Local structure and composition

in additively manufactured bulk metallic glasses and composites

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Abstract

Additive manufacturing enables the production of complex multi-material geometries and bulk metallic glass parts beyond their critical casting thickness. The local modification of structure, composition, and properties is explored in this thesis with the aim to design novel composite materials and functional gradients. The present work contributes to the process understanding required to produce bulk metallic glass composites in the laser powder bed fusion process. The investigated material systems include zirconium and iron based metallic glasses, metallic glass - nitride composites, as well as laser nitriding of titanium.

The onset of devitrification of metallic glasses due to the processing or post-processing heat treatments induces the formation of nanoscale clusters. Features of > 1 nm can be detected and reliably distinguished from random fluctuations by atom probe tomography. The progression of crystallisation depends on the oxygen content of the samples and the applied heating or cooling rates. In-depth understanding of the crystallisation processes can be used to optimise both compositions and processing conditions. The process atmosphere contains reactive species such as oxygen or nitrogen, which can be incorporated during different stages of processing by surface oxidation of the powder or substrate pieces as well as by reactions with the gas during processing. While an inert gas atmosphere with a low residual oxygen content is sufficient to hinder reactions with residual oxygen, a nitrogen atmosphere can be used for local laser nitriding and, thus, the fabrication of metallic glass – ceramic composites. Due to the decompositions of nitrides formed in the preceding process steps and the tendency of a metallic glass matrix to crystallise, which limits the processing conditions, the incorporation of nitrogen is restricted to the first few hundred nm from the surface for a Zr-based amorphous alloy. In titanium, as a crystalline example, nitrogen is incorporated throughout the molten pool.

The nitride composites exhibit increased hardness depending on the local nitride fraction, which can thus be used to fabricate specific property gradients within or on a printed piece. With optimised process parameters, the amorphous fraction of a printed Fe-based bulk metallic glass can be tailored for improved soft magnetic properties.

Keywords: additive manufacturing, bulk metallic glasses, nanoscale clustering, convective flow, laser nitriding, laser powder bed fusion, metallic glass - ceramic composites, oxygen impurities, mechanical properties, magnetic properties, viscosity

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I’d learned quite a lot, over the years, by avoiding what I was supposed to be learning

Margaret Atwood
(Moral Disorder)
# Contents

Abstract ........................................................................................................... ii

Contents ......................................................................................................... v

List of publications .................................................................................... vii

1 Introduction ............................................................................................ 1

2 Devitrification of metallic glasses .......................................................... 5
   2.1 Nanoscale cluster identification (paper I) ........................................... 6
   2.2 Rapid crystallisation (paper VII, unpublished) ............................... 9

3 Control of composition .......................................................................... 11
   3.1 Oxygen impurity incorporation (paper II) ....................................... 12
   3.2 In-situ laser nitriding (papers III, IV) .............................................. 14

4 Properties and tailoring ......................................................................... 17
   4.1 Viscosity - from fragile to strong (paper V) .................................... 19
   4.2 Mechanical properties of composites (papers III, IV) .................... 20
   4.3 Magnetic properties - from powder to printed (paper VI) . 22

5 Conclusions and outlook ........................................................................ 25

6 Materials and methods .......................................................................... 27
   6.1 Sample preparation ........................................................................ 27
   6.2 Characterisation ............................................................................... 28
   6.3 Sample description .......................................................................... 30

7 Popular scientific summary ...................................................................... 33

8 Acknowledgements ................................................................................... 35

Bibliography .............................................................................................. 37

Acronyms ..................................................................................................... 44
This thesis is based on the following papers:

I  Nanoscale clustering in an additively manufactured Zr-based metallic glass evaluated by atom probe tomography
   Inga K. Goetz, Janis A. Sälker, Marcus Hans, Björgvin Hjörvarsson, and Jochen M. Schneider
   Under review at: Materials & Design

II Convective flow redistribution of oxygen by laser melting of a Zr-based amorphous alloy
   Inga K. Goetz, Victor Pacheco, Carl J. Hassila, Ulf Jansson, Jochen M. Schneider, and Marcus Hans
   Submitted to: Scientific Reports

III Reactive metal additive manufacturing: Surface-near ZrN - metallic glass composite formation and mechanical properties
   Inga K. Goetz, Maciej Kaplan, Marcus Hans, Petter Ström, Ulf Jansson, Björgvin Hjörvarsson, and Jochen M. Schneider
   Under review at: Additive Manufacturing

IV Sequential nitriding depth profiles in titanium, obtained under reactive additive manufacturing conditions
   Inga K. Goetz, Marcus Hans, Ulf Jansson, Björgvin Hjörvarsson, and Jochen M. Schneider
   Manuscript

V Viscosity of metallic glass-forming liquids based on Zr by fast-scanning calorimetry
   Raschid Al-Mukadam, Inga K. Götz, Moritz Stolpe, and Joachim Deubener
   Acta Materialia 221, 117370 (2021) (reprint: accepted ms.)
VI Laser powder bed fusion process development and magnetic contrasting of the magnetic domains and melt pool characteristics in a Fe-based bulk metallic glass
Julia Löfstrand, Inga K. Goetz, Jithin James Marattukalam, Björgvin Hjörvarsson, Björn Skårman, Zhou Ye, Martin Sahlberg, Petra E. Jönsson
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VII High resolution measurements and modelling of ultra-fast crystallisation kinetics in Zr-based metallic glass with added oxygen
Mattias Tidefelt, Julia Löfstrand, Inga K. Goetz, Anders Ericsson, Xiaoliang Han, Petra E. Jönsson, Martin Sahlberg, Ivan Kaban, Martin Fisk
Manuscript

VIII Transforming laboratory experiments for digital teaching: remote access laboratories in thermodynamics
Matthias Weiszflog and Inga K. Goetz
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**Contribution statement**

My contribution to each paper is briefly described below:

I  I planned the investigation, participated in parts of the atom probe tomography (APT) measurements at RWTH Aachen, and had the main responsibility for the manuscript.

II I planned the investigation and carried out the experiments together with Victor Pacheco and Marcus Hans. I had the main responsibility for the manuscript.

III I planned the investigation and planned and carried out most experiments. I participated in the time-of-flight elastic recoil detection analysis (ToF-ERDA) and nanoindentation measurements and had the main responsibility for the manuscript.

IV I planned the investigation, fabricated the samples, carried out the initial characterisation, and participated in parts of the advanced characterisation. I had the main responsibility for the manuscript.

V I planned the initial investigation, participated in parts of the fast-scanning (flash) differential scanning calorimetry (FDSC) measurements at TU Clausthal and had the main responsibility for the introduction section of the manuscript.

VI I planned the investigation together with the co-authors. I participated in the process parameter development, fabricated the single tracks, and carried out parts of the characterisation. I took part in structuring and writing the manuscript.
Crystallinity infers a periodic arrangement of the constituent elements leading to long range order in addition to the local order, which is already present in the liquid state [1]. Solid materials are traditionally linked to crystalline materials. Notwithstanding this common ascription of solid to ordered, disordered materials, lacking long-range periodicity, are vested in nature and technology [2], for example, volcanic glasses, polymers, window glasses, and amorphous silicon solar cells. Glasses exhibit the near-infinite viscosity of solids but the absence of long range order and resulting isotropic properties typical for liquids [1].

