties even with high-temperature irradiation [16].

The chemical nature of the oxide nano-dispersoids is an essential aspect to consider in order to achieve these properties. Yttria (Y$_2$O$_3$) shows noteworthy stability at high temperature and irradiation conditions, making it interesting for the purpose of ODS steel manufacturing. In fact, it is very common to find it as the oxide of choice to produce this material [15], [16].

**Mechanical alloying**

The ball mill is a machine where a grinding jar, containing the powders and the grinding balls, quickly revolves around its own axis while simultaneously revolving with the planetary disk, as in Figure 7.

This motion gives rise to Coriolis forces that induce the movement of the balls as displayed in Figure 7. The balls impact the powder, fracturing the brittle particles, reducing their size, and flattening and welding the ductile particles. Over time, the ductile particles become work hardened and start going through a cycle of fracturing and rewelding, which reduces their size as well. The mechanical alloying process occurs in this system as the two powders mix
together and as the brittle particles get trapped and embedded in the ductile ones. If the components of the system are soluble, a solution will be produced, with composition converging to the average composition of the whole powder batch with increasing milling time. The morphology of the powder particles also improves with time, where initially they will exhibit a mostly flattened and elongated shape, which gradually converts to a regular, almost spherical shape.

![Figure 7: Working principle of a ball mill](image)

The speed of the ball mill affects the process by determining the amount of energy that is provided to the system via grinding balls impacts and friction. It has to be mentioned that this is overall a very low efficiency process, hence a higher energy also contributes to an increase in temperature. This may be advantageous if diffusion is required, as it will be enhanced in these conditions [18].

Process control agents may be added to reduce the rate of cold-welding between particles, which facilitates size reduction and decreases the amount of time required to reach convergence. This does, however, introduce another component in the system that may be incorporated by the final product [18].

In ODS steel mechanical alloying, experimental results show that Yttria particles are either dissolved or reduced to very small sizes very quickly during the mechanical alloying process [19]. In a study, Alinger et al. postulate the same two different incorporation processes: fine fragmentation and trapping of the brittle oxide particles into the steel matrix or actual dissolution of Yttria, with the production of a highly supersaturated solution, as Yttria is not soluble in iron. The latter is considered the prevalent process by Alinger et al. [20]. Oxide nanoparticles would then precipitate once again during the thermal consolidation process.
I. Introduction - Nanoparticle formation process

The size and distribution of these nanoparticles can be affected by additions such as Ti, which promotes the formation of Y-Ti-O ternary oxides and a reduction in size of the dispersoids, which is generally considered beneficial to the properties of the material.

Nanoparticle formation process

A complete understating of the current theories of nanoparticle formation dynamics is imperative for the purpose of optimizing the fabrication process and dopant introduction in ODS steel, so that the established goal of obtaining a high density of nano-sized precipitates may be achieved.

The process starts during mechanical alloying, where the oxide particles are fragmented into nano-sized clusters and incorporated into the steel matrix. As already pointed out, some results support the complete dissolution of the Y$_2$O$_3$ powder into the matrix, where a supersaturated and heterogeneous solution is produced. The resulting solute would appear in the form of localized clusters, but their distribution would be homogenous throughout the matrix.

Other studies hypothesize that rather than the dissolution into single atoms, nano-sized and sub-nanometer sized particles are produced by the mechanical alloying and incorporated into the metal matrix [20], [21]. The dispersed fragments would then experience amorphization and agglomeration, including incorporation of metal atoms from the matrix or the alloying elements. This is supported by the study of Dai et al. [22], who report the fragmentation of Yttria into irregularly shaped particulate, with only a minor portion of dissolution into the atomic components of the oxide in the matrix. Following the evolution of the particulate, the transition from an ordered phase into a disordered phase and finally into a fine-grained nanocrystalline structure is also observed.

During the consolidation process, recrystallization or growth of the nano-precipitates would occur, possibly with the formation of a core-shell structure, where the shell does not necessarily share the high-temperature stability of the postulated Yttria core. The specific structure formation is dependent on the available elements in the composition, as some specific elements show high affinity for Yttria, such as Al or Ti. The intensity of the growth appears to be connected with temperature, as higher temperature appear to be beneficial to the process, but this does not appear to also affect the final size of the precipitates. Dai et al. [22] report in their study no significant difference in the dimensions of precipitates annealed at temperatures of 891 K and 1023 K, but they do point out that the growth of the particles is visible with XRD only with a minimum T of 891 K. The morphology of the identified particles also changes from irregular fragments to roughly spherical particles.
Coarsening of the particles can occur if ODS steel is applied at temperatures higher than 1300 °C, which results in dispersoids growing in size at the expense of the smaller precipitates, which in turn produces a decrease in the number density of particles [23].

**Selective laser melting**

Additive manufacturing is a novel fabrication process where a 3-dimensional object is manufactured by subsequently adding layers of materials on top of one another and then consolidating them. Commonly, the geometry of the object is provided with a Computer Aided Design (CAD) file and then the machine prints according to the instructions and parameters set by the operator.

![Overview of SLM manufacturing process](image)

*Figure 8: Overview of SLM manufacturing process [24].*

In SLM, the powder particles spread on the build platform and a high-power laser melts the area corresponding to the first layer of the object. Tunable parameters are the laser power, the scanning speed, the hatch spacing and the layer thickness. Typically, particle sizes are in the range of 10-60 µm and the morphology is as close to spherical as possible to produce optimal results [25]. This fabrication method allows producing parts with complex designs and to consolidate multiple parts in a single object in situations where conventional consolidation processes are not suitable. It allows production of parts on demand and in-situ, reducing the need for stocking, and it is very beneficial to prototyping. Because of the aforementioned advantages, it is quickly becoming widespread in many different fields, such as aerospace engineering, automotive and healthcare, for more than just prototyping but for the rapid supply of replacements for structural components.

The properties of the final product are strongly dependent on the print parameters, the geometry and on the thermodynamics of the consolidation after melting, which is considerably complex to model due to the wide variety of process conditions. Overall, the
process is capable of resulting in high-density specimens, but the mechanical properties can differ greatly from those of the same material produced with a different consolidation process. A most common property of these samples is the anisotropy of their properties: this is a result of a grain structure that is commonly elongated in the print direction, as thermal gradients drive grain growth in this way. It must also be noted that, usually, objects produced in additive manufacturing may experience strong residual stresses diffused in the object, which suggest that subsequent thermal treatments may be very beneficial to the performance of the part.

Description and aim of the study

In this study, Eurofer97, a 9%Cr-Fe steel, one of the options as a reduced activation ferritic martensitic steel, is employed as the steel of choice, whereas Yttria is chosen to produce the nano-dispersoids required to attain the improvement of properties desired in ODS steel. The starting materials are supplied as powders and mechanically alloyed in a ball mill; following this, the powder are consolidate with Selective Laser Melting (SLM).

The goal of the analysis is to reach a good understanding of the effects of the fabrication process on the microstructure of the material and on the presence and distribution of nano-dispersoids. Large structures induced with SLM, such as melt pools and layering are also explored, to determine whether they affect the material properties and the oxides distribution.

Numerous techniques are employed to reach these goals, such as:

- Metallographic techniques;
- Light Optical Microscopy (LOM);
- Scanning electron microscopy (SEM);
- Energy dispersive X-ray Spectroscopy (EDSX);
- Transmission electron microscopy (TEM);
- Synchrotron-based x-ray diffraction (XRD).

This master thesis is being performed as a conclusion to the joint Master’s degree programme in Nuclear Engineering of EPFL and ETHZ. The production of the powders and the analysis of the specimens is carried out mostly at Paul Scherrer Institute. The fabrication process is carried out at the Swiss Federal Laboratories for Materials Science and Technology (EMPA) in Dübendorf.
II. **Experimental method**

**Powder production and analysis**

The mechanical alloying process has been performed with a Retsch PM100 planetary ball mill. The amount of powder fed was 400 g, 398 g of which were Eurofer97 steel powder and 2 g of which were Yttria powder, with the composition specified in Table 1.

<table>
<thead>
<tr>
<th>Powders</th>
<th>Final elemental composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eurofer97</td>
<td>Fe</td>
</tr>
<tr>
<td>99.5%</td>
<td>89%</td>
</tr>
<tr>
<td>Yttria</td>
<td>Ta</td>
</tr>
<tr>
<td>0.5%</td>
<td>0.12%</td>
</tr>
</tbody>
</table>

Table 1: Composition of the manufactured ODS steel.

The quality of the powders was assessed based on two parameters: powder particle mean size, with the Feret diameter as size indicator, and flowability, evaluated with angle of repose measurements.

![Retsch PM100 planetary ball mill](image)

*Figure 9: Retsch PM100 planetary ball mill.*
II. Experimental method - Powder production and analysis

The powder was milled for 40 h at a rotation speed of the planetary disk of 600 rpm. A mill-and-pause rhythm was setup in order to prevent excessive heating of the grinding jar, as this can lead to the ball mill automatic interruption of the process. The powder was milled for 10 min and then stopped to cool down for 15 min, after which the milling is resumed with inverted rotation direction.

A 250 ml tungsten carbide grinding jar was employed, as it is the one recommended by the manufacturer to minimize the erosion in case of milling of hard metals. The grinding medium consists of 800 g of steel grinding balls of 5 mm in diameter, which fills the grinding jar up to 2/3 of its volume, leaving space for the movement of the balls and the powder, as advised in the operation guidelines. However, this produces a 2:1 ball charge ratio, which is lower than the typical values employed of 10:1 or 5:1. In Figure 10, the parameter space of milling time and rotational speed for several of the considered studies is shown.

