

Manufacturing and aging behavior of CuCr1Zr powder: Analysis and modelling of close-coupled gas atomization of CuCr1Zr and its impact on the melt beam disintegration and analysis powder oxidation kinetics

Heinrich von Lintel^{a,*}, Ivo Šulák^b, Katrin Jahns^a, Ulrich Krupp^c

^a Faculty of Engineering and Computer Science, University of Applied Sciences Osnabrück, Osnabrück, Germany

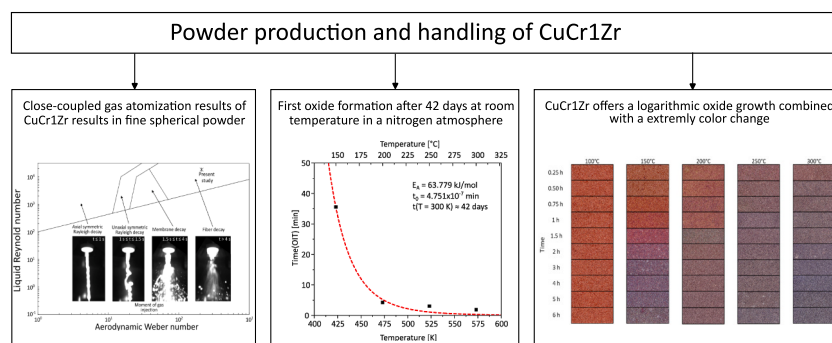
^b Institute of Physics of Materials, The Czech Academy of Sciences, Brno, Czech Republic

^c IEHK Steel Institute, Chair Materials Engineering of Metals, RWTH Aachen University, Aachen, Germany

HIGHLIGHTS

- The critical diameter for secondary disintegration is estimated using gas pressure.
- Close-coupled atomization at 8 bar argon pressure yields particles up to 200 μm .
- CuCr1Zr powder offers a logarithmic oxide growth including an extreme color change.
- First oxide formation is predicted after 42 days in a nitrogen atmosphere.
- Pre-aged powder reduces microhardness and conductivity in aged PBF-LB/M samples.

GRAPHICAL ABSTRACT



ABSTRACT

Powder bed-based additive manufacturing methods represent an increasingly vital role in industrial applications. Specifically, there has been considerable focus on highly reflective metals, such as CuCr1Zr, in recent years. However, current research primarily revolves around developing appropriate manufacturing parameters e. g. laser powder bed fusion (PBF/LB-M) and assessing the corresponding mechanical and electrical properties of CuCr1Zr. The impact of manufacturing routines and oxidation behavior of CuCr1Zr powder are seldom discussed in additive manufacturing. Therefore, the present study addresses the analysis of powder production and the oxidation behavior of CuCr1Zr powder via close-coupled gas atomization to analyze the disintegration of a CuCr1Zr melting jet during gas atomization of CuCr1Zr by using a high-speed camera. Critical conditions for secondary disintegration were calculated as a function of the initial gas pressure. Additionally, calorimetric measurements and isothermal oxidation experiments were conducted to quantify oxide formation and growth. According to the results, initial oxide formation occurs after 42 days with CuCr1Zr powder at room temperature in a nitrogen atmosphere. Subsequently, oxide growth follows a logarithmic law, associated with the formation and conversion of Cu_2O to CuO .

1. Introduction

Powder bed-based manufacturing has seen significant advancements

in additive manufacturing in recent years [1]. Particularly, there has been extensive research on highly reflective metals such as copper and low-alloyed copper alloys [2]. One of the most commonly used low-

* Corresponding author.

E-mail address: heinrich.von-lintel@hs-osnabrueck.de (H. von Lintel).

<https://doi.org/10.1016/j.powtec.2024.120356>

Received 19 August 2024; Received in revised form 3 October 2024; Accepted 8 October 2024

Available online 10 October 2024

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alloyed copper alloy in additive manufacturing involves the CuCrZr alloy system, which finds applications, e.g., as heat exchangers in the aerospace industry due to its high thermal conductivity and strength [1]. The application of CuCr1Zr in powder bed-based additive manufacturing spans across various techniques including laser powder bed fusion (PBF-LB/M), electron beam powder bed fusion (PBF-EB/M), and laser powder direct energy deposition (DED-LB/M) [2]. However, these different manufacturing routines require distinct particle size distributions. Typically, particle sizes for PBF-LB/M range from 10 μm to 60 μm [3], while PBF-EB/M necessitates particles between 60 μm and 105 μm [3], and for DED-LB/M, particle sizes from 50 μm to 150 μm are commonly used [4]. Commercially, powders for additive manufacturing are frequently produced using gas atomization due to its good scalability. Here, gas atomization is based on the pulverization of a molten metal jet through lateral gas injection and is categorized into free-fall application (FFA) and close-coupled application (CCA) [5]. In both cases, fine and spherical particles can be produced, ranging from a particle diameter of approximately 100 μm to 200 μm for FFA [6,7] and approximately 40 μm to 80 μm for CCA [6,8], respectively.

The current research on powder production via gas atomization concentrates on the impact of appropriate process parameters on the particles size distribution of pure copper [9]. In general, it can be concluded that the particle size can be controlled by the ratio of the gas mass flow to the melt mass flow [5,9,10]. Moreover, a decreasing particle size can be achieved by increasing the melt overheat [9]. The higher the ratio of the gas mass flow to the melt mass flow and the melt overheat, the finer the particles [5,9]. However, the critical condition to produce fine CuCrZr powder as a function of manufacturing parameters is scarcely reported in literature.

Furthermore, it is known that metallic powder has a high oxygen affinity due to the high ratio between the surface to the volume of powder particle [11,12]. Therefore, metallic powders are very susceptible to the formation of surface oxides. As a result, the degree of absorption changes with different surface conditions [13]. Hence, using the same set of manufacturing parameters can result in different microstructures and consequently in different properties depending on the stage of oxide formation. Therefore, the storage condition and the use at elevated temperatures during additive manufacturing is crucial for reproducibility of reported mechanical and electrical properties of CuCrZr in additive manufacturing. Mostly, the oxygen concentration is given in literature for this purpose. However, it is difficult to assess the surface oxide formation based on the reported oxygen concentration.

The present study aims to address this research gap by analyzing the atomization process as well as the oxidation behavior of CuCr1Zr. For this purpose, the CCA atomization process was recorded with a high-speed video camera. A detailed overview of the kinetic and thermal behavior of the powder particles was obtained by modelling the gas velocity, the droplet velocity as well as the cooling process of the droplets. Furthermore, the oxide formation and growth were estimated through calorimetric measurements and isothermal oxidation experiments.

2. Material and methods

2.1. Powder manufacturing of CuCr1Zr

In this study, oxygen-free copper (Cu-OFE), CuCr10 alloy, and CuZr50 alloy were utilized as raw materials for CuCr1Zr powder production using an Indutherm AU300 atomizer. The weighed raw materials were inductively heated in a graphite crucible up to 1450 $^{\circ}\text{C}$ and held at this temperature for 10 min.

Using pre-alloyed raw materials reduces the holding time to 10 min, as the overall liquids temperature of a homogenous melt is approximately 1080 $^{\circ}\text{C}$ [14] so that an overheating of 370 $^{\circ}\text{C}$ can be applied at the atomization process. In contrast, utilizing pure Cr and Zr results in a longer holding time to fully dissolve the coarse metal pieces, due to the

higher melting temperatures of Cr and Zr [15]. This approach decreases the likelihood of sudden nozzle blockage caused by the solidification of residual Cr or Zr particles within the nozzle.

Afterwards, the sealing rod was lifted, allowing the molten metal to pass through a CCA nozzle of 1.5 mm diameter. After a delay of 1.5 s, an argon jet with a pressure of 0.8 MPa (8 bar) was activated. Here, the atomization process was recorded using a high-speed video camera (Photron type Fastcam SA-Z/15.000 fps). The droplets solidify within a stainless steel vessel and the resulting powder particles are then collected at the bottom of the vessel. Throughout the atomization and subsequent cooling processes, the atomization chamber was purged with argon.

The chemical composition was verified by means of wet chemical analysis using an Agilent 5110 inductively coupled plasma optical emission spectroscopy (ICP-OES) machine. The remaining oxygen concentration was determined via carrier gas hot extraction process using a LECO RO 41DR analyzer. Particle size distribution was assessed before and after powder preparation using dynamic image analysis by a Cam-sizer X2. The desired particle size distribution for PBF-LB/M fell within the range of 10 μm to 63 μm [3]. Therefore, post-processing of the powder utilized sieving (mesh size = 63 μm) and air separation to adjust the upper and lower limit of the particle size.

Metallographic measurements of polished powder samples were conducted using analytical techniques in a high-resolution scanning electron microscope (field emission SEM Zeiss Auriga) in combination with energy dispersive X-ray spectroscopy (EDS Oxford X-Max 80). The samples were initially ground with silicon carbide paper to achieve a surface roughness of approximately 18 μm . Diamond suspension with diamond sizes of 9 μm , 3 μm , and 1 μm were applied. The final preparation step utilized a colloidal silica suspension with a silica size of 0.06 μm and a pH value of 10.

Lamellae for transmission electron microscopy (TEM) analysis were prepared in a dual beam field emission SEM Tescan Lyra 3 XMH. By means of focused ion beam (FIB) milling in combination with micro-manipulator and gas injection system site-specific TEM lift-outs were carried out. The surface of future lamellae was protected by a platinum layer, applied using electron then ion deposition. Rough milling via gallium ions at 30 keV, 1–4 nA produced a parallel-sided wall (1.5 $\times$ 15 μm) which is then platinum welded to an OmniProbe™ grid, fine milled (at $\pm 1.5^{\circ}$) to electron-transparency $\approx$ 80 nm (Ga^{+} , 30 keV, 0.1–1 nA) and eventually polished (Ga^{+} , 2 keV, 100 pA). The lamellae were examined in a Talos™ F200i TEM operating at 200 kV in scanning (STEM) mode in combination with a high-angle annular dark field (HAADF) detector, using bright field (BF) and dark field (DF) imaging. The TEM instrument is equipped with energy-dispersive X-ray (EDS) spectroscopy that, in combination with unique absorption correction in Velox software, empowers very accurate quantification.

2.2. Thermal analysis of CuCr1Zr powder

The oxidation behavior of metallic powder is a critical topic in powder handling, encompassing all stages of powder manufacturing and its use. The first oxide formation can already occur directly after the powder production by removing the hot powder from the collecting vessel. Typically, the powder cools down in an inert gas atmosphere. When the powder is removed at elevated temperatures, it reacts immediately with ambient oxygen. Consequently, the oxygen concentration of the powder changes due to oxidation, making it unsuitable for use in additive manufacturing. In most cases, lower temperatures and oxygen concentrations such like during PBF-LB/M are sufficient enough to start the oxidation reaction. Metallic powder is typically stored in a dry inert gas atmosphere at room temperature between the powder production and its use. During storage, the powder undergoes a natural aging process, resulting in an increasingly thick oxide layer around the powder particles. Thus, the feedstock for additive manufacturing changes in its chemical composition with prolonged storage.

Consequently, the corresponding manufactured component part offers a different chemical composition, which results in a deviation in the electrical and mechanical properties.

Thermal analyses are a helpful method to quantify the boundary and framework conditions for the formation and growth of oxides. The aim of the investigations is to use the results of the thermal analysis to optimize the powder handling of CuCr1Zr powder. To determine the formation temperatures of the oxides, TGA measurements are carried out followed by isothermal oxidation experiments to determine the diffusion kinetics. In addition, calorimetric measurement methods can be used to simulate oxidation under defined conditions such as atmosphere and temperature and to predict the first oxide formation at room temperature.

2.2.1. Thermogravimetry of CuCr1Zr powder

The initial step of the thermal analysis entails measuring the temperature range for oxide formation of CuCr1Zr powder within a highly oxygenated environment. To achieve this, thermogravimetric analysis (TGA) was conducted using the Mettler Toledo TGA/SDTA 851, ranging from 25 °C to 950 °C. During the heating the sample was heated up with a rate of 20 K/min within a ceramic crucible, while oxygen was supplied at a flow rate of 50 ml/min. The mass increase is recorded as a percentage throughout the measurement, and the first derivative is calculated from this recorded data. These analyses delineate the critical temperature range significant to the short-term application of CuCr1Zr powder within a highly oxidizing atmosphere. Consequently, the outcomes of the TGA serve as foundational data for subsequent thermal investigations, such as calorimetric and isothermal oxidation tests.

2.2.2. Oxidation induction time of CuCr1Zr powder

The experimental setup for oxidation induction time (OIT/ Mettler Toledo DSC 823) measurements uses two open aluminum crucibles. One crucible contains the powder sample, while the other remains empty and serves as a reference (see Fig. 1a). At all OIT measurements, the sample weight is amounted between 90 mg and 100 mg. Both crucibles are heated in a protective inert gas atmosphere, using the same heating rate of 20 K/min until reaching a predetermined temperature. For the present study, the conditions for oxidation were changed by altering the temperature and atmosphere so that the OIT measurements can be divided into two parts. In the first setup of OIT measurements, varying oxygen flow rates ranging from 5 ml/min to 15 ml/min were employed. Here, the sample crucible and the reference were heated to

150 °C. Subsequently, the temperature was maintained for 5 min in a nitrogen atmosphere with a flow rate of 15 ml/min. After 5 min, the atmosphere transitioned from nitrogen to oxygen. In the second setup, experiments were conducted at different temperatures, ranging from 100 °C to 300 °C, with increments of 50 °C, all within a protective nitrogen atmosphere with a flow rate of 15 ml/min.

The results are then evaluated by recording the heat flow as a function of time. During the heating, the temperature is independently monitored for each crucible. After a specified duration, the atmosphere transitions from a protective inert gas to an oxygen atmosphere. By knowing the mass of the sample, the heat flux can be measured. In the absence of any reaction, the heat flux remains constant, defining the baseline of the analysis (see Fig. 1b). The oxidation process begins once the activation energy of reaction is surpassed, the oxidation process initiates (see Fig. 1c). As a result of the exothermic reaction, a deviation in temperature becomes detectable (see Fig. 1d), leading to a fluctuation in heat flux. Hence, oxidation is indicated by this deviation from the baseline. Upon completion of the reaction, the heat flow of the sample returns to equilibrium, establishing a new baseline. The OIT time is determined using an onset method between these two baselines.