The production chains for many material systems have been influenced by the advances in 3D printing, more formally referred to as additive manufacturing (AM). The new techniques have changed production pathways in industry and enabled new geometries, designs, and rapid prototyping [3]. For the production of metal components, laser powder bed fusion (LPBF) is one of the most common technologies for AM [3]. The basic operation of such a process is the laser scanning and local melting of one powder layer in a specified pattern to form one slice of the desired component. Subsequently, the next powder layer is spread on top, and the process is repeated until the specified component has been built up layer-by-layer. Beyond implications for component design, this approach enables the processing of bulk metallic glass (BMG) compositions, for which more traditional routes like casting and melt spinning impose severe limitations on the attainable geometries [4]. Prior to processing with AM, the fabrication of BMG parts was limited to geometries for which overall sufficiently high cooling rates could be attained. For many technologically promising compositions, this, in effect, limited the producible geometries to thin ribbons or sheets. In parallel to the rapid development of AM, the research into metallic glass (MG) transformed from a small research field to production and technological application [1] for example as structural and magnetic materials [5].
From a thermodynamic perspective, the glassy or vitreous state of a material can be described as a frozen in, under-cooled liquid. According to this definition, glasses can be described as non-equilibrium solids, as visualised in Figure 1.1a. When cooling a melt with a sufficiently high cooling rate, a metastable melt is attained in the temperature range between the glass transition temperature ($T_g$) and the melting temperature ($T_m$) instead of observing crystallisation at $T_m$. The viscosity of the supercooled liquid increases further upon cooling so that the atomic rearrangement in the liquid slows down with decreasing temperature [2]. At $T_g$, the metastable liquid is kinetically frozen in, the time-scale of the atomic rearrangements drops below the observable time-scales. $T_g$ depends on the cooling rate, as a lower cooling rate allows the material to stay in the supercooled liquid state down to lower temperatures [2]. This is visualised by a time-temperature-transformation (TTT) diagram (Figure 1.1b). The slowest sufficient cooling rate to quench a glass without crystallisation is denoted as the critical cooling rate (CCR). The cooling rates in LPBF are estimated to be around $10^3$–$10^8$ K/s [6], exceeding the CCRs of most BMGs, and are therefore sufficient for the additive production of BMG parts [4].

![Schematic diagrams on glass formation.](image)

**Figure 1.1:** Schematic diagrams on glass formation. (a) Temperature dependence of volume (adapted from [7]). $T_m$ and $T_g$ are indicated. (b) TTT-diagram. The indicated cooling process represents the slowest cooling rate leading to vitrification.

By employing AM, bulk metallic glasses components are no longer confined to size and geometry constraints dictated by the available cooling rate for a complete component, which was considered their most serious disadvantage [8]. Additional to the fast cooling rates in the metal AM process, the successive nature of the process enables an additive production of a larger geometry out of local segments with sufficiently high cooling rates. Consequently, reports on successfully printed metallic glass components have increased remarkably since 2015 [4]. The successive local processing additionally allows the integration of structural, chemical, and functional local gradients into an AM part. Scanning strategies can be used to tailor the microstructure and texture of crystalline printed components [9–11]. The parameter settings can also be utilised to print composites, for example, by partial crystallisation of MGs and forma-
tion of bulk metallic glass composites (BMGC) [12], interactions with reactive gases [13–16], or multi-material processes [17]. For LPBF, typical melt pool sizes are in the 50 - 500 μm range, therefore regions with adjusted characteristics can also be achieved on this length scale. With these possibilities to influence the structure, composition, and thus properties locally at selected positions within a build, AM can be used for the functionalisation of these variations.

In the present work, AM of BMGs is studied for the Zr-based composition AMLOY-ZR01, previous trade name AMZ4, Zr$_{59.3}$Cu$_{28.8}$Al$_{10.4}$Nb$_{1.5}$ (Amloy), and a Fe-based composition. Along with the successful processing of many bulk metallic glass components (e.g. [18–22]), there is a need for adequate characterisation of the process and the obtained components to enhance process understanding and process control. The characterisation of MGs presents an experimental challenge due to the deciding features on the near-atomic scale and the materials’ proneness to crystallisation. The characterisation of crystalline alloys often focuses on microstructure in order to influence the material properties, while for MGs, the local structure (short-range order) and its packing in the few-nm range (medium-range order) are defining the macroscopic properties [23]. Amloy is chosen as a model system to study the production of amorphous parts and assess nanoscale clustering in paper I. The crystallisation mechanisms under LPBF can differ from other production methods as they depend on the rapid heating and cooling rates and the thermal cycling caused by adjacent laser tracks and powder layers [18], and are thus challenging to predict or simulate. Thermal conductivity and viscosity influence the transport of heat and mass in and around a melt pool with fluctuating velocities [24]. The viscosity is thus an important material property, but its experimental determination near $T_g$ is challenging due to rapid crystallisation. A possibility to circumvent this difficulty by employing FDSC is presented in paper V. Additionally, kinetics play an important role, especially considering the high heating and cooling rates, which is studied in project VII. Finally, contaminants are known to influence the glass forming ability (GFA) and may either hinder or accelerate the crystallisation of MGs in AM, but their incorporation and redistribution is not fully understood. The role of oxygen and nitrogen is studied for the model system Amloy in papers II and III. Nitride formation is also studied for the Ti-N system in paper IV, which allows to investigate local property variations and nitrogen inclusion in a crystalline two-component system. Single tracks are a strategy to study the most basic building block of LPBF bulk materials without the influence of thermal cycling due to adjacent laser tracks. Following the studies on single tracks, modifications of areas and bulk parts are investigated for Amloy-ZrN composites in paper III. For soft-magnetic BMGs, composition and LPBF process optimisation for both favourable
magnetic properties and crack-free, dense builds present an additional challenge. The interdependence of bulk processing and local property modifications is studied for a Fe-based BMG system regarding the magnetic properties of the powder, LPBF bulk components, and single laser tracks in paper VI.

Based on the above mentioned publications, the studied possibilities to attain local structural, compositional, and property variations by LPBF are summarised in the following chapters:

(1) In the second chapter on devitrification of metallic glasses, the evolving spatial heterogeneity in metallic glasses upon crystallisation is explored on different length scales. In the first part, the influence of LPBF processing on nanoscale clustering and the distinction between random and non-random APT reconstructions is assessed. In the second part, the influence of rapid heating on the microstructure and phase evolution is analysed.

(2) In the third chapter, the attainable control of composition and compositional variations in LPBF-processed materials from the pathways of oxygen impurity incorporations to controlled laser nitriding of titanium and a Zr-based MG is examined. The influence of 0.3 and 1.3 at.% oxygen impurity on the glass forming ability is investigated and oxygen incorporation through the transport of surface oxides is explored. By switching between the inert process gas argon and nitrogen as a reactive gas, the introduction of hybrid processing strategies for composite formation is tested.

(3) In the fourth chapter, properties of metallic glasses and property tailoring is investigated. The viscosity is assessed for commercial compositions used for LPBF. The potential and limitations for property tailoring by LPBF process design is explored for local mechanical and magnetic characteristics of printed components.
Chapter 2

Devitrification of metallic glasses

As non-equilibrium solids, glasses undergo crystallisation when heated to temperatures above the glass transition. The properties associated with the amorphous nature are altered upon crystallisation, which can degrade the performance for a specific application. Therefore, knowledge about the crystallisation process and its dependence on the process route is essential to fabricate parts with specific and reproducible characteristics. The emerging heterogeneity when an MG starts to crystallise spans over many orders of magnitude in length scales, from nm-scale clustering to the growth of μm-sized crystalline grains. The choice of characterisation and detection of such composites thus depends on the analysed length scale. Two ranges were investigated for the Amloy composition: The onset of decomposition and its detection as nanoscale clustering by APT and the crystallisation pathway on a few-nm to μm scale with \textit{in-situ} scattering experiments.

Multiple studies have analysed the crystallisation pathway and the relationship between LPBF processing and crystalline phase fractions for this system. The Amloy composition is studied in 35\% of the published papers on AM of Zr-based BMGs [4]. Small angle neutron scattering (SANS) was employed to study early stages of the crystallisation and showed that isothermal annealing at 370 °C for 90 minutes resulted in a mean cluster radius of about 3 nm [25]. For the industrial grade composition with \(\sim 1\) at.\% oxygen, a lower thermal stability than for the same composition produced from high purity raw materials was observed with the formation of the Cu\(_2\)Zr\(_4\)O phase at 440 °C [26]. Furthermore, CuZr\(_2\) [25–27], Al\(_3\)Zr\(_4\) [25, 26], and Al\(_2\)Zr\(_3\) [26] have been observed upon partial or complete crystallisation of the alloy. α-Zr [28] and Cu\(_2\)Zr\(_4\)O [26, 28, 29] nanocrystals were observed in as-produced LPBF samples.
2.1 Nanoscale cluster identification (paper I)

I: Nanoscale clustering in an additively manufactured Zr-based metallic glass evaluated by atom probe tomography

The investigation of nanoscale clusters can give crucial information about the onset of crystallisation, the characterisation of clusters on this length scale is, however, experimentally challenging. APT, combining mass spectrometry and projection microscopy, is a state of the art tool to investigate the spatial chemical distribution on the nm-scale [30, 31]. The study conducted in paper I investigates the clustering on this length scale by means of APT for Amloy produced by LPBF and uses isotopes in the metals Zr and Cu as a reference for a random spatial configuration.