The employed parameters result from the analysis of the resulting powder with different milling conditions of a 200 g initial batch and a 4:1 ball charge. The low rotational speed of 200 rpm produced a powder consisting of very large particles, with a very low yield below 45 µm. Some unknown contamination was produced while milling this batch of powder. It is possible that the cause of the contamination is the detachment of material that was cold-welded to the walls of the grinding jar during previous use. It is very unlikely for the contamination to be the result of direct erosion of the walls themselves, due to the high hardness of Tungsten Carbide. Similarly, contamination of the batch was also noticed for the rotation speed of 450 rpm, along with strong static electricity in the produced powder, which was deemed completely unusable. The presence of contamination is likely not linked to the milling parameters, but to the inadequate condition of the grinding jar, but these issues prevented the assessment of the quality of the resulting powder. The 600 rpm batch showed the smallest particle size, the highest yield after sieving below 45 µm and the least amount of contamination. Based on this, this powder was selected as the best option for further advancements of the project. A 400 g batch, 2:1 ball charge, milled for twice the time, was produced, in order to avoid any difference in the processing conditions in the powder destined for the additive manufacturing process, and studied to assess its compatibility with the manufacturing process.
II. Experimental method - Powder production and analysis

The use of process control agents (PCA) was considered and tested. The resulting powders displayed very small particles, below the requirements of additive manufacturing and very poor flowability, with angles of repose significantly greater than 40°. Based on these results, the use of PCAs was discarded.

The powders were milled in an Argon atmosphere to minimize the oxidation, especially because it is facilitated by the temperature increase produced by the milling.

The as-milled powders were sieved manually with a three-stage sieve stack, with mesh sizes of 150 µm, 100 µm and 45 µm. No other treatment of the powders was performed before analysis and printing.

Two powder batches were prepared with the same milling parameters: a mechanically alloyed ODS steel one and a non–ODS Eurofer97 steel as reference. To produce an adequate amount of powder for the print, two batches of the non-ODS reference powder were produced. A summary of the milling parameters, together with the resulting powder properties, is shown in Table 2.

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**Figure 10:** Milling parameter space commonly explored for the purpose of mechanical alloying of ODS steel powders, not specific to one consolidation process [19], [26]–[32]. The dots in black represent the chosen parameters in this study.
The ODS steel powder and the reference Eurofer97 steel powder were produced in the exact same MA process, but resulted in different properties of the powders. This might have occurred because of the presence of Yttria in the ODS steel powder batch, which, by entering the metal as a sub-nanometer dispersoids or as a supersaturated solution, might be affecting the ductility and hardness of the system. This, in turn, could have reduced the time required to reach the asymptotic results of MA, thus producing a powder with smaller particle size. Priority has been given to preserving the same manufacturing process rather than attempting to produce powders with the exact same characteristics.

Table 2: Milling parameters and resulting properties of the powders prepared for additive manufacturing

<table>
<thead>
<tr>
<th>Sample</th>
<th>Input mass</th>
<th>Milling time</th>
<th>Mill</th>
<th>Pause</th>
<th>RPM</th>
<th>Ball charge</th>
<th>Ball size</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODS steel</td>
<td>400 g</td>
<td>40 h</td>
<td>10 min</td>
<td>15 min</td>
<td>600</td>
<td>2:1</td>
<td>5 mm</td>
</tr>
<tr>
<td>Reference steel 1</td>
<td>400 g</td>
<td>40 h</td>
<td>10 min</td>
<td>15 min</td>
<td>600</td>
<td>2:1</td>
<td>5 mm</td>
</tr>
<tr>
<td>Reference steel 2</td>
<td>400 g</td>
<td>40 h</td>
<td>10 min</td>
<td>15 min</td>
<td>600</td>
<td>2:1</td>
<td>5 mm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Output mass</th>
<th>Angle of repose</th>
<th>Avg. size</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODS steel</td>
<td>289.07 g</td>
<td>40.67 ± 1.51</td>
<td>10.2 ± 5.5</td>
</tr>
<tr>
<td>Reference steel 1</td>
<td>156.97 g</td>
<td>39.95 ± 2.10</td>
<td>18.0 ± 6.8</td>
</tr>
<tr>
<td>Reference steel 2</td>
<td>160.5 g</td>
<td>39.97 ± 1.87</td>
<td>18.7 ± 6.0</td>
</tr>
</tbody>
</table>

1 Evaluated after sieving below 45 µm.
2 Uncertainty of ± 0.01 g.
3 1-σ error bar of the set of measurements.

Figure 11: Particle size distribution of the ODS steel powder produced for additive manufacturing.

An example of the size distribution of the powder particles is reported in Figure 11. Elongated particles of Feret diameter > 45 µm can still pass through the sieve, thus a tail of large particles is present in the size distribution. The size distribution analysis was performed...
with the image processing and analysis software ImageJ. Pictures of the morphology and size of the powders are shown in Figure 12, taken with LOM and SEM. It must me noted that the SEM picture of the powder refers to an ODS sample milled for 20 h with a 4:1 ball charge, whereas the LOM picture refers to the ODS steel powder that was employed in the SLM fabrication process. In Figure 13, a representative angle of repose measurement picture is displayed.

![Figure 12: On the left, SEM picture of the chosen ODS steel powder produced during the parameter optimization study; on the right, LOM picture of the steel powder employed in SLM.](image)

![Figure 13: Angle of repose measurement picture for the ODS steel powder used in SLM.](image)

Sample printing

The samples were printed with SLM at EMPA. Ten samples were produced for each batch. The ODS steel samples will be referred to as B-series samples, from B1 to B10, whereas the reference steel samples will be referred to as C-series samples, again from C1 to C10. The printing parameters are shown in Table 3. The print was performed under a protective Argon atmosphere to avoid the oxidation of the specimen and the layer thickness was 40 µm. During the print, a continuous laser scans the sample horizontally. The scanning direction rotates 90° between layers, so that adjacent layer have perpendicular scanning directions.
A preliminary characterization of the quality of the print was carried out at EMPA measuring the density with Archimedes’ principle. The resulting densities are plotted in Figure 14. Overall, the values are very close to the theoretical value of steel density, but there is a distinct decrease in density for the reference steel samples. Since the uncertainty of the measurement with Archimedes’ principle is ~1%, it cannot be excluded that the difference is only a statistical variation. If the decrease is assumed real, then the reason may lie in the larger average size of the particles for the reference steel powder compared to the ODS steel one. A relatively large variation of the density also occurs for samples B9 and B10, which were manufactured with a smaller hatch spacing. To perform this print, the scanning speed was dramatically increased, as a smaller hatch spacing would otherwise push the energy density to a point where the sample’s integrity may be compromised. This difference in fabrication parameters is considered at the root of the difference in density, although it may again be just a result of the inaccuracy of the density measurement method.
Table 3: Printing parameters employed in the production of the ten ODS steel and reference steel samples.

<table>
<thead>
<tr>
<th>Laser power</th>
<th>Scanning speed</th>
<th>Hatch spacing</th>
<th>Energy density</th>
</tr>
</thead>
<tbody>
<tr>
<td>(W)</td>
<td>(mm/s)</td>
<td>(µm)</td>
<td>(J/mm³)</td>
</tr>
<tr>
<td>B1</td>
<td>175</td>
<td>400</td>
<td>125</td>
</tr>
<tr>
<td>B2</td>
<td>175</td>
<td>350</td>
<td>125</td>
</tr>
<tr>
<td>B3</td>
<td>175</td>
<td>240</td>
<td>125</td>
</tr>
<tr>
<td>B4</td>
<td>175</td>
<td>175</td>
<td>125</td>
</tr>
<tr>
<td>B5</td>
<td>150</td>
<td>400</td>
<td>125</td>
</tr>
<tr>
<td>B6</td>
<td>150</td>
<td>300</td>
<td>125</td>
</tr>
<tr>
<td>B7</td>
<td>150</td>
<td>240</td>
<td>125</td>
</tr>
<tr>
<td>B8</td>
<td>150</td>
<td>175</td>
<td>125</td>
</tr>
<tr>
<td>B9</td>
<td>175</td>
<td>500</td>
<td>80</td>
</tr>
<tr>
<td>B10</td>
<td>150</td>
<td>500</td>
<td>80</td>
</tr>
</tbody>
</table>

Figure 15: Measured dimensions of the ODS steel printed samples.

The printed samples appear to have picked up powder on the sides beyond the 5 mm of the design. The measured samples’ dimensions range between 5.5 mm and 5.9 mm in “x” direction, 5.5 mm and 5.75 mm in “y” directions, where for both directions higher energy density samples appear to be larger, and between 4.5 and 4.6 mm in “z” direction, which is the printing direction. Designation numbers are printed on top of the surface of the samples, but they have been neglected in this measurement. This description is shown in Figure 15.

An in-depth analysis of the microstructure and the nanoparticle distribution is performed for samples B4, B5, B6, B7 and B8 and for the corresponding reference steel samples.
II. Experimental method - Metallographic preparations

**Metallographic preparations**

The analyzed samples were treated in various ways to display the desired structures and microstructures or to be readied for a specific examination technique. Most of the decisions on how to treat the samples are based on internal knowledge of PSI scientists and technicians of the Laboratory for Nuclear Materials (LNM) department. These techniques will be thoroughly described in the following paragraphs.

**Cutting**

Sample pieces were cut from the bulk of the samples for the analysis. The cut slices were ~800 µm thick and always perpendicular to the printing direction. The cutting was performed with a Well diamond wire saw over the course of about 1h, although different samples appeared to require different times to cut. This could be a consequence of small variations in the geometry of the samples or in a difference in hardness induced by the different printing parameters. Afterwards, the samples were treated in an ultrasonic shaker in an acetone bath, then an ethanol bath and finally a deionized water bath, to remove the residuals of the thermal glue utilized to attach the sample to the sample holder.

