In situ modification of case-hardening steel 16MnCr5 by C and WC addition by means of powder bed fusion with laser beam of metals (PBF-LB/M)

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Abstract

Typical high-strength products are made from carbon-rich steels possessing relatively high carbon content, thus reducing weldability. In this work, preliminary studies on designing and tailoring a low-alloyed steel for the laser-based powder bed fusion (PBF-LB/M) process by adding carbon black (C) nanoparticles and tungsten carbide (WC) particles for enhancing the material properties are provided. First, the base material 16MnCr5 is modified with different concentrations of C and WC. It was found that an increased C and WC content resulted in an elevated material hardness in the as-built state. However, this comes at the cost of a poorer processability as pore formation increased for C-modified and crack tendency increased for WC-modified 16MnCr5. When applying a post-process quenching and optional tempering heat treatment, material hardness in the range of 615 HV can be achieved for C-enriched 16MnCr5 in the tempered state, which would be suitable for bearing and gearing applications. The addition of WC particles favored an improved wear resistance which is twice as high as the one of C-modified material for similar material hardness, showing the enormous potential of WC addition for reducing the wear rate. Complementary SEM and EDX analyses show that both the dilution and bonding zone of the WC particles are affected by the processing conditions and the WC concentration. Furthermore, it was found that a nearly defect-free fabrication of WC-enriched 16MnCr5 was possible for up to 2.5 wt.-% of WC, proving that the occurring defects are highly sensitive to the WC concentration.

Keywords Additive manufacturing · PBF-LB/M · Selective laser melting · Case-hardening steel · In situ alloying · Hardness · Wear resistance · WC

1 Introduction

Case-hardening steels such as 16MnCr5, 20MnCr5, and 17CrNiMo6 are commonly used in various fields including bearing and gear applications [1]. These low-alloyed materials typically provide excellent ductility. However,

as high contact forces demand elevated material hardness, subsequent chemical carburizing or nitrating are necessary before quenching and tempering steps are performed for increasing the strength and hardness of the workpiece. Resulting products are characterized by a highly ductile core and wear-resistant case due to the increased C or N content. This leads to energy-intensive process chains on the one hand. On the other hand, carburizing effects can support warping of the workpiece or lead to irregularities on the surfaces of the workpiece, which is especially crucial for highly complex parts. According to Palaniradja et al. [2], about 10% of all case-hardened products are characterized by unwanted defects. Such sophisticated products, which could be characterized by, e.g., internal cooling or lightweight structures, can be produced by means of additive manufacturing (AM). One commonly used technology is laser-based powder bed fusion of metals (PBF-LB/M). This AM

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process is characterized by several iterative steps including the application of powder material, selective illumination, and solidification using an energy source, and lowering of the build platform by a defined height. Due to the small size of the powder used, typically in the range of 20 to 63 μm , and potentially small laser spot sizes varying between 50 and 250 μm , fine structures can be produced. Furthermore, laser-based AM processes possess extremely high cooling rates in the range of 10^3 to 10^5 K/s, thus supporting ultrafine grain formation [3]. This can lead to superior part properties compared to conventional manufacturing processes [4].

In the field of powder bed-based AM processes, low-alloyed case-hardening steels such as 16MnCr5 have only been investigated recently. Kamps [5] focused his work on generating lightweight gears using the PBF-LB/M process. By applying a post-process carburizing step, similar hardness values for additively and conventionally manufactured specimens were observed. Conventionally manufactured specimens were generated through continuous casting and forging. Schmitt et al. [6] also studied the general processability of 16MnCr5 by means of PBF-LB/M. Furthermore, the researchers presented results on the overhanging angles and the influence of contour scans on the corresponding roughness values. Within their work, Bartels et al. [7] studied the carburizing and hardening of additively manufactured 16MnCr5 specimens. They found that an increased hardness and case-hardening depth can be observed for additively manufactured specimens from case-hardening steels. Schmitt et al. [8] have also shown the processability of these steels using PBF-LB/M, building on their previous publication from 2018, while also investigating case-hardening behavior and tensile properties of additively manufactured samples. Aumayr et al. studied the processing of a newly developed low-alloy steel E185 AMPO. Relative part density was determined to be above 99.5% [9]. Material hardness in the as-built state was in the range of 38 HRC, which is approximately 370 to 380 HV. After case-hardening, peak hardness of 720 HV0.5 was found, similar to case-hardened 16MnCr5 specimens from bulk material. Yang and Sisson investigated the processing and case-hardening behavior of 20MnCr5 [10]. In the as-built state, an average material hardness of 287 HV0.5 was determined. Measured hardness for case-hardened samples increased up to 857 HV0.5 near the surface.

Zumofen et al. [11] investigated AM of tempering steel 30CrNiMo8 using PBF-LB/M. This steel is characterized by higher carbon content between 0.26 and 0.34 wt.-% compared to case-hardening steels. They found out that a nearly defect-free processing was possible for a defined processing window for varying laser power and exposure time. Mechanical testing in quenched and tempered state showed properties similar to conventionally fabricated specimens from bulk material.

