Developing Tungsten-Filled Metal Matrix Composite Materials Using Laser Powder Bed Fusion

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Abstract: The additive manufacturing technique laser powder bed fusion (L-PBF) opens up potential to process metal matrix composites (MMCs) with new material pairings free from limitations of conventional production techniques. In this work, we present a study on MMC material development using L-PBF. The generated composite material is composed of an X3NiCoMoTi 18-9-5 steel as matrix and spherical tungsten particles as filler material. A Design of Experiment (DoE)-based process parameter adaption leads to an Archimedean density close to the theoretical density in the case of 60 vol% tungsten content. A maximum ultimate tensile strength of 836 MPa is obtained. A failure analysis reveals a stable bonding of the tungsten particles to the steel matrix. This encourages the investigation of further material combinations. An additional heat treatment of the MMC indicates the potential to design specific material properties; it also highlights the complexity of such treatments.

Keywords: metal matrix composite; additive manufacturing; laser powder bed fusion; tungsten; MS1 (1.2709/X3NiCoMoTi 18-9-5)

1. Introduction

Metal matrix materials (MMCs) are able to combine favorable properties of their components. The resulting mechanical properties of MMCs can even be superior to the properties of each component itself. Thus, material properties like specific strength, specific stiffness or wear resistance can be improved to a higher level [1–3]. Conventional processing methods are often constrained in terms of process control, dispersion control, mechanical properties or shape complexity [4]. The choice of matrix and filler materials is therefore limited. On the contrary, additive manufacturing (AM) offers possibilities of generating new materials which are challenging or unfeasible to produce by conventional means. Such new materials enable the adaption of their mechanical properties for specific applications [4,5]. Kang et al. report on laser powder bed fusion (L-PBF) of tungsten carbide reinforced maraging steel composites whose tensile properties are dependent on the tungsten carbide content. Moreover, especially regarding the topic of phase composition, it is stated that there is still a lack of knowledge [5]. Chen et al. point out the potential of excellent compressive strength combined with high ductility in WC-reinforced iron-based composites by L-PBF [6]. Biedunkiewicz et al. describe the increasing reinforcement effect of 316 L stainless steel with increasing amounts of TiC nanoparticles [7].

Generally, multiple combinations of materials are possible. Thus, metallic particles as well as ceramic components can be applied as filling material of a metallic matrix. However, L-PBF-related studies focus on ceramically reinforced MMCs, and only some literature on metal–metal composites is available. An example for the latter is tungsten heavy alloys, which are manufactured by conventional process routes like infiltration techniques. First attempts to generate similar material systems by laser powder bed fusion (L-PBF) are described in the works concerning W-Ni alloys by Zhang et al. [8], and regarding W-Ni-Fe-Co composites by Chen et al. [9]. Zhang et al. demonstrate the influence
of the Ni content on the microstructure evolution. The microstructure changes from bar-shaped to dendritic to honeycomb structure with increasing Ni content. In addition, W dendrites are observed indicating a partial melting of the particle [8]. This study emphasizes the importance of microstructural investigations of new MMC systems. Chen et al. report on the effects of laser process parameters and chemical compositions on densification, microstructures and tensile properties giving evidence of the complexity of this topic [9].

This study focuses on a strategy to access new material combinations. The development of process parameters for single materials is already especially elaborate for L-PBF. There is currently no common procedure for the development of process parameters. Because of possible interactions between different materials in the manufacturing process, achieving appropriate process parameters for material combinations is therefore challenging as well. In this work, two metallic materials are combined as a proof of concept. The findings shall be transferred to application-specific material combinations in the future. To observe as many potential effects as possible, two stock materials with the greatest differences in process-relevant material properties are selected. Tungsten, a heavy element with high melting point that is known as extremely brittle itself, is chosen as filling material. For the matrix material, a common X3NiCoMoTi 18-9-5 steel (MS1) is selected because the L-PBF processing parameters are already available. Moreover, MS1 represents an extreme option because it needs to be heat-treated after processing to develop its full mechanical performance. This enables the investigation of heat treatment effects on metal–metal composites.