**Surface grinding and polishing**

The samples have been ground and polished to display a mirror-like surface, a necessary prerequisite for many examination techniques. A Struers Labopol-5 Metallurgical Grinder Polisher was used to aid in the preparation. The samples’ surfaces were polished with silicon carbide grinding paper with increasing grit size, starting at the rough grit size 500, then 1000, then 2000 and finally the very fine grit size 4000. The grinding was always performed under a steady stream of water to remove any item that might compromise the process by scratching the surface.

After grinding, the samples were polished with the aid of the same device. The SiC paper was replaced with a polishing cloth covered with a thin layer of diamond suspension to further refine the surface quality. Three polishing steps were employed with different diamond dispersoids size: first 6 µm, then 1 µm and finally 0.25 µm. Afterwards, the ultrasonic shaker solvent treatment is applied.

**Vibrational polishing**

Vibrational polishing was applied to further refine the sample surface for advanced analysis techniques. For this purpose, a Buehler Vibromet-2 was used along with the OP-S colloidal silica solution. The samples were placed three at a time in the Vibromet for 1h at
a power of 20%. Afterwards, the colloidal silica is removed by washing the surface of the samples with soap and the ultrasonic shaker solvent treatment is applied.

This process produced a completely scratch free surface, but it also resulted in a certain accentuation of the topography of the sample. Possibly, this is caused by the presence of different phases or grain orientations, which may be affected differently by the vibrational polishing and the OP-S solution. Some copper contamination of unidentified origin has appeared on some of the samples treated with this method, as visible in Figure 16.

**Chemical and electrochemical etching**

Etching is a process where a sample is treated with a specific chemical mixture in order to highlight different structural or phasic characteristics. During chemical etching, the polished sample is completely immersed in a bath of etching fluid for a set amount of time. During electrochemical etching, the sample is acting as the anode in a galvanic cell and it is subject to removal of material from the surface under the action of an electrolyte; with this method, both voltage and time are crucial parameters for a successful etch. Chemical etching and electrochemical etching procedures were attempted with limited knowledge of the phase content of the samples, as with additive manufacturing, unexpected minor phases may appear [33]. Different manufacturing conditions, specifically concerning the chosen scanning speed, may also strongly affect the microstructure of a sample, favoring the preferential formation of one phase over the others. There is a connection in particular
between increased scanning speed and ferrite phase refinement and austenite formation [34], [35].

Chemical etching was performed using the V2A reagent and a contrast medium, based on the internal knowledge of steel etching of PSI and EMPA. The etching was attempted both at room temperature and at 50 °C, both for 20s, in order to assess the best fitting procedure. The higher temperature process resulted in several large structures on the surface of the material, most likely stains from the contrast agent added to the acid solution, based on their appearance with LOM (Figure 17). This indicates an added difficulty in using the contrast agent at higher temperatures.

Another attempt at a comparison was performed on sample B4, etched at room temperature and at 50 °C, both again for 20s. The resulting structure is clearly visible at room temperature, but it appears to be overtly etched at 50 °C, showing large holes on the surface of the sample, as in Figure 18. Based on these tests, etching with V2A was limited to room temperature. An influence of the process used to clean the samples afterwards was also noticed. By using the aforementioned ultrasonic shaker treatment, the temperature increase due to the ultrasonic waves, coupled with the interaction with acetone and acid residuals, may be affecting the surface finish, worsening the definition of the microstructure. Because of this, the ultrasonic shaker was avoided in cleaning the samples after the chemical etching process and static acetone, then ethanol, then deionized water baths were used instead.
Electrochemical etching was performed with a solution of 10% oxalic acid in deionized water, at a voltage of 6V and for a time of 20s. The voltage and the electrolyte are a product of PSI internal knowledge, whereas the time is the product of a study of the evolution of the microstructure with increasing etching time. Overall, this etching procedure showed different effectiveness for different samples, and, while it was always possible to find regions where the relevant information could be gathered, it usually produced strong pitting in the samples. With this method, however, it was always possible to highlight quite clearly the melt pool structure in all of the samples, which was not always the case with V2A etching. Further optimization of this etching method is likely to yield better and more consistent results.
II. Experimental method - Electron microscopy

Electron microscopy

Electron microscopy techniques have been used to analyze the microstructure and the nanoparticles present in the sample. A Zeiss Nvision electron microscope was used to perform SEM, EDSX and STEM, whereas a Jeol JEM 2200 FS was used to gather TEM data.

Scanning Electron Microscopy

In an SEM, an electron beam scans the surface of a sample. The electrons interact with the atoms in the specimen in several ways, inducing the release of secondary electrons, of X-rays, or simply being scattered. The two detectors of the Zeiss Nvision electron microscope that have been used most prominently are the InLens detector and the Secondary Electron detector (SE2). The former collects electrons with high efficiency directly in the column of the electron gun. It results in high-contrast information about phases with different electron density, which can be linked to the atomic number of the atoms present in the phases. The latter is positioned so that it faces the sample’s surface at an angle and because of this it carries a lot more information about the topography of the sample. A comparison of the two image types can be seen in Figure 20: with the use of the SE2 detector, it is possible to recognize the circular features in the image as pits and particles on the surface.

Several configurations of voltage and distance were used. Most of the images were taken with a voltage of 3 kV as it results in less charge deposited in the sample and increased spatial resolution. The sample is routinely placed at a 5 mm or higher working distance from the electron gun to prevent accidental damage to the microscope.

![Figure 20: On the left, InLens picture of the pitting in sample B7; on the right, SE2 picture of the same region.](image-url)
**II. Experimental method - Electron microscopy**

*Energy dispersive x-ray spectroscopy*

This is a technique used to extract information on the composition of a sample based on the energy of the characteristic x-rays emitted under electron irradiation. As the electrons penetrate into the specimen and interact with the atoms, they may excite an inner shell electron of one atom to the point where it is expelled. This creates a vacancy that can be filled by an electron in an outer shell. Since outer shells are higher in energy compared to inner ones, the transitioning electron emits the difference in energy in the form of a characteristic x-ray, which is specific to the interacting atom. Detecting the x-ray and its energy with high accuracy can lead to the identification of the atom that produced it.

![Figure 21: Time-lapse image of the drift over 40 min with a sample mounted on carbon tape.](image)

In this study, a voltage of 6 kV is used for the acquisition of EDSX spectra and elemental maps. The increased voltage is required to efficiently excite some of the atoms in the material, specifically Yttrium, but it is also necessary to avoid too strong an increase of the interaction volume. EDSX has been used mainly to confirm the composition of the nanoxide particles or other unidentified objects in the samples. In order to differentiate as well as possible between peaks from different elements, the highest available time setting was chosen for the resolution of the x-ray energy. Due to drifting issues and the small size of the nanoparticles, short acquisition times were employed, which at times resulted in poor statistics. An analysis of the different drifting conditions for different magnetization state and mounting has been performed in an attempt to optimize the EDSX acquisition; the time-lapse images of the drift are shown in the appendix. Unfortunately, this phenomenon appeared to be unpredictable and poorly controllable.
II. Experimental method - Electron microscopy

Generally, the resolution of the EDXS measurements is relatively low, partly because of the drifting effects. This makes it so that the very small dispersoids found in the samples cannot be characterized in terms of composition.

![Figure 22: Example of EDSX mapping for a large yttrium oxide nanoparticle.](image)

**Transmission electron microscopy**

Transmission electron microscopy is a technique that shows some similarities to SEM, but the voltage is considerably higher ($\geq 200$ kV, compared to $\leq 30$ kV for the SEM used in this study) and information about the sample is gathered through the electrons that pass through the sample and are collected by the detector on the other side. This can be used to extract mass-thickness contrast, or based on the atomic number, or on the presence and orientation of ordered structures in the system. It is also possible to detect electrons that experienced elastic scattering and produce a diffraction pattern. This allows to study in detail the presence and type of ordered structures in the sample.
The TEM investigations of the sample had the specific purpose of identifying the Yttria nanoparticles and assessing their size, morphology and density. The Jeol JEM 2200FS was used for this purpose and it was operated at a voltage of 200 kV, in bright field imaging.

The Zeiss Nvision electron microscope can also be operated in STEM mode. This allows to explore the sample with a scanning electron beam rather than a parallel beam. The operating voltage is 30 kV, which for TEM results in worse spatial resolution compared to 200 kV. Images are taken both in bright field mode and dark field mode, with an emphasis on the identification of nanoparticles. This device is capable of resolving particles as small as 2.5 nm in diameter, which makes it unsuitable to probe the very small Yttria nanoparticles, in the below 2 nm in diameter, whose presence has been confirmed in commercial ODS steels [21].

**TEM sample preparation**

The samples were ground with SiC grinding paper down to a thickness of roughly ~100 µm. Afterwards, a disc of 1 µm in diameter was punched out of each sample and placed in a hole of the same size in a 3 µm disc of 316L stainless steel, where it was fastened with 2-component glue. The glue residuals where removed from the surface by grinding once again with SiC grinding paper with a grit of 2500. Finally, jet electropolishing was performed with a Struers TenuPol-5, in order to thin down the sample to the point of producing a hole, which creates a thin enough region in its surroundings to be analyzed with TEM. The electropolishing was performed using a 5.5% Perchloric acid solution in methanol at -20 °C, at a voltage of 25 V.
II. Experimental method - X-ray diffraction

**X-ray diffraction**

![X-ray diffraction pattern](image)

*Figure 23: Example of 1-D XRD pattern compared to phases found in literature.*

The sample has been analyzed through XRD to gain more information on the metallic phases present. The analysis was performed on one of the B5 samples prepared for TEM, in the microXAS beamline at the Swiss Light Source (SLS). The SLS is a synchrotron light source with an energy of 2.4 GeV, used to produce high-brightness photon beams of tunable energy from the excitation of beam electrons. Numerous beam lines are supported, for very diverse research areas, ranging from biology to material science studies. The microXAS beamline is a hard x-ray microprobe facility, dedicated to x-ray fluorescence, spectroscopy and diffraction of active and inactive samples, with x-ray energy ranging from ~3 keV to ~23 keV.