2.2.3. Isothermal oxidation experiments

Based on the temperature region of interest resulting from the above-mentioned TGA experiments and the information about the time scale of oxide formation via OIT, isothermal oxidation experiments can be performed to obtain additional information about the diffusion kinetics. For isothermal experiments, the mass gain normalized with the sample surface is measured against the time at a constant temperature. Disk-shaped samples are normally used for bulk material making the sample surface is easy to determine. However, the definition of the oxidizing surface for powders is rather difficult. Decreasing particle size increases the specific surface area of the powder particles [16]. Consequently, the surface area of the particle increases stronger compared to its volume so that smaller particles offer a high chemical activity. Hence, metallic powders with small particle diameter are very sensitive to e.g. oxygen [11,12]. However, it is very difficult to measure the mass gain for single particles with different diameters. The approach in the present study is to measure the average mass gain of a powder with a defined particle size distribution. Therefore, the thickness of the sample is reduced at least to one to two powder layers so that the main oxidizing surface corresponds to the cross section as shown in Fig. 2. During the experiments, the mass gain per oxidated surface of CuCr1Zr is measured for a duration of six hours at temperatures from 100 °C to 300 °C with steps of 50 °C in lab air, and the oxygen concentration is measured via ICP-OS. Based on the different colors between copper and its types of oxides, the change in color is recorded with a digital microscope (Keyence VS5000). For a reproducible comparison of the oxidation levels, the color images were converted into an 8-bit grayscale image so that the oxidation levels can be categorized on a scale between 0 and 255. The mean grey scale of the red spectra of each image is then plotted as a function of time.

2.3. Impact of pre-aged CuCr1Zr on LPBF

The impact of using pre-aged powder can be estimated with PBF/LB-M samples, which are made from strongly oxidized powder. Accordingly, CuCr1Zr was treated at a temperature of 200 °C for 2 days in lab air. Afterwards, the powder was used for a printing job using AMCM EOS M290 customized PBF/LB-M printer. The manufacturing parameters include a laser powder of 125 W, a scanning speed of 400 mm/s and hatching distance of 100 µm. For all iteration steps, cubic samples with a length of 8 mm are built. The scanning vectors rotate after each layer by about 67°. The layer thickness is adjusted to 20 µm and the laser beam has a beam diameter of approximately 50 µm at the field edge of the intensity distribution. The pre-heating of the building-platform (made of 316 L stainless steel) is 80 °C and an oxygen concentration of 0.1 % is

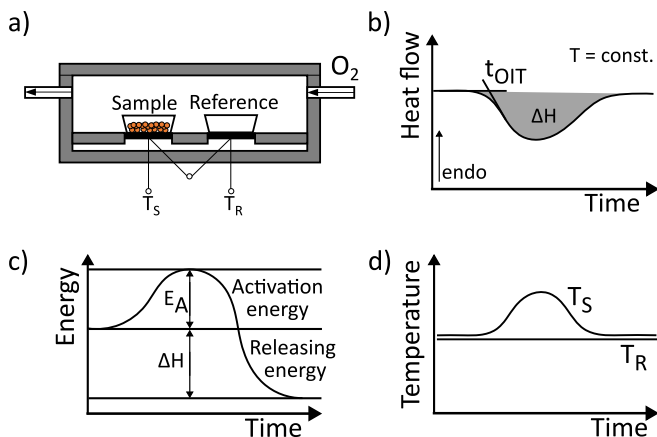


Fig. 1. Schematic illustration of a) experimental setup of the OIT measurement by illustrating of the furnace chamber with the sample crucible and a reference in an oxygen atmosphere, b) the energy condition of the sample as a function of the reaction time at an oxidation with c) the corresponding temperature distribution of the sample and reference showing an increase of temperature of the sample at an oxidation and the d) the corresponding measured heat flow of the sample an oxidation time.

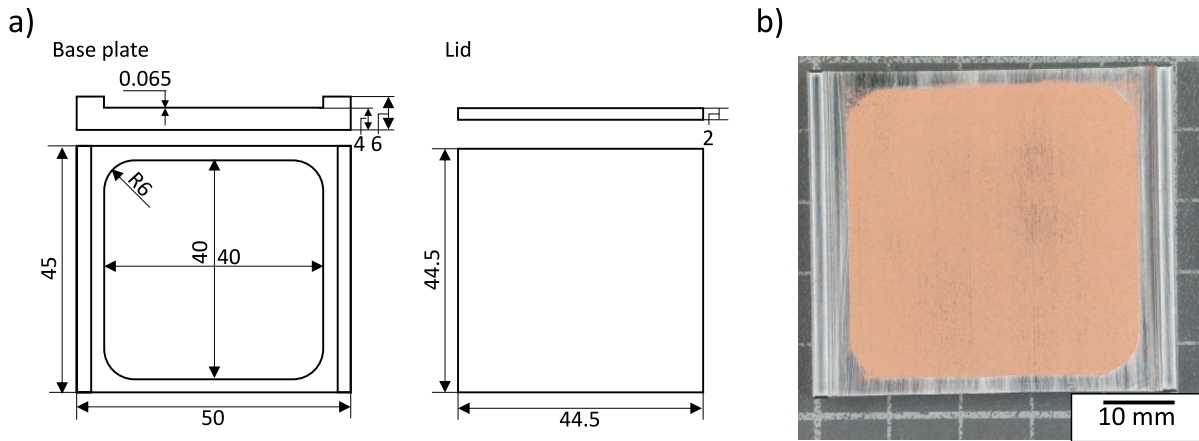


Fig. 2. a) Technical drawing (number in mm) of experimental set-up for testing a single powder layer during the isothermal oxidation test and b) a filled example with CuCr1Zr powder.

maintained in the process chamber. The analysis of the chemical composition and the metallographic preparation and analysis is described in section 2.1. Further properties of the additively manufactured CuCr1Zr are microhardness HV0.1 measured by the Fischerscope HM2000 (Fischer GmbH) and the analysis of the electrical conductivity via eddy-current principle (Sigmatest 2.069 / FOERSTER Holding GmbH) within the as-built condition as well as after a precipitation-hardening treatment at 480 °C for 2 h.

3. Modelling of kinematic and solidification conditions during atomization process

3.1. Modelling of gas velocity

The powder production via gas atomization is based on the interaction between the dripping melt jet and surrounding atomizing medium. Therefore, the thermal and kinematic conditions during the manufacturing process play a crucial role. According to Lee et al. [17], the gas velocity u_g can be determined using

$$u_g = u_0 \cdot \left(1 + \left(\frac{x}{\alpha \cdot \sqrt{A_e}} \right)^{20} \right)^{-0.05} \quad (1)$$

where u_0 is the initial axial gas velocity, x the axial flight distance, α an empirical constant related to gas dynamics viscosity (here $\alpha = 10.5$ [17]), and $A_e = \frac{\pi}{4} \cdot d_n^2$ the nozzle exit area.

Engineering devices such like nozzles essentially operate without exchanging heat ($dQ = 0$) with its surroundings [18]. Hence, the entropy of a fixed mass of the atomization medium does not change during the disintegration of the droplet. Thus, isentropic condition can be used as a suitable model for real process [18] like gas atomization utilizing a CCA-nozzle. When a perfect gas flows isentropically, its pressure and density are related to temperature in the following ways [19]:

$$\frac{\rho_0}{\rho} = \left(\frac{T_0}{T} \right)^{1/(\gamma-1)} \quad \text{and} \quad \frac{p_0}{p} = \left(\frac{T_0}{T} \right)^{\gamma/(\gamma-1)} \quad (2)$$

where ρ_0 and ρ the (initial) gas density, T_0 and T the (initial) gas temperature, and γ the specific heat ratio of the atomization medium. Experimental data showed that the gas temperature remains constant at room temperature during the manufacturing process. As a consequence the ratio T_0/T is one and therefore it can be assumed that the gas density is constant at the gas atomization inside the atomization chamber and during the disintegration of the droplet. This approach has been used several times in literature to estimate the gas velocity during [17,19,20]. Thus, the initial axial gas velocity can be evaluated from the isentropic

gas flow relation given by [19]:

$$u_0 = \frac{\dot{m}_g}{\rho_g \cdot A_e} \quad (3)$$

with

$$\dot{m}_g = \frac{A_e \cdot p_0 \cdot \sqrt{\gamma \cdot \left(\frac{2}{\gamma+1} \right)^{\frac{\gamma+1}{\gamma-1}}}}{\sqrt{R_s \cdot T_0}} \quad (4)$$

where $\dot{m}_g$ is the mass gas flow, ρ_g the density of the used atomization gas, $R_s = \frac{R}{M}$ is the specific gas constant of the atomization gas resulting from the ratio between the universal gas constant ($R = 8.314 \text{ J/(mol}\cdot\text{K)}$) and the molar mass of the atomization medium, γ the specific heat ratio of the atomization gas, p_0 the gas pressure and T_0 the initial gas temperature.

3.2. Modelling the droplet velocity

The flying droplets are accelerated and decelerated due to the high velocity differences of the atomization medium to the droplet velocity. By neglecting the fluctuating gas velocity due to turbulences, the motion of the droplet can be described as a spherical rigid body in a one-dimensional gas flow. In this case, the acceleration can be estimated by the Newton's second law. Considering that only inertia forces, gravitational forces and droplet drag forces are acting during the flight (see Fig. 3), the acceleration of the droplet can be estimated via [21]

$$\frac{du_d}{dt} = g \cdot \left(1 - \frac{\rho_g}{\rho_d} \right) - \frac{3}{4} \frac{c_d}{d} \cdot |u_g - u_d| \cdot (u_g - u_d) \quad (5)$$

where u_d , ρ_g are the velocity, and the density of the droplet, respectively and g the gravitational acceleration. The term du_d/dt represents the acceleration of the droplet. Since the gas velocity in Eq. (1) is a function of the axial flight distance, it is beneficial to express the droplet velocity as a function of the axial flight distance as well. Consequently, the expression for du_d/dt in Eq. (5) can be rewritten as:

$$\frac{du_d}{dt} = \frac{dx}{dt} \cdot \frac{du_d}{dx} = u_d \cdot \frac{du_d}{dx} \quad (6)$$

To calculate the droplet velocity, Eqs. (5) and (6) can be combined, resulting in a differential equation for du_d/dx :

$$\frac{du_d}{dx} = \frac{g \cdot \left(1 - \frac{\rho_g}{\rho_d} \right) - \frac{3}{4} \frac{c_d}{d} \cdot |u_g - u_d| \cdot (u_g - u_d)}{u_d} \quad (7)$$

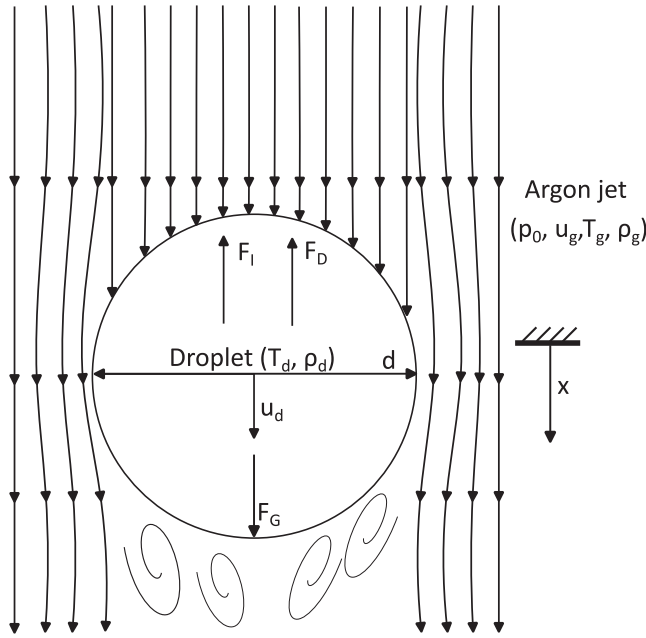


Fig. 3. Schematic illustration of the balance of forces showing the gravitational force (F_G), the inertial force (F_I) and the drag force (F_D) of a droplet with the velocity u_d , diameter d , temperature T and density ρ_d in an argon jet with the velocity u_g , temperature T and density ρ_g and the gas pressure p_0 .

Eq. (7) now represents a straightforward differential equation that can be solved numerically. Furthermore, the flight distance and flight time can be estimated using the droplet acceleration term, as acceleration is the second derivative of flight distance with respect to flight time.

$$\frac{du_d}{dt} = \frac{d^2x}{dt^2} = g \cdot \left(1 - \frac{\rho_g}{\rho_d}\right) - \frac{3}{4} \frac{c_d}{d} |u_g - u_d| \cdot (u_g - u_d) \quad (8)$$

The drag force c_d can be approximated with the empirical equation given by [22]:

$$c_d = 0.28 + \frac{6}{\sqrt{Re}} + \frac{21}{Re} \quad (9)$$

where Re is the aerodynamic Reynolds number determined by [17,23,24]

$$Re \equiv \frac{\rho_g \cdot d \cdot |u_g - u_d|}{\mu_g} \quad (10)$$

with d as the droplet diameter and μ_g as the gas dynamic viscosity. The term $|u_g - u_d|$ expresses the relative velocity v_r of the droplet to the atomization medium. In addition, the liquid Reynolds number Re_l is often used as a characteristic value for quantification of atomization behavior of metal melts by replacing the gas density with the density of the melt ρ_d [25]:

$$Re_l \equiv \frac{\rho_d \cdot d \cdot |u_g - u_d|}{\mu_g} \quad (11)$$

The effort to form a sphere is influenced by the surface tension and inertial forces. In the area of fluid mechanics, the aerodynamic Weber number is used for this purpose. Hence, the aerodynamic Weber number quantifies the ratio of acting inertial forces to stabilizing surface tension forces [24]:

$$We \equiv \frac{\rho_g \cdot v_r^2 \cdot d}{\sigma_l} \quad (12)$$

where σ_l the surface tension of the copper melt. The amount of the

Weber number is an indicator whether the inertial forces or the surface energy dominates the process. The higher the Weber number, the higher the influence of the inertial forces, where the driving force is the relative velocity of the droplet to the atomization medium. In the case that the aerodynamic Weber number is much higher than 1, inertial forces dominate the flow behavior. Consequently, the formed droplets are capable to disintegration in smaller droplets. In contrast, at Weber numbers much lower than 1, the surface energy forces of the droplet dominate the process and stabilize the spherical shape of the droplet. Therefore, the Weber number classify the different regimes of disintegration conditions [25].