While APT provides the unique advantages of imaging a 3-dimensional nanoscale reconstruction of the position and chemistry of individual ions, it comes with the disadvantage of a non-isotropic and poorly defined spatial resolution [32]. The spatial resolution is limited by detection efficiency, trajectory aberrations, and the reconstruction protocol. With a detection efficiency $<1$, the random removal of atoms from segregations leads to a more random appearance of the data reconstruction than in the material before the measurement [31]. For the ions that do get detected, it has to be taken into consideration that their recorded positions are affected by trajectory aberrations in the flight path, as illustrated in Figure 2.1. Trajectory aberrations arise from a range of experimental parameters, such as the temperature and electric field strength [33] and the specimen shape [34]. Homogeneous materials typically reach a steady-state shape during field evaporation process, yet heterogeneous materials entail variations which lead to changes in the reconstructed density due to the associated different magnifications [34, 35]. Consequently, APT resolution is anisotropic and better in depth than laterally [33]. Finally, the reconstruction of the gathered data (affected by detection and trajectory aberrations) is a third contribution to the spatial resolution and determines to a large extent the depth resolution [32].

Naturally, these spatial resolution limitations are more eminent the smaller the features of interest are. For the analysis of small clusters below 1 nm in radius, De Geuser and Gault [32] show that the effective resolution caused by trajectory aberrations is the dominant factor for many cases that have previously been considered detection-limited. The positional shift of the ion in the reconstruction compared to the material results in particle ions being reconstructed within the matrix and vice versa. As the magnitude of the aberrations depends on the specimen, experimental conditions, and system, the spatial resolution differs too [32].
For the study presented in paper I, LPBF-processed Amloy samples from the process parameter development study presented in [28] are analysed with respect to nanoscale clustering. The absence or presence of such heterogeneities could indicate how wide the parameter window of the LPBF processing is to obtain a homogeneous BMG or how susceptible the output is to a change in parameters. The samples analysed in paper I were produced with laser powers ranging between 55 - 85 W while the other processing parameters were kept constant [28]. As a reference, heat treated samples comparable to such showing nanoscale clustering [25] are analysed. To further address the above described challenge of distinguishing nanoscale clustering from random fluctuations, two random references are evaluated: Experimentally, the spatial isotope distributions in Zr and Cu and computationally, a simulation of complete spatial randomness for the respective composition.

![Figure 2.1](image)

**Figure 2.1:** Schematic illustrating the challenges associated with limited APT resolution: The $< 1$ detection efficiency leads to a random loss of atoms, and the ions that do reach the detector are affected by aberrations and thus shifted in their 3-dimensional positions in the reconstruction.

The challenge associated with this research question due to the above stated spatial resolution limitations is depicted in Figure 2.1: From the original configuration of ions in the sample in a nm-sized sub-volume, schematically illustrated by the red dots on the left, a fraction is randomly selected by the detection process with the probability of the detection efficiency. Furthermore, the limited resolution leads to trajectory aberrations. To extract information about the arrangement of atoms in the sample from the measured configuration in the reconstruction, the resolution thus has to be taken into account as a crucial factor. In the present study, the measured nm-scale tips are divided into $1^3 - 5^3$ nm$^3$ voxels, and statistical methods are used to determine the deviation of the observed configuration from a random one.

A selection of two of the Amloy tips analysed for paper I is depicted in Figure 2.2 as the reconstruction of specific ions. From visual inspection, all as-printed samples, spanning a LPBF processing parameter window of 55 - 85 W laser power, show a homogeneous distribution of the different ion types. The as-printed 75 W sample depicted in Figure 2.2a includes an oxygen-rich region at the top of the tip, which was excluded from the
clustering analysis as it likely stems from surface oxidation. The results of the approach adapted to statistically analyse deviations from a random configuration (i.e., the presence of clustering) are presented in the graph in Figure 2.2a for the as-printed sample: For each voxel size, the filled symbols show the standard deviation normalised by the average of a specific ion type per voxel, calculated with the voxels filling the entire tip. The circles show the same metric, not for the measured distribution of ions, but for a simulated one, which exhibits spatial randomness with respect to the ion positions. The correspondence of experiment and simulation strengthen the first visual impression: There is no indication of clustering on the probed length scales. This finding was consistent for all analysed as-printed samples irrespective of the laser power parameter setting, and additionally for the powder prior to processing. To assure that a random spatial configuration is reliably detected as such by the applied statistical approach, spatial isotope distributions of Zr and Cu are analysed: In both cases, a similar result as shown for the as-printed Amloy (Figure 2.2a) was observed with an excellent correspondence between simulation and experiment.

![Graph showing standard deviation normalised by average of specific ion type per voxel for as-printed and annealed samples.](image)

**Figure 2.2:** Experimental results for (a) as-printed and (b) 5h annealed (390 °C) Amloy samples and a simulated random reference. The reconstructed tips show the distribution of Zr, Cu, Al, and O. Adapted from paper I.

One of the annealed samples is represented in Figure 2.2b. From visual inspection, there is already an indication for clusters with higher oxygen concentration. These samples are printed with the same parameters as the sample depicted in Figure 2.2a, and subsequently annealed at 390 °C for 1, 5, and 10 hours. Shown in Figure 2.2b is the sample annealed for 5 hours, which shows a distinct difference between the simulation of a random arrangement of the ions (open circles) and the experimentally measured distribution (filled symbols). This sample shows a clear deviation from a random spatial arrangement and demonstrate that cluster sizes \(> 1\) nm in diameter are reliably detected for these analysis con-
2.2 Rapid crystallisation (paper VII, unpublished)

VII: High resolution measurements and modelling of ultra-fast crystallisation kinetics in Zr-based metallic glass with added oxygen

In the study conducted for paper VII (unpublished), the phase evolution is followed over a much wider range than the onset of decomposition studied in chapter 2.1 and employs fast heating with up to $\sim 10^4$ K/s [36]. This adds to the understanding collected from ex-situ studies on post-AM samples [27–29, 37] and in-situ heating experiments carried out with much slower heating rates of e.g. 20 K/min [26]. With resistive heating [36] and in-situ high time-resolved small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) at the beamline P21.2 (Petra III, DESY [38]), the structural evolution can be followed and analysed. The measurements give insight into the nucleation and growth of crystalline phases. The Amloy composition was produced in batches with different oxygen content by arc-melting. The samples were subsequently suction cast, and compositions with $1.3 \pm 0.1$ to $4.3 \pm 0.2$ at.% oxygen were obtained according to ToF-ERDA measurements.

TEM has been used to complement the diffraction results and was performed on the samples after the in-situ heating experiments. The analysed lamella was taken from the centre of the sample with 1.3 at.% oxygen annealed with a 12 A current for 5 seconds with a peak temperature of $\sim 1000$ K. Figure 2.3 highlights the main findings of a wide range of grain sizes with both amorphous rings and crystalline diffraction spots visible in SAED (Figure 2.3b). EDS (Figure 2.3d) revealed three main contrast consisting of aluminium rich, poor and intermediate regions, which all in turn showed a mix of crystalline and amorphous diffraction features when analysed with nanobeam diffraction. Furthermore, the EDS shows that the potential respective phases appear to be far from their stoichiometric compounds, suggesting a notable substitu-
Devitrification of metallic glasses

Figure 2.3: TEM investigation of a sample with 1.3 at.% oxygen content heated with 12 A: (a) Overview transmission electron microscopy (TEM) bright field image. (b) selected area electron diffraction (SAED) on encircled area showing both amorphous and crystalline fractions. (c) TEM dark field image showing the region analysed with (d) energy dispersive X-ray spectroscopy (EDS). Unpublished data.

tion between Al and Cu in the respective crystalline phases. Nanobeam diffraction confirmed the presence of the CuZr$_2$ phase in the area shown on in Figure 2.3c. The other main candidates (Al$_3$Zr$_4$ and Cu$_2$Zr$_4$O) could not be identified for this sample. None of these three contrast corresponds to the amorphous matrix, but small amorphous regions remain in all fractions. The domain sizes observed were as small as $\sim 1$ nm.