X-ray diffraction exploits the phenomenon of elastic scattering of X-ray waves in the atomic lattice of the sample. If there are regular structures in the sample, the photons’ scattering will interfere constructively in specific directions which satisfy the Bragg condition. This constructive interference produces peaks in specific locations in a 1-D diffraction pattern, which can be compared to the literature found in an XRD database. In this study, the crystal
lattice information of the Inorganic Crystal Structure Database (ICSD) of FIZ Karlsruhe was used as reference.

In order to probe the thin area of the TEM sample, in the close proximity of the hole, while still maintaining good signal to noise ratio, an energy of 17.2 KeV was used for the beam, which corresponds to a wavelength $\lambda=0.7208$ Å. The diffraction spectra were acquired in a 400 μm x 200 μm region surrounding the hole, with 2 μm steps and 1 s of acquisition time.
III. Results and discussion

Melt pools and layers

Figure 24: Close up of the melt pools on sample C6 (left) and of the layers on sample B1 (right).

The manufacturing process relies on the continuous build-up of the sample by adding material on top of the already solidified portion and melting it with a high-power laser. The melting process and the layering leave traces on the samples that can be clearly identified with the appropriate chemical treatment. Both V2A etching and Oxalic Acid etching proved effective in highlighting the presence of the structures from additive manufacturing, although the latter appears far superior to the former in this respect showing the structure noticeably more.

Figure 25: Sample B4, etched with Oxalic Acid (left) and with V2A (right).

Different samples treated in the exact same process also show inconsistent results in terms of visibility of the additive manufacturing structure. This may be an indication that changing the fabrication parameters may lead to differences in the chemical behavior, which could
occur e.g. with the preferential formation of diverse phases, thus affecting the susceptibility to the etching process. Another possibility is that the characteristics of the powder are not homogeneous for all the different samples, which could lead to the first printed sample (B1/C1) to have different properties from the last printed sample (B10/C10).

Finally, ODS steel and Eurofer97 samples also show a different response to etching. The visibility of the AM induced structures is considerably stronger in the C-series specimens, for all of the analyzed processing conditions. This can be a result of the different properties of the powders, as the C-series powder had a considerably larger powder size, or a consequence of the different composition. The latter can be further separated into two possible reasons: the effect on the chemical susceptibility of the surrounding metal matrix might be a result of the presence of Yttria nanoparticles or of the formation of complex Y-Fe-O oxides or other iron-yttrium phases [36], [37].
Results and discussion - Melt pools and layers

Since a likely theory concerning the introduction of oxide powders during mechanical alloying sees the Yttria (Y$_2$O$_3$) molecule dissolving in the metal matrix as its single atoms, it cannot be excluded that their presence could lead to the formation of phases that change the behavior of the sample. Further studies to extrapolate the reason for these differences are beyond the scope of this study.

Overall, the melt pool average size appears to be unchanging across all regions in the sample, except for the sides of the print, which in some samples show a slightly larger and more regular melt pool size. The melt pools themselves show non-negligible variation, with some being several times larger than the others, as pointed out by the red arrows in Figure 27. In some areas, the melt pool structure is lost, and only a large band can be seen, stretching perpendicular to the printing direction and with no clear distinction of individual pools, as pointed out by the yellow arrow in Figure 27. This phenomenon is commonly seen across all the samples. A possible reason for this lies in the large spread in the particle size distribution of the initial powder: differently sized powder aggregates are likely to give rise to differently sized melt formations during the fabrication process. To correct this behavior, it could be proposed better control the milled powder processing, utilizing multiple sieving steps to reduce the spread of sizes in the powder particles, such as by sieving away particles deemed too small for the SLM process while also using finer sieves in the to reduce the maximum size allowed. It is necessary to consider that such a process would come at the cost of a lower yield of powder, reducing the overall efficiency of the process significantly. Another possibility is that the area below the melt pool currently forming experiences itself some partial or complete re-melting, which leads to the loss of its characteristic structure.

Figure 27: Close up of melt pools of sample C4, showing different morphology and sizes.
III. Results and discussion - Melt pools and layers

Figure 28: Layer thickness trend with energy density.

A quantitative analysis of the AM structures is reported in Figure 28 and Figure 29. The data points are representative of the samples, in order of energy density, i.e. B5→B6→B7→B8→B4 (same order for the C-series samples).

Overall, the layer thickness appear to agree with the value set during the fabrication process. Although the individual layers appear to vary in size across their length and even if the melt pools tend to span areas larger than the layer thickness, it is still possible to identify traces belonging to adjacent layers. The individual traces do not strictly correspond to the preset 40 µm value, but over a large portion of the sample, the result average to the expected value. The difference in thickness of the individual layers can be seen at the very top and bottom of the samples, where there is no averaging. Sample B7 shows a non-negligible deviation from the set parameter, but this is most likely caused by the poor visibility of the layers in this specimen, rather than being interpreted as an actually occurring difference.
The melt pool size behaves similarly to the heat-affected size of the layers with increasing energy density. The Eurofer97 steel samples show a roughly linear increase in the radius of the structures, as expected with increased energy deposition into the powder. The ODS steel samples, however, show an erratic behavior, maintaining a hint of the size increase, but without clear consistency between adjacent data points. Sample B7 in particular, shows a decrease of the melt pool size compared to sample B6, which is completely different from what is seen for samples C7 and C6. As these are the samples containing dispersed Yttria in the powder, it is possible that the presence of the different phase is at the root of the inconsistency; however, the mechanism inducing this variation is unclear. Another possible cause lies in the different properties of the initial powders, as the ODS steel powder has smaller particle size and slightly higher angle of repose. However, this variation is best suited to explain the overall larger melt pool radii for the ODS steel samples compared to the reference steel ones. The change in the stacking of powders with different mean particle sizes and flowability could be leading to different conditions in the formation and propagation of the melt under laser heating. In particular, smaller particles could more easily be incorporated into the forming melt, which enables a larger pool size.

The most likely explanation for the incoherent trend of the ODS steel samples is likely to be found in the different response to etching. The C-series sample show very clearly and homogeneously the presence of well-defined melt pools, whereas it takes more effort to identify them in the B-series samples. If specific size-classes of the melt structures are more
prone to identification after etching, it is possible that the results are affected by a bias towards the most visible ones, which may not be completely representative of the average, as the ODS steel samples do not show a homogeneous distribution of well-defined melt pools.

Table 4: Complete results of the AM structure analysis, focusing on the thickness of the layers and the radii of the melt pools as characteristic properties of their size. The samples are ordered by increasing energy density.

<table>
<thead>
<tr>
<th>Energy density</th>
<th>Avg. layer</th>
<th>Avg. melt pool</th>
<th>Avg. layer</th>
<th>Avg. melt pool</th>
</tr>
</thead>
<tbody>
<tr>
<td>B5</td>
<td>C5</td>
<td>75</td>
<td>37.95</td>
<td>91.27 ± 18.36</td>
</tr>
<tr>
<td>B6</td>
<td>C6</td>
<td>100</td>
<td>38.84</td>
<td>102.51 ± 11.28</td>
</tr>
<tr>
<td>B7</td>
<td>C7</td>
<td>125</td>
<td>39.71</td>
<td>92.73 ± 17.59</td>
</tr>
<tr>
<td>B8</td>
<td>C8</td>
<td>171</td>
<td>40.17</td>
<td>150.92 ± 53.33</td>
</tr>
<tr>
<td>B4</td>
<td>C4</td>
<td>200</td>
<td>37.68</td>
<td>146.89 ± 52.27</td>
</tr>
</tbody>
</table>

Table 5: Samples dimensions in X, Y and Z and energy densities; the Z direction is the printing direction.

<table>
<thead>
<tr>
<th>Energy density</th>
<th>Dimensions [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[J/mm³]</td>
<td>X</td>
</tr>
<tr>
<td>B1</td>
<td>88</td>
</tr>
<tr>
<td>B2</td>
<td>100</td>
</tr>
<tr>
<td>B3</td>
<td>146</td>
</tr>
<tr>
<td>B4</td>
<td>200</td>
</tr>
<tr>
<td>B5</td>
<td>75</td>
</tr>
<tr>
<td>B6</td>
<td>100</td>
</tr>
<tr>
<td>B7</td>
<td>125</td>
</tr>
<tr>
<td>B8</td>
<td>171</td>
</tr>
<tr>
<td>B9</td>
<td>109</td>
</tr>
<tr>
<td>B10</td>
<td>94</td>
</tr>
</tbody>
</table>

On a final note, the morphology of the melt pool cross section appears mostly circular, which allows the use of the radius to characterize the average size. However, there are instances of flattened or elongated structures, especially near the edges of the sample and towards the side where the non-molten powder is present. Most likely, it is easier for the melt to propagate and pick up small, untouched powder particles than to affect the already solidified previous melt pool, which promotes the elongation in one direction while inhibiting growth in the other. This behavior can be seen also in the lateral dimensions of the ODS steel specimens, which appear to grow larger as the energy density increases. The vertical dimension does not show the same trend.
Microstructure analysis

The chemical etching with V2A solution and the electrochemical one with Oxalic acid allowed revealing the microstructure of the samples. The analysis was carried out using the image analysis software ImageJ, while the grain size measurements were performed with the Hilliard single-circle procedure, according to the ASTM E112 standard [38].