3.3. Modelling the droplet cooling and temperature condition

Various mechanisms are affecting the cooling behavior of droplets from its liquid to solid stage. Important to highlight is that the convective cooling dominate the cooling process [26]. Due to the small volume of the formed droplets, it is assumed that they offer a homogeneous temperature distribution throughout their entire volume. This allows the cooling process to be described by the Newtonian heat transfer formulation [17].

3.3.1. Cooling in the liquid state

Based on the given assumptions, the temperature evolution during the liquid state can be determined by means of the following equation [17,23]:

$$\frac{dT_d}{dt} = - \frac{6 \cdot h \cdot (T_d - T_g)}{\rho_d \cdot c_L \cdot d} \quad (13)$$

where T_d is the droplet temperature, T_g the gas temperature ($T_g = T_0 = 27^\circ\text{C}$), c_L the specific heat capacity of the liquid droplet and h the convective heat transfer coefficient. The value of h can be estimated with the correlation of Ranz and Marshall [27]:

$$h = \frac{k_g}{d} \cdot \left(2 + 0.6 \cdot \sqrt{Re} \cdot \sqrt[3]{Pr}\right) \quad (14)$$

with k_g as the gas thermal conductivity and Pr known as the Prantel number, which is determined by [24]:

$$Pr \equiv \frac{c_{p,g} \cdot \mu_g}{k_g} \quad (15)$$

where $c_{p,g}$, μ_g is the specific heat and dynamic viscosity of the atomization medium.

3.3.2. Nucleation and recalescence

Gas atomization is a highly dynamic process so that a heterogeneous nucleation (see Fig. 4) is assumed in literature [17,23]. Here, the nucleation depends on the undercooling of the melt and can be described with the nucleation frequency J_V per unit volume [28–30]:

$$J_V = K_V \cdot \exp\left(-\frac{16\pi}{3 \cdot k_B \cdot T_d} \cdot \frac{T_L^2 \cdot \sigma_{SL}^2 \cdot f(\theta)}{\rho_d^2 \cdot \Delta H_f^2 \cdot (T_L - T_d)}\right) \quad (16)$$

where K_V is the kinetic parameter taken here as $10^{40} \text{ m}^{-3} \text{ s}^{-1}$, k_B the Boltzmann constant, σ_{SL} the solid-liquid interfacial energy, $f(\theta)$ the contact angle factor with a wetting angle θ , which describes the catalytic potency. Assuming an inverse relationship between the catalytic efficiency [31], the calculation catalytic potency can be simplified via

$$f(\theta) = \frac{2 - 3 \cdot \cos(\theta) + \cos^3(\theta)}{4} = a_1 + \frac{a_2}{d} \quad (17)$$

with the constant $a_1 = -5.025 \cdot 10^{-3}$ and $a_2 = 1.005 \mu\text{m}$.

In a continuous cooling process, the nucleation temperature can then be defined as [29,30]:

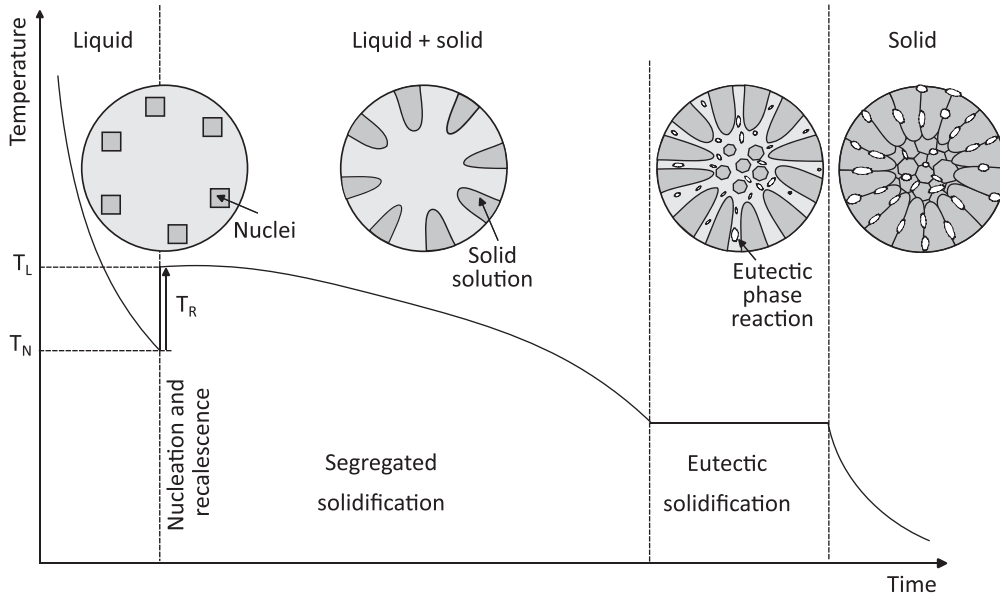


Fig. 4. Schematic diagram of the solidification process, illustrating temperature as a function of time for a single droplet. The diagram highlights key stages including recalescence due to nucleation, segregated solidification in both the liquid and solid phases, the eutectic phase reaction, and the temperature decline during the solid phase.

$$\int_{T_N}^{T_L} \frac{V_d \cdot J_V(T_d)}{\dot{T}} \cdot dT_d \approx 1 \quad (18)$$

where $\dot{T}$ is the cooling rate, which is given in Eq. (13). During the cooling process, the convective heat transfer coefficient h changes extremely due to the fast changing of the relative velocity. Therefore, the expression of the relative velocity is simplified for nucleation calculation with [17,23]

$$|u_g - u_d| \approx u_0 \cdot \left(\frac{T_d - T_g}{T_i} \right)^2 \quad (19)$$

where T_i is the melting temperature at the starting point of the atomization process.

After reaching the nucleation temperature, the temperature rises to the melting temperature T_L . This process is called recalescence (see Fig. 4). The temperature increase can be determined with the eq. [23]:

$$\frac{dT_d}{dt} = \frac{(\Delta H_f - (c_L - c_s)(T_L - T_d)) \cdot K \cdot (T_L - T_d)}{c_L \cdot d} \quad (20)$$

where K is a constant for the solid/liquid interface mobility (taken here as $10^{-2} \text{ m/(s} \cdot \text{K)}$ [32]). The percentage of the formed solid fraction f_s can be estimated with the expression [23]

$$\frac{df_s}{dt} = \frac{K \cdot (T_L - T_d)}{d} \quad (21)$$

The recalescence is finished, when $\frac{dT_d}{dt}$ is equal to 0. The corresponding amount of solid fraction is then termed as f_r . It should be pointed out that the Eq. (20) is only valid for a plane solidification front.

3.3.3. Segregated solidification

Due to the high cooling rates of the atomization process, the further segregated solidification takes place according to [33,34], where Scheil condition influence the temperature gradient and the calculation of the solid fraction:

$$\frac{dT_d}{dt} = \frac{(\Delta H_f - (c_L - c_s)(T_L - T_d))}{c_L} \cdot \frac{df_s}{dt} \cdot \frac{dT_d}{dt} - \frac{6 \cdot h \cdot (T_d - T_g)}{\rho_d \cdot c_s \cdot d} \quad (22)$$

with

$$f_s = 1 - (1 - f_r) \cdot \left[\frac{T_m - T_L}{T_m - T_d} \right]^{\frac{1}{1-k_0}} \quad (23)$$

and

$$\frac{df_s}{dt} = - \frac{1 - f_r}{(1 - k_0)(T_m - T_L)} \cdot \left[\frac{T_m - T_L}{T_m - T_d} \right]^{\frac{2-k_0}{1-k_0}} \quad (24)$$

In Eqs. (23) and (24) is T_m the melting point of pure copper and k_0 is the equilibrium partition coefficient, which is estimated here as 0.1 [35].

3.3.4. Eutectic solidification

When the droplet temperature reaches the eutectic temperature (T_E) of CuCr1Zr, the temperature remains stable until the remaining liquid is completely solidified ($f_s = 1$ / see Fig. 4). The time of the constant temperature can be estimated with the equation [17,23]

$$\frac{df_s}{dt} = \frac{6 \cdot h \cdot (T_E - T_g)}{(\Delta H_f - (c_L - c_s)(T_E - T_d)) \cdot \rho_d \cdot d} \quad (25)$$

3.3.5. Cooling in solid state

The cooling process at the solidified droplet can then determined by [17,23]

$$\frac{dT_d}{dt} = - \frac{6 \cdot h \cdot (T_d - T_g)}{\rho_d \cdot c_s \cdot d} \quad (26)$$

with c_s and ρ_d as the specific heat capacity and density of the solid droplet.

The parameters in Table 1 were used for the calculation of kinematic and thermal conditions during the atomization process. The above differential equations were solved with Matlab R2020a.

4. Results

4.1. Gas atomization of CuCr1Zr and resulting powder properties

4.1.1. Close-coupled atomization of CuCr1Zr

After reaching a defined length, the surface tension becomes

Table 1

Physical parameters of copper, CuCr1Zr and argon for the modelling process.

Parameter	Unit	Value	Reference
Melting temperature of pure copper (T_m)	°C	1083	[15]
Melting temperature of CuCr1Zr (T_i)	°C	1080	[14]
Eutectic temperature of CuCr1Zr (T_E)	°C	961	[36,37]
Latent heat of fusion of copper (ΔH_f)	kJ/kg	208.69	[38]
Density of liquid copper ($T = 1450$ °C) (ρ_d)	kg/m ³	7650	[39]
Solid-liquid interfacial energy of copper (σ_{sl})	J/m ²	0.189	[40]
Surface tension of copper ($T = 1450$ °C) (σ_l)	N/m	1.35	[38]
Specific heat capacity of liquid copper ($c_{p,l}$)	J/(kg·K)	571.76	[38]
Specific heat capacity of solid copper ($c_{p,s}$)	J/(kg·K)	370	[38]
Density of argon ($T = 27$ °C) (ρ_g)	kg/m ³	1.78	[38]
Specific heat ratio of argon (γ)	–	1.66	[38]
Specific gas constant of argon (R)	J/(kg·K)	208.1	[38]
Dynamic viscosity of argon (μ_g)	Pa·s	$2.25 \cdot 10^{-5}$	[38]
Kinematic viscosity of Ar (ν_g)*	m ² /s	$1.27 \cdot 10^{-5}$	
Dynamic viscosity of Cu (μ_m)	Pa·s	$3.69 \cdot 10^{-3}$	[41]
Kinematic viscosity of Cu (ν_m)*	m ² /s	$4.83 \cdot 10^{-7}$	
Nozzle exit diameter (d_n)	mm	1.5	present study
Gas mass flow ($\dot{m}_g$)	kg/h	300	present study
Melt mass flow ($\dot{m}_m$)	kg/h	103	present study
Ratio of gas mass flow to melt mass flow (GMR)	–	2.91	present study

* Calculated via $\nu = \mu/\rho$.

insufficient to counteract the force of gravity, leading to the necking of the melt stream and subsequent dripping of droplets. This phenomenon is referred to as an axial symmetric Rayleigh decay, cf. [25] (see Fig. 5a). In the current study, axial symmetric decay occurs within just 1 s after the nozzle opening. With increasing length of the CuCr1Zr melt jet, an interaction with the surrounding argon atmosphere intensifies, so that turbulence arises at the surface of the liquid stream. Due to the irregular shape of the stream, this regime is termed uniaxial Rayleigh decay, cf. [25] (see Fig. 5b). After a delay time of 1.5 s after the nozzle opening, lateral gas injection with Argon at a pressure of 0.8 MPa (8 bar) commences. Between 1.5 s and 4 s, an area of low-pressure was formed, causing a back pressure regime that pushes the melt to the edge of the nozzle, which is characteristic for the membrane decay, cf. [25] (see Fig. 5c). After a total time of 4 s, a stable area of low pressure is established, inducing a highly turbulent flow condition. At this point, the CuCr1Zr stream becomes highly unstable after passing through the nozzle due to the high forces exerted by the area of low pressure. If smaller melt streams emerge, the disintegration regime is referred to as

fiber decay, cf. [25] (see Fig. 5d)

At a stable atomization process, the aerodynamic Weber number and the liquid Reynolds number for the current study can be estimated using Eqs. (10) and (12) with a nozzle diameter (d_n) of 1.5 mm, a relative velocity (v_r) of 326 m/s (see section 4.1.2) and using the physical properties listed in Table 1. Consequently, an aerodynamic Weber number of 210.2 and a Reynolds number of $1.81 \cdot 10^4$ can be assumed for the primary disintegration observed in the present study.

4.1.2. Results of the modelling gas velocity, droplet velocity and aerodynamic Weber number

The dripping of the droplets from the ligaments during the primary disintegration results in a sudden acceleration and subsequent deceleration of the droplets. Depending on the droplet size and velocity, a further secondary disintegration may occur. The calculation of the droplet velocity with different diameter and corresponding Weber number is shown in Fig. 6.

The acceleration of droplets is influenced by the initial gas velocity (see Fig. 6a). Applying a gas pressure of 0.8 MPa (8 bar), an initial gas velocity of 326 m/s was calculated for the argon stream, which remains constant for a distance of 0.12 m. Afterwards, the gas velocity decreases significantly to 91 m/s at an axial flight distance of 0.5 m. It can be assumed that smaller droplet sizes experience higher acceleration and deceleration. For droplets with a diameter of 25 μ m, the maximum velocity is approximately 147 m/s after 0.31 m, followed by a decrease in velocity. Conversely, a droplet diameter of 400 μ m results in a maximal velocity of 14.7 m/s after an axial flight distance of 0.5 m.

Based on the distribution of gas and droplet velocities, the relative velocity can be calculated (see Fig. 6b). Initially, the differences between various droplet sizes are minor and can be estimated using the initial gas velocity. The distribution of relative velocity forms the basis for estimating the aerodynamic Weber number of different droplet sizes (see Fig. 6c). Here, droplets with a diameter of 25 μ m have an initial Weber number of 3.5. As the droplet diameter increases, the Weber number increases as well. The droplets with a diameter of 400 μ m have an initial Weber number of 56. Due to the rapid decrease in relative velocity of droplets, the Weber number exhibits a similar trend. Consequently, the Weber number decreases to 2 after a flight distance of 0.5 m for a droplet diameter of 400 μ m.