Another possibility for improving the material strength is provided by in situ alloying. This term describes the generation of a material within the manufacturing or solidification process itself. In PBF-LB/M, this can be achieved by pre-mixing a base powder with additional elements, leading to a modified material after solidification with adjusted part properties.

One adjusting lever in steel modification is increasing the carbon content as material strength significantly rises with higher carbon content. The theoretically achievable martensitic hardness can be approximated knowing the carbon content of a material [12]. Typical carbon contents for case-hardening steels are in the range from 0.4 to 0.8 wt.-% leading to material hardness between 600 and 800 HV after hardening and annealing.

This has already been investigated by Bischof et al. for FE4800 which has been modified with varying carbon concentrations of up to 0.3 wt.-% [13]. However, additively manufactured carbon-rich steels (>0.4 wt.-% C) typically require a post-process heat treatment for hardening and achieving the theoretically possible material hardness [14]. Process-intrinsic heat treatment in PBF-LB/M leads to tempering effects in underlying layers, thus resulting in reduced hardness values. Schmitt et al. also studied the in situ alloying of 16MnCr5 by adding different carbon concentrations. They claim that a defect-free processing with high relative densities above 99.8% is possible. When scaling the experiments towards gear parts, an increase in porosity was observed, which is attributed to the unsuited contour illumination strategy. When analyzing the material properties, a rise in hardness was observed for increased carbon contents. Furthermore, the ductility of the specimens decreased with higher carbon contents [15].

In laser metal deposition, Hentschel et al. studied the influence of carbon black (CB) nanoparticle addition on material hardness for tool steel 1.2343 [16]. With the addition of 0.1 wt.-% carbon black nanoparticles, hardness increased by approximately 50 HV1 up to 700 HV1. Further enhancing the carbon content to 0.2 wt.-% also resulted in higher hardness even though the rise was not as significant as before. Here, determined hardness was in the range of 725 and 750 HV1.

WC addition provides a second opportunity for improving mechanical hardness and wear resistance of material systems. For PBF-LB/M, different investigations on the reinforcing effects of different WC-concentrations have been performed by Yan et al. [17]. They found that a WC content of approximately 2% led to a rise in hardness of approximately 100 HV0.2 for MS300 steel. Kang et al. [18] in contrast only observed a slight increase in hardness of 50 HV (350 to 400 HV) when adding 15 wt.-% WC to maraging steel. Gu et al. [19] also investigated the addition of WC to an iron-based matrix. Their results also show an

improved wear resistance, which is partially attributed to a novel microstructure and the interface of the carbide with the matrix. These observations are also in accordance with the previously discussed results.

Shi et al. found that the size of WC particles significantly affected crack formation and bonding in Inconel IN718 [20]. Different particles with a medium size of 21 μm , 10.5 μm , and 5.25 μm were used. It was observed that smaller particles favored a finer microstructure as well as a more homogeneous distribution of internal stresses within the specimens.

Grünenwald et al. investigated the effects of laser surface alloying on the material hardness and wear behavior of case-hardening steel 16MnCr5 by adding carbon and tungsten. While increasing carbon content led to increased hardness, wear resistance was only improved until a threshold value of carbon content of approximately 0.8 wt.-%. They also observed that with increasing tungsten contents, the wear rate was constantly reduced. However, pore and crack susceptibility increased for excessive tungsten contents above 20 wt.-% [21].

From literature review, it is seen that carbon-enhancement of steels is rarely performed for PBF-LB/M materials. This can be attributed to reduced weldability of steels for higher carbon content. Thus, improving material hardness is generally achieved by following conventional processing routes including resource-intensive carburizing and heat treatment steps. In PBF-LB/M, WC particles are more commonly used for improving wear properties compared to the base material.

The following work aims at investigating the effect of different potential hardening mechanisms for increasing the material hardness of case-hardening steels during the additive manufacturing process. By this, energy-intensive heat treatment strategies could be avoided. Two different approaches are followed: on the one hand, CB nanoparticles are added for increasing the total carbon content within the material as the martensitic hardness is typically characterized by the amount of carbon. Therefore, carbon content will be increased by adding carbon nanoparticles. On the other hand, the addition of hard particles gives the opportunity for significantly

improving material hardness and wear resistance when embedded into the matrix material. In both cases, the interdependencies are mostly unknown for low-alloyed steels such as 16MnCr5. The aim of this experiment is to find upper limits for the maximum concentration for the addition of carbon and WC particles while still possessing a good processability. Based on these results, energy-consuming post carburizing and ideally heat treatment steps could potentially be avoided. The latter, however, would require the processing of ready-to-use components with sufficient high material hardness in the as-built state. Target hardness should exceed 56 HRC, which is equivalent to approximately 615 HV.