Figure 30: From left to right, top to bottom: sample B4, etched with V2A; sample B5, etched with V2A; sample B6, etched with V2A; sample B7, jet electropolished with a 5.5% perchloric acid solution in methanol; sample B8, electrochemically etched with a 10% Oxalic acid solution in water.

The appearance of the grains and their morphology varies strongly based on many factors, such as their position in the sample or their position in the melt pool or even the conditions
of the areas neighbouring analyzed melt pool. Due to the strong temperature gradients, the continuous re-heating or even re-melting of material when building the following layers and the difference in average temperature of the substrate as the printing process continues, the sample’s microstructure is not expected to be isotropic. In particular, it is very common for metals produced with AM to show characteristic elongated grains that are parallel to the direction of the temperature gradient, i.e. they point from the outside towards the center of the melt pool [39]. Because of the high cooling rates, it is also expected for the specimens to be fine-grained and for the phase structure to show unexpected characteristics, such as a mixture of austenitic, ferritic and martensitic phases. Residual stresses are also commonly found in the as-printed samples, therefore a thermal treatment of the sample is often applied to recover the stresses and stabilize the phases and the microstructure.

Similarly to the case of the visibility of the melt pools, the etching process appears to have reached different degrees of success in the different samples. The V2A solution appeared optimal to reveal the grains, especially in the low energy density samples, but its efficacy dwindles with some of the high energy density samples. The oxalic acid electrochemical etching process was effective in revealing the grains, but it also induced strong pitting in some regions of the samples, where the structural information was lost. Finally, samples B5 and B7 response to the jet electropolishing process for the TEM sample preparation allowed the clear identification of the grains as well.

Table 6: Average grain size for five ODS steel samples and the five reference steel samples corresponding to the same fabrication process parameters.

<table>
<thead>
<tr>
<th>ODS Sample</th>
<th>Avg. grain size [nm]</th>
<th>EUROFER97 Sample</th>
<th>Avg. grain size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B4</td>
<td>951.5 ± 382.4</td>
<td>C4</td>
<td>850.4 ± 77.6</td>
</tr>
<tr>
<td>B5</td>
<td>537.7 ± 95.29</td>
<td>C5</td>
<td>816.1 ± 209.8</td>
</tr>
<tr>
<td>B6</td>
<td>851.8 ± 310.9</td>
<td>C6</td>
<td>1328.9 ± 510.5</td>
</tr>
<tr>
<td>B7</td>
<td>809.0 ± 250.0</td>
<td>C7</td>
<td>873.2 ± 187.5</td>
</tr>
<tr>
<td>B8</td>
<td>1097.1 ± 225.3</td>
<td>C8</td>
<td>1180.4 ± 156.9</td>
</tr>
</tbody>
</table>

Overall, it is quite easy to see the elongated grains in samples B5, C5 and B7, whereas for the other samples the grains appear to have a shape closer to equiaxed. Both of these types of morphology are expected in a sample produced via laser melting. The edge of the melt pool, which experiences the strongest thermal gradients, often presents an elongated structure, whereas the center of the sample tends to shift towards a more regular shape.

It is apparent that the thermodynamic conditions during the cooling are strongly connected to the microstructure formed. An example in favor of this, by a specific region of sample B5, where the formation of a melt pool appears to have produced a contraction of the material, which inhibited full contact with the already solidified substrate. The porous layer most likely acted as thermal isolation, preventing the fast cool down experienced by the other melt
III. Results and discussion - Microstructure analysis

pools. As a result, the grains appear equiaxed and their average size of 1237.7 nm is considerably larger than that of the rest of the sample, 537.7 nm.

Another example of cooling conditions influencing the development of the grains can be seen by comparing the size of grains in different regions of the sample. The continuous melting process, occurring at the top of the sample as it builds, leads to more and more heat spreading into the system. This in turn leads to an increase of average temperature of the sample as the printing progresses, not only because more heat is transferred, but also because, as the sample gets thicker, it becomes increasingly harder for the substrate heat sink to dissipate it at the same rate.

In Figure 32, sample B6 clearly shows this increased grain size. While the average grain size is 851.8 nm, in the top portion of the sample it increases to 1302.3 nm. The shape of the grains does not appear to change considerably, although a clear separation between the equiaxed and elongated grains cannot be confirmed, neither in the top of the sample or in the bulk. The majority of the spots visible in this picture are from pits created during electrochemical etching, which resemble round particles with the InLens imaging mode, but some of them are actually particulate laying on the surface of the sample. The characteristics of this particulate are explored in the Nanoparticle Analysis section.
Figure 32: Morphology and size of the grains in the top portion of sample B6. The grains are considerably larger than the average size in the bulk of the sample. The dark spots are carbon stains, possibly induced by the solvents used to remove the etching solution or by an accumulation of the contrast agent used in the etching process.

Figure 33: On the left, equiaxed grains in the C5 sample; on the right, columnar grains. The sample is aligned so that the printing direction is exactly vertical, thus the columnar grains are differently oriented.
Figure 34: Micrograph of a melt pool from edge to center (indicated by the red lines). The elongated structure follows the full development of the melt pool, some spanning more than half of the full length.

It is worth exploring in greater detail the microstructure present in sample C5, as it presents the clearest view on the formations typical of AM. The equiaxed grains are considerably smaller, on average, compared to the columnar ones. The two types do not cover equal portions of the surface, rather the elongated structures are significantly more numerous. In some melt pools, no equiaxed grain formation can be identified, whereas it is possible for the elongated grains to extend from the edge of a melt pool to the border of the next one. This may be caused by the continuous remelting process: in the previous section, it was reported that the melt pools are larger than the thickness of the layers, which means that in the bulk of the sample, only the outer portion of the melt pools will be visible. The center of the newest melt pool lies at the top of the newest layer, hence, when the subsequent layers are created, it will be melted again, becoming the edge of the new melt pool. This also has the effect of transforming the previously equiaxed grains into elongated ones.
Some of the columnar grains of sample C5 show curved grain boundaries, obtaining a shape reminiscent of hourglassing or bambooing. In some regions, the effect is strong enough to connect the opposing GBs, actively producing a segmentation of the whole grain. It is not clear what kind of conditions are causing this peculiar shape, as most of the other elongated grains in the sample show roughly straight GBs. One possible scenario sees the bamboo-shaped grains starting out not as columnar grains that undergo segmentation, but as the result of growth of equiaxed grains in a preferential direction. Due to the reheating of the sample, it is possible for grains, which have already formed fully in a previous solidification step, to experience growth again and to connect, creating a thinner juncture point. This would produce an hourglass-shaped grain, which, with the same process, could grow into a bamboo-shaped grain.

The grains do not always appear to be single crystal structures. In some occasions, as shown in Figure 36, it was possible to see an irregular sub-grain structure in the columnar grains. The size is approximately in the order of 200 nm, while the shape is approximately equiaxed, though they appear to be aligned in the direction of the elongation of the grain containing them. The presence of nanosized grains, or sub-grain structures, was also theorized for ODS steel sample B8, as during TEM analysis, an polycrystalline, almost powder-like, electron diffraction pattern was acquired, strongly hinting at the presence of superimposed ordered structures even in a relatively thin region.
III. Results and discussion - Porosity

![Sub-grain structure in an elongated grain of sample B10.](image)

**Figure 36: Sub-grain structure in an elongated grain of sample B10.**

Porosity

An analysis of the porosity of the samples has been performed. For this purpose, images of the polished surfaces have been used in order to quantify the percentage covered by the pores. The image analysis software ImageJ has been used to calculate the percentage. This method is very effective in assessing the porosity shown by the single surface of the sample, but, in this study, the distribution of the pores is not assumed homogenous, thus the single surface porosity cannot be assumed representative of the conditions of the whole specimen. Most of the polished surfaces have undergone cutting with a diamond wire saw, grinding and polishing before the assessment of the porosity.

The density for the base Eurofer97 steel is reported in literature between 7.75 g/cm$^3$ and 7.79 g/cm$^3$, with a postulated theoretical density of 7.82 g/cm$^3$ [40][41][42].

The densities reported in this study (see Figure 14) are on the low end of the reported range, albeit the uncertainty of the Archimedes’ principle density measurement is ~1%; it also appears that for the ODS steel sample, a lower porosity is present compared to the reference Eurofer97 steel. This result is consistent with the density measurements executed at EMPA. The cause of this difference is attributed to a difference in the characteristics of the starting
powders, which can easily lead to changes in the packing of the particles and in overall different thermodynamic development of the system.

Table 7: Porosity of all the analyzed samples.