2. Materials and Methods

The experiments of this study were conducted on the L-PBF system EOS M 100 by EOS GmbH (Germany) equipped with a 200 W laser unit (YLR-series, CW-laser, wavelength 1070 nm, Gaussian TEM00 mode). The maraging steel MS1 (1.2709/X3NiCoMoTi 18-9-5, particle size distribution D_{10}: 17 µm, D_{50}: 31 µm, D_{90}: 54 µm) was mechanically mixed with spherical tungsten powder (particle size distribution D_{10}: 20.8 µm, D_{50}: 29.0 µm, D_{90}: 43.4 µm). The mixed powder was processed in 20 µm layers. During the process, the steel particles were molten and solidified around the tungsten particles. A series of powder mixtures with tungsten contents of 40–70 vol% was used to build test cubes of 1 cm³. An argon-based inert gas atmosphere of O₂ < 0.1% was applied in order to avoid oxidation.

The densities of the resulting test cubes were measured by the Archimedean principle according to DIN-EN-ISO-3369 at a Kern ABT 220-5DM (with the readability δ = 0.01 mg and the calibration value e = 1 mg) and considered as a first quality criterion. This method was chosen as it is known to give reliable and repeatable results [10]. The principle consists of measuring the sample mass, mₐ in air and mₗ in liquid (distilled water), and calculating the density of the sample ρₛ by using the known density of the liquid ρₗ:

$$\rho_s = \frac{m_a}{m_a - m_l} \cdot \rho_l. \quad (1)$$

Subsequently, the cubes were prepared by standard metallographic means and analyzed using light microscopy regarding aspects such as the distribution and shape of the tungsten particles as well as the porosity of the composite material. For the microscopic investigations, a Zeiss Axio Imager.Z2m system was used.

For generating the SEM images shown in this article, a Zeiss EVO 15 system was used. In addition to a secondary electron detector for topographical investigation, a backscattered electron detector was applied in order to identify material contrasts. The intensity of the detected signal represented in greyscale values is dependent on the mass of the element. Heavy elements enhancing the number of backscattered electrons appear brighter in the image than lighter elements. This enables the differentiation between heavy tungsten particles and the lighter steel matrix. A coupled Octane Plus detector by EDAX Inc. was employed for energy-dispersive X-ray spectroscopy (EDS), which gives information on the local elemental composition due to specific X-rays emitted by the elements.

Quasi-static tensile tests were carried out according to DIN EN ISO 6892 on an Instron 8033. The strain was measured by a tactile extensometer.
Heat treatments were executed in a Nabertherm LHT 04/17 oven. The MMC samples were placed inside the heating chamber at room temperature. After the heat treatment the samples were water quenched.

3. Results

3.1. Process Parameter Development

For the processing of MMC materials, suitable process parameters need to be developed. In order to investigate the impact of different process parameters, a randomized full factorial DoE (Design of Experiment) experimental plan was created based on the starting parameters. The main factors—laser power and exposure speed—were varied on two levels by ca. ± 10% relative to the central point of the experimental plan. The hatching distance as the third common main factor was not adapted [11]. Tungsten content started at 40 vol%. This value is found to be one of the highest particle volume contents investigated in L-PBF studies regarding steel-based MMCs [7]. The central point of the 40 vol% experimental plan presents the starting parameters developed for MS1 by the methodology of Pfaff et al. [11]. In each experimental plan, three control points were used for the center. Each sample was measured three times by the Archimedean principle. Each plan was executed once. All experimental plans are listed in Table 1. The hatch distance was set as 0.09 mm. However, the final experimental plan (W, 60 vol% 2nd adaption) was repeated with different hatch distances of 0.07 mm and 0.05 mm to check its influence. As the overall picture regarding density does not change, only the measurements for 0.07 mm are depicted in Figure 1. Slim experimental plans were chosen in order to keep the number of samples within one build cycle low. This can prevent cross-contaminations by side products, faulty recoating or unsuitable positioning in the building volume (e.g., side positions).

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The theoretical density ($\rho_{\text{theo}}$) that can be expected from the corresponding tungsten content ($V_{\text{Tungsten}}$) is calculated by the ideal linear rule of mixtures

$$\rho_{\text{theo}} = \rho_{\text{Tungsten}} V_{\text{Tungsten}} + \rho_{\text{MS1}} (1 - V_{\text{Tungsten}}),$$

with $\rho_{\text{Tungsten}} = 19.25 \text{ g/cm}^3$ and $\rho_{\text{MS1}} = 8.1 \text{ g/cm}^3$. 