The rapid heating rate and influence of oxygen contents in the few at.% range connects to typical LPBF conditions. The sample presented in Figure 2.3 exhibits a similar oxygen content to LPBF fabricated samples based on the industrial grade Amloy alloy with $\sim 1$ at% oxygen [28]. Due to the high heating rates and short anneal times, kinetics limit the phase formation and, consequently, non-stoichiometric compositions of the crystalline phases as well as remaining amorphous fractions are observed (Figure 2.3b-d). The heating rates in the LPBF process are, however, even higher with approx. $10^6$ K/s [39]. These effects become especially relevant for the heat affected zone (HAZ), which describes the region surrounding the molten pool, which does not reach sufficiently high temperatures to melt. This zone is especially prone to crystallisation [40], for which the explored measurement conditions provide insights into the crystallisation kinetics. Furthermore, X-ray diffraction methods are suitable to capture an integral picture of the crystallisation, while the presented TEM adds local information on the grain size and crystallinity.
Control of composition

Reactive species pose both a source of unintended contamination as well as a possibility for tailored composites. As a source of contamination, the incorporation of oxygen in the different stages of the LPBF fabrication remains a challenge for process control. The powder form of the raw material with the corresponding high surface area and the purity of the inert gas atmosphere during processing are two possible contributing factors to impurity incorporation. An oxygen content of around 1 at.\% is reported for the powder used for the studies on Amloy, which was not found to increase in the printed part [28]. Oxygen incorporation has been reported to decrease both the GFA and the thermal stability of Zr-based alloys by inducing the formation of crystalline particles [26, 41–43]. The mechanisms for oxygen incorporation and redistribution under LPBF conditions are investigated in paper II and summarised in the following section.

The same mechanisms suspected of constituting a risk for oxygen impurity incorporation during the processing through reactions between the molten metal and residual reactive species in the inert gas atmosphere, can be employed for targeted composite formation. \textit{In-situ} composite formation can be achieved, for example, by combining laser nitriding and LPBF. By changing between an inert and a reactive atmosphere, an additional printing parameter to control composition and phase formation is introduced. As a well-studied laser nitriding material system, Ti-N was adapted for such experiments [13–16]. Titanium laser nitriding under LPBF conditions is thus explored to enhance process understanding as well as to outline the limitations (paper IV).

Typical metallic glass compositions consist of three or more elements according to Inoue’s empirical rules [44], which makes the investigation of the nitride formation mechanisms more intricate to study than for the Ti-N system. Additionally, the amorphous matrix is prone to crystallisation and has thus to be taken into account in the choice of parameters.
Control of composition

By a successful combination of metallic glasses and ceramic phases, the advantages of both materials can be combined: In additions to the bulk properties of the metallic glass, for example, typically high strength exceeding 3 GPa, along with increased wear resistance and an elastic elongation limit of around 2 % [45], a ceramic layer can add protection against crystallisation upon short-term high temperature exposure of the part [46] and increase the corrosion resistance [47, 48]. The potential advantage of adding such layers or regions in the AM process is twofold: The choice of position within and on a build is, due to the successive nature of the process, free for design down to the size of the individual melt pools. Additionally, a smooth integration can be ensured, and adhesion problems, observed, for example, for ex-situ sputter deposition [46], can be avoided.

3.1 Oxygen impurity incorporation (paper II)

II: Convective flow redistribution of oxygen by laser melting of a Zr-based amorphous alloy

Oxygen impurities are an important factor in the devitrification of metallic glasses, as already presented in chapter 2. Nevertheless, the mechanisms for their incorporation and redistribution in the LPBF process remain partly unclear and are thus studied for Amloy to enhance process control. To study the oxygen pathways under LPBF conditions, the methodology presented in Figure 3.1 was adopted in paper II: Substrates of the chemical composition based on the commercial Amloy composition were prepared by arc-melting and splat-quenching with two different oxygen concentrations (0.3 and 1.3 at.%). These two substrates allowed the investigation of the impact of the different compositions with respect to the oxygen content. X-ray diffraction (XRD) showed that the substrate with less oxygen (0.3 at.%) was X-ray amorphous, while the substrate with a higher oxygen content (1.3 at.%) exhibited a crystalline fraction. The cooling rate of splat-quenching, estimated around $10^5$ - $10^8$ Ks$^{-1}$ [49], is evidently not sufficient to avoid crystallisation due to the lower GFA (and thus higher CCR required for glass formation) of the alloy with an oxygen concentration increased by 1 at.% compared to the reference. Additionally, the results from differential scanning calorimetry (DSC) showed that the sample with higher oxygen content exhibits a slightly lower crystallisation temperature (466 compared to 468 °C for a heating rate of 20 K/min). These results highlight how narrow the compositional range of a BMG composition can be if a certain GFA is required due to cooling rate limitations and how small variations in oxygen concentrations, for example, through the choice of high-purity or
3.1 Oxygen impurity incorporation (paper II)

(more cost-effective) industrial grade raw materials, can lead to crucial differences in processability and hence component properties.

Figure 3.1: Preparation of BMG samples with different oxygen content used to study oxygen incorporation and redistribution. Substrate fabrication by arc-melting and splat-quenching, followed by characterisation with ToF-ERDA, XRD, and DSC. Single laser track processing of substrate materials and characterisation of cross sections by scanning electron microscopy (SEM), APT, and TEM. Adapted from paper II.

For an AM component, the impurity concentration in the raw materials is, however, not the only possible source of oxygen, as outlined in the introduction of this chapter. The large surface area of the powder entails the incorporation of surface oxides, and a reactive formation of oxides from residual oxygen in the processing atmosphere and the molten metal may occur. To separate these steps in the LPBF process, the two substrates presented above were scanned with a single laser track under LPBF conditions (Figure 3.1). From their cross section, the incorporation and redistribution of oxygen and oxides can be analysed.

Figure 3.2: Process understanding gained from single tracks in cross section: Surface oxides seemingly undergo redistribution into the melt pool during LPBF processing. (a) SEM backscatter imaging of melt pool. (b) Schematic representing the melt pool. (c) Bright field scanning transmission electron microscopy (STEM) image of band of ZrO nanocrystals. (d) APT reconstruction showing Zr ions and O isosurfaces. Adapted from paper II.

APT and SEM imaging using backscatter electrons revealed that the single tracks on the two substrates with different oxygen content did not show any systematic differences. Both exhibited a similar melt pool shape and similar contrasts within the melt pool, as well as oxygen-enriched regions not only in the APT tips extracted from the cross sections but also in those extracted from the substrate sheets. Despite the
difference in oxygen concentration, which was shown to have a clear effect on the crystallinity and thermal stability of the substrates, these oxygen-rich particles were detected within the melt pool of the sample with lower oxygen content as well. The particles observed as dark contrast bands in the melt pools (Figure 3.2) likely stem from surface oxides, as they were also found on the surface of the substrate sheets. Their distribution in the melt pool and abundance in both samples suggest that they were transported by the convective flow of the liquid metal in the melt pool, rather than nucleated from the (more or less, depending on the sample) oxygen-rich melt. The discovery of these particles both on the surface of the substrates and in the melt pools after laser-scanning suggests that the oxides were not reactively formed on the surface during processing, but stem from the surface oxide layer. This surface oxide was observed by ToF-ERDA measurements on the substrates prior to processing. During laser-processing, oxide particles from the surface oxide layer are presumably swept into the melt pool and show as bands of nanocrystals in the cross sections after solidification of the metallic glass matrix. For the LPBF processing conditions, this entails that such nanocrystalline oxides, which may act as heterogeneous nucleation sites, could be included from surface oxides on the powders used for processing. This suggests an additional mechanism for impurity incorporation other than the printing atmosphere and the raw material purity.

