

Tailoring metal powders by dry nanoparticle coating for powder bed fusion applications

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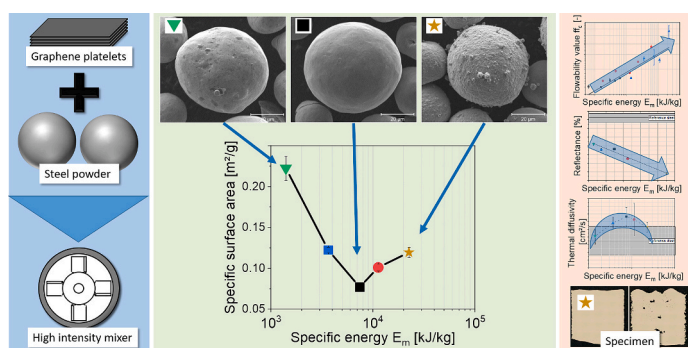
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HIGHLIGHTS

- The particles' surface roughness is adjustable by high intensity mixing.
- The specific energy while mixing defines the flowability and reflectivity of powder.
- Tailored particles for PBF with increased bulk densities and heat diffusivities.
- Enhanced mechanical properties of manufactured parts for tailored particles.

GRAPHICAL ABSTRACT



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ABSTRACT

The influence of high intensity mixing of graphene platelets with stainless steel particles in the scope of additive manufacturing is investigated. Therefore, 0.75 vol% graphene platelets were coated onto conventional stainless steel powder as a model material, resulting in very homogenously distributed graphene layers. The specific energy input during mixing was found to be the main factor for increasing the flowability and decreasing the reflectivity of the powder. Furthermore, the resulting surface roughness of the coated powders could be correlated with a theoretical consideration of van der Waals forces. In this way, the mixing process can be controlled regarding its specific energy input to achieve tailored powders for the application in PBF-LB/M. Cubic parts were produced with different laser parameters and analysed. As a result, the admixing of graphene at lower specific energies resulted in a wider process window and parts with a relative density of 99.99% were achieved.

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1. Introduction

Additive manufacturing (AM) of metals is used particularly in the automotive [2], aerospace [3] and medical industry [4]. A main advantage of AM processes is the realisation of complex structures with reduced geometric restrictions, especially in lightweight and prototype construction [5–7]. Major challenges are still low productivity and high costs of AM processes [8], which is why an application in series production is not easy to be implemented as a standard. Among the many different AM process categories, which are classified in DIN EN ISO/ASTM 52900 [9], Powder Bed Fusion of Metals using a Laser Beam (PBF-LB/M) is considered a promising technique for the transition from rapid prototyping to series production. PBF-LB/M is further described as the most effective powder-based AM method to manufacture high-density parts [10–12]. In PBF-LB/M, a powder layer is applied to a build platform and selectively molten with a laser beam. This procedure is repeated until the complete component is built up layer upon layer. Currently, an increase in productivity is typically achieved by higher laser intensities or the use of multiple lasers, leading to an increase in investment and operating costs [13,14]. Hence, the approach to modify and improve the powder feedstock is gaining importance not only in research but also in industrial attention [15]. This is extensively done by adding nanoparticles/nanomaterials to the feedstock powder to build Metal Matrix Nanocomposites (MMNCs) [1,15]. MMNCs are composed of a metal or an alloy as a continuous phase and a reinforcement material, which can be particles, short fibres or continuous fibres [16]. MMNCs combine the properties of both matrix and reinforcement. Therefore, MMNCs exhibit superior characteristics compared to the original alloy [17]. According to Chawla [16], there are three main processing routes: liquid-state processes (i.e. casting, liquid infiltration, spray-forming) solid-state processes (i.e. diffusion bonding, spray deposition, chemical vapour deposition, physical vapour deposition) and in situ processes (i.e. self-propagating high-temperature synthesis, PBF). In-situ processes are advantageous in terms of dispersing and wetting of reinforcement materials, since the composite material is processed in one step. Especially PBF-LB/M is suitable to form high-quality MMNCs with more homogenous distributed reinforcement material than conventionally processed MMCs [17]. One of the key factors here is to prepare the powder feedstock in a way, that the nanomaterial is well distributed in or rather onto the powder, and a homogeneous dispersion is realized [18–22]. Another important factor is the flowability of the powder, affecting the spreadability and therefore the powder bed density and thus the final part density [23,24]. According to Beitz et al. [25] also the shape of the spreading device and the direction of powder deposition influence the mechanical properties of additively manufactured parts. Parts built in recoating direction exhibited an 18% higher tensile strength and nearly 50% higher fracture strain values than parts built in other directions.