Table 1. Experimental plans for the development of suitable process parameters. Hatching distance is set constant. Central points are fabricated three times and are marked in bold font. Each experimental run is executed fully randomized.
Figure 1 presents the measured Archimedean density in comparison to the theoretical value. With an increase in tungsten content from 40 to 50 and 60 vol% (black data points), a descending trend in density was observed. This behavior can be explained by the fact that the tungsten particles had an influence on process-relevant properties such as thermal conductivity or absorptivity of the laser energy. Therefore, the boundary conditions in the powder bed changed. This leads to the necessity of adapting the process parameters in order to counteract the descending densities with increasing tungsten content. Consequently, adapted DoE matrices were applied to shift and expand the process parameter variations. Additionally, the powder bed, which was not heated for the starting parameters, was heated to ca. 90 °C. These measures led to an improvement in the overall density level in the case of 60 vol% tungsten. However, a further descending density from 60 to 70 vol% tungsten was monitored (red data points). Concentrating on the 60 vol% tungsten volume content, another optimization iteration of the process parameters resulted in densities close to the theoretical density (green data points).

The measured density is influenced by porosities as well as the actual tungsten volume content. Thus, low porosity leads to high densities, whereas high porosity results in lower densities. Figure 2a,b highlights these two cases. The tungsten volume content can differ from the nominal value. Illustrative images of corresponding microstructures are presented in Figure 2c,d, respectively. This phenomenon can arise because of inhomogeneity originating in the mixing process or because of the mechanical interaction of the recoater blade of the L-PBF machine with the powder bed. Another reason for this phenomenon can be the application of an excessive energy density. This can lead to temporary, high local temperatures above the melting point of tungsten, allowing single tungsten particles to fuse or deform during a short period. The resulting change in morphology is shown in Figure 2c. The change in tungsten content explains why positive deviations of the expected relative densities can be observed.
The observed characteristics “porosity”, “tungsten content” and “particle morphology” proved to be challenging for an analysis of the experimental plans in Table 1. Density measurements by the Archimedean principle, as they are common for the development of L-PBF process parameters, are insufficient because all characteristics mentioned above impact the result. The use of μCT measurements has been tested within this work. However, because of the high X-ray absorption of tungsten, the quality of the results was insufficient for an evaluation (not presented within this publication). While the tungsten content and the porosity can be quantified based on microscopical images, there is no approach to quantify the particle morphology. DoE approaches, as they are used for the development of process parameters for monomaterials, should therefore be adapted for MMCs. This could be done by moving the process window of the experimental plans into an area where no or low fusion of filling particles can be observed. Single laser track experiments, as shown by Pfaff [11], could be used to define a suitable process window. Because of the time-consuming sample preparation and analysis by microscopy, it is advisable to keep the experimental design as lean as possible (e.g., fractional designs). Because of the described challenges, a thorough analysis of the experimental designs in Table 1 was not possible. However, because the process parameter variation should mainly serve to fabricate a material of sufficient quality for a proof-of-concept of the material combination, the parameter combination resulting in the lowest porosity was picked out of all samples showing no excessive deformation or fusing of the tungsten particles. All following investigations were based on the main process parameters of 90 W, 500 mm/s, 0.07 mm and W 60% vol%, resulting in the following characteristics: ~1.1% porosity, ~58% tungsten content and “spherical” morphology.

Energy-dispersive X-ray spectroscopy (EDS) measurements confirmed the presence of tungsten particles surrounded by an iron-based matrix. In Figure 3a, the measured EDS profile of the matrix is shown, exhibiting all major constituting elements of the matrix as well as tungsten in the background. Part (b) shows the corresponding profile measured on a tungsten particle.

Figure 3. EDS measurements. (a) Spectrum of the MS1 matrix with tungsten in the background. (b) Spectrum measured on a tungsten particle.
3.2. Tensile Test

In order to obtain first information on the mechanical behavior of the generated MMC material, three tensile test specimens with 60 vol% tungsten content were built with the same processing parameters (90 W, 500 mm/s, 0.07 mm and W 60% vol%, see Section 3.1) and tested afterwards. The resulting stress–strain curves are shown in Figure 4a. The corresponding microstructure is depicted in (b) and (c).

Ultimate tensile strengths (UTS) of 758, 833 and 836 MPa were measured at strains between 0.5 and 1.0%. It can be stated that all samples exhibited similar failure behavior, pointing out a homogenous and stable building process. Moreover, the results showed that the material tolerated some plastic deformation. However, the ultimate tensile strength was below the UTS of about 1100 MPa of pure MS1 [12]. The corresponding microstructure revealed some porosity, which might affect the mechanical performance. This indicates a possible improvement of the MMC, e.g., by further adjusting the process parameters.

3.3. SEM Analysis of Failure Surface

A scanning electron microscopy (SEM) analysis of the failure surface of one tensile test specimen is shown in Figure 5.