3.2 In-situ laser nitriding (papers III, IV)

III: Reactive metal additive manufacturing: Surface-near ZrN - metallic glass composite formation and mechanical properties

IV: Sequential nitriding depth profiles in titanium, obtained under reactive additive manufacturing conditions

Nitrogen and argon are explored as examples to examine the process gas as an additional printing parameter. With a reactive gas such as nitrogen, compared to an inert gas such as argon, local compositional and structural modifications can be attained. Figure 3.3 shows the equilibrium phases for the systems Ti-N and Zr-N, for which nitriding is investigated in papers III and IV. The stability regions for TiN and ZrN exhibit many similarities for both systems. Furthermore, the solubility of nitrogen in the metal liquid is, in both cases, well below 50 at.%, thus not permitting to re-obtain pure stoichiometric nitrides after melting the respective nitride without supplying additional nitrogen during cooling. Another consequence is that when the respective nitride is melted, nitrogen is lost to the gas phase, and the nitride is partly decomposed. This decomposition has been experimentally observed for laser-melting ZrN.
(paper III). With these thermodynamic considerations, the experimental processes can be investigated with the aim to attain specific composites. The main experimental findings concerning the process understanding for laser nitriding of titanium and the Zr-based metallic glass Amloy under LPBF conditions is summarised in Figure 3.4.

![Figure 3.3: Phase diagrams for (a) Ti-N, (b) Zr-N, showing the stability regions for the respective nitrides. Adapted from papers III and IV.](image)

A study on Ti laser nitriding under LPBF-like conditions suggested a slow laser speed as beneficial [13]. We, therefore, explored a 50 mm/s laser scanning speed together with different laser power settings and number of remelts along a single track. Figure 3.4a shows a cross-section SEM image of a laser track melted three times in total. The image shows electron backscatter contrast, thus the darker contrast corresponds to overall lighter elements, in the present case indicating nitrogen incorporation. This result was complemented with electron backscatter diffraction (EBSD) from the cross sections and XRD from the top of the laser tracks. Both techniques confirm TiN formation and a dispersion of TiN in an $\alpha$-Ti matrix. With a number of melts along the same single track line, the nitrogen incorporation and nitride fraction increased.

For the fabrication of metallic glass - ceramic composites, the optimal parameters for maximising the nitride fraction have to be regarded in the context of the optimal parameters for printing the metallic glass. If an overall higher energy input per scanned area is chosen by increasing the laser power or decreasing the scan speed, this additionally impacts the level of crystallinity of the matrix. If a metallic glass matrix with dispersed nitride particles or a nitride layer is envisioned, the optimal parameters for printing the metallic glass (see [28] for process parameter development for the here studied composition) are the starting point.

Two different printing strategies regarding the processing atmosphere were explored. The reactive gas was either used for the complete printing process or for remelting the surface of a part printed in an inert atmosphere. The two approaches resulted in similar nitrogen and nitride distributions: A maximum of up to 34 at.% at the surface with an
Control of composition

Figure 3.4: Results overview of the nitriding studies on (a) TiN and (b) ZrN. (a) Single tracks on Ti substrates in nitrogen atmosphere resulted in an increased nitride fraction with multiple melts and incorporation depths of > 200 μm. (b) Nitriding of Amloy in nitrogen atmosphere resulted in dispersed ZrN nanocrystals up to ∼500 nm depth from the surface and enhanced crystallisation in the bulk. Adapted from papers III and IV.

exponential decrease in the first 200 nm from the surface. The samples for which every 20 μm powder layer was processed in nitrogen did only exhibit this feature on the surface of the last powder layer, i.e., the surface of the build, but no evidence for such layers in the bulk was found. The integral nitrogen concentration in the bulk ranged around 0.4 - 0.6 at.%, which is increased compared to inert processing (0.16 ± 0.04 at.% nitrogen), but nevertheless a very low concentration. The nitrides formed at the surface after processing thus seem to undergo decomposition and a possible redistribution in the bulk if another powder layer is added on top of a nitrided layer.

Due to these mechanisms, homogeneous or layered bulk composites could not be attained under the employed processing conditions. Yet the fabrication of parts with a nitrogen and ZrN-rich surface-near layer and a gradient profile, while limiting the crystallisation of the metallic glass matrix, is possible. The results on titanium laser nitriding highlight that this limitation for the attainable Amloy-ZrN composites is likely connected to the necessary parameter range for processing BMGs with much higher laser speeds (2000 mm/s compared to 50 mm/s presented for titanium laser nitriding).
Properties and tailoring

The time-dependence of glass formation, illustrated in the introduction (Figure 1.1), entails that the glass properties depend on the cooling (and heating) rates and, thus, the processing. A different thermal history evokes a different frozen in configuration as well as different sizes and number densities of crystallites. By processing metallic glasses with LPBF, a complex thermal history is imprinted into the component due to the single laser passes spaced next to each other and the layers stacked upon each other. While each single laser track is written, the thermal gradient and the solidification front influence strain and phase formation, while the HAZ is especially prone to crystallisation for metallic glasses. The HAZ is the material at the rim of the melt pool, which is not melted by the laser pass but exposed to a heat flux from the melt pool to the bulk resulting in an increased temperature.

A first impression of the differences in the glass structure associated with different processing conditions for Amloy fabricated in the same LPBF machine is shown in Figure 4.1: Three samples produced with laser power settings of 60, 75, and 105 W are heated with 20 K/min up to 450 °C. The heat-flux DSC measurement records the difference in heat flow rate to the sample and to an empty reference pan during the controlled heating program by measuring the temperature difference between the two [50]. The difference in temperature is translated to a difference in heat flow rate by a specified calibration with known materials. The first upscan (heating segment) reflects the thermal history associated with the production of the glass, in the present case, the printing process. The second upscan reflects the thermal history stemming from the controlled downscan [51]. The difference between the two curves relates to the enthalpy released during the first upscan, which originates from the excess internal energy stored during the initial fast quenching [51] in the LPBF process. The larger area between the two up-scans marked in Figure 4.1 indicates a faster cooling for lower laser
Properties and tailoring

power parameters. This can be rationalised by the relation between laser power and melt pool size in the LPBF process: With an increase in laser power at a constant speed, the larger energy density generates larger melt pools [52], leading to lower cooling rates and slower solidification. Furthermore, samples fabricated with 105 W show a crystalline fraction already after LPBF production [28]. Consequently, the sample volume contributing to the observed glass transition is reduced, and a smaller endothermic contribution is observed for this sample compared to the X-ray amorphous samples with 60 and 75 W. This example illustrates how a seemingly small change in the processing affects the quenched-in configuration of the glass.

Figure 4.1: DSC scans with 20 K/min on samples produced with LPBF according to [28] employing the laser powers 60, 75, and 105 W for different samples. Each sample is heated up to 450 °C, just above the glass transition. To avoid crystallisation as much as possible, the samples are immediately cooled down after reaching this temperature. Subsequently, the quenched samples are subjected to a second heating cycle. Unpublished data.

While the complex processing can be a challenge for a homogeneous product quality and properties, the advantage likewise lies in the modifyable size range. Down to the melting of single laser tracks of a few μm in diameter, the processing can be locally chosen to give rise to specific properties. Chapter 3 presented how reactive gases can give rise to local modifications, and nitride-rich regions can be incorporated on the surface down to regions of 10 - 100 μm across and hundreds of nm to hundreds of μm deep with a single laser track. This raises the question of how well the associated property changes can be controlled locally.

In this section, the viscosity is analysed as one example of a glass property that influences the processing. Furthermore, two examples of properties that can be (locally) modified by means of LPBF are shown: mechanical and magnetic characteristics.
4.1 Viscosity - from fragile to strong (paper V)

V: Viscosity of metallic glass-forming liquids based on Zr by fast-scanning calorimetry

The viscosity of the metallic melt at different temperatures plays an important role in the LPBF process [53]: The viscosity needs to be low enough to ensure smooth spreading on the previously melted surface and an enclosure of unmelted solid particles if present (this is relevant for example for the nitrides discussed in chapter 3 with a significantly higher melting point than the metal matrix). On the other hand, low viscosity melts can lead to balling phenomena in the processing, causing an uneven surface [53].