4.1.3. Solidification of the CuCr1Zr droplets

After the droplets have left the nozzle, the cooling and solidification process ensues, exhibiting considerable variations depending on droplet size (see Fig. 7 a + b). Small particles with a diameter of 25 μ m solidify within a time span of less than 2 ms. In contrast, droplets with a diameter of 400 μ m require 115 ms for a complete solidification. Here, the first nuclei are formed after 49.9 ms. Afterwards, a continuous solidification takes place. Thereby, the segregated solidification needs 63.97 ms and is followed by the eutectic phase reaction, which is completed within 1.13 ms.

Furthermore, the nucleation temperature and undercooling of the droplets vary. Generally, smaller droplet diameters correspond to higher undercooling. However, the calculated temperature distribution does not exhibit a linear relationship between droplet size and nucleation temperature. Consequently, nucleation commences at an approximate temperature of 1023 °C for droplets with a diameter of 25 μ m, while for droplets with a diameter of 400 μ m, the nucleation temperature is calculated to be 1075 °C.

Throughout the solidification process, the droplet undergoes recalcence, segregated solidification, and the eutectic reaction. Due to differing cooling behavior, varying amounts of solid fraction were formed at each stage. During recalcence, the highest amount of solid fraction, 0.1552, is calculated for a droplet diameter of 25 μ m, decreasing to 0.003 for a droplet size of 400 μ m. Generally, the highest amount of solid fraction occurs during segregated solidification, ranging from 0.823 for a droplet diameter of 25 μ m to 0.972 for a droplet

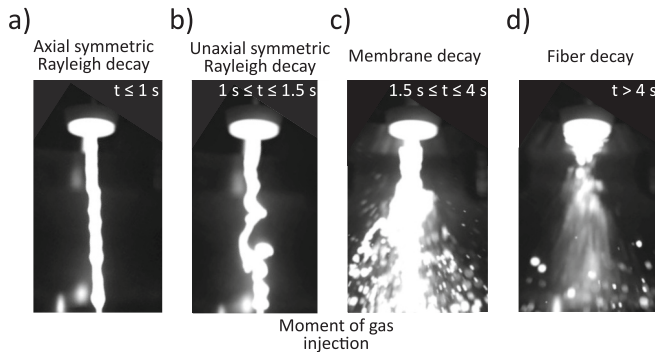


Fig. 5. Recordings of high-speed camera of the close-coupled atomization process showing a) the axial Rayleigh decay, b) uniaxial Rayleigh decay, c) membrane decay and d) a stable atomization process with a Fiber decay.

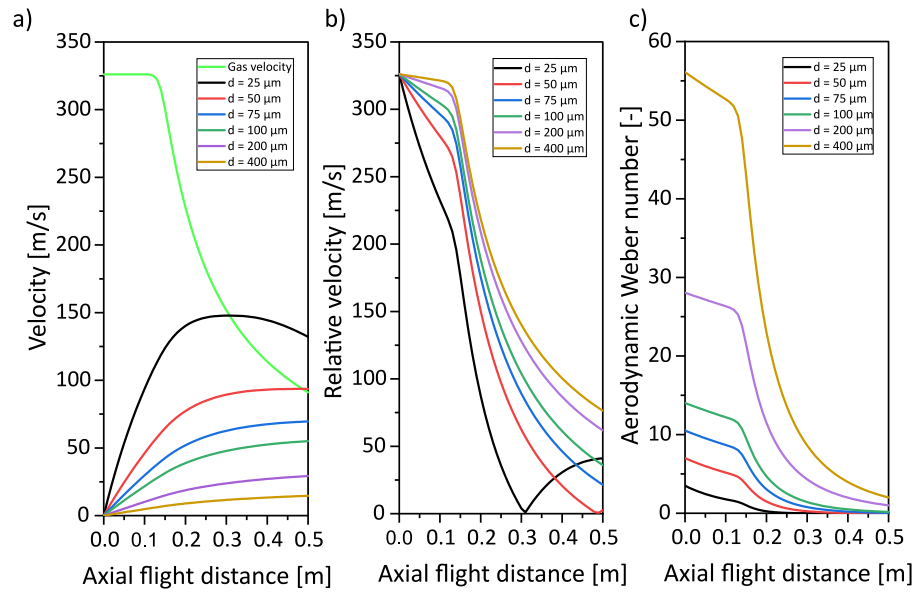


Fig. 6. Results of modelling a) the gas velocity distribution ($u_0 = 326 \text{ m/s}$), droplet velocity distribution for droplet diameters in the range of 25 μm and 400 μm , and c) the corresponding relative velocity and aerodynamic Weber number.

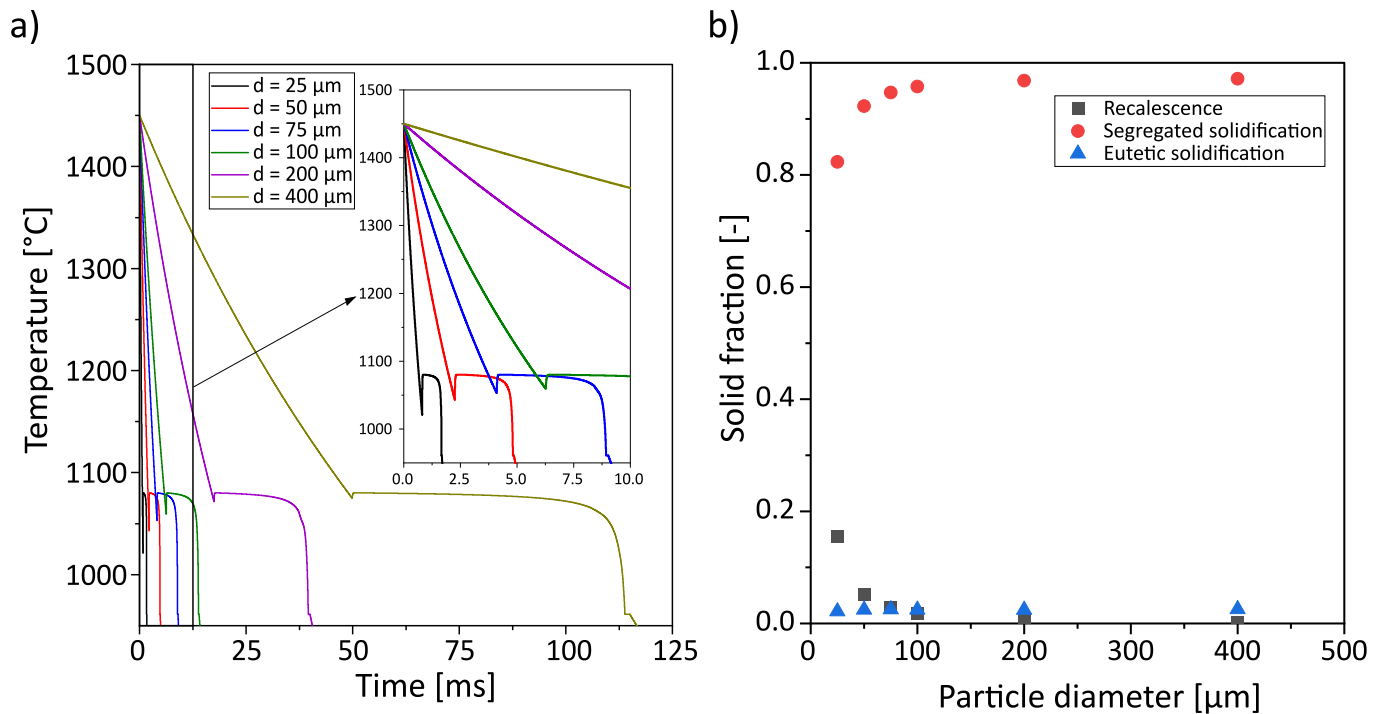


Fig. 7. Results of modelling a) the temperature profile during the cooling process of droplets with diameters in the range of 25 μm to 400 μm , and b) the percentage of solid fraction during the recalescence, the segregated solidification and the eutectic solidification as a function of the particle diameter.

diameter of 400 μm . Regarding the eutectic reaction, the values for solid fraction are very similar, resulting in a slight increase in solid fraction from 0.0215 for droplets with a diameter of 25 μm to 0.0254.

4.1.4. Powder properties

Most particles resulting from membrane and fiber decay exhibit the desired particle diameter for additive manufacturing. As mentioned above, for PBF-LB/M a particle size between 10 μm and 60 μm is preferred. Therefore, larger particles must be removed from the raw feedstock via sieving with a mesh size of 63 μm . Conversely, smaller particles can be eliminated through air separation. The particle size

distribution, along with corresponding overviews before and after sieving and air separation, is illustrated in Fig. 8. Prior to powder preparation, a significant proportion of very small and large particles are observed. Consequently, the $d_{10.3}$ value is measured at 16.81 μm , while the $d_{90.3}$ falls within the range of 88.83 μm . The corresponding mean diameter, $d_{50.3}$, is calculated to be 42.30 μm . Following powder preparation, the particle size distribution exhibits a considerably narrower range of diameters. Consequently, the $d_{10.3}$ value increases to 20.12 μm , while $d_{50.3}$ is 35.58 μm , and $d_{90.3}$ is 56.40 μm . Furthermore, the atomized powder shown in Fig. 8b exhibits agglomerations, which can form due to van-der-Waals forces, electrostatic forces, and liquid bridges

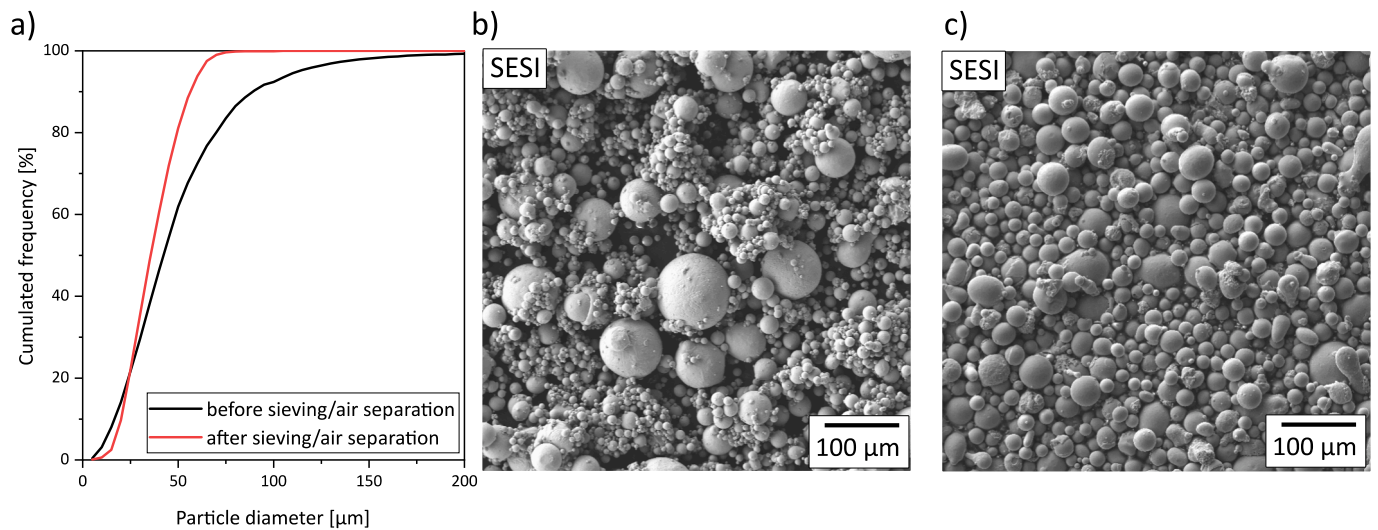


Fig. 8. Illustration of the powder properties by showing a) the particle size distribution before and after powder preparation and overview of the morphology b) before the powder preparation and c) after the powder preparation recorded via SEM.

between particles [42]. However, agglomerations caused by van-der-Waals and electrostatic forces are reversible, meaning they can be removed after powder preparation.

Fig. 9a) depicts the morphology of the powder particles following powder preparation. Gas atomization results in highly spherical particles, with a measured roundness of 0.95. According to Powers' roundness grading system [43], particles with a roundness exceeding 0.7 are

classified as well-rounded.