2 Materials and methods

In the presented work, different in situ approaches are investigated for improving the material hardness. First, pure 16MnCr5 powder is processed for determination of an adequate processing window as well as a benchmark for achievable hardness of the base material. In a second step, the influence of both carbon and tungsten carbide addition on material properties is investigated. Different carbon and tungsten carbide concentrations and their respective influence are examined. By means of optical microscopy and pixel brightness analysis, relative part density as well as defect formation is determined. Energy-dispersive X-ray (EDX) measurements are performed for analyzing tungsten distribution within the specimen. Additionally, dispersing effects and connectivity zone of these tungsten carbides are studied. In the next step, material hardness for different specimens is investigated. Finally, samples for wear analysis by means of pin-on-disc tests are manufactured. Our goal is to manufacture ready-to-use samples that possess material properties similar to conventionally carburized and hardened 16MnCr5. The methodological approach is presented in Fig. 1.

In the first step, a processing window for the nearly defect-free ($\rho_{rel} > 99.7\%$) fabrication of unmodified 16MnCr5 specimens is determined. Powder material was supplied by Nanoval GmbH, Berlin, Germany. Subsequent particle analysis was performed at FIT AG (Lupburg,

Fig. 1 Methodological approach for in situ material modification and subsequent analysis of this research work

Germany) using a CamsizerX2 (Microtrac Retsch GmbH, Haan, Germany). Characteristic particle size d_{10} , d_{50} , and d_{90} were determined to be 17.23 μm , 27.86 μm , and 40.69 μm , respectively. Experiments are performed on a commercially available AconityMINI (Aconity GmbH, Herzogenrath, Germany). The machine is characterized by a maximum build envelope of $\varnothing 140 \times 200 \text{ mm}^3$ and is equipped with a 1 kW single mode fiber laser ($\lambda = 1070 \text{ nm}$). All experiments were performed in a reduced build envelope of $\varnothing 55 \text{ mm}$ with no additional platform pre-heating. Argon was utilized as shielding gas. Typical remaining oxygen content in the machine was below 500 ppm.

Key process parameters such as laser power and scanning speed are varied within test samples. Investigated laser power P_L was varied from 250 to 350 W in steps of 50 W. Scanning speed v_s was modified in steps of 100 mm/s from 500 to 900 mm/s. Hatch distance h , layer thickness H , and spot size were set constant to 120 μm , 50 μm , and 120 μm , respectively. Contour laser power $P_{L,c}$ and contour scanning speed $v_{s,c}$ were chosen at 250 W and 900 mm/s, respectively. These parameter ranges were selected based on common literature values for the processing of low-alloyed steels. As specimen, geometry cubes with an edge length of $6 \times 6 \times 6 \text{ mm}^3$ were manufactured in all tests. Even though transferability to large-scale applications is not provided in this work and thus needs further investigation, these samples are used as an indicator for potentially achievable material properties.

Based on the most promising processing window for the manufacturing of 16MnCr5 specimens, a parameter range for the fabrication of CB- and WC-enhanced 16MnCr5 was determined. Carbon black nanoparticles were added in different concentrations leading to a total C content in the powder material of 0.28 wt.-%, 0.44 wt.-%, and 0.52 wt.-%,

respectively. The last carbon concentration was chosen as experiments showed that a slightly higher carbon content than 0.4 wt.-% in the solid would be suitable considering potential post-process heat treatment strategies as well as tempering at around 200 °C. Previously determined best parameter combinations for the fabrication of 16MnCr5 specimens were used as an indication and were varied further. Carbon black nanoparticles of type N550 were procured from Harold Schold & Co. GmbH, Partenstein, Germany. Carbon concentration both in powder and in solidified material was determined using an ELEMENTRAC CS-i carbon and sulfur analyzer produced by ELTRA GmbH, Haan, Germany.

For WC addition, different concentrations of 2.5, 5, and 10 wt.-% were admixed to 16MnCr5 base material prior to fabrication. WC microparticles of type DS 250 were provided by H.C. Starck GmbH, Goslar, Germany. Since the effect of WC-particles on processability is unknown, a wider parameter range was studied. All powders were mixed using an automatic periodic tumbling unit and are mixed for at least 2 h prior to processing.

Optical analysis is performed to evaluate the homogeneity of the powder mixture as well as determining potentially process-hindering defects. For carbon addition, attached CB nanoparticles can be found distributed over the entire surface of 16MnCr5 powder after tumbling, as shown in Fig. 2.

In some places, smaller agglomerations of these particles can be observed. Performing Hall-flowmeter tests showed that flowability of these powder materials decreased slightly from 17.28 to 21.81 s for 0.44 wt.-% C. Second, WC particles were added to 16MnCr5. An exemplary SEM image is shown in Fig. 3.

In contrast to the carbon-enriched powder, larger agglomerations of WC particles can be found on the surface of the base material. These accumulations might act obstructively

Fig. 2 SEM images of a 16MnCr5 and carbon black powder mixture at 500 $\times$ magnification (a) and 5,000 $\times$ magnification (b)

Fig. 3 SEM images of a 16MnCr5 and WC powder mixture at 500× magnification (a) and 3000× magnification (b)

while processing due to their irregular shape, leading to hooking effects during powder supply. This can also be seen during Hall-flowmeter testing as the investigated powder mixtures do not flow through the capillary. However, recoating of powder during PBF-LB/M process was possible. Furthermore, it can be observed that larger particles did not adhere to the surface of the base material. This is the result of insufficient adhering forces due to too large particle size. During processing, this could result in WC losses during powder supply or inhomogeneous WC distribution within the manufactured specimen. Additional images of the WC particles can be found in the [Appendix](#) of this work (Fig. 20).