A peculiar aspect of the viscosity temperature dependence of many metallic glass forming liquids has been analysed in paper V: The compositions Amloy [54] and Vitreloy 105, Zr\textsubscript{52.5}Cu\textsubscript{17.9}Ni\textsubscript{14.6}Al\textsubscript{10}Ti\textsubscript{5} (Vit105) [55] are reported to potentially undergo a fragile-to-strong transition. The viscosity of a liquid determines its flow kinetics and can be described as the friction between different internal layers in relative motion to each other [1]. Glasses can be divided by their viscosity into strong and fragile liquids according to the classification first proposed by Angell [56]. Strong liquids behave similar to an Arrhenius temperature dependence, the temperature dependence of the viscosity when approaching the glass transition remains almost linear in a logarithmic plot [1]. Contrarily, fragile liquids are characterised by rapid changes in viscosity upon temperature changes [1]. Metallic glasses are challenging for direct viscosity measurements at intermediate temperatures close to their glass transition temperature, as they undergo rapid crystallisation, which was shown for Amloy in chapter 2. It is however this intermediate region which is of interest for a potential fragile-to-strong transition: At low temperatures, many metallic glass systems exhibit a strong behaviour, whereas at high temperatures, they exhibit a fragile behaviour. The transition thus would occur in the inaccessible region.

Liquid-liquid transitions are presumed to lie behind the transition phenomenon. Since the first observations in 1979 [57, 58], transitions between amorphous states have been observed for many compositions [59]. For the Zr-based compositions Viteloy 1 [60] and Vitreloy 106a [61], the associated structural changes have been studied. The kinetic crossover is related to a disorder-order liquid-liquid transition connected to the evolution of medium-range order [62]. Except for Vitreloy 1, most bulk metallic glass compositions do not allow for sufficient experimental time to perform viscosity measurements throughout the supercooled liquid region due to rapid crystallisation [62]. Such experimental limitations for direct viscosity determination can be circumvented by using FDSC,
as demonstrated by Al-Mukadam et al. for oxide melts [63, 64]. With this approach, the accessible temperature range can be broadened, as presented for Amloy in Figure 4.2.

Figure 4.2: FDSC has been used to determine the viscosity in the not directly accessible intermediate temperature range prone to crystallisation. The result for Amloy shows the crossover temperature estimated by a fit encompassing a strong behaviour at low and a fragile behaviour at high temperatures. The red circles show the previously available data from [54]. Adapted from paper V.

The range accessed by FDSC is highlighted in grey in Figure 4.2. Together with the previously available data [54], a Mauro-Yue-Ellison-Gupta-Allan (MYEGA) [65, 66] fit encompassing both the strong and fragile behaviour can be attained, which is shown as the back line with strong behaviour dominating at low and a fragile behaviour dominating at high temperatures. No transition from the strong to the fragile behaviour was observed within the range determined by FDSC, the strong behaviour persists in this temperature range and narrows down the temperature range in which the transition presumably takes place. With the current fit, the crossover for Amloy is centred at 0.66 T_g/T.

4.2 Mechanical properties of composites (papers III, IV)

III: Reactive metal additive manufacturing: Surface-near ZrN - metallic glass composite formation and mechanical properties
IV: Sequential nitriding depth profiles in titanium, obtained under reactive additive manufacturing conditions

The fabrication of nitride-metal composites by reactive printing is discussed in chapter 3. One interest for integrating nitriding steps into the LPBF processing of a part is the mechanical properties, particu-
4.2 Mechanical properties of composites (papers III, IV)

larly modifications in hardness. Thus, samples from the different types of produced composites from the studies presented in paper III and IV were chosen for nanomechanical testing. Three different composite types were considered: Single laser-nitried tracks on Ti sheets, the surface of reactively laser-remelted Amloy samples, and Amloy samples reactively printed in nitrogen. Cross sections from the first and last sample types are displayed in Figure 4.3.

![Figure 4.3: Nanoindentation mapping of hardness on cross sections of laser-nitried samples. The dark contrast at the top of the images stems from the embedding material. (a) Single laser track on Ti sheet with 50 W laser power and 50 mm/s laser speed, scanned three times. (b) Melt pool at the surface of a reactively printed Amloy sample (60 W, 2000 mm/s). Adapted from papers III and IV.](image)

For the single laser nitried track on a titanium sheet shown in Figure 4.3a, the transition in the locally measured hardness, from the unaffected titanium sheet on the right into the melt pool on the left, is clearly visible not only by the backscatter contrast in the image, but also by the increased hardness (colour map). Averaged over 190 indents, the hardness of the titanium substrate sheet (outside of the nitried melt pool) is $2.2 \pm 0.4$ GPa, which is in good agreement with other results on commercially pure titanium grade II [67, 68]. Within the melt pool area, the hardness variation is more pronounced, reflecting the distribution of TiN in Ti matrix. A maximum of 20.8 GPa is observed, which is close to the hardness reported for pure TiN coatings of $\sim 24 - 27$ GPa. [69]. This example demonstrates that such a hardness variation is attainable in the process on the length scale of few hundred μm and down to $>100$ μm melt pool depth.

The laser nitried Amloy (Figure 4.3b), for which a dispersion of ZrN nanocrystals was observed in the surface-near region, exhibited an increased surface hardness of $6.8 \pm 0.9$ GPa compared to $5.3 \pm 0.5$ GPa for the surface without the nitriding, when the processing conditions were optimised for a nitride surface finish. For a build completely printed in nitrogen, shown in cross section in 4.3b, the observations made concerning the bulk, a low incorporation of nitrogen, and no detectable ZrN
fraction, are also reflected in the hardness. Compared to the hardness of 5.0 ± 0.3 GPa for the cross section of a sample processed in argon, the nitrogen processing did not lead to increased hardness. Even though the average hardness did not vary between argon and nitrogen processing, larger variations between the individual indents were observed with 5.0 ± 0.7 GPa. This variation may be caused by a small fraction of dispersed crystalline particles, which are suspected to have lead to accelerated crystallisation of the BMG compared to argon processing.

These examples show that laser nitriding can be used to locally modify the mechanical properties. For the well-know Ti-N system, the hardness can be locally varied from the titanium base material (∼2 GPa) up to approaching the hardness of pure TiN (∼21 GPa). For adding an *in-situ* hard coating onto a specified position of the BMG composition Amloy, LPBF can be used to avoid potential adhesion and local placement challenges when adding such a coating *ex-situ*. Howbeit the present approach comes with challenges associated to the attainable gradients and coating thicknesses and the linked mechanical properties. While a high fraction of ZrN nanoparticles could be attained in the surface-near region, increasing the surface hardness by around 30 %, only a small dispersed fraction of the ceramic phase is assumed in the bulk, not notably changing the mechanical properties and adversely leading to a reduction of glass forming ability during processing. Finally, it is noteworthy that the employed thermodynamic calculations could be used to predict if nitrides are formed in the process and serve as a starting point for process parameter optimisation to tailor mechanical properties.

### 4.3 Magnetic properties - from powder to printed (paper VI)

*VI: Laser powder bed fusion process development and magnetic contrasting of the magnetic domains and melt pool characteristics in a Fe-based bulk metallic glass*

The links between the properties of the powder and LPBF processed parts, and the resulting consequences for the processing are discussed in paper VI for a Fe-base BMG composition. An SEM image and a DSC measurement of the as-received powder is shown in Figure 4.4a. The as-received powder was XRD-amorphous, and the DSC scan shows a glass transition around 470 °C directly succeeded by the first crystallisation event. In total, three exothermic crystallisation events are visible with the onsets at 486, 528, and 649 °C, respectively, and the first melting onset is observed at 904 °C.
Heat treatments show the structural and magnetic property changes associated to the three crystallisation steps: Three powder batches heat-treated at 500, 540, and 670 °C respectively, exhibited more than one crystalline phase, with likely candidates being $\alpha$-Fe, Fe$_3$P, Mo$_{73}$Fe$_{27}$ and Mo$_2$Fe$_{23}$C$_6$. With increasing annealing temperatures, the remaining amorphous phase decreased, while the crystalline peaks present did only change in their relative intensity. The three exothermic crystallisation events (Figure 4.4a) could thus not be attributed to specific phases. The magnetic characterisation shows an increase of the magnetic saturation and the coercivity for the heat-treated, partially crystallised powders compared to the as-received, amorphous powder. The supposed advantage of an increased magnetic saturation from a crystalline fraction is outweighed by the increase in coercivity, which deteriorates the soft magnetic properties. A predominantly amorphous part is thus preferable for this composition.