The manufactured CuCr1Zr powder has a chromium concentration of 0.941 wt.-%, a zirconium concentration of 0.158 wt.-%, and an oxygen concentration of 55 ppm, respectively. Moreover, a network of chromium precipitates was observed predominantly at the grain boundaries of the powder particles' surface. The size of these precipitates ranges up to 625 nm. Due to the location at the surface of the particle in

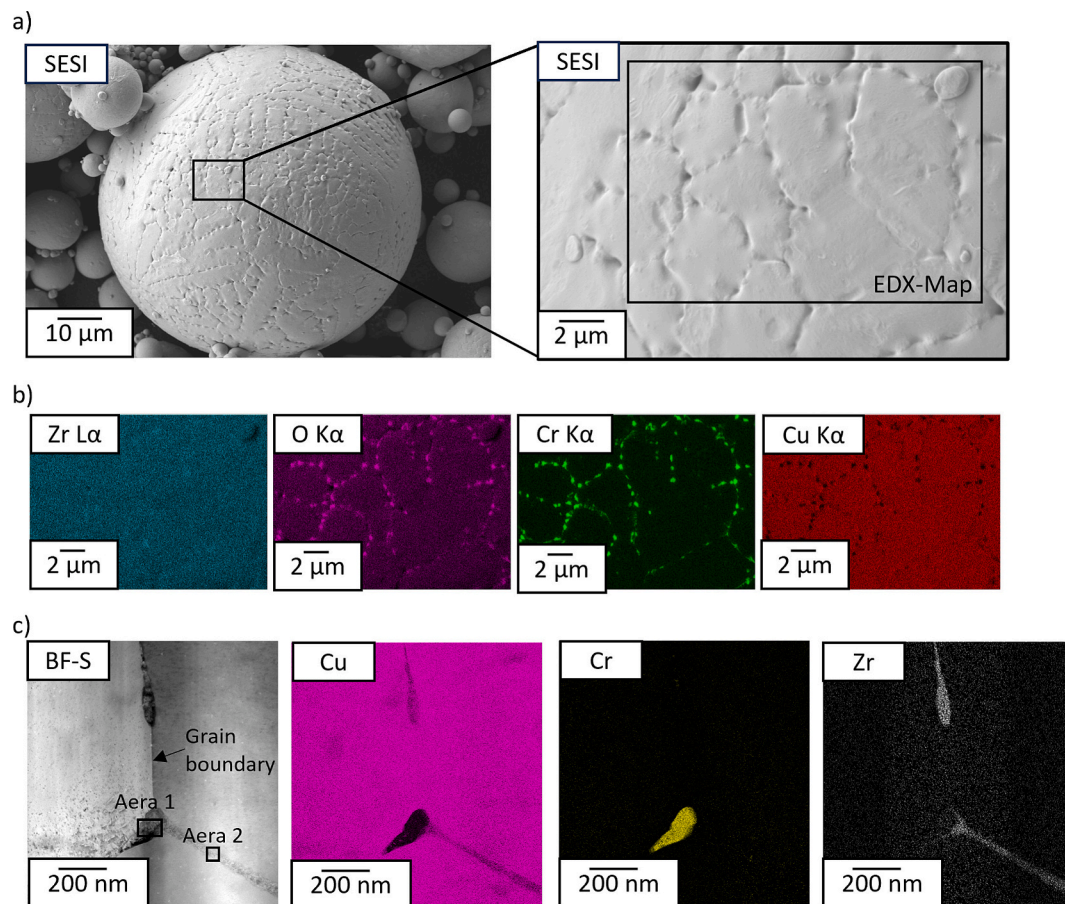


Fig. 9. a) Overview of a single CuCr1Zr-particle with b) an EDX-map of particle surface showing a network of chromium oxide and c) cross section of a powder particle via STEM and corresponding elemental distribution.

combination with a high oxygen affinity of Cr results in a fast oxidation of the precipitates. Therefore, a selective oxidation can be seen at the particles surface of CuCr1Zr (see Fig. 9b). The oxidation of the Cr precipitates may have occurred during powder handling in the powder preparation process. Afterward, the powder was stored in a hermetically sealed container filled with Ar. A similar network is discernible within the powder particles, as depicted in Fig. 9c. However, the observed particles consist predominantly of Cr and Cu/Zr. In area 1, the Cr concentration is approximately 79.9 at.-%, with Cu comprising approximately 13.4 at.-%. However, the reported concentration of Cu in Cr is amounted to max. 2.2 at.-% [44] so that it can be concluded that parts of the surrounded Cu matrix were also measured. It is noted in literature that copper-rich Cr precipitates form due to the low solubility of Cr in a copper melt, which is approximately 0.7 wt.-% [15,45–48]. Additionally, in area 2, the Cu concentration is approximately 68.4 at.-%, and Zr constitutes approximately 7.1 at.-%. Thermodynamic calculations suggest the potential formation of various intermetallic compounds between Cu and Zr, distinguished by their chemical composition and structure [49]. Commonly reported stoichiometries of such compounds include Cu_4Zr , Cu_5Zr , and $\text{Cu}_{51}\text{Zr}_{14}$ in conventional materials [15,45–48]. Here, similar phases were observed in other manufacturing processes with comparable cooling rates, such as laser-based powder bed fusion, where cooling rates between 10^4 K/s and 10^6 K/s have been reported [2]. In comparison, gas atomization provides cooling rates of up to 10^5 K/s [50].

4.2. Temperature limit

According to the TGA measurement and its first derivation (see Fig. 10), no mass gain could be measured at temperatures up to 200 °C in a strongly oxidizing atmosphere. Afterwards, the recorded curve increases continuously, which indicates the first oxide formation. At a temperature of 235 °C, the initial mass gain stops and changes into a plateau, which implied the end of the oxide reaction. A renewed increase of the derived curve starts at temperatures from 350 °C and ends at 380 °C. Hence, the thermal analysis indicates a second oxide reaction in this temperature regime. The greatest increase in slope is recorded at a temperature of around 590 °C followed by a rapid decrease of the derived curve. The rapid increase and decrease in mass gain suggests the formation of a dense passivation layer around the particles, which hinders further oxygen diffusion and thus prevents additional oxidation. Thus, a decrease in mass gain were overserved. At a temperature around 790 °C, a renew strong decrease can be observed.

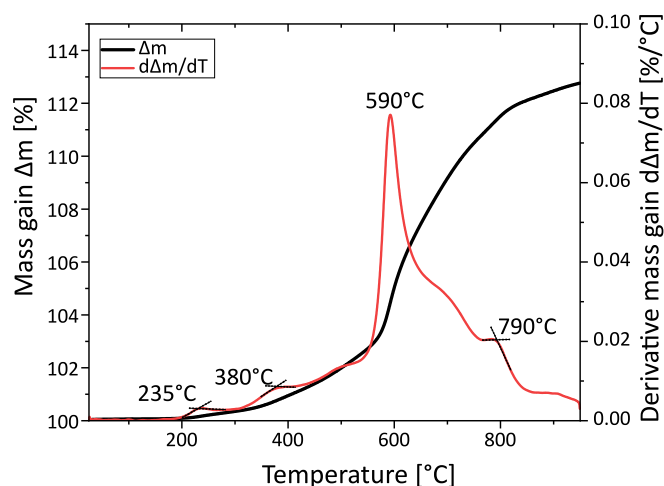


Fig. 10. Thermogravimetry of CuCr1Zr powder and its derivative in the temperature range from 25 °C to 950 °C with a heating rate of 20 K/min and an oxygen flow rate of 50 ml/min showing the oxidation the powder.

4.3. Oxidation resistance

At a temperature of 150 °C, the onset of oxidation exhibited only slight variations at different oxygen levels (see Fig. 11a). Specifically, at flow rates of 15 ml/min and 10 ml/min, the change in heat flow was measured at approximately 1.3 min. At the lowest flow rate of 5 ml/min, the starting time increased slightly to 1.86 min. Consequently, it is imperative to store CuCr1Zr powder in a protective gas atmosphere. OIT measurements can also be conducted at temperatures ranging from 100 °C to 300 °C within a protective nitrogen atmosphere of 15 ml/min (see Fig. 11b). At 300 °C, oxidation commenced after 1.9 min, accompanied by a substantial release of energy at -27.27 J/g. With decreasing temperature to 250 °C, the onset of oxidation increased to 3.07 min, and at 200 °C, it reached 4.24 min. Notably, at 200 °C, there was a significant decrease in released energy, from -20.42 J/g to -7.71 J/g. In the temperature range of 150 °C, oxidation set in after 35.56 min, with the measured energy being very low at -4.65×10^{-3} J/g. At the lowest temperature of 100 °C, defining the onset of oxidation proved challenging. Here, two options must be considered. The first option is that oxidation starts after 60 min, which is beyond the measurement duration. Considering the fact, that the released energy at 100 °C must be lower than at 150 °C, the minimal change in heat flow at 100 °C makes it difficult to distinguish a decrease in heat from the baseline.

4.4. Oxide growth

In a good agreement, the oxidation-induced mass gain at all temperatures follows a logarithmic rate law. The different evolutions of the oxidation-induced mass gains can be characterized with the temperature dependent constant k and the integration constant τ (see Fig. 12a). The range for k has risen constantly from 0.02698 mg/cm² at 150 °C to 0.12415 mg/cm² at 300 °C (see Table 2). Whereas τ differs from 0.71349 h at 150 °C to 0.21741 h at 300 °C. After 6 h at the different temperatures, the mass gain at 150 °C was up to 0.0701 mg/cm² and 0.43337 mg/cm² at 300 °C. It should be noted that the oxygen concentration increases more rapidly after exceeding 4 h at 300 °C than the logarithmic prediction suggests. A possible explanation for this is the onset of breakaway oxidation [51], where the formed oxide layer spalls off the powder particles, exposing fresh copper surfaces that can oxidize again. As a result, a higher mass gain is observed. This spalling of the oxide layer is supported by the presence of strong oxides in the powder, as shown in Section 4.6, Fig. 14. The mass gain at a temperature of 100 °C cannot be measured with this technique. However, for the estimation of state of oxidation for temperature between 100 °C and 300 °C, the oxygen content was measured with hot gas extraction (see Fig. 12b). Here, the curve progression indicates also a logarithmic oxide growth behavior. For 100 °C, the oxygen concentration differs between 55 ppm and 193 ppm. For temperatures of 150 °C, the oxygen concentration is almost in the same order of magnitude and has a maximal value of 360 ppm. The highest increase of the oxygen content can be measured at 300 °C. After 6 h at this temperature, the oxygen content increases to 7320 ppm.

A much easier way of quantifying the state of oxidation is the change in color (see Fig. 13). Here, the recorded pictures of the digital microscope were analyzed with the software ImageJ. For the image analysis, each image was separated into the color component red, blue, and green. The color separated images were then shown in a grey value. The mean grey scale value were then measured and plotted as a function of time. For 100 °C, no change in color is visible. Therefore, the grey scale is almost constant at 174 for the time increment of 6 h. The same amount of grey scale can be observed at 150 °C only for 1 h. Afterwards the values decrease to values of 130 at 3 h. At temperature from 200 °C to 300 °C, there is an immediate change in color. The highest change in color is observed at 300 °C. After 6 h of heat treatment, the values decrease from 174 to 115.

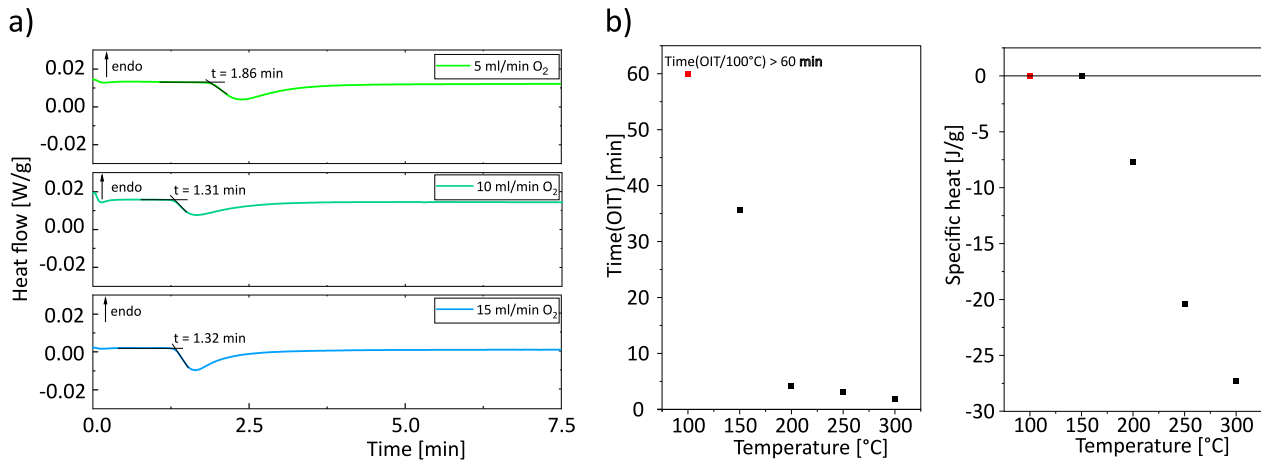


Fig. 11. a) Results of the OIT-measurement at different oxygen flow rate from 5 ml/min to 15 ml/min ($T = 150\text{ °C}$) illustrating an oxidation starting time in the range from 1.31 min to 1.86 min and b) illustration of OIT-time at different temperatures from 100 °C to 300 °C at nitrogen flow rate of 15 ml/min and the corresponding specific heat during oxidation.

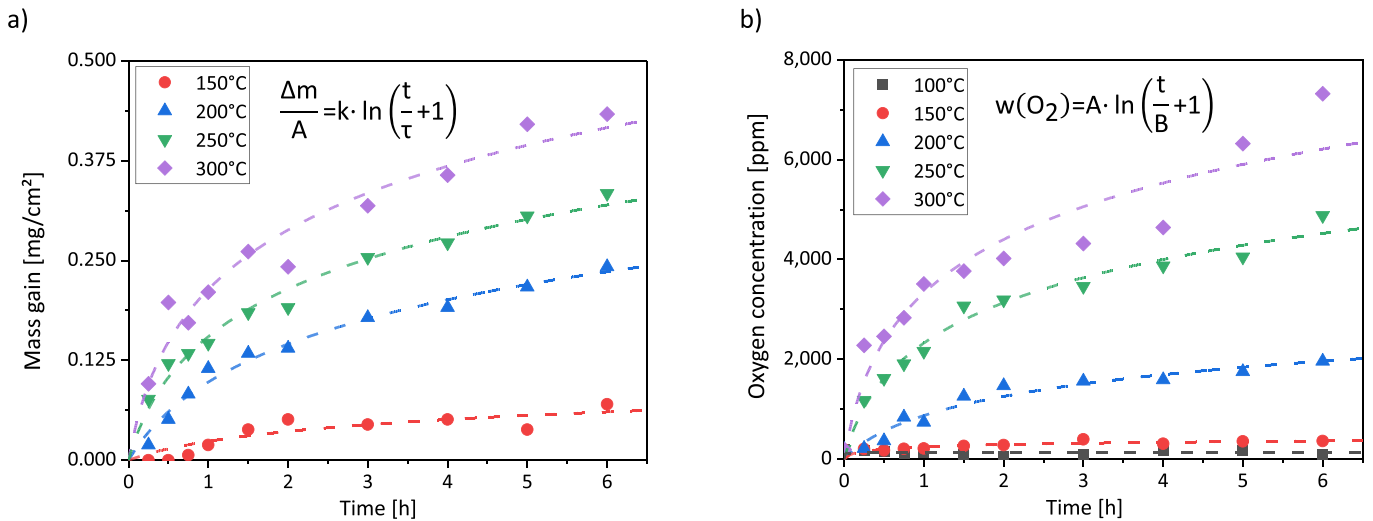


Fig. 12. a) Mass gain of CuCr1Zr powder at temperatures from 150 °C to 300 °C at lab air and b) the corresponding oxygen concentration including the temperature of 100 °C.