Table 1 lists the investigated process parameters and their range for the corresponding experiments using the different powder mixtures.

After processing, all manufactured specimens are analyzed in a metallographic laboratory. This procedure includes powder analysis before processing as well as the investigation on manufactured samples. Test cubes are embedded at 150 °C in a resin matrix for optical analysis, and built-up direction is from left to right in all cases. For this, all samples need to be grinded and subsequently polished to 1 μm using a diamond suspension. Relative part density is

determined using magnified (25× and 50×) images of cross-sections that are evaluated manually using GIMP (magn. 25×) or (magn. 50×) by use of an analysis module in the Image Management System (Imagic Bildverarbeitung AG). These images are binarized based on a determined threshold value, thus separating defect-free regions from defect-prone regions. Influence of WC-particles on microstructure is determined using scanning electron microscopes (SEM) of types TESCAN MIRA3 and TESCAN VEGA (TESCAN ORSAY Holding, a.s., Czech Republic).

Thirdly, hardness testing was performed on embedded cross-sections using a Qness Q10 A+ microhardness tester (ATM Qness GmbH, Germany). Material hardness is tested according to Vickers with a test load of 5 kp (HV5) supporting comparison of manufactured samples. Nine points in the inner region of the manufactured specimens were measured per sample. Three cubes were built for every validated parameter set. Furthermore, material hardness of wear specimens was determined along build direction. For case-hardened specimens, hardness profile is determined using HV1.

Analysis of tribological material properties of additively manufactured samples is performed by means of pin-on-disc tests using an SRV 4 tribometer (Optimol Instruments

Table 1 Investigated process parameters

Parameter	16MnCr5	16MnCr5 + CB	16MnCr5 + WC
Laser power P_L	250–350 W	250–300 W	250–350 W
Scanning speed v_s	500–900 mm/s	500–900 mm/s	500–900 mm/s
Hatch distance h	120 μm	120 μm	120 μm
Layer thickness H	50 μm	50 μm	50 μm
Focal diameter d_f	120 μm	120 μm	120 μm
Contour laser power P_{LC}	250 W	250 W	250 W
Contour scanning speed $v_{s,c}$	900 mm/s	900 mm/s	900 mm/s

Table 2 Selected parameters for pin-on-disc testing

Parameter	Value
Contact force (normal force)	180 N
Testing period	1 h
Velocity	0.05 m/s
Lubrication	FVA 3
Temperature	Ambient

Prüftechnik GmbH, Germany). These investigations aim at qualitative comparison of different alloying systems, thus deriving most promising compositions for improving wear resistance in the as-built state. Testing discs with the diameter of 35 mm and a height of 8 mm were built using the best parameter combinations for pure 16MnCr5, 0.44 wt.-% carbon in 16MnCr5, and 2.5 wt.-% WC in 16MnCr5. Manufactured discs were machined to the final diameter of 31 ± 0.1 mm and height of 4 mm. As pin, a cylindrical roll of type ZRB5 $\times$ 10 made from conventional bearing steel was used. The length and diameter of this pin were 10 and 5 mm, respectively. Testing conditions for tribological analysis are listed in Table 2.

By continuously measuring friction force while maintaining a constant contact force, the coefficient of friction is determined. Furthermore, roughness measurement on worn disc surfaces allows the estimation of wear loss. This supports at least a qualitative analysis of the performance of different material systems.

3 Results and discussion

In the following section, the results on optical analysis, hardness measurement, and wear testing are provided for unmodified base material 16MnCr5, carbon black-enriched 16MnCr5, and WC-reinforced 16MnCr5.

Fig. 4 Cross-section and relative part density (determined by GIMP) of additively manufactured 16MnCr5 specimen for parameters $P_L = 350$ W and $v_s = 500$ mm/s (a) and $P_L = 250$ W and $v_s = 600$ mm/s (b)

		Scanning speed in mm/s				
		500	600	700	800	900
Laser power in W	350	99,146%	99,837%	99,938%	99,916%	99,900%
	300	99,576%	99,850%	99,944%	99,956%	99,898%
	250	99,903%	99,941%	99,962%	99,919%	99,793%

Fig. 5 Illustration of the relative part density (determined by IMS) depending on the applied processing parameters during PBF-LB/M for one exemplary specimen each using $50\times$ magnification

3.1 Optical analysis

This section aims at presenting results on the part density analysis by means of optical imaging. Results are divided into base material 16MnCr5, carbon black-modified 16MnCr5, and tungsten carbide-modified 16MnCr5.

3.1.1 Base material 16MnCr5

First, results on relative density analysis for different in situ alloyed materials are presented. Unmodified 16MnCr5 base material is used as benchmark for further comparison. Higher laser powers lead to an increased amount in pores within the material. Cross-sections for additively manufactured samples with high and low laser power can be seen in Fig. 4. Here, an increased amount of defects is obvious for a laser power of 350 W and a scanning speed of 500 mm/s (Fig. 4a) compared to a power of 250 W and scanning speed of 600 mm/s (Fig. 4b).