<table>
<thead>
<tr>
<th>ODS Sample</th>
<th>Avg. porosity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>0.12</td>
</tr>
<tr>
<td>B2</td>
<td>0.35</td>
</tr>
<tr>
<td>B3</td>
<td>0.52</td>
</tr>
<tr>
<td>B4</td>
<td>0.72</td>
</tr>
<tr>
<td>B5</td>
<td>0.96</td>
</tr>
<tr>
<td>B6</td>
<td>0.47</td>
</tr>
<tr>
<td>B7</td>
<td>0.32</td>
</tr>
<tr>
<td>B8</td>
<td>0.97</td>
</tr>
<tr>
<td>B9</td>
<td>0.20</td>
</tr>
<tr>
<td>B10</td>
<td>1.37</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>EUROFER97 Sample</th>
<th>Avg. porosity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B4</td>
<td>0.72</td>
</tr>
<tr>
<td>C4</td>
<td>1.79</td>
</tr>
<tr>
<td>B5</td>
<td>0.96</td>
</tr>
<tr>
<td>C5</td>
<td>1.57</td>
</tr>
<tr>
<td>B6</td>
<td>0.47</td>
</tr>
<tr>
<td>C6</td>
<td>1.32</td>
</tr>
<tr>
<td>B7</td>
<td>0.32</td>
</tr>
<tr>
<td>C7</td>
<td>2.13</td>
</tr>
<tr>
<td>B8</td>
<td>0.97</td>
</tr>
<tr>
<td>C8</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Figure 37: Overview of the porosity of four B-series ODS steel samples: B5 (top left), B6 (top right), B7 (bottom left) and B8 (bottom right).
III. Results and discussion - Porosity

The porosity of the B-series samples appears to be quite low, as it stays consistently below 1%, aside from one sample. The pores appear to have regular shapes, with no sharp edges, and most of them are roughly circular. These could have formed due to the trapping of a gas bubble. Other pores are oriented in a semicircle or in a crescent moon shape, where a more or less visible circular portion of the sample is bulging into the pore. These pores may be caused by contraction of the powder contraction of the powder when the melt forms, which could inhibit complete cohesion of two adjacent layers of material. These pore shape is typical for samples produced with laser melting.

Generally, SLM is credited with the ability to produce high-density samples with low degrees of porosity, hence some calculated porosities exceed the expectations. In particular, two samples, namely sample B5 and B10, show very high uncertainty in the measurement: this is a result of very high porosity localized in specific regions of the specimen, while in other areas the specimen appears very compact. Some of this large pores show typical morphology for metals produced via AM, whereas other pores, do not show a connection to the surrounding macrostructures, thus other creation processes must be postulated. As an example, the large pore in the lower left corner of picture of sample B5 (see Figure 39) does not appear to occur in the interface between one layer and the following one, which is the expected position: in fact, judging by its dimensions alone, it is obvious that it spans multiple
layers and melt pools. However, other pores in the same image appear to be consistent with the AM structures, showing the melt pool and the incomplete attachment to the substrate.

The metallographic preparation steps for these samples require the use of a diamond wire saw and of mechanical grinding with SiC grinding paper. Both of these methods actively remove material, which is visible during both procedures, from the surface of the sample and leave the polished side in a mechanically deformed state. A hypothesis is formulated: it is possible to have an ineffective melting process, which could lead to a localized region having very weak cohesion with the surrounding metal, leaving very susceptible to being removed during rough mechanical treatments, such as cutting and high-grit size grinding. Theoretically, this could lead to the formation of very large holes, not necessarily coherent with the structure of the melt. To explore this possibility further, LOM images of the other side of the cut portion of sample B5 have been examined.

![Figure 39: On the left, polished side of the cut of sample B5; on the right, as-cut surface of the opposite side of the cut. The holes are in mirrored positions, as expected of the two faces of the cut.](image)

In Figure 39, it is possible to see the two sides of the cut. In the same quadrant of the sample, on the two sides, two large pore formations appear, but the distance between the two is not the same in the two images. The cause of this could be the non-negligible amount of material that has been removed between the two, both from grinding and from the diamond wire, which has a measured thickness between 250 µm and 300 µm. Regardless, it is possible to connect the pore-surrounded melt pool in the two images, as the melt pool structure is already clearly visible.

In order to confirm whether these large pores are produced during the manufacturing process or from the metallographic preparations, a study of the evolution of the pores in depth is carried out. The starting point is the highly porous surface of the cut piece of sample B5. The sample is ground down until 200 µm are removed from the surface and images are taken every 50 µm to assess the condition of the pores.
The results show that the pores develop gradually at this step size. Some of the pores open up, which could be cause either by preexisting voids or by the grinding action on the surface. Some other pores, however, appear to be gradually closing down, strongly suggesting that they were already present after the fabrication steps.

Because of the presence of these localized large pores, the uncertainty of the porosity values of these samples is substantially higher than the rest of the sample. As the distribution and size of the pores are clearly not homogenous across one or multiple surface, the porosity result cannot be considered representative of the conditions of the entire sample.
Nonetheless, it is possible to hypothesize that the conditions of the printing might vary strongly during the process, leading to strong differences in different portions of the sample. For these reasons, different techniques should be employed to assess the complete porosity, such as a complete X-ray tomography of the sample or of a portion that can be deemed representative of the whole object.

**XRD analysis**

Synchrotron x-ray diffraction has been employed to characterize the phases present into this sample. It has been reported that several ferrous phases can be found in samples produced via AM, with austenite and ferrite being present even when a fully austenitic phase would be expected based on the alloying elements [43]. The reason for this lies in the very quick transition from a solid powder to a melt and finally again to solid metal, which does not allow the metal matrix enough time for the phases to stabilize. For these samples, the base metal matrix is the Eurofer97, a RAFM steel, for which the prevalent microstructure should be BCC α-ferrite.

![Image of a sample used in XRD analysis](image)

*Figure 41: Vicinity of the hole the TEM-ready B5 sample used in XRD analysis. The hole is positioned right in the middle of one of the melt pools.*

One of the B5 samples prepared for TEM was used in the XRD analysis. This ODS sample is the one for which the melt pool structure in the vicinity of the hole was clearest, which would allow for a complete phase characterization through the whole span of a melt pool. Two acquisitions were made, with different sizes and steps. The resulting intensity maps can be found in the Appendix. Some of the acquired 1D XRD spectra have been compared with those reported in the ICSD of the Karlsruhe Institute of Technology (KIT) for
Austenite (ICSD #76800), α-ferrite (ICSD #634069), martensite (ICSD #9860), (acquired at a temperature of 70°), cementite (ICSD #30256), and crystalline Yttria (ICSD #23811), [44]–[48].

The 1D XRD spectrum reported in Figure 42. Here the prevalence of α-ferrite in the system can be seen very clearly, based on the complete correspondence of the peaks. Austenite does not appear strongly in this specific location; the shoulder of the large ferrite peak around 20° could be cause either by diffraction on austenite, martensite or cementite. Based on the rest of the peaks and on other acquired spectra, such as in Figure 43, it is deemed very likely for austenite to be present, whereas there is little correlation between the ODS steel peaks and those of martensite throughout the whole spectrum. In the 20° to 30° range, the signal is reminiscent of that of cementite. Due to the large presence of α-ferrite, the weak presence of austenite and the inconclusive information regarding martensite, it is expected that, during the solidification process, the diffusion of carbon would have been...
successful in forming a certain amount of Fe$_3$C$_4$. Finally, the peak structure below the 20° scattering angle can be weakly linked to the diffraction pattern of crystalline Yttria, especially for the (2,1,1) diffraction peak, hence indicating that there is at least a portion of the ODS particles which possess an ordered structure rather than an amorphous one. Nonetheless, the signal is weak and not entirely coherent with the intensities of the peaks reported in literature, hence it cannot be excluded that their origin may lie in other unexpected phases. The overlapping between the Yttria and cementite peaks in the 20° to 30° range is also detrimental to the correct identification of the actual structure of the material.

![Figure 43: Other example of an XRD spectrum of B-series ODS steel superimposed to the spectra of possible present phases. The presence of austenite is very clear in this acquisition, as there is a complete correspondence between the peaks of ODS steel and those of the reported austenite phase.](image)

**Nanoparticle characterization**

Two of the main properties defining the quality and performance of ODS steels are the size of the nanoprecipitates and their density. Overall, finer and more numerous particles are conducive to better properties. Usual results for experimental ODS steels show an average around and below 5 nm and a density of fine nanoparticles above $10^{23}$ particles per cubic
III. Results and discussion - Nanoparticle characterization

Some studies also report the presence of diverse size classes for the precipitates, highlighting the presence of particles both very small, below 10 nm in diameter, and very large, over 50 nm [49]. This gives rise to the speculation that different types of particles may be forming, with different average sizes and distribution behaviors. It is known that the addition of dopants can influence the type of particles that form. In particular, the refining effect of titanium on the oxide clusters [51] has often been subject of study and it is considered the most promising candidate as dopant to reach the desired high number density and small particles size.

The analysis of the particles has been performed through SEM, TEM and low-resolution STEM. The size and distribution visible for each of these techniques is confined by their specific detection limit. Two classes of visible particles are analyzed: above and below 10 nm, in accordance with what can be seen with the aforementioned microscopy techniques. The average size of the visible particles is reported in Table 8.

Table 8: Average size of the visible nanoparticles for the ODS steel samples. The results are shown for the two separate class sizes.

<table>
<thead>
<tr>
<th>ODS Sample</th>
<th>Above 10 nm Nanoparticle avg. diameter [nm]</th>
<th>Below 10 nm Nanoparticle avg. diameter [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>60.15</td>
<td>6.61&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>B2</td>
<td>63.02</td>
<td>1.12&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>B3</td>
<td>54.14</td>
<td>5.99&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>B4</td>
<td>64.15</td>
<td>1.86&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>B5</td>
<td>98.68</td>
<td>4.58&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>B6</td>
<td>49.31</td>
<td></td>
</tr>
<tr>
<td>B7</td>
<td>58.34</td>
<td></td>
</tr>
<tr>
<td>B8</td>
<td>41.17</td>
<td></td>
</tr>
<tr>
<td>B9</td>
<td>50.43</td>
<td></td>
</tr>
<tr>
<td>B10</td>
<td>63.22</td>
<td></td>
</tr>
</tbody>
</table>

<sup>1</sup> Obtained with STEM.<br><sup>2</sup> Obtained with TEM.