Table 2

Corresponding values of mass gain and oxygen concentration.

Temperature [°C]	Mass gain		Oxygen content	
	k [mg/cm ²]	τ [h]	A [–]	B [h]
100	/	/	1.233	$8.4167 \cdot 10^{-45}$
150	0.02698	0.71349	67.733	0.0147
200	0.09644	0.56849	723.509	0.4268
250	0.10415	0.29253	1345.623	0.2159
300	0.12415	0.21741	1734.114	0.1718

4.5. Properties of PBF/LB-M component using pre-aged CuCr1Zr powder

Fig. 14 illustrates the use of strong oxidized CuCr1Zr powder for a printing job. After an artificial aging at 200 °C for 2 days in lab air, a thick oxide layer was formed around the surface (see Fig. 14a). Here, a spalling of the brittle oxide layer from the particle surface was observed. As a result, coarse oxides phases were incorporated into the matrix material by using pre-aged powder for PBF/LB-M (see Fig. 14b). The shown EDS elemental maps indicate that the formed oxides consisted mainly of Cr and Zr, which are not reported by applying the same

manufacturing routine [52]. Based on the presence of coarse oxides in the microstructure, the different electrical and mechanical properties were measured compared to the reported values in [52]. In the as-built condition, a microhardness of 112HV0.1 was measured by using the presented pre-aged CuCr1Zr powder (see Fig. 14c). A similar value for the microhardness is reported in literature, where a microhardness of 109HV0.1 was listed. A higher difference can be seen by a comparison of the electrical conductivity. Here, the samples with coarse oxides in the as-built condition had an electrical conductivity of 27.7 MS/m, while the sample without the coarse oxides offer a conductivity of 11.11 MS/m. According to Nordheim's rule, the fewer foreign atoms or imperfections in the copper matrix, the better the electron transport through the lattice, leading to higher electrical conductivity [53]. When using unused CuCr1Zr powder for PBF-LB/M, it is assumed that more Cr and Zr dissolve into the copper matrix compared to pre-aged powder. This increased amount of dissolved elements causes greater lattice distortion, which in turn reduces electrical conductivity. In contrast, a significant portion of Cr and Zr in pre-aged powder is consumed in oxide formation, leaving fewer alloying elements to dissolve in the copper lattice. As a result, higher electrical conductivity is observed when using pre-aged powder.

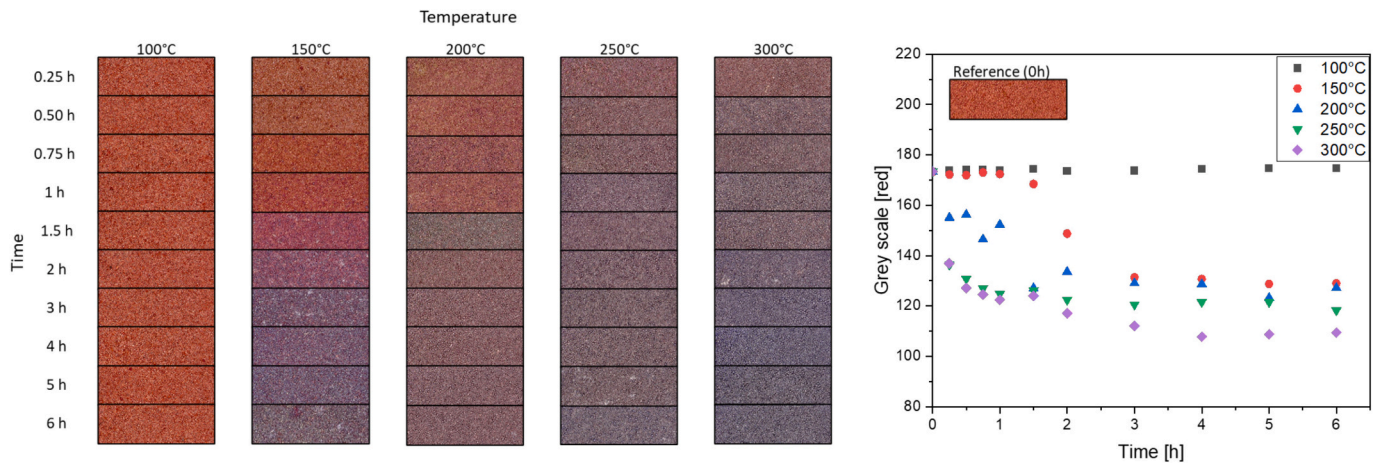


Fig. 13. Illustration of the color change due to oxidation of CuCr1Zr powder in a time scale up to 6 h in a temperature range between 100 °C and 300 °C and the corresponding change of the grey scale.

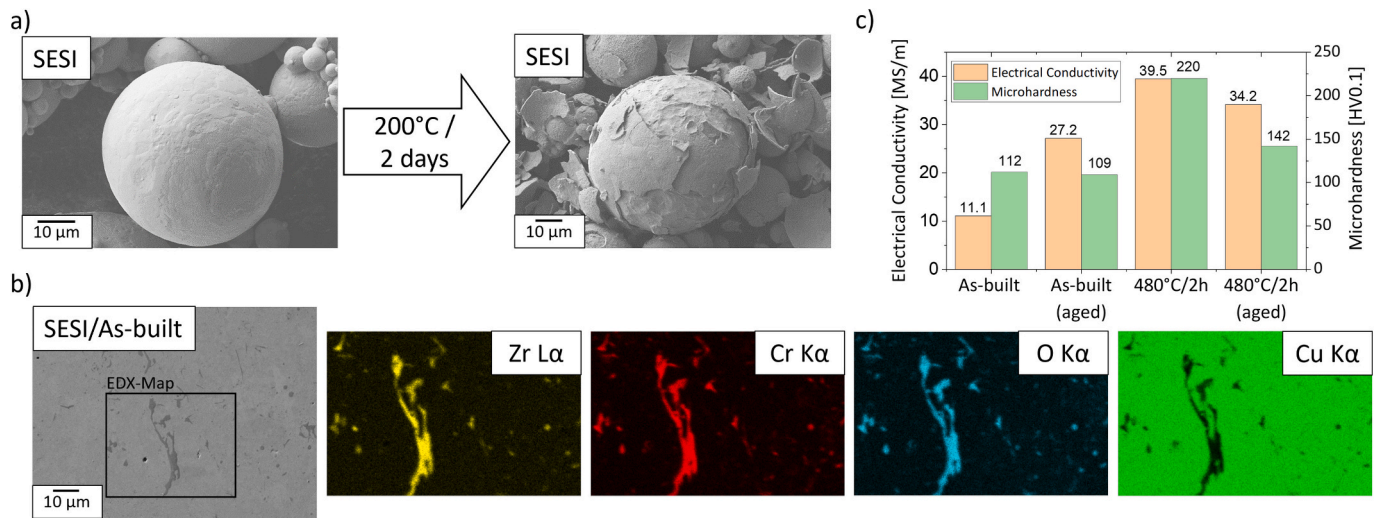


Fig. 14. Impact of aging CuCr1Zr powder showing a) the oxide layer formation ($T = 200\text{ °C}$ for 2 days) in lab air, b) incorporation of Chromium- and zirconium oxide into the matrix and c) the resulting microhardness and electrical conductivity (reference values taken from [52]).

After a heat treatment at 480 °C for 2 h, the microhardness of the samples of the pre-aged powder rise to a value of 142HV0.1, while the use of powder without a thick oxide layer results in a microhardness of 220HV0.1 after precipitation hardening. In contrast, the electrical conductivity shows a different behavior after precipitation hardening compared to the as-built condition. Before the heat treatment at 480 °C for 2 h, the samples, which were built with the pre-aged CuCr1Zr powder offered a higher electrical conductivity. After the precipitation hardening, these sample had with 34.2 MS/m a lower conductive compared to the reference value of 39.5 MS/m. After precipitation hardening, the formation of intermetallic compound clusters reduces the amount of dissolved elements, leading to a significant increase in conductivity. According to the literature, the higher the concentration of dissolved elements, the lower the activation energy required for cluster formation [54]. Since pre-aged powder contains fewer dissolved elements, a higher activation energy is needed for precipitation hardening. Consequently, less cluster formation occurs compared to fresh powder, leaving more dissolved elements in the copper matrix. As a result, lower microhardness and electrical conductivity were measured in CuCr1Zr samples after precipitation hardening when using pre-aged powder.

5. Discussion

The present study of powder manufacturing and handling of CuCr1Zr shows that a gas pressure of 0.8 MPa argon results stable fiber decay of the melting beam as a primary disintegration. Here, the unprepared powders showed particles size up to 200 µm. Furthermore, the results have shown that the particles are composed of a network of Cr and CuZr phases, which have formed preferentially at the grain boundaries. In addition, the present study illustrates that CuCr1Zr powder manifests a high reactivity with respect to an oxygen atmosphere. Therefore, the first oxide formation appears within a short time space followed by a fast logarithmic oxide growth. Therefore, the following discussion should explain the critical conditions for further secondary disintegration as a function of the manufacturing parameter. Further, a detailed description of the oxidation mechanisms will be given. At the end of the discussion, the effects of oxidation of CuCr1Zr powder for use in additive manufacturing will be described.

5.1. Gas atomization of CuCr1Zr

The focus of gas atomization is based on the adjustment of a defined particle size distribution so that amount of powder for additive

manufacturing with the desired particle size can be maximized. Therefore, material and manufacturing parameters, as well as the properties of the atomization medium have to be considered. Overcoming the critical conditions for a secondary breakup is the crucial factor. This study aims to gain further insights into secondary breakup by integrating simulated cooling processes (see Fig. 7) with calculated Weber numbers (see Fig. 6).

5.1.1. Droplet formation of CuCr1Zr during CCA atomization

For an evaluation of the high-speed images of CCA atomization, Chigier and Fargo [25] had established a classification of the disintegration regimes by plotting the liquid Reynolds number as a function of the aerodynamic Weber (see Fig. 15a). An axially symmetric Rayleigh

decay only occurs at very low Weber numbers smaller than 25, cf. [25]. Lefebvre et al. [24] estimated the droplet dimensions in this area to be 1.89 times the nozzle diameter in this regime (see Fig. 15c). By reacting with the surrounded atmosphere, the axially symmetric decay changes to an unaxially symmetric Rayleigh, which represents a transitional form to other disintegration types. Therefore, this type of disintegration is only valid in a small range of Weber numbers between 25 and 75, cf. [25]. After starting the gas injection, a stagnation front (see Fig. 15d) can be developed at the impact point of the gas jet so that a back press regime (see Fig. 15e) of the melting beam occurs [55]. Here, the melt is pressed to the top and to the side until the rising melt reaches the nozzle. Arriving at the nozzle, the melt is pushed aside by the incoming melt from the crucible. By reaching the edge of the nozzle, the melting beam

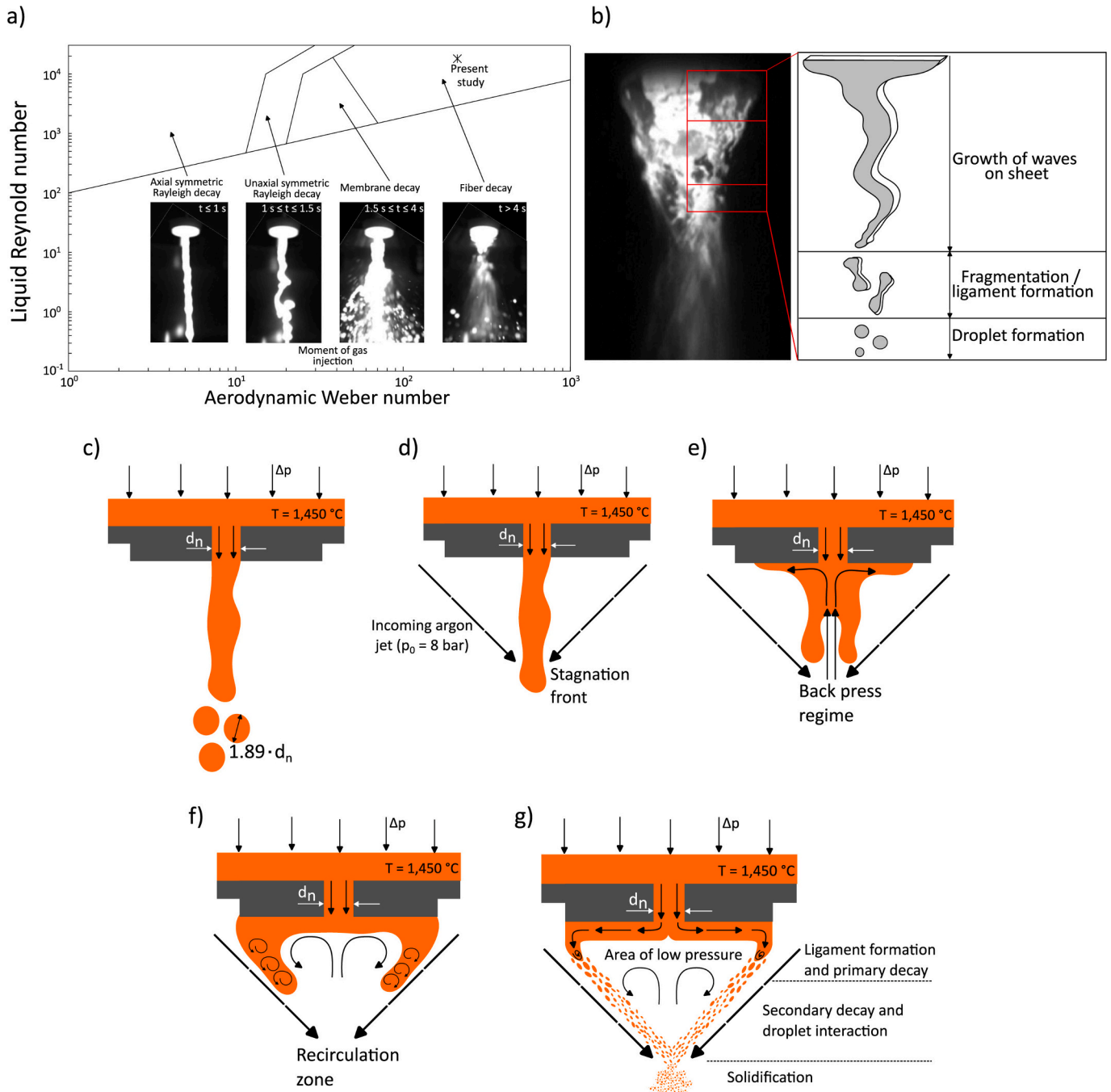


Fig. 15. a) Classification of the recorded decomposition types as a function of the liquid Reynolds number and aerodynamic Weber number, b) formation of primary droplets via wave motion and decomposition of ligaments and c)-d) schematic representation of gas atomization.

is pressed downwards again due to a renew impact with the lateral gas jet. The constant repetition of rising and displacement of the melting beam creates a recirculation zone (see Fig. 15f) with an area of low pressure in the interior (see Fig. 15g) [55]. Zhang et al. [56] and Ting et al. [57] studied the gas flow field both experimentally and through numerical simulations, confirming the formation of a stable recirculation zone throughout the entire atomization process. However, due to limited studies on the atomization mechanism and metal melt flow behavior in CCA-atomization, the impact of turbulent and irregular gas flow remains unclear. Therefore, further experimental investigations and numerical simulations are required to address this issue.