Furthermore, a higher number of pores can be found in the outer regions of the manufactured specimens. This is the result of non-optimized contour parameters which could potentially result in pores due to deep penetration welding. Contour porosity could potentially be countered

by optimizing the parameter set by, e.g., increasing the scanning speed to reduce the energy input.

Increase in porosity can be attributed to higher laser powers evaporating elements within the matrix material. These defects might also be the consequence of deep penetration welding as shielding gas is entrapped inside the solidified layer. This is the case for instable and thus collapsing key-holes during welding. The identified process window and the corresponding relative part densities for further parameter combinations are illustrated in Fig. 5.

A constant decrease in relative part density with increasing laser powers is obvious. However, increasing the scanning speed for higher laser powers leads to reduced porosity in the final specimen as total energy decreases. Based on determined relative part density, the process window for further experiments with CB-addition is constricted to laser powers between 250 and 300 W as well as scanning speeds in the range of 600 to 900 mm/s. These best results are also similar to Kamps [5], Schmitt et al. [8], and Bartels et al. [7], who all have found a relative part density above 99.9%.

3.1.2 Carbon black–modified 16MnCr5

The following subsection focuses on the addition of different carbon black concentrations to base material 16MnCr5. Similar to processing of the base material, a comparison of parameter combinations resulting in the lowest and highest relative part density is presented. For a measured C content of 0.28 wt.-%, relative part densities between 99.72% (a, $P_L = 250$ W, $v_s = 600$ mm/s) and 99.88% (b, $P_L = 300$ W, $v_s = 700$ mm/s) can be determined using previously well-suited parameter combinations, as shown in Fig. 6.

Increased carbon content in the material requires an increased laser power for the fabrication of nearly defect-free specimens. Nevertheless, for a carbon content of 0.28 wt.-%, specimens can be manufactured with satisfying part densities. In the next step, the addition of further 0.16 wt.-% C

is investigated, leading to a total of 0.44 wt.-% in the material. Again, a defect-free fabrication of samples is possible. Relative part densities of up to 99.89% can be achieved as illustrated in Fig. 7.

When comparing to the specimens with a total carbon content of 0.28 wt.-%, no clear decrease in porosity can be found. The pores in the center of the material, however, possess a larger size. Finally, specimens with a total carbon concentration of 0.52 wt.-% in the powder were manufactured additively. Figure 8 presents the results for the most and least porous cross-sections.

In contrast to lower carbon contents, an increased porosity is found for the worst parameter combination investigated. This shows that the potential process window shrinks for higher carbon concentrations, which could be expected as the defect-affinity increases. The increase in porosity compared to preliminary experiments on processing the unmodified 16MnCr5 powder can be attributed to both a higher energy input due to the carbon black nanoparticles and the higher defect affinity of carbon-enriched steels. Next, carbon content was measured both for the pre-mixed powder material and for manufactured test samples using the ELEMENTRAC CS-i analyzer. It was observed that the carbon content in the powder was typically higher by about 10% compared to the content of manufactured specimens. This trend observed throughout all carbon-enriched powders is listed in Table 3.

Losses between powder and specimen can possibly result from adhesion on the surface of the glass container after tumbling and during the powder supply during the process.

3.1.3 Tungsten carbide–modified 16MnCr5

The second investigated approach for in-situ modification is the addition of WC-microparticles to unmodified 16MnCr5 base material. By adding these carbides, an increase in wear resistance is targeted. However, analyzing the corresponding

Fig. 6 Most (a) and least (b) porous cross-sections of 0.28 wt.-% carbon black–modified 16MnCr5 test cubes used for density measurements, process parameters: $P_L = 250$ W, $v_s = 600$ mm/s (a) and $P_L = 300$ W, $v_s = 700$ mm/s (b)

Fig. 7 Most (a) and least (b) porous cross-sections of 0.44 wt.-% carbon black–modified 16MnCr5 test cubes used for density measurements, process parameters: $P_L=250$ W, $v_s=900$ mm/s (a) and $P_L=250$ W, $v_s=650$ mm/s (b)

relative part density is more complicated compared to carbon addition as polished cross-sections show darker zones around WC particles, which appear like defects within the sample, as can be seen in Fig. 9. An automated determination of the relative part density is not feasible as pores cannot be distinguished from the embedded carbides. Therefore, information on the relative part density is omitted at this stage. To assess whether the dark spots are pores or carbides, a more in-depth analysis of the microstructure including SEM and EDX imaging of these cross-sections is required.

As the presence of these WC particles appears to be highly dependent on the energy input, it can be assumed that these particles are either partly or completely solved within the matrix material. For a higher energy input, less of these dots can be found (see Fig. 9a). Using a larger magnification reveals the differences between pores and WC particles within the material, as illustrated in Fig. 10.