In the backscatter image (a), it can be seen that the heavy tungsten particles (bright grey) were distributed over the whole sample surface. The dark areas represent the lighter steel matrix phase. However, porosity was clearly visible, e.g., the dark hole at the right side of the image. Regarding the failure behavior, tungsten intraphase failure and a few cracks in the steel matrix can be stated (indicated by red arrows). Having a closer look at the failure surface (b), it can be observed that the tungsten particles were thoroughly embedded in the steel matrix. Thus, the tungsten particles were not ripped off the matrix during the tensile test, but cleavage planes of the particles dominated the failure surface. This indicates that the contact between the matrix and reinforcing particles was strong enough to withstand the applied tensile forces.
The pure matrix material MS1 is supposed to be heat treated at 490 °C for 6 h [12] to reach higher UTS and hardness. However, this heat treatment was not considered to be expedient, as it would possibly promote the formation of intermetallic phases. Because of the nickel-rich MS1, the growth of Ni-W precipitates at the interface between the tungsten particles and steel matrix would be most likely. Such intermetallic precipitates are known to embrittle the interface and reduce the toughness of the material [13]. In contrast to this, a dissolution of potential Ni-W precipitates is desirable. According to Ellinger and Sykes [14] and Walsh and Donachie [15], the dissolution of N-W phases takes place at temperatures above 1093 °C. Therefore, heat treatment at a sufficiently high temperature of 1200 °C and a shorter duration of 1 h, followed by quenching in water, was attempted. The SEM analysis of a metallographic specimen (60 vol% tungsten) after this heat treatment is presented in Figure 6.

Figure 6. Backscatter images of a metallographic specimen after heat treatment (1200 °C, 1 h). (a) Overview at low magnification; (b) Close-up revealing the formation of an interphase exhibiting cracks probably caused by thermal stress relief.

After a look at the backscatter image of the metallographic specimen, it can be stated that the heat treatment led to the formation of a pronounced interphase (medium grey). The tungsten particles (bright grey) dissolved into the steel matrix (black). The fact that the medium grey areas exhibited no transition from a brighter to a darker grey underlines the formation of an interphase. Moreover, cracks in the interphase were visible. Thermal stress due to heat treatment might be the reason for this phenomenon. This also indicates a brittle behavior of the interphase. EDS measurements...
(see Figure 7) revealed that the interphase contained all measurable elements of the matrix and the reinforcement particles.

![Figure 7. EDS measurement of the interphase. The spectrum contains all measurable elements of the MSi matrix and tungsten.](image)

Additionally, a fracture surface of a heat-treated sample was analyzed in the SEM. From Figure 8a, it can be concluded that the interface between tungsten particles and steel matrix was weakened due to heat treatment. A ripping-off of the particles at the fracture surface can be stated. Moreover, a radial pattern around the particles can be observed, indicating diffusion processes taking place during the heat treatment. In the backscatter image (b), a cracked tungsten particle can be seen. A core-shell-like structure was formed because of the diffusion processes started by the heat treatment.

![Figure 8. Dissolution of tungsten particles at a fracture surface of a tensile test specimen due to heat treatment (1200 °C, 1 h, water quenched). (a) Ripping-off of particles can be observed; (b) Core-shell-like structures can be found. This phenomenon can be explained by radial diffusion processes inside the particles during the heat treatment.](image)

This attempt effectively shows that MMCs can be modified by applying heat treatment steps. This might be used for the design of specific material properties. However, the combination of more than one material enhances the complexity of heat treatments themselves. Therefore, for shorter developing times it might be more expedient to generate MMCs by employing starting materials not necessary to be heat-treated after the building process.
4. Discussion

In this study, the feasibility of generating an MMC by processing two metal powders with L-PBF is presented. The experiments show that the process parameters require adaptations for an increasing amount of filler particles. The application of a DoE-based approach leads to an improvement in the resulting material properties, such as the density. However, this approach is not ideal for MMCs. The analysis of the experimental designs requires high characterization efforts. Therefore, DoE approaches need to be adapted for MMCs. Tensile test data indicate potential for further material optimization. This encourages the investigation of further application-specific material combinations.

A heat treatment procedure test led to the formation of a pronounced interphase and inferior mechanical behavior of the MMC. This gives a glimpse of the complexity of the development of MMCs whose performance is dependent on a heat treatment procedure to fully unfold their potential. Material combinations not requiring additional heat treatment steps are therefore considered to be less time-consuming in development. Such MMCs are promising materials for civil as well as for defense applications in the near future.

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Conflicts of Interest: The authors declare no conflict of interest.

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