The agglomeration of nanoparticles is addressed as the main influence factor hindering MMNCs to outperform conventional alloys [26]. Herewith, according to Gu et al. [27], it is possible to manufacture ‘designed materials’ with beneficial properties, which cannot be produced by conventional techniques.

Among other possible reinforcements in MMCs (i.e. intermetallic compounds, oxides and nitrides, [26] and ceramics [1]), graphitic materials, especially graphene, have gained enormous interest in the manufacturing of MMNCs [17]. Graphene is defined as an allotrope of carbon in the form of a 2D hexagonal crystal lattice. Each atom forms one corner of the lattice and is bound by an sp^2 hybridisation [28]. In particular, a reinforcement with graphene or rather graphene platelets is of great interest because of the outstanding properties of graphene. Particularly a high thermal conductivity up to 5400 W/mK [29,30], an extremely high mechanical strength, a high surface area, chemical inertness, and a possible self-lubrication behaviour are worth to be mentioned [31]. This leads to MMNC components with good wear resistance [32,33], good thermal conductivity [1], low thermal

expansion coefficients [29], and enhanced tensile strengths [32,34–36] as well as higher hardness values [37]. Dadkhah et al. [17] conclude that the main challenge of reinforcing MMNCs with graphene is the uniform distribution of graphene while maintaining strong interfacial bonding. Most studies of MMNC reinforced with graphene deal with Aluminum, Magnesium and Copper. Detailed reviews about graphene-enhanced MMNCs are performed by Hu et al. [38] and Dadkhah et al. [17]. For steel or stainless steel, few research articles can be found in the literature. Lüddecke et al. [1] prepared few-layer graphene through a wet mechanical grinding process and coated the flakes, among others, on stainless steel 1.4404 and tool steel 1.2709 in a fluidized bed system with a focus on the coating process itself and powder properties. They could show a very homogenous coating of FLG on the powder surface and measure the lowest reflection of laser light for FLG coatings in contrast to silicon carbide and iron oxide black. In a consequent study from Pannitz et al. [39], they observed a rapid heat dissipation of 0.75 vol% FLG/14404 coatings during the PBF melting process. Han et al. [40] prepared 316 L/GNPs powders via magnetic stirring in ethanol suspension and ultrasonic treatment, resulting in a fair distribution of graphene platelets on the metal particle surface. The authors assume, that graphene is dispersed in the melt and preserved at the grain boundaries, leading to an increase in tensile strength of 17.9%.

Another method for preparing steel-graphene MMNC is the dispersion of graphene in dry mixing processes, such as ball milling or high intensity mixing. The aim is to distribute smaller particles onto the surface of metal particles for the application in PBF-LB/M [27,41–43]. For the latter, the distribution of these so-called guest particles has to be performed without an alteration of the powder morphology to maintain a good flowability [1,27,42]. In addition, the distribution of the guest particles has to be as homogenous as possible. Mandal et al. report dry mixing of graphene in a planetary ball mill and subsequent fabrication of PBF-LB/M parts achieving up to 25% higher Vickers hardness, 70% higher yield strength [41], a reduced wear rate [33], and decreased thermal expansion [29]. Das et al. [44] showed the importance of PBF parameters for the fabrication of stainless steel matrices modified with graphene platelets. For the highest volume energy density of 240 J/mm³, they achieved the highest relative density of 95%.