Here, a small but bright dot, which could either be a WC carbide or oxidized particles, can be identified within the center of the majority of the black spots. As these spots are both irregularly shaped and surrounded by a darker bonding region, it is assumed that these dots are WC particles. This is due to the WC particles possessing an irregular shape compared to the base powder material. Pores, on the other

hand, possess a more spherical shape than the WC particles. A similar differentiation of pores and WC-particles was already presented by Kang et al. [18]. In a next step, EDX line scans are performed for measuring the W content of these potential WC particles within matrix. This supports the assumption that these darker sections within the specimen are the consequence of bonded WC particles and not pores or other defects like oxidation. An exemplary EDX line scan of the tungsten concentration in two different directions is shown in Fig. 11.

EDX analysis shows that these brighter regions within the material are characterized by an increased W peak. Furthermore, a drastic fall in Fe content is detectable. This supports the assumption that not all dark spots in Fig. 12 are defects such as pores or cracks within the specimen. Furthermore, the diffusion zone of these WC particles within the 16MnCr5 matrix needs to be analyzed. SEM images also show asymmetrical diffusion zones of these WC particles as well as elongated diffusion zones, in addition to spherical zones as shown in Fig. 11, within the matrix. These effects can be seen in Fig. 12.

This elongated diffusion zone can also be referred to as a W tail, which was already reported by Schaak et al. in previous work [22]. Additional EDX line scans of this tungsten tail are

Fig. 8 Most (a) and least (b) porous cross-sections of 0.52 wt.-% carbon black–modified 16MnCr5 test cubes used for density measurements, process parameters: $P_L=300$ W, $v_s=500$ mm/s (a) and $P_L=250$ W, $v_s=700$ mm/s (b)

Table 3 Carbon content in powder material and additively manufactured specimens

Powder mixture	Powder	Specimen
16MnCr5	0.177 ± 0.002	—
0.28 wt.-% C	0.279 ± 0.004	0.259 ± 0.002
0.44 wt.-% C	0.445 ± 0.006	0.400 ± 0.004
0.52 wt.-% C	0.528 ± 0.004	0.448 ± 0.011

presented in the [Appendix](#) (Fig. 21), proving that the brighter region is the consequence of tungsten within the material.

Finally, SEM analysis of the diffusion zone of WC particles was performed. Our goal was to investigate the occurrence of potential defects after solidification. Exemplary images of two WC particles within the 16MnCr5 matrix are presented in Fig. 13.

Here, the formation of a carbide network starting from the embedded WC particles can be observed. The carbide network appears to form with a preferred direction within the specimen. However, further investigation on the development of this network structure is necessary for fully understanding its propagation. Furthermore, bonding defects surrounding the WC particle can be found consistently. These defects are characterized by darker spots that form both directly at the WC particle and in the surrounding diffusion zone. One potential reason for these defects is insufficient wetting behavior of the WC particles within the matrix in the molten state. One potential approach for minimizing bonding defects is the use of Co-coated WC particles, allowing a better wetting of the added particles within the matrix. However, additional research needs to be performed for fully understanding the origin of this defect formation. Besides the micro-scale bonding defects near individual particles, it can be concluded that the addition of 2.5 wt.-% WC to 16MnCr5 base material still allows the fabrication of nearly defect-free specimen. An increase of pores in the outer regions of the specimens is evident.

Furthermore, addition of 5 wt.-% and 10 wt.-% WC to unmodified 16MnCr5 has been investigated. Here, a significant increase in defects, which includes gas porosity and crack formation, can be found after processing, even for all investigated parameter sets. Exemplary cross-sections of WC-modified 16MnCr5 are shown in Fig. 14.

In both cases, crack formation can be identified in the outer edges of the specimen. With increasing WC content (10 wt.-%), crack tendency in the center of the specimens also increases (see Fig. 14b). Here, the cracks appear to spread between the pores which originate from the embedded carbides. Similar effects were observed by Chen et al. [23] even for lower carbide contents. Further microstructure is investigated by means of SEM for determining the dilution zone of the WC particles, as depicted in Fig. 15.

In contrast to modification with 2.5 wt.-% WC, a more pronounced carbide network can be found in the area surrounding the added particles. However, presumably due to insufficient wetting behavior, an increased amount of WC particles, and a harder matrix material, crack formation in the region of WC particles drastically increases. These cracks probably result from internal stresses occurring during processing and form during cooling and solidification of the melt pool. This crack formation could possibly be avoided by integrating a high-temperature platform heating at least for a WC content of 5 wt.-%. Another potential solution for avoiding this crack formation lies in using even smaller particles in the sub-micron scale, as it was reported by Chen et al. [24].

In summary, processing of WC-enriched base material is possible for low contents of 2.5 wt.-%. For higher contents, defect-affinity drastically increased as crack formation was initiated.

3.2 Hardness analysis

Material hardness was determined for different carbon and tungsten carbide concentrations in the final specimens.