The process parameter development study consequently focused on optimising the process parameters to obtain amorphous bulk samples. A suitable parameter space with a laser speed of 1200 mm/s, laser powers of 110 to 170 W, and hatch spacings of 130 to 220 μm was identified for the production of bulk pieces up to a few mm height. Samples produced with 110 - 130 W laser power and 130 - 140 μm hatch were observed as predominantly amorphous and investigated further. These samples exhibited low coercivity, and a magnetic saturation of around 0.9 T. Kerr imaging on the top surface revealed a wide range of heterogeneous domain sizes and shapes, with up to hundreds of μm large features as well as maze-like patterns with a characteristic size of tens of μm.

To investigate the properties associated with the printing process and relate the builds to the powder properties, single tracks were written...
onto one printed piece, and the melt pool studied in cross section. The
cross sections did not show any contrast related to the melt pool of the
single track or within the printed piece in SEM, but with Kerr imaging,
shown in Figure 4.4c, magnetic domain contrasts are visible. With the
technique, the melt pool associated with the single laser track is clearly
visible with a finer domain pattern within, while larger domains are visi-
ble outside the melt pool, reaching down to the stainless steel substrate.
The magnetic contrast thus gives a possibility to observe the melt pool
geometry. The disposition of the larger domains around the melt pool
indicates stress, which causes anisotropy connected to the solidification
of the molten pool.
AM can be used to circumvent cooling rate limitations of conventionally fabricated BMG parts and offers flexibility to create complex geometries or multi-material parts. BMGs encompass promising characteristics, but are challenging to study due to their (non-equilibrium) glassy state depending on their thermal history and unusual characteristics like liquid-liquid transitions in the observable temperature and pressure range.

The partial or complete crystallisation of MGs results in property changes. To control the properties, process understanding concerning the crystallisation related to the AM processing is thus required. The onset of devitrification denoted by nanoscale decomposition is challenging to detect and analyse, for which simulations of random distributions of elements can aid the identification of evolving ordering. With the, commonly unintentional, addition of oxygen to the composition, the GFA is reduced, and oxygen-rich heterogeneous nucleation sites are formed. For compositions with higher oxygen content, higher critical cooling rates are thus required to attain amorphous components.

Multi-material AM can, among others approaches, be achieved by reactive processes. Laser nitriding is chosen to analyse these processing options in the present studies. The nitride formation and incorporation depth depends on both thermodynamics and kinetics and is thus not simple to predict for multi-component systems out of equilibrium (containing amorphous phases). Under specific processing conditions, multiple remelts with the laser can increase the nitrogen uptake and nitride fraction, while under others, decomposition balances out with formation. If nitride-BMG composites are targeted, crystallisation of the amorphous matrix can be avoided by informed parameter selection, this, however, limits the processing window for optimising the nitrogen uptake considerably.

With an understanding of these processes, properties can be tailored. Nitriding, and hence the introduction of ceramic particles, gives rise to
localised hardness changes that can be used to build up specific gradients and patterns. Laser nitriding is shown to locally increase the hardness from the substrate material hardness to close to the one of the pure nitride for crystalline titanium. BMGs are very promising for soft magnetic applications, the domain structures depend on the complex processing history and can be influenced by the distribution of nanocrystals and stress induced by the LPBF processing.

Systematic approaches to characterising nucleation and growth and to relating mechanical and magnetic properties to the AM processing conditions can aid not only the process understanding for the respective specific alloy compositions. The developed methodologies may also be used for further work to systematically screen for optimised compositions for specific applications. Additionally, the gathered material data from crystallisation and viscosity studies can be used as a basis for improved simulations. Finally, the interconnection between short-to medium-range order and the intricate processing history of a LPBF-fabricated BMG is an intriguing area for further study to enable property tailoring at the near-atomic scale.
Chapter 6

Materials and methods

The experimental techniques utilised for the presented projects are briefly described below. Experimental details for all projects can be found in the respective manuscripts.

6.1 Sample preparation

Arc-melting and splat-quenching

Arc-melting has been employed to produce the alloy compositions with different oxygen content. The respective metals are weighed in manually from high purity raw materials and placed in one of several Cu moulds in a water-cooled plate. The intended oxygen concentration was added via CuO powder, which was enclosed in Cu foil to avoid loss of the powder during the melting. The chamber is purged with argon gas and evacuated several times before flooding it with argon for the melting. An arc is struck with a tip on a Ti getter, which is melted several times to purify the atmosphere further. Subsequently, the alloy is melted several times to ensure homogeneity.

By releasing a copper piston onto the molten material shortly after terminating the arc, the alloy solidifies with high cooling rates up to $10^5 - 10^8$ Ks$^{-1}$ [49] on the water-cooled copper plate. The produced pieces are thus thin, circular sheets.

Laser powder bed fusion

All samples produced or modified with LPBF were fabricated using an EOS M100 equipped with a Yb-fiber laser with a constant speed and minimum beam diameter of 40 μm at the focal plane [70]. After each powder layer, the build plate is moved down by 20 μm, and a new powder layer is spread. The laser melting is carried out either in an inert argon
atmosphere (purity > 99.9997%) or in reactive nitrogen atmosphere (purity > 99.999%) with an overpressure of 30 - 60 mbar compared to 1 atm. Variable parameters are the laser power, laser speed, hatch distance (the distance between the single laser passes) and the scan pattern. For the Amloy builds, the commercial industrial grade powder from Hereaus GmbH [71] was used. To study single laser tracks on bulk substrates or modify the surface of an existing part, the surface of the substrate was placed at the focal spot of the laser, similar to a single powder layer.

6.2 Characterisation

Optical and Kerr microscopy

Optical microscopy uses visible light for imaging and is used for the inspection of sample surfaces and the imaging of melt pools in the few-hundred μm range.

Kerr microscopy uses polarised light for imaging. Changes in the analysed polarisation compared to the incident polarisation are used to image magnetic domains under an applied external magnetic field.

Electron microscopy

SEM systems are based on an electron beam and can be used to image with secondary or backscattered electrons. Imaging with backscattered electrons provides a contrast based on the elastic scattering of the incoming electrons. Generally, heavy elements produce a stronger signal and thus a brighter contrast than light elements.

Focused ion beam techniques (FIB) systems include an additional gallium ion or xenon ion plasma column, which can be used to observe and manipulate a sample with electron and ion imaging simultaneously. The ion beam can be used to cut into the material or deposit layers of material such as platinum and carbon on the surface for protection. The ion beam allows to cut out specific sample geometries for further analysis, for example, lamellae to observe in TEM or tips to field evaporate and reconstruct in APT.

Transmission electron microscopy uses the signal obtained from a high kV electron beam passing through a sample < 100 nm in thickness. Typical sample sizes are in the few-μm-range. Different instrument modes can be used to image diffraction or mass contrast, inspect the sample from different angles, and obtain diffraction patterns from small areas with SAED, convergent beam electron diffraction (CBED), or nanobeam diffraction. The diffraction patterns can be analysed with respect to crystal symmetry, lattice parameters, and observed zone axis.
EDS can be performed with additional detectors in both SEM and TEM systems. By analysing spectra of characteristic X-rays emitted by the material interaction with the incident electron beam, local chemical compositions can be measured. By a point-wise scanning of a specified area on the sample surface, mapping of an area of interest and its chemical variations can be obtained.

**Atom probe tomography**
APT is an atom probe microscopy technique that uses the specimen ions of a nm-sized tip to build a 3-dimensional reconstruction [72]. The technique is based on field-evaporating atoms from the apex of the tip successively, accelerating the ions towards a position-sensitive detector, and building a reconstruction based on their flight times and positions. This allows to study nanoscale variations in chemistry.

**Elastic recoil detection analysis**
ToF-ERDA relies on a source of heavy ions impinging on the studied sample surface. Recoil atoms ejected from this surface are analysed with respect to their energy and time-of-flight, giving information not only about the chemical element, but also the depth from which the atom was ejected. Thus, the technique allows to calculate depth profiles down to hundreds of nm from the surface.