Based on the sudden acceleration of the melting, the Weber number rises to values up to 100, cf. [25]. The corresponding disintegration type is called membrane decay, cf. [25]. After the development of a stable recirculation zone, the primary droplet formation starts with the arisen of a network of aerodynamic wave motion of the recirculated melt at the edge of the nozzle [58] (see Fig. 15b). These waves grow until they reach a critical length. Afterwards parts of the waves break off and can form smaller ligaments. The fragments of unstable ligaments contract by surface tension subsequently break down into primary droplets [58]. The primary droplet formation appears at Weber number between 100 and 500, which belongs to the area of the fiber decay, cf. [25].

A successful secondary disintegration of the primary droplets is responsible for a fine particle size distribution, which is based on a further interaction between the atomization medium and the primary droplets. However, a strong competition between the surface tension, which is the driving force for the formation of a spherical body, the fast solidification and the relative velocity occurs after the primary disintegration. Smaller droplets have a high affinity to form a stable spherical body and offers fast solidification. The higher the droplet diameter, the higher the tendency for the secondary disintegration. Here, the critical Weber number (We_{crit}) defines the boundary condition, where the surface tension force and the drag forces are balanced. Consequently, the critical Weber number (We_{crit}) highlights the minimal diameter d_c where a secondary disintegration can occur. According to [24], the critical diameter can be estimated with the drag coefficient at a known relative velocity of the droplet:

$$\left(\frac{\rho_g \cdot v_r^2 \cdot d_c}{\sigma} \right)_{crit} = \frac{8}{c_d} \quad (27)$$

Below the critical diameter, the surface tension forces stabilize the droplet so that secondary disintegration is improbable. In the case that the droplet diameter is greater than the critical value, the drag forces

dominate the process and secondary disintegration can occur. The results of the modelling indicate (see Fig. 6a and b) that the critical Weber number is not stable during the atomization process due to the high changes of the relative velocity. Based on a similar relative velocity at the beginning of the atomization process, it can be assumed that the initial gas velocity is equal to the relative velocity ($v_{r,0} \approx u_0$) and therefore, the initial critical Weber number ($We_{crit,0}$) and diameter ($d_{crit,0}$) can be estimated with the initial gas pressure p_0 . Hence, the Eqs. (3), (4), (9) and (10) can be added in Eq. (27). Hence, a gas pressure of 0.8 MPa (8 bar) results in a critical diameter of 149 μm and a critical Weber number of 21 is calculated for the present study. The calculated critical value is in a good agreement with the measured particle size distribution before the powder preparation as shown in Fig. 8. Here, only 1.9 % of the particles are greater than the critical diameter. As a result, the assumption for the study were accurate enough to describe the secondary disintegration of gas atomization of CuCr1Zr.

Since the relative velocity depends on the gas pressure, Fig. 16 shows the critical droplet diameter and the critical Weber number as a function of the initial gas pressure and the corresponding types of the secondary disintegration. Here, the diagram indicates an extreme change of the critical diameter for a secondary disintegration. In general, the higher the initial gas pressure, the smaller the critical diameter for a secondary disintegration. Here, the critical diameter decreases to 7.7 μm and a critical Weber number of 15.1 is obtained for an initial gas pressure of 3 MPa (30 bar).

In general, the secondary disintegration is based on two breaking mechanisms. The first mechanism includes under the combined action of positive pressure and friction from the gas, the droplets deform until they break up [59]. Whereas the second mechanism contained a movement with an angular momentum so that a certain amount of centrifugal force. At sufficient angular velocity, the droplets will also break up [59]. Furthermore, the type of the secondary disintegration can be classified with known Weber number. According to Lou et al. [60], a so-called vibrational breakup mode takes place at Weber numbers between 6 and 35, where disintegration is induced by the vibration of the droplet in the natural frequency [58] (see Fig. 16b). At higher droplet diameter and gas pressure, which results in Weber number between 35 and 80, the bag breakup mode is the dominated type of secondary disintegration. Here, the droplet is compressed and became a membrane and collapse afterwards. At higher Weber numbers up to 350, a sheet-thinning breakup mode appears. In addition, Pilch and Erdman [58] reported a catastrophic breakup at Weber numbers higher than 350. Based on the calculated critical Weber number, only a small number of

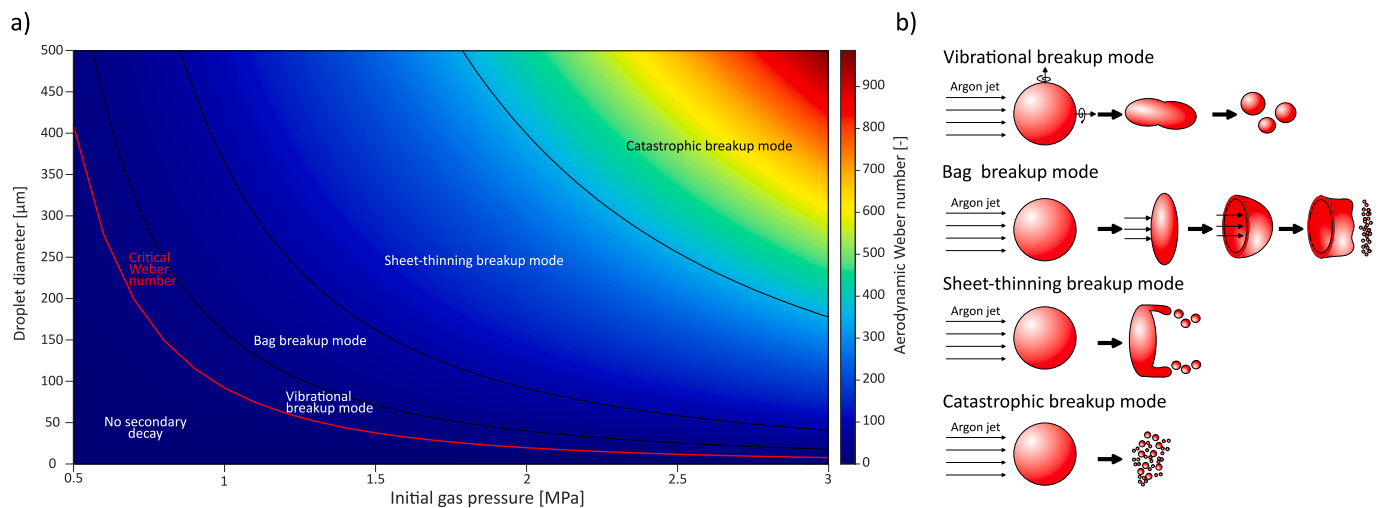


Fig. 16. a) Calculated Weber number for copper as a function of the droplet diameter and initial gas pressure with highlighted light with the critical Weber number and reported areas with the different types of secondary disintegration and b) schematic illustration of the vibrational breakup mode, bag breakup mode, sheet-thinning breakup mode and (based on [58]).

droplets are capable to disintegration via vibrational breakup for the present study. For the used manufacturing parameters, the most droplet disintegration is via bag breakup mode. The Sheet-thinning mode appears at gas pressure of approximately 1.1 MPa the first time. The catastrophic breakup occurs the first time for droplets with a diameter of 500 μm at a gas pressure of 1.8 MPa.

A complete overview of the process conditions over the axial flight distance is given in Fig. 17. With known solidification time corresponding to flight time. Hence, the flight time and solidification time, respectively, correspond to a specific flight distance so that the aerodynamic Weber number can be plotted as a function of droplet size, the phase condition and type of secondary disintegration for an initial gas pressure of 0.8 MPa (8 bar). Here, the competition between the fast solidification and the secondary disintegration can be illustrated. The highest probability for a secondary disintegration falls within the distance of the liquid and liquid+solid phase. In general, droplets with a diameter of 200 μm can disintegrate in the distance up to 0.0473 m. According to [60], the corresponding type of a secondary disintegration is the vibrational breakup mode. In the case of a droplet of 400 μm , the distance for the disintegration increases to 0.0781 m.

Due to the mutual interaction of the droplets, a further opportunity for a disintegration can occur. Two droplets can disintegrate at a collision of two droplets with enough kinetic energy and mass [61]. In addition, it can be concluded from Fig. 17 that a successful secondary disintegration can be achieved by increasing the overheating of the melt so that the liquid and liquid+solid phase can be enlarged.

Furthermore, the probability of occurrence of the location of defects such as cavities in the particles along the axial flight distance can be estimated with Fig. 17. Defects in powder particles occurs at a collision of two particles, where at least one particle consists of a liquid + solid phase. At the collision, the liquid part of the droplet will be removed so that the remaining solid part build the particle. This can mostly occur at the end of the liquid+solid regime, whereas the formation of unround particles occurs mainly at the beginning of the liquid+solid regime where a slight amount of solid fraction at the surface hinders a further deformation and hence a beginning secondary disintegration. Furthermore, non-decomposable droplets can form unround particles due to the reaction with the surrounded atmosphere turbulences.

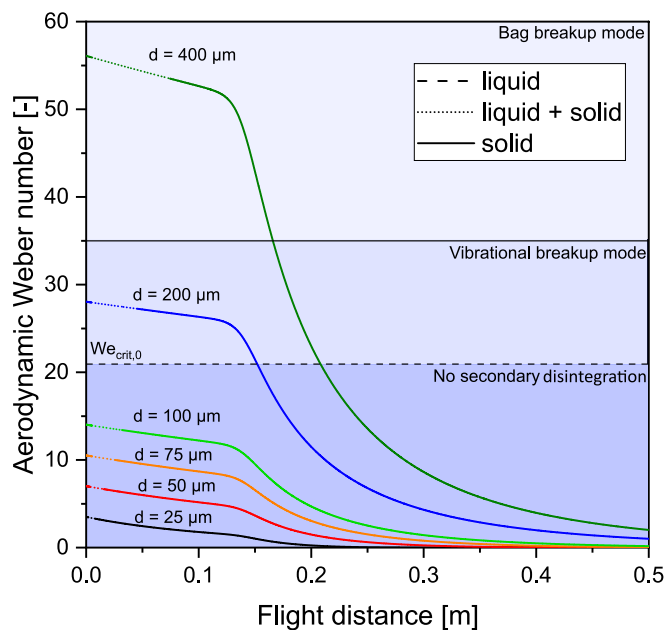


Fig. 17. Gas velocity and corresponding Weber number for a gas pressure of 0.8 MPa (8 bar) with corresponding secondary disintegration.

5.1.2. Prediction of particle size distribution

As shown in the discussion above, the prediction of the particle size distribution is very difficult by means of an analytical approach. Lubanska [10] established an often-used empirical equation for the median mass diameter $d_{50,3}$, which contained the physical properties of the material and also technological properties of the given experimental setup:

$$d_{50,3} = k \cdot d_n \cdot \sqrt{\frac{\nu_m}{\nu_g \cdot \text{We}_n} \left(1 + \frac{1}{\text{GMR}}\right)} \quad (28)$$

Where d_n is the melt diameter at the nozzle exit, ν_m and ν_g the kinematic viscosity of the melt and gas, respectively, and We_n is the liquid Weber number with nozzle diameter d_n as the characteristic length value. GMR expressed the ratio of gas mass flow $\dot{m}_g$ and the melt mass flow $\dot{m}_m$. The constant k is determined experimentally and characterizes the setup of each atomization unit [10,62], the properties of the applied metal melt [63], the adjusted gas pressure [64] and properties of the used atomization medium [9]. Therefore, the reported values for the constant k differ extremely from each other. By using FFA atomization, values in the range of 40 to 50 are mentioned [10]. However, the value of k increases by the use of CCA atomization of Cu to 124 [9]. By applying Eq. (28) with the required physical parameter from Table 1 with a diameter of 1.5 mm and a relative velocity of 326 m/s results in a Weber number of 903,900. With the measured mean diameter of $d_{50} = 42.30 \mu\text{m}$ results in a constant k of 118.60, which is slightly lower than the estimated constant given in [9] for a CCA atomization. It is reported that constant k is valid for the use argon and nitrogen [9] so that the main reason for the deviation of the constant k could be explained with different geometry of the atomization unit due to the use of the same material. In addition, it should be pointed out that the prediction of the mean mass diameter using Eq. (28) results in a mean error of $\pm 9 \mu\text{m}$ [9,62]. Instead, Urionabarrenetxea et al. [9] suggested the prediction according to Kishadaka [65] for of the mean mass diameter of pure copper powder:

$$d_{50,3} = k_1 \cdot d_n \cdot \text{Re}_n^a \cdot \text{We}_n^b \cdot \text{GMR}^c \quad (29)$$

where k_1 ($k_1 = 42.09$), a ($a = -0.34$), b ($b = -0.18$), c ($c = -0.42$) are experimentally determined constants and Re_n the melt Reynolds number, which can be calculated with the eq. [9]:

$$\text{Re}_n = \frac{d_n \cdot \rho_m \cdot v_r}{\mu_m} \quad (30)$$

where ρ_m and μ_m are the density and dynamic viscosity of the melt. Based on the parameters provided in Table 1, a Reynolds number of 1,012,733 can be calculated. However, in the present study, the four independent constants could not be determined, as this would require a larger number of test series. In contrast, Urionabarrenetxea et al. [9] used 66 different combinations of manufacturing parameters—such as varying atomization mediums, gas pressures, and overheating levels—to determine these constants. The application of the Kishadaka method, as reported, reduced the mean error of the mean mass diameter to 4 μm for close-coupled atomization of pure copper [9]. However, applying the reported constants to the current study yields a mean particle diameter of 31 μm , which is 11 μm smaller than the measured diameter. In [9], the manufacturing parameters included gas pressures ranging from 10 to 60 bar (using argon, nitrogen, and helium), overheating temperatures up to 500 $^{\circ}\text{C}$, and melting overpressures between 0.25 and 0.4 bar. Therefore, the constants of the Kishadaka method are highly influenced not only by the atomization unit but also by the physical properties of the atomization medium and the metal melt.