Fig. 9 Cross-sections of 2.5 wt.-% WC-modified 16MnCr5 test cubes with (b) and without (a) dispersed WC particles visible, process parameters: $P_L = 350$ W, $v_s = 600$ mm/s (a) and $P_L = 300$ W, $v_s = 900$ mm/s (b)

Fig. 10 Microscope analysis of WC-enhanced 16MnCr5 with dispersed WC particles at magnification of 100-times (a) and 200-times (b)

Furthermore, samples with a carbon content of 0.52 wt.-% were also heat-treated prior to indentation measurement. Determined material hardness for different carbon-modified materials is shown in Fig. 16.

Additively manufactured 16MnCr5 specimens are characterized by a mean material hardness of 337 HV5 for the favored parameter set. Hardness of the conventionally fabricated and case-hardened reference system was determined to be 602 ± 9 HV5 for a carbon content of 0.4% in the case. Average material hardness for CB-modified base material was determined to be 375 HV5 for 0.28 wt.-% and 436 HV5 for 0.44 wt.-%, respectively.

Further increasing the carbon content to 0.52 wt.-% in the powder, which is equivalent to a carbon content of approximately 0.45 wt.-% in the specimen after PBF-LB/M, leads to a material hardness of 458 ± 24 HV5 in the as-built state. After austenitization at 860 °C for 30 min and subsequent quenching, these specimens possess an indentation hardness of 725 ± 7 HV5, which falls to 617 ± 3 HV5 after a subsequent tempering step at 200 °C with a holding time of 2 h. This temperature was selected as it is commonly used for quenched and tempered specimens. The observed drop in material hardness supports the assumption that the martensitic phase is dominant after heat treatment, as other

Fig. 11 SEM images of dispersed WC particle within the etched base material (a) as well as EDX line scans for determining the elemental composition (b, c)

Fig. 12 SEM images of WC particles with asymmetrical diffusion zones (a) and elongated W tails (b)

phases, e.g., bainite, possess a higher tempering stability. Comparing the results of the material hardness with the ones presented by Hutchinson et al. [25] supports the assumption that a primarily martensitic phase is present after hardening, as the hardness values are similar. At this point, it is evident that solely increasing the carbon content of the powdery material does not result in a sufficiently increased material hardness. This can be attributed to the process intrinsic heat treatment leading to a continuous tempering of lower layers, resulting in reduced material hardness compared to the theoretically achievable one. Therefore, additional XRD analysis was performed which show that the content of retaining austenite was approximately 4% for manufactured specimens. Considering the high hardness of martensite, this leads to the assumption that a microstructure possessing a lower hardness must underlie. Etched cross-sections of carbon black-modified 16MnCr5 are displayed in Fig. 17.

From the presented images, no clear increase in dark needle formation, which could potentially represent an enhanced martensite formation, is detectable. This supports the assumption that the present microstructure is not solely martensitic in the as-built state. Furthermore, the addition of CB-nanoparticles might lead to a finer microstructure,

which is characterized by smaller martensitic needles with increasing carbon contents. This would correlate with the observations made by Reinert et al. [26] that carbon nanotubes and nanoparticles result in grain refinement. The finer grain then favors an increase in material hardness, as shown in the studies by Hall [27]. Coupled with an improved martensitic hardness due to an increased carbon content, the rise in material hardness can be explained. Further analysis on the average grain size needs to be performed. This, however, falls within the scope of future investigations. The obtained results lead to two main findings: On the one hand, specimens from a carbon-enriched 16MnCr5 can be manufactured nearly defect-free, showing the possibility to avoid a post-process chemical heat treatment for increasing the carbon content. On the other hand, however, heat treatment is still required for achieving a desirable material hardness.

In the next step, material hardness of WC-enhanced 16MnCr5 specimens was determined. Obtained results for different WC concentrations are depicted in Fig. 18.

Firstly, material hardness is constantly increasing with higher WC concentrations. A rise in hardness of approximately 80 HV5 per additional 2.5 wt.-% WC compared

Fig. 13 SEM images of individual particles containing mainly defects in the diffusion zone (a) and bonding defects (b)

Fig. 14 WC-modified 16MnCr5 base material with 5 wt.-% WC (a) and 10 wt.-% WC (b)

to the base material can be assumed. This is in accordance with the results presented by [17], who reported an increase by approximately 100 HV for 2 wt.-% WC. Furthermore, in comparison to C-addition, a significant increase in material hardness can be determined already in the as-built state. This could be attributed to the comparably high hardness of WC particles compared to the base material, dispersion hardening effects, or other hardening mechanisms. Standard deviations also tend to increase drastically for larger WC contents. One possible reason for this is the increasing number of defects within the sample.

3.3 Wear analysis

Finally, qualitative wear analysis tests were performed for determining wear rate of manufactured test specimens. Conventionally fabricated and case-hardened 16MnCr5 samples were used as reference system. Furthermore, additively manufactured and case-hardened specimens as well as in situ modified samples with enhanced carbon or WC content were studied. For comparability, roughness values R_a (mean arithmetic roughness) and R_z (maximum height of a specified profile) and R_t (maximum roughness entire sample) are determined. Measurement points (b) as well as

corresponding roughness in μm (a) for different material systems are presented in Fig. 19.