**X-ray diffraction**
The intensities and angles of diffracted incident radiation can be used to study the crystallinity, crystal structure, and texture of materials. All presented in-house characterisation was obtained with Cu K-α radiation. A broad halo is associated with amorphous structures, while crystalline phases result in well-defined lattice planes that give rise to sharp diffraction peaks. A sample is described as X-ray amorphous when no such crystalline peaks are observed, which cannot rule out the presence of nanocrystallites, for which, for example, TEM analysis can be used. The fraction of nanocrystallites not detectable by XRD is estimated around 2% [73].

**Differential scanning calorimetry**
Thermal analysis is carried out by DSC to determine the glass transition temperature, crystallisation temperatures, and melting temperatures during a specified heating and cooling program. Conventional DSC employs mm-sized crucibles to encapsulate the sample under analysis and typically provides heating rates of 0.1 to 100 K/min and cooling rates
of -10 to -20 K/min [50]. FDSC uses much smaller samples, such as a single powder grain of around 20 μm diameter mounted on a measurement chip, as shown in Figure 4.2. Heating and cooling rates of up to 2,400,000 K/min can be reached [74].

**Nanoindentation**
Mechanical properties for papers III and IV were analysed using nanoindentation. An indenter tip is pressed against the surface of the material under analysis according to a specified load protocol while the displacement is measured. From the response of the material, hardness and elastic modulus can be calculated. By arranging a number of individual indents as a grid on the sample surface, the mechanical properties can be mapped.

**Thermodynamic calculations**
Thermodynamic calculations were carried out with the Thermo-Calc software [75], which is based on the Calphad approach. Calphad allows the calculation of the Gibbs energy and other thermodynamic properties to construct, for example, phase diagrams as presented in Figure 3.3, for which the TCHEA3 database was chosen.

### 6.3 Sample description

**Amloy powder (papers I, III, V)**
The Amloy powder supplied by Heraeus Amloy Technologies GmbH is used for all prints of the Zr-based material and is additionally directly chosen for measurements for the viscosity study presented in paper V.

**Amloy samples printed in argon (Papers I, II)**
Ar-prints produced from the Amloy powder were supplied by Jithin James Marattukalam [28]. Heat treated samples for paper I were provided by Victor Pacheco.

**Amloy samples printed or remelted in nitrogen (paper III)**
The reactively printed samples for Paper III were fabricated by LPBF from the Amloy powder in nitrogen atmosphere based on the earlier parameter development for argon gas [28]. The reactively remelted (surface remelted) samples were Ar-printed samples [28] that were laser-melted in a scan pattern across the surface in nitrogen atmosphere. The pa-
parameters were optimised to reach full coverage of the surface with lower power parameters.

**Arc-melted Amloy-based samples with controlled oxygen addition (papers II and VII)**

The alloys with different oxygen contents were produced by arc-melting with the nominal composition $\text{Zr}_{59.3-x}\text{Cu}_{28.8}\text{Al}_{10.4}\text{Nb}_{1.5}\text{O}_x$ with $x = 0, 1$ for Paper II and $x = 0, 0.2, 0.4, 0.6$ for paper VII. The samples for paper II were splat-quenched into substrate sheets, while the samples for paper VII were cast. The oxygen contents were analysed by ToF-ERDA after these additional processing steps. The actual oxygen content of these further processed samples was higher than the nominal composition with 0.3 and 1.3 at.% for paper II and 1.3 - 4.3 at.% for paper VII.

**Printed Fe-based samples (paper VI)**

For paper VI, the Fe-based composition $\text{Fe}_{73.8}\text{P}_{10.6}\text{Mo}_{4.2}\text{B}_{2.3}\text{Si}_{2.3}\text{C}_{6.7}$ was used for LPBF in argon to produce bulk pieces of approx. 1 mm build height.

**Single laser tracks (Papers II, III, IV, VI)**

Single laser passes were produced by placing bulk samples at the focal distances from the laser into the AM machine, as for one layer of powder, but without any supply. In the programme controlling the laser melting, the hatch distance was set to a large value to avoid any influence of the adjacent tracks upon each other and the other parameters were set as specified. Single tracks were produced on splat quenched sheets (paper II), bulk ZrN (paper III), Ti sheets (paper IV), and printed samples (paper VI).
Fasta ämnen är traditionellt associerade med atomärt välordnade kristallina material med en genomgående symmetri. Ett metallglas är ur ett termodynamiskt perspektiv ett material som uppvisar en "frusen" flytande struktur i ett fast tillstånd. Dessa material uppvisar en ordnad struktur på längdskalar upp till endast några få nanometer, och saknar därför en väldefinierad och genomgående kristallstruktur. En sådan struktur kan med tillräckligt höga kylhastigheter i princip uppnås för alla material, det är dock experimentellt utmanande för metalliska legeringar, då dessa kräver höga kylhastigheter. För tillverkningsprocesser så som gjutning innebär detta att endast små provstolekar kan erhållas för välutvecklade sammansättningar, eftersom ett större prov ger längre kylhastigten.


Metallglas kan kombineras med andra ämnen för att erhålla specifika egenskaper. Syre, till exempel, kan leda till en accelererande ordnad struktur (kristallisation), och bör därför undvikas under tillverkningsprocessen. Inkorporering av syre kan härröra från en rad processer, till exempel den omgivande gasen under smältning, råvaror, eller oxider på ytan som
förts in i materialet när den smälts av lasern. Liknande processer kan användas för att medvetet bilda specifika och gynnsamma partiklar. Ett exempel är nitridpartiklar, som lokal kan öka hårdheten och korrosionsbeständigheten.
Chapter 8

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Bibliography

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Acronyms

AM Additive Manufacturing. 1, 2, 3, 5, 9, 12, 13, 25, 26, 31
Amloy AMLOY-ZR01, Previous Trade Name AMZ4, Zr$_{59.3}$Cu$_{28.8}$Al$_{10.4}$Nb$_{1.5}$.
3, 5, 6, 7, 8, 9, 10, 11, 12, 15, 16, 17, 19, 20, 21, 22, 28, 30, 31
APT Atom Probe Tomography. ix, 4, 5, 6, 7, 13, 28, 29
BMG Bulk Metallic Glass. 1, 2, 3, 4, 5, 7, 12, 13, 16, 22, 23, 25, 26
BMGC Bulk Metallic Glass Composites. 3
CBED Convergent Beam Electron Diffraction. 28
CCR Critical Cooling Rate. 2, 12
DSC Differential Scanning Calorimetry. 12, 13, 17, 18, 22, 23, 29
EDS Energy Dispersive X-ray Spectroscopy. 9, 10, 29
FDSC Fast-scanning (flash) Differential Scanning Calorimetry. ix, 3, 19, 20, 30
FIB Focused Ion Beam Techniques. 28
GFA Glass Forming Ability. 3, 11, 12, 25
HAZ Heat Affected Zone. 10, 17
LPBF Laser Powder Bed Fusion. 1, 2, 3, 4, 5, 6, 7, 10, 11, 12, 13, 14, 15, 17, 18, 19, 20, 22, 23, 26, 27, 30, 31
MG Metallic Glass. 1, 2, 3, 4, 5, 25
MYEGA Mauro-Yue-Ellison-Gupta-Allan. 20
SAED Selected Area Electron Diffraction. 9, 10, 28
SANS Small Angle Neutron Scattering. 5, 9
SAXS Small Angle X-ray Scattering. 9
SEM Scanning Electron Microscopy. 13, 15, 22, 23, 24, 28, 29
STEM Scanning Transmission Electron Microscopy. 13
**Acronyms**

*Tg* Glass Transition Temperature. 2, 3  
*Tm* Melting Temperature. 2  
**TEM** Transmission Electron Microscopy. 9, 10, 13, 28, 29  
**ToF-ERDA** Time-of-flight Elastic Recoil Detection Analysis. ix, 9, 13, 14, 29, 31  
**TTT** Time-temperature-transformation. 2  
**Vit105** Vitreloy 105, Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_{5.1}$  
**WAXS** Wide Angle X-ray Scattering. 9  
**XRD** X-ray Diffraction. 12, 13, 15, 22, 29
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