High intensity mixing for coating applications was originally discovered by Japanese researchers looking for new mechanical grinding methods. The driving mechanism of dry coating is the presence of host particles and guest particles (one or two magnitudes smaller than the host), and the mixing of these two components. The term “ordered mixing” is strongly related to dry particle coating [45]. The guest particles adhere to the larger particles due to van der Waals forces, whereas the adhesive force between the two particle species is larger than the weight force of the guest particles. This results in host particle surfaces, which are covered with guest particles. Gärtner et al. show that the nanoparticle amount and mixing time have a decisive role for the distribution of nanoparticles onto the powder, which significantly affects the flowability of the powder [46]. Depending on the kind (spherical particles or platelets) and the distribution of guest particles, different surface appearances and roughnesses are generated [47]. In a previous publication [1], the van der Waals forces for a graphene-induced nanoroughness could be calculated. Theoretically, a roughness of around 10–20 nm results in the lowest van der Waals force (see Fig. 1).

In dry coating, high shear and compaction forces are applied [48], ensuring the deagglomeration of the smaller components [49]. If these forces are very high and cause an alteration of the surface, a so-called surface fusion is possible. These changes can be physical (adhesion, embedding) or even of chemical nature [50,51]. The involved processes are then called mechano-fusion or even mechano-chemistry [49]. In high intensity mixing, these forces can be reached easily, which is used in several industries for product formulations. Also, metal particles were already coated with ceramics [52,53] for example to prevent oxidation of iron particles [54]. More recently, He et al. [55] reported combined ball milling with high intensity mixing. The production of Aluminum

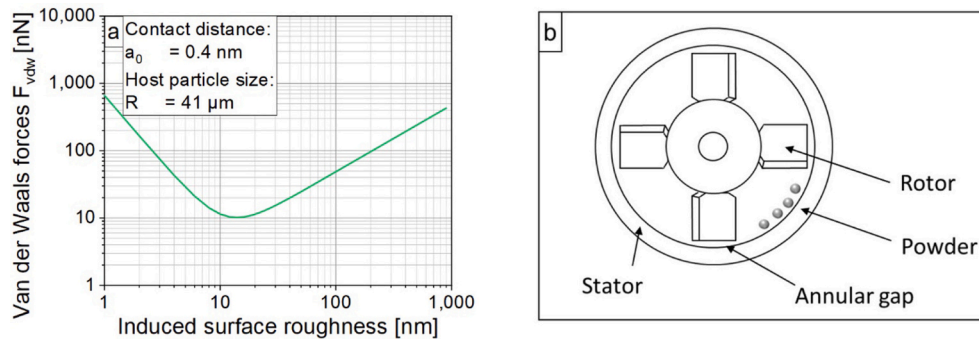


Fig. 1. Theoretical van der Waals forces in relation to the induced nano-roughness according to [1] (a), principle of the high intensity mixer Picobond Nobilta 80 according to HOSOKAWA ALPINE (b).

nanoflakes increased the surface area of spherical Al particles and enabled the homogenous distribution of high SiC loadings up to 10 wt% SiC. As a result, increased tensile and yield strengths were reached.

In general, processes for the production of graphene-modified powders focus on the PBF-processing and final part properties. However, a detailed investigation of the influence of process parameters such as different specific energy inputs and stressing conditions is missing. Consequently, the focus of this work is the production of graphene coatings by high intensity mixing, the distribution of the graphene platelets on the surface and the resulting surface and powder properties of spherical metal particles. In this study, conventional stainless steel 1.4404 was used as a model material, due to the well-known properties of the powder and corresponding manufactured parts as well as the significance in research and industry [5]. Therefore, the authors can explicitly differentiate between the properties of the MMNC-reinforced and conventional powder. Overall, the high intensity mixing of metal powder and graphene enables an adjustable surface roughness and therefore improved powder for the PBF process. The relation of surface roughness, flowability, thermal diffusivity and its influence on the laser absorption, PBF process and additively manufactured part properties is, to the author's knowledge, not reported in the literature so far.