Overall, the size of the particles cannot be correlated with the manufacturing parameters, as no clear trend can be identified that links these values with the scanning speed, the laser power or the energy density. However, it can be said that the smallest particle size is found in a high energy density sample (B8, 171 J/mm³), while the highest is found in the lowest energy density one (B5, 75 J/mm³).
Morphologically, most of the particles appear to be spherical, but there are some that show very well-defined octahedral shape, which is consistent with the expected crystalline structure of Yttria. Occurrences of strongly elongated particles can also be found in these samples. The crystalline structure is only seen for the larger particles, whereas for the very small ones the morphology is always spherical. These characteristics indicate that some particles may form as crystalline, whereas others may be polycrystalline or even amorphous or even that entirely different processes lead to the production of these different types.

The composition of these particles has been identified as containing Yttrium, Oxygen and a depletion in the Iron content, although this is not always the case for the smaller particles,
as the electron beam and the x-ray are penetrating enough to carry information regarding the iron matrix below the particles. Furthermore, due to the drift issues, it was not possible to perform long acquisitions that would result in more complete information and better contrast between the particle and the substrate. A typical EDSX acquisition spectrum can be seen in Figure 46.

This spectrum shows very clearly the peaks for Fe, C, Cr (the peak right before Fe) and O. The Y and the W peaks can be seen, respectively, at 1.922 keV and at 1.774 keV. The peaks of the alloying elements are commonly and definitively identifiable throughout all of the acquisitions, whereas Y usually appears as a weaker signal, at times completely overtaken by the spread around the W peak.
During the analysis of the reference Eurofer97 steel samples, it was also possible to see some form of precipitate being present in the matrix. The EDSX analysis resulted in the conclusion that these particles are complex Vanadium oxide particles, sometimes also incorporating other alloying elements. It is not surprising to find Vanadium-based precipitates in steel samples containing it, since it is a known and exploited characteristic of this metal, used in steel metallurgy [52]. Nevertheless, it cannot be excluded that the software misinterpreted the signal due to the very close proximity of the characteristic x-ray energy peaks for V and O in the explored energy range, as the Lα peak of V appears at 0.511 KeV, while the Kα peak of O appears at 0.525. Once again, it must be noted that the morphology of this particles is mixed, with some showing an approximately round shape and some others being heavily faceted, possibly crystalline.

The appearance of this Vanadium oxides also prompted the investigation of their presence in ODS steel samples. Indeed, some of the identified oxide particles also show an affinity for V, which is not unheard of in literature [53], while also incorporating C, a typical element involved in the precipitation process of V [52]. The referenced particle can be found in Figure 51.
III. Results and discussion - Nanoparticle characterization

Figure 48: EDXS acquisition of a vanadium oxide particle in sample C5.

Figure 49: Particle damaged during a targeted EDXS acquisition, showing possibly a core-shell structure where the shell is made of low-melting point material.

Another interesting behavior can be observed with respect to the contrast of the oxide particle analyzed with STEM in dark field mode. In dark field, it is typical for solid particles to appear brighter than their surroundings, as by scattering more they generate more signal for the annular detector designed to capture deflected electrons. However, not all of the acquired particles appear brighter, some actually appear darker. A possible explanation could be found in the internal structure of the particle: a crystalline precipitate naturally appears darker in TEM analysis, due to the stronger scattering produced, while an amorphous one would appear featureless, with little contrast compared to the surrounding matrix, and produce little scattering. If this internal structure difference is indeed present it is possible that it might producing the observed deviation from the expected contrast conditions. Another possibility lies in the low voltage of the acquisition: it is possible that due to the low energy of the electrons, they may not be able to propagate through thicker particles, thus they would result dark in the acquisition. Since there is little evidence of a difference in vertical thickness in the observed particles, the former hypothesis is considered more likely than the latter.
Finally, during targeted acquisitions on oxide particles, it is not uncommon to see damage occurring, where a portion of the particle appears to have molten, whereas a central core appears unaffected. This could lead to the idea that the oxide nanoparticles actually form with a core-shell structure, possible with the shell material having a lower melting point with respect to the core material. The shell structure was also observed during TEM acquisitions for some of the oxide particles, with varying thickness across multiple instances. As an affinity for V was already documented, it may be hypothesized that a compound of V and other alloying elements may be forming on the surface, such as Vanadium Pentoxide, which has a remarkably low melting point (690°C) compared to Yttria (2,425 °C).
III. Results and discussion - Nanoparticle characterization

Figure 51: EDXS of two particles found in sample B6, showing varying degrees of presence of Y, O, V, C and Fe.

In many acquisitions, the larger particles do not appear to have a homogenous composition, not only collectively, but also inside the individual particle. In at least one instance, shown in Figure 52, a nanoprecipitate shows an ordered atomic lattice with TEM, with an interatomic spacing of 2.303 Å. The same particle also shows different degrees of contrast in the outer region: this is coherent with the morphology observed in SEM analysis, where some of the larger particles appeared to be missing relatively large chunks after treatment.
with perchloric acid. This can be interpreted as differential etching rates on the same particle, which could be caused by a heterogeneous composition, where one phase appears to be more susceptible to acid attack with perchloric acid. To further analyze the morphology of the dispersoids, FIB tomography coupled with high resolution EDSX could be employed, so as to reconstruct, layer by layer, the full complete composition as well. Another option would be to employ APT, which would also provide information on both morphology and composition.

Figure 52: ODS steel nanoprecipitate showing hints of ordered atomic layers in a visibly self-contained region and differential contrast along the rim.

Finally, the possibility of a different distribution of the particles across a melt pool is considered. During the vertical building of the samples, depending on when the particles actually form during the evolution of the melt, it possible that the lighter Yttria dispersoids (Yttria has a density of 5.01 g/cm³) would naturally relocate towards the center of the melt pool, the most elevated position. If the particles form early and there are no complex fluid-dynamic conditions that would oppose this relocation, then it is expected to see a higher concentration in the center of the melt pool. An example of the presence of these particles across a melt pool is reported in Figure 53. There does not appear to be any change in the
distribution, which leads to two possible conclusions: either the nanodispersoids form during the later stages of the solidification process, thus not in the presence of the melt, through diffusion an recrystallization in the matrix, or the melt is too quick and/or viscous to allow the nanoprecipitates free movement. A complete thermal fluid-dynamic simulation of the melt pool development in the presence of already formed dispersoids could aid in the verification of the latter hypothesis, which, if refuted, would leave only the later formation as possible explanation.

Concerning the particles below 10 nm, the size of the dispersoids does not appear to be influenced by the manufacturing parameters. However, while the density of the larger class of particles is significant, the smaller ones are few, sparse and not characterized in terms of composition, as EDSX with high enough resolution could not be performed. It is also important to mention that the identification has only been carried out through the visual inspection of the TEM and STEM micrographs and a certain degree of uncertainty is present, as the samples are still in as-built conditions, with no thermal treatment applied, thus large a high dislocation density is also visible, complicating the analysis considerably.

Across all of the analyzed samples, regardless of the microscopy technique employed, the results show that the sample with the highest density of small nanodispersoids is B6, at least in the limited regions visible with STEM. The presence of at least a few small precipitates could be confirmed for all of the analyzed samples between B4 and B8. The smallest identified particles expectedly appear in samples B5 and B8, as the resolution limit of the employed TEM exceeds the one of the STEM. Possibly, particles as small as 0.32 nm have been identified in sample B5, however it is also possible that even more powerful microscopy techniques would reveal the presence of even smaller particles, hence the size distribution analysis must be weighted with the detection limit of the specific techniques employed.
An example of the very small particles present in sample B5 is reported in Figure 55. It is possible to clearly see some particles with a diameter of ~1 nm on the edge of the sample, overhanging on the hole produced during the sample preparation. The position of these particles is consistent with the larger particles, which also frequently appear on the edge of the metal (see Figure 52). There are also very small particles in the inner region of the sample, but they are not as visible, as the thickness of the sample and the superimposition over the metal microstructure interfere with the identification. An attempt to assess the particle density in the thin region of sample B5 (as seen in Figure 55) resulted in a value of $6.23 \times 10^{23}$ particles per cubic meter, where a sample thickness of 10 nm was assumed. This assumption comes with large uncertainties, as the thickness of the sample in this region is expected to lie between 10 and 100 nm. An additional uncertainty component is introduced by the superposition with the microstructure, which can easily hide some particles or produce false positive results.

It is suggested that a high-resolution STEM equipped with an EDSX detector be used for further analysis and characterization of the samples, with a specific regard towards identifying definitively the nature of the very small nanodispersoids, to confirm or deny whether they are Yttria-based. The beneficial properties of the nanoparticle distribution is clearly strongly tied to their elemental nature, as otherwise the remarkable temperature and irradiation stability, required for future nuclear installations, would not be guaranteed.

![Figure 54: Sample B6 region showing a high density of small nanoprecipitates in the bottom right portion and a complex dislocation network in the center of the image.](image-url)
III. Results and discussion - Nanoparticle characterization

Figure 55: Sample B5 very thin region, showing on particles on the edge, overhanging on the hole, and a larger particle in an inner region. Some very small particles appear to be visible also in the inner region, but the sample’s thickness and the low resolution hinders the identification. Some of the particles are highlighted with red arrows. Two regions showing presence of very small particles are highlighted in the purple (left) and orange (right) boxes.
IV. **Conclusions and further plans**

The goal of this study was to fabricate Fe-9%Cr ODS steel via mechanical alloying followed by selective laser melting and to explore its characteristics in terms of structures from the solidification process, microstructure and nanoparticle size and distribution. The impact of changes in the manufacturing parameters was also to be explored.