System 4, which was manufactured conventionally and subsequently carburized to a carbon content of approximately 0.4% in the case, was set as a reference value. After 1 h of testing, measured R_z value is $0.40 \pm 0.02 \mu\text{m}$. For unmodified 16MnCr5, the roughness R_z was determined to be around $2.4 \pm 0.59 \mu\text{m}$. As-built specimens of system 2 (16MnCr5 with a total of 0.42 wt.-% C) result in a significantly higher maximum height of the profile of almost $1.9 \pm 0.16 \mu\text{m}$. This increase can be attributed to the comparably low hardness in the as-built state. In contrast, specimens with added WC (system 3) show significantly improved wear behavior ($R_z = 0.8 \pm 0.16 \mu\text{m}$) compared to carbon-enriched specimens (system 2). The material hardness in the as-built state is similar for both WC-enriched and CB-enriched material. Therefore, this decreased surface roughness can be attributed to the more wear-resistant carbide network within the test disc. Presented results show the potential of carbide addition, already in the range of 2.5 wt.-%, for improving the wear resistance of additively manufactured samples from case-hardening steels. Here, compared to pure 16MnCr5, a reduction in roughness by factor 3 was realized. However, even as both system 2 and system

Fig. 15 SEM images of WC particles in a 10 wt.-% WC specimen at 10,000 $\times$ (a) and 20,000 $\times$ magnification (b)

Fig. 16 Mean hardness of C-modified 16MnCr5 at different concentrations and processing parameters in as-built and heat-treated conditions

3 possess similar hardness, wear rate for WC-enriched specimens is reduced by more than 50%. Considering that hardness of WC-enhanced 16MnCr5 (437 ± 2 HV5) compared to C-enriched 16MnCr5 (458 ± 3 HV5) is comparable, it can be concluded that wear resistance is not primarily affected by material hardness. This was already observed by Gore and Gates in 1997 when they found that cast irons in the as-built state possessed a lower wear rate against a dry sand rubber wheel compared to carbon-reduced cast iron. However, changing the material of the wheel to steel resulted in opposite results. This is similar to the findings of this work as material hardness is not the sole indicator of a material wear rate [28]. Further studies by Tjong [29] have also shown that a moderate addition of 5 wt.-% TiB₂ to stainless steel already resulted in a significantly reduced wear loss.

Analysis of μ shows a lower coefficient of friction after 60 min of testing for conventionally manufactured and case-hardened samples ($\mu=0.036$) compared to additively fabricated ones. For carbon-enriched 16MnCr5, coefficient of friction was determined to be around 0.66, which is similar to the one of the unmodified base materials. WC addition resulted in the lowest coefficient of frictions of approximately 0.030. This reduced coefficient of friction could be another potential indicator for the significantly improved wear performance of WC-modified specimens. Due to the possibility of nearly defect-free fabrication, the addition of WC-particles to 16MnCr5 base material in low concentrations allows for both a significant increase in material hardness and wear resistance. However, even longer testing periods are required for analyzing the removal of hard particles out of the ductile matrix material.

Fig. 17 Etched cross-sections of unmodified (a) and carbon black modified to 0.44 wt.-% C (b)

Fig. 18 Mean hardness of WC-modified 16MnCr5 at different concentrations and processing parameters

Fig. 19 Mean roughness for different wear samples tested for different material systems (a) and measurement points on a worn disc (b)

4 Conclusions

In the presented work, in situ material modification using low-alloyed case-hardening steel as base material and carbon black nanoparticles as well as tungsten carbide microparticles as additional alloying component was investigated. Both C- and WC-enriched 16MnCr5 steels were processed successfully using the PBF-LB/M process. In the following, the key findings are summarized:

- The processing of low-alloyed case-hardening steels with carbon contents of up to 0.52 wt.-% is possible by means of PBF-LB/M
- Increasing the carbon content only slightly improves the material hardness in the as-built state, therefore demanding a post-process heat treatment
- Applying a conventional heat treatment proves that the required material hardness for industrial applications of above 615 HV can be achieved
- Carburizing heat treatment strategies for increasing the carbon content could be replaced in the future as materials with an increased carbon content can

already be processed nearly defect-free by means of PBF-LB/M

- The addition of WC particles resulted in an increased material hardness and drastically improved wear resistance even for small concentrations in the as-built state
- Carbide reinforcing of the material provides a significant potential for tailoring the wear resistance of additively manufactured specimens as the wear resistance is increased by the factor of two for similar hardness values compared to the as-built material

Based on these results, future work will focus on the combined addition of carbon black and carbide hard particles to further improve the wear resistance of the material. Furthermore, the presented approach can be applied to manufacture highly complex products like gears using a combination of the PBF-LB/M process for generating the main body and the DED-LB/M process for tuning the wear resistance of the product.

Appendix

Fig. 20 SEM images of WC particles at 1,500×(a) and 5000×(b) magnification

Fig. 21 Bright shimmering tail within WC modified 16MnCr5 (a) and the corresponding EDX line scan proving the presence of tungsten (b)

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Availability of data and material The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Declarations

Ethics approval The authors respect the ethical guidelines of the journal.

Consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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