2. Materials and methods

2.1. Feedstock material

Conventional steel powder type 1.4404, manufactured by ThyssenKrupp Materials GmbH, was employed as the base material in this study. The chemical composition provided by the supplier is depicted in Table 1. The powder exhibits a monomodal particle size distribution (PSD) with a $x_{50,3}$ of 41 μm , a span ($x_{90}-x_{10}/x_{50}$) of 0.77 and a nearly spherical particle shape. The nanoparticulate guest graphene platelets (6–8 nm thick) were acquired from IOLITEC GmbH and exhibit a high specific surface area of 162 m^2/g . The morphology and particle sizes can be seen in the supporting information (Fig. S1 for graphene platelets and Fig. S2 for the stainless steel powder).

2.2. Powder processing

High-intensity mixing was performed at 10, 20 and 30 m/s in a picoline mixer (Hosokawa Alpine, Germany), with a picobond configuration and a Nobilta 80 rotor (see Fig. 1b), containing a gap width s of 2 mm. The mixing times were 2, 5, 10, 15, and 30 min. For each

experiment 0.75 vol% graphene (corresponding to 0.2 wt%) platelets were used. Since the size and thickness of coated graphene platelets differ depending on the mixing energy (see supporting information Fig. S4) a theoretical surface coverage is hardly calculable. Therefore, we consider the thickness of theoretical graphene layer around the particle. 0.75 vol% graphene addition corresponds thereby to a theoretical layer thickness of 50 nm around the host particle. In this way, it is possible to adjust the high intensity mixing process in a way that favorable surface roughness results.

2.3. Material analysis

The XRD-measurements of powders were conducted by an Empyrean series 2 diffractometer (MalvernPanalytical, Almelo, The Netherlands) with Cu-K α radiation ($\lambda = 1.5419$ nm, K α_2 : K $\alpha_1 = 0.5$, Cu LFF HR as X-ray source) and a PIXcel3D detector was applied to record diffractograms from 20° to 90° 2 θ with a step size of 0.053°. The samples were prepared on a Si sample holder and measured in reflection mode (Bragg–Brentano geometry). Additionally, the carbon content was measured with Leco Series 744 via combustion under oxygen and analysed via NDIR.

Raman spectroscopy (alpha300R, WITec) was used to determine the structural changes of the graphene platelets caused by the high intensity mixing. The used wavelength was 532 nm at a low power input of 2 mW to avoid sample alteration. 10 single spectra were recorded on different particles and then averaged.

2.4. Particle and particle surface characterisation

Laser diffraction (Mastersizer 3000 dry module, Malvern) was used for the particle size analysis of the dry feedstock AM powder and MMNC powders. It was operated dry with a dispersion pressure of 2 bar.

The specific surface area was determined by nitrogen absorption via the BET method (Nova 200e/Quantacrome). A Multi-Point BET approach was used to determine the specific surface area. Atomic force measurements were conducted in tapping mode (AFM/ Nanowizard 3, JPK Instruments) and evaluated with the JPK data processing tool. Consequently, the average roughness value (Ra-value) was calculated using the following equation:

$$Ra = \frac{1}{L} \int_0^L |z(x)| dx \quad (1)$$

With L is the length of measurement and $z(x)$ the profile height

Table 1

Chemical composition of the model material 1.4404 stainless steel in wt%.

Element	Fe	C	Si	Mn	P	S	Cr	Mo	Ni
wt%	Balance	0.02	0.4	1.1	<0.01	0.004	17.1	2.2	11.3

function.

For the evaluation of the surface coating quality and morphology, a scanning electron microscope (SEM), Helios G4 CX, was employed (FEI/ThermoFisher Scientific). A coupling energy dispersive x-ray detector (EDX) was used to determine the elemental distribution (especially for the qualitative evidence of carbon) on the particle surfaces. SEM pictures in the supporting information are performed with Phenom XL (Thermo Fisher Scientific).

The Nicolet iS20 FTIR spectrometer (Thermo Fischer Scientific, Waltham, MA, USA) was used to measure the reflectance of the powder. The device is equipped with a XT-KBr beam splitter, a MCT/A detector and the diffuse reflection accessory DiffusIR (Pike Technologies, Madison, WI, USA). The spectral resolution is 4 cm^{-1} and Wavenumbers from 4000 to $10,000\text{ cm}^{-1}$ were used to record sample spectra over a wide range. For every sample, 16 scans were performed for 3 samples of each powder.