The samples were close to the theoretical density, showing relatively low porosity across all of them, with some isolated instances of large pores, most likely strongly related to the solidification process. A small connection to the printing parameters was found, in that the ODS steel samples showing the highest degree of porosity were also the samples manufactured with the lowest energy density; this trend was not reproduced by the reference samples. However, the limited information a single polished surface can provide has to be taken into account, suggesting that statistical trends or deviations from the expected behavior of the porosity need to be considered as possibly a result of limited statistics. To attempt to determine whether the large pores present in some of the samples originated from the fabrication process or from mechanical treatment, a study of the evolution of the pores in depth was performed. The results are in support of the former hypothesis. To further explore the formation of pores, x-ray tomography of the sample is an option. Since the pores are in the range of tens or even hundreds of micrometers, they should be easily detectable with this technique, and this would also allow to confirm whether the distribution of pores across the sample is homogeneous or not.

The melt pool and layer structure appear quite clearly in all of the samples treated with Oxalic acid and they follow the expected behavior. Although the individual layers do not necessarily conform to the set value of 40 µm per additive step across their full length, their average size still tends towards that value. The melt pools appear to increase in size with increasing energy density for the reference steel samples, but a deviation from this is observed for the ODS steel ones, where the increase in size is present on average but not necessarily from one sample to the next one in energy density. This could be a result of the presence of oxide particles affecting the morphology of the melt pool, although the dispersoids do not appear to be distributed in a way that would inhibit melt formation. It could also be a result of etching being most effective for a specific class of melt pools, possibly showing a specific phase structure that naturally makes it more chemically susceptible to Oxalic acid. Finally, it could be a result of feed quality, as it may happen that during the print of several samples, the quality of the feed in terms of packing density and size distribution is no longer optimal for the print, producing large variations between different regions of the sample.

In terms of microstructure, all of the samples appear to be fine grained, with average grain sizes between 800 and 1200 nm, with the notable exception of sample B5, which appeared
IV. Conclusions and further plans

considerably finer with an average size of 537 nm. The reference steel samples appeared to have slightly larger grain size, which could be a result of the larger feed powder particle size or of the presence of the ODS steel particles, which may hinder grain growth to a certain extent. The typical microstructure of samples produced via AM is observed in these specimens as well. Columnar grains appear in several samples, most of the time at the border of the melt pool, as expected since, during the solidification process, that is the region experiencing the strongest thermal gradients and the highest cooling rates, thus driving the growth of the grains parallel to the direction of the temperature difference. Sharp changes in the inclination of the columnar grains can be observed at the interface between two adjacent melt pools. The equiaxed grains typical of the slower-cooling center of the melt pool do not always appear in the bulk of the sample, as the continuously overlapping melt pools might be reforming them into equiaxed grains in later stages of the printing process. Different regions of the samples show variations grain structure, most of the time consistent with expected differences in the cooling rate. A melt pool, isolated from the previous layer substrate by different pores, shows a considerably larger grain size and exclusively equiaxed grains, as it is likely that the pores created during the melt pool contraction act as thermal insulator, thus preventing the strong thermal gradients and the formation of columnar grains. Grain structure near the upper portion of the sample also appears to be larger, as it forms on a substrate that has been heated repeatedly in the additive building of layers, thus possessing a higher average temperature compared to what all the previous layers experienced. Finally, peculiar hourglass/bamboo shaped grains were observed in sample C5, possible formed as multiple equiaxed grains consolidating as a single one during the continuous reheating or as columnar grains separated in an unidentified thermodynamic process.

With the use of synchrotron XRD, it was possible to identify some likely candidate phases composing the sample. The most evident, as expected, appears to be $\alpha$-ferrite, while there is also a significant content of austenite. The phase ratio appears to vary in different regions of the sample, although it could be a result of different orientation of the samples, but these two are almost always present. Martensite has not been observed in any of the analyzed 1D diffraction spectra, although the considerable overlapping of its peaks with $\alpha$-ferrite peaks could have hidden its presence. Cementite appears to have formed in at least one region of the sample, its complex peak structure appearing in one spectrum. Finally, there is at least one instance of one of the characteristic peaks, specifically the (2,1,1) peak, of the Yttria spectrum appearing in the B-series ODS steel sample spectrum. However, the rest of the most prominent peaks in the Yttria spectrum do not appear, which may be indicating that another unidentified phase with peaks overlapping with Yttria might be present.

The results indicate that a large amount of particles with diameter above 10 nm is present and it appears that they are homogeneously distributed across the sample. Some particles below 10 nm were also identified, although some difficulties arose because of the rich underlying microstructure and the limited resolution of the detector. An attempt has been made to assess the number density of particles below 10 nm but although the results are
promising, they come with very large uncertainties, due to the necessary assumptions made in the calculations. The particle size does not appear to trend in any way with the printing parameters. The morphology of the particles hints towards the possibility of both crystalline and amorphous structure, possibly with different compositions, as EDXS acquisitions resulted in a high concentration of alloying elements at times, together with the expected Y and O. Some of the particles react differently to treatment with perchloric acid and some possess a well-defined core-shell structure, with different nature in terms of composition. Vanadium appears to be a possible element for the shell of the dispersoids, but a false positive result of EDXS cannot be completely excluded due to the proximity of the V and O peaks in the analyzed x-ray energy region. Increasing the energy and time of the acquisitions is suggested, in order to improve the quality of the results and to confirm definitively the complete composition of the particles, provided that the drift related problems can be solved. High-resolution STEM coupled with EDXS is also suggested, to obtain the fullest possible characterization of the sizes of the particles and to characterize the composition of the very small nanodispersoids as well. Introducing Ti as a refining agent to attempt to reduce the size of the oxide particles is also recommended. Finally, FIB tomography could also help explore the possible porous structure and heterogeneous composition that some of the particles show.

Further suggestions to complete the characterization of the samples include mechanical testing and annealing studies. A study of the mechanical properties is imperative, in order to determine the extent of the strengthening effects, compared to the base Eurofer97 steel, induced by the presence of nanoparticles even with samples produced with AM. Due to the state of the samples after this consolidation process, with non-negligible residual stress and dislocation density, annealing is always a required step. A full study of the changes in the mechanical properties with different annealing temperatures, as well as of the size and distribution of the nanodispersoids, to confirm their thermal stability, would be ideal. This would allow to determine the optimized recipe for the complete fabrication of the sample, starting from the mechanical alloying and finishing when the part has reached its nominal properties and it is ready to be employed. Finally, studies of the mechanical properties and the stability of the dispersoids under irradiation might also be conducted, especially in light of the presence of austenite in the matrix, which could lead to swelling of the component regardless of the ferritic composition of the base metal.
Acknowledgements

I would like to thank first my supervisor, Dr. Peter Warnicke, for his helpfulness and constant effort in making many of the envisioned studies a reality. His patience and knowledge during long discussions about the often-unexpected results have been exceptional and invaluable. I would like to thank PD Dr. Manuel A. Pouchon, for sparking the interest in the subject in my mind and for its excellent input and suggestions on the development of the project.

I am grateful to Prof. Dr. Minh Quang Tran, my tutor and professor, for his willingness to supervise this work as well, despite the distance and the many bureaucratic hurdles.

I cannot thank enough Dr. Elisabeth Müller and Dr. Emiliya Poghosyan for their great support in the use of the electron microscopy facilities; with them, the work has been allowed to progress unhindered, and their effort in training and assisting is profoundly appreciated. My only hope is that I have not given them too many troubles and too much strife during my user experience.

I thank Dr. Jia-Chao Chen, Dr. Liliana Duarte, Prof. Dr. Philippe Spätig, Lijuan Cui, Alina Horwege, Hans Kottmann, Roger Brün, Roger Schwenold and Dr. Pascal Grundler for their help in many aspects of this project, in particular regarding the training and help in the use of many of the facilities available at PSI.

Thanks to Dr. Anthony De Luca and Dr. Christian Leinenbach and to EMPA for their collaboration in this project and the information provided about the sample and additive manufacturing in general. It is safe to say that, without them, the project could not have existed.

I want to thank the colleagues of my Master programme for the feeling of camaraderie during these two years of study and for listening to all of my numerous complaints, offering valuable advice in return.

I am deeply grateful to my girlfriend, Claudia Anibaldi, for her unwavering support in this endeavour and for helping me see my worth when I was most in doubt. I hope I can return this help even just half as well.

I thank my family, for supporting me during all my life and here in Switzerland, for helping me endure the long distance from home and for putting their best effort in advising me in the most complicated situations I had to face.

Last, but absolutely not least, I want to thank all my friends from Rome, always present and always cheerful, always pushing me to do the best I can.

Without even just one of the people mentioned, I believe that this work would have been less. I thank you all deeply.
References


References


References


Appendix

Drift study micrographs

Figure 56: 30 min drift for an ODS steel sample mounted on copper tape.

Figure 57: 30 min drift for a clamped ODS steel sample.
Figure 58: 30 min drift for an ODS steel sample mounted on carbon tape.

Figure 59: 40 min drift for an ODS steel sample, which was magnetized in plane, mounted on carbon tape.
XRD transmission and iron content maps

Figure 60: X-ray transmission map recorded at 17.2 keV of the entirety of an instance of sample B5 prepared for TEM, obtained with a 20 µm spacing in between data points.

Figure 61: X-ray transmission map recorded at 17.2 keV of the entirety of an instance of sample B5 prepared for TEM, obtained with a 2 µm spacing in between data points.
Figure 62: X-ray fluorescence map of Fe Kα at 17.2 keV of the entirety of an instance of sample B5 prepared for TEM, obtained with a 2 µm spacing in between data points.