The Lubanska method provides a fast and efficient approach for predicting the mass mean diameter in atomization processes, as it requires only one independent parameter in its equation. This simplicity makes it highly practical for real-time applications in manufacturing

environments. The method can be applied using a single set of manufacturing parameters, where the constant k can be interpreted as a characteristic number of the atomization process. As a result, k can serve as a process control number, providing a means of monitoring and adjusting the atomization process. By adjusting k with different atomization parameters—such as variations in gas pressure—the method can be refined to improve accuracy. This adaptability makes it suitable for use with different atomization parameters, units, and media, enabling the knowledge gained from one atomization process to be transferred to other close-coupled atomization (CCA) machines.

In contrast, the method proposed by the Kishadaka approach, provides a more accurate prediction of the mass mean diameter by incorporating four independent parameters as reported in [9]. Once these parameters are determined, the Kishadaka method results in a lower error in the prediction of the mass mean diameter. However, the accuracy of this method is highly dependent on several factors, including the specific atomization unit, manufacturing parameters, and the physical properties of the atomization medium and metal melt.

5.2. Low temperature oxide formation of CuCr1Zr powder

The results of the isothermal oxidation experiments indicate a logarithmic rate law for the oxide growth of CuCr1Zr powder, which can be

explained with the high surface area to volume ratio. The aging process starts with a selective oxidation at the particle surface, where elements with a high oxygen affinity can easily react with the surrounded atmosphere. In the case of CuCr1Zr, the oxidation of the surface-near dense network of chromium and zirconium-rich copper precipitates forms chromium and zirconium oxides, which protect the copper matrix (see Fig. 18 a + b). As oxidation time increases, the oxidation of these precipitates should progress. However, due to the lack of experimental studies on the oxidation kinetics of CuCrZr powder in the literature, it remains unclear whether the early stage of oxidation leads to partial or complete oxidation of the precipitates. Therefore, further investigation is required for a valid conclusion. Afterwards, the oxidation process of the copper matrix starts. Honkanen et al. [66] investigated the oxidation behavior of pure bulk copper within the temperature range of 200 °C to 350 °C, noting localized formation of copper-I-oxide (Cu_2O) at temperatures around 200 °C. Here, the shift to the measured at 235 °C for the first oxide formation can be explained with the protective effect of selective oxidation. Additionally, Lee et al. [67] highlighted that the Cu_2O layer exhibit a thickness ranging between 50 nm and 100 nm for bulk copper at 200 °C after 10 min. At the further oxidation process is dominated by a conversion of the Cu_2O to monoclinic copper-II-oxide (CuO) at temperature greater than 320 °C [67] (see Fig. 16c + d). In this temperature regime, oxygen diffuse favorable along the grain

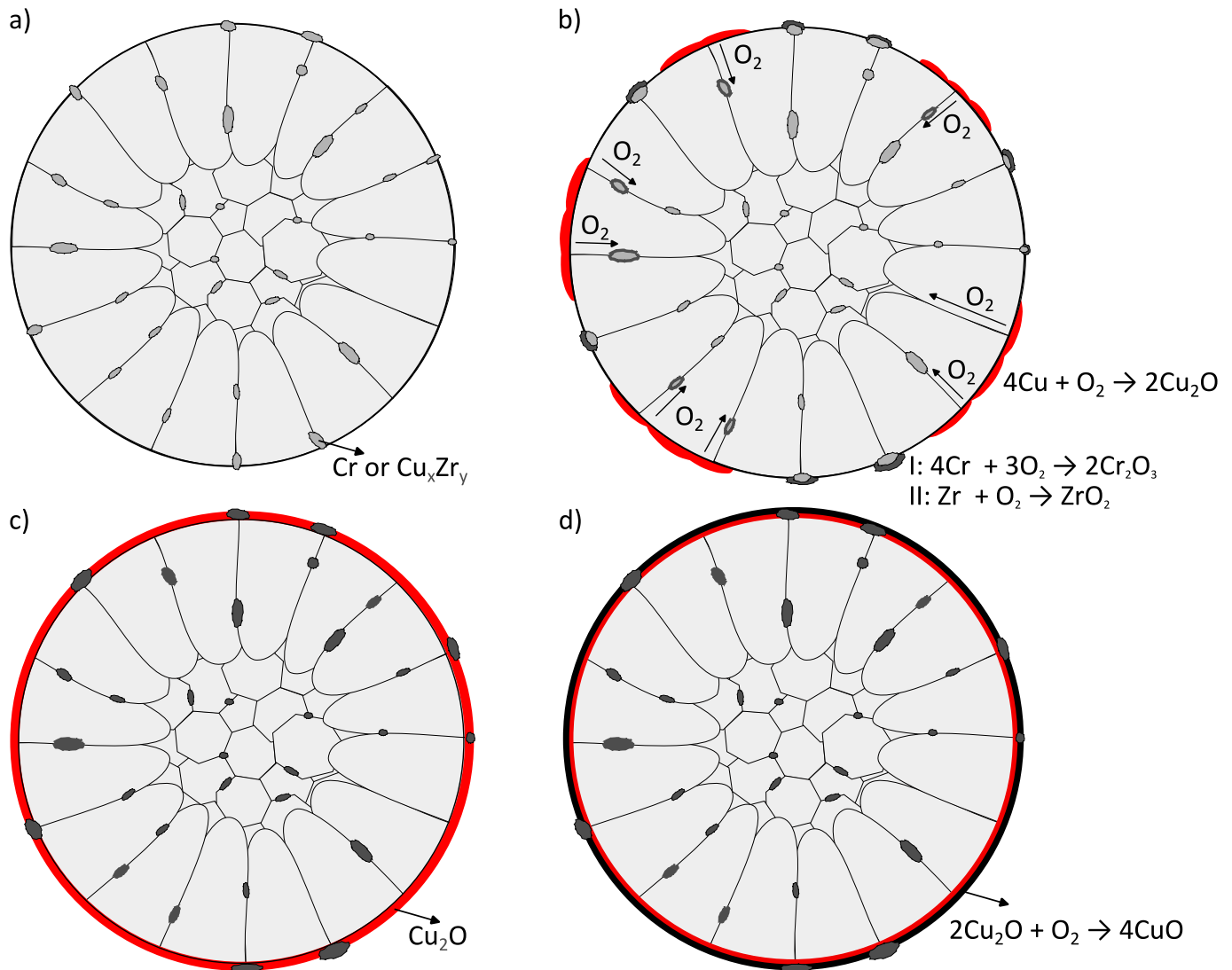


Fig. 18. Schematic illustration of the powder oxidation by showing a) unaged powder, b) the beginning of the oxidation with the formation of chromium and zirconium oxide (Cr_2O_3 and ZrO_2) and c) a dense layer of copper-I-oxide (Cu_2O) and d) the transformation to copper-II-oxide (CuO).

boundary [68,69] so that the located chromium and zirconium rich copper precipitates at the grain boundary hinder a further grain boundary diffusion of oxygen [68,69] by the formation of further chromium and zirconium oxides inside the powder particle. Consequently, the reported conversion reaction to CuO takes place at temperatures around 380 °C as seen at the TGA measurement of CuCr1Zr powder. Therefore, the second part of the oxidation process is dominated by the movement of the cations and anions into the oxide layer, so that a transformation of Cu₂O to CuO takes place [70]. As a result, a lower mass gain can be observed with increasing reaction time.

As the results show, the oxidation process is a temperature activated process. Therefore, the logarithmic constant k follows an Arrhenius function [51]:

$$k = k_0 \cdot e^{-\frac{E_A}{R \cdot T}} \quad (31)$$

Where k_0 is a pre-exponential factor, E_A is the activation energy of the system in J/mol, R the gas constant ($R = 8.314 \text{ J/(mol} \cdot \text{K)}$) and T the temperature in K. Fig. 19 a) illustrates the calculation of the activation energy via Arrhenius plot. The shown experiment setup offers an activation energy of 19.58 kJ/mol with a pre-exponential factor of 0.2646 mg/cm².

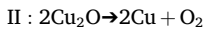
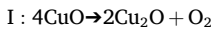
Similarly, the approximate oxidation starting time can be estimated by the OIT data with an Arrhenius [71]:

$$t(\text{OIT}) = t_0 \cdot e^{\frac{E_A}{R \cdot T}} \quad (32)$$

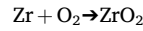
Using an inert gas atmosphere, the activation energy increases to 63.779 kJ/mol. According to Eq. (32), the estimated OIT for room temperature is approximately 42 days (see Fig. 19b).

5.3. Impact on pre-aged powder at LPBF

At temperatures exceeding 1,100 °C, CuO is reduced to Cu₂O, and afterwards to Cu under the release of molecular oxygen [15]. Therefore, the surface oxides can serve as a source of oxygen at the melting stage of PBF-LB/M:



Hence, elements with a high oxygen affinity like zirconium can react with the releasing oxygen in the copper melt and can potentially be form nanoparticles, as described in [52,72]:



Therefore, the reported nanoparticles were considered as a function of the copper surface oxides and consequently as a result of the powder aging. However, Due to the high cooling rates during PBF-LB/M, ranging from 10⁴ K/s to 10⁶ K/s [2], and the varying amounts of copper surface oxides, it remains unclear whether partial or complete oxidation of the zirconium can occur. Further experimental and simulation studies are needed to validate this hypothesis. The nanoparticles are beneficial for the mechanical properties due to oxide-dispersoid strengthening (ODS). However, after the development of nanoparticles based on the oxidation reaction during the heating and cooling phase, the amount of dissolved elements in the matrix decreases. Consequently, the amount of intermetallic compounds, which can be formed during the precipitation hardening, decreases. In conventional manufactured CuCr1Zr, an sufficient increase in strength is based on the development of Cr precipitates and various intermetallic compounds between Cu and Zr such like Cu₄Zr, Cu₅Zr, and Cu₅₁Zr₁₄ [15,45–48]. Therefore, with a massive increase in coarse chromium and zirconium oxides may decrease the strength as well as the electrical conductivity.

6. Conclusion

The present study provides a detailed overview of the powder production and handling of CuCr1Zr powder. For this purpose, the CCA atomization process and the oxidation behavior has been intensively analyzed. Based on the shown results and discussion, it can be concluded that

- the primary droplet formation of CuCr1Zr by using argon as atomization medium and a gas pressure of 8 bar is caused by a stable fiber decay of the melting beam.
- a critical droplet diameter of 149 μm was calculated at a gas pressure of 8 bar.
- the majority of the decomposable droplets disintegrated at the bag breakup mode.
- the first oxide formation is predicted after 42 days at room temperature in a nitrogen atmosphere via calorimetric measurements, followed by a logarithmic oxide growth.
- the oxidation state can be determined based on the color change of the copper oxides.
- no color change and therefore no oxidation can be observed at temperature beneath 100 °C.

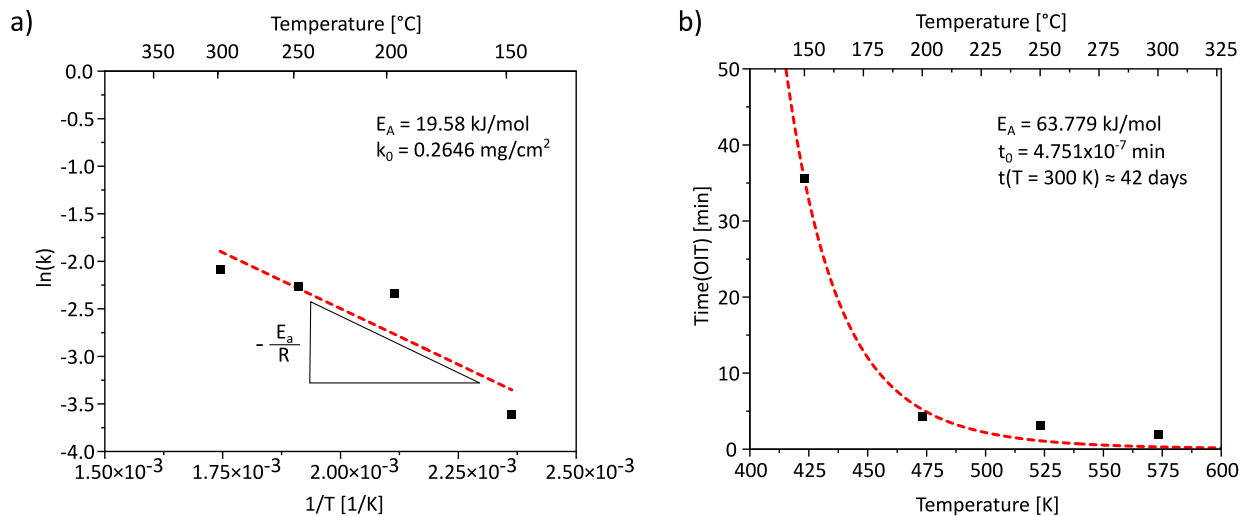


Fig. 19. Calculation of the a) activation energy of CuCr1Zr in an oxygen atmosphere and b) calculation of the oxidation starting time of CuCr1Zr in a nitrogen atmosphere (15 ml/min).

- nanoparticles in PBF/LB-M component parts can be formed by the decomposition of the copper surface oxides during the heating and cooling stage.

CRedit authorship contribution statement

Heinrich von Lintel: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Ivo Šulák:** Writing – review & editing, Visualization, Methodology, Data curation. **Katrin Jahns:** Writing – review & editing. **Ulrich Krupp:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

Ivo Šulák thanks for the financial support from the Czech Academy of Sciences.

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