2.5. Powder characterisation

Ringshear measurements at low pre-shear stresses of 1 and 3 kPa were performed in a Ringsheartester XS (Schulze, Germany) with a medium shear cell ($V = 31\text{ cm}^3$). The definition of a profound flowability value (ff_c) is according to Jenike [56] the ratio of the consolidation stress σ_1 and the unconfined yield strength σ_c . Hereby, a free-flowing powder exhibits a ff_c value above 10 and a cohesive powder between 2 and 4. For further background on how shear tests are performed, the authors refer to Schulze [57], where a holistic explanation of shear testers and the behaviour of bulk materials is given.

Additionally, the dynamic angle of repose was determined using a rotating drum with transparent lateral glass frames (Granudrum, Granutools). For each test, 50 ml of powder was filled into the drum and the measurement was repeated three times. The operation speeds were increased stepwise from 1, 2, 4, 6, 8, 10, 20, 40 to 60 rpm and decreased thereafter. An integrated CCD camera automatically took 50 pictures at each speed and the software calculated the dynamic angle of repose, by detecting the powder surface with an edge detection algorithm [58,59].

The carbon content (C-content) of the powders was analysed via combustion with oxygen in a Leco CS300 (Laboratory Equipment Company, USA). The incidental exhaust gas from the combustion passes a catalyst to convert CO to CO_2 . Consequently, the C-content is analysed from the CO_2 content with a nondispersive infrared sensor (NDIR sensor).

The laser flash technique was employed to measure thermal diffusivity using an LFA 1000 laser flash analyzer (Linseis Messgeräte GmbH, Germany). Measurements were performed using a container depicted in Fig. 2. This device features a container made of DIN EN 1.4404, enveloped at its upper and lower ends by quartz glass discs composed of Suprasil® 1. This measurement setup facilitated the direct assessment of thermal diffusivity for the powder material. The thickness (L) was established by the spacing between the quartz glass discs and set at 2 mm for this particular study. A precise description of the measurement principle can be found in a work published by Berger et al. [60].

2.6. PBF-LB/M processing and specimen characterisation

PBF-LB/M of processed powder at 30 m/s tip speed in the high intensity mixer was performed on a TruPrint 1000 (Trumpf GmbH + Co. KG, Ditzingen, Germany) equipped with a 200 W Laser with a spot size of $30\text{ }\mu\text{m}$. The diameter of the build platform was 34.5 mm. The samples (cubes) of the build job had a base area of $4.5 \times 4.5\text{ mm}^2$ and a height of 6 mm. The layer thickness was $30\text{ }\mu\text{m}$. A constant hatch distance of $60\text{ }\mu\text{m}$ was used. The laser scan speed ranged from 600 mm/s to 1200 mm/s (300 mm/s step size). The nominal laser power ranged from 150 W to 170 W (10 W steps). This is equal to volumetric energy densities of $69.4\text{--}157.4\text{ J/mm}^3$. The build job was performed under a nitrogen atmosphere ($< 100\text{ ppm}$ oxygen content) with a starting orientation of the scan vectors of 45° , rotating 90° every layer. As the cubic-shaped samples have been rotated by 45° along the z-axis, the scan vectors were orientated parallel to the edges of the samples. The as-built cubic parts were ground stepwise (320 to 1000 grit size) and sequentially polished with a grain size of $9\text{ }\mu\text{m}$, $3\text{ }\mu\text{m}$, and oxide polishing suspension. Three cross-sections of each sample have been metallographically prepared. A

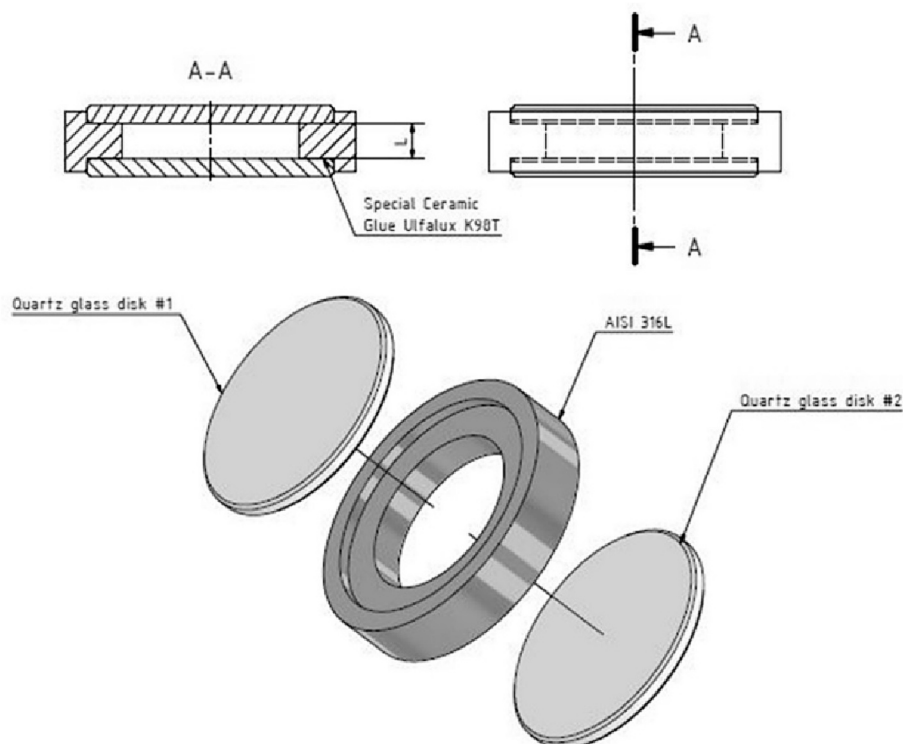


Fig. 2. Measurement container setup for an eased evaluation of thermal diffusivity for powder materials. Extracted from [60].

VHX 6000 digital microscope (Keyence Corporation, Japan) was used to take images of the prepared cross-sections. The relative density was then measured in an area with a width of 3.5 mm and a height of 3 mm. An automated calculation of the threshold value for each cross-section was performed using the Isodata algorithm of the Python library scikit-image to derive a binary image. In the end, the relative density was calculated by the ratio of black to white pixels.

The hardness and Young's modulus of the manufactured specimen were determined by nanoindentation. The indenter (TriboIndenter, Hysitron Inc.) was equipped with a high load transducer (SN 5/310/18) and a Berkovich tip (TI 065 fluid). The load function was displacement controlled with a depth of 4000 nm, a load rate of 800 $\mu\text{N/s}$, a Set Point of 250 μN and a Drift of 2/5. An indentation pattern of 5×5 with a distance of 75 μm between indents was established, resulting in 25 indents per specimen. The specimens produced at 150 W and 600, 900, and 1200 mm/s for powders processed at 30 m/s were tested. In depth-sensing indentation techniques were used to obtain the hardness H_{IT} and Young's modulus E_{IT} according to [61]. The indentation hardness is derived from the mean contact pressure of the indenter (see Eq. (4)). Whereas the load P is measured and the projected area of the contact A is given by the depth of the "plastic" penetration h_p and the known geometry of the indenter. h_p is thereby the depth of penetration measured from the area of contact.

$$H_{IT} = \frac{P}{A} \quad (2)$$

With $A = 3\sqrt{3}h_p^2 \tan^2 \theta$ and $\theta = 65.27^\circ$ for a Berkovich tip results:

$$A \approx 24.5 h_p^2 \quad (3)$$

And finally

$$H_{IT} = \frac{P}{24.5 h_p^2} \quad (4)$$

The Young's modulus E_{IT} can be derived from the slope of the unloading curve of the load-displacement measurements at maximum load.

$$E_{IT} = \frac{1}{2} \frac{\sqrt{\pi}}{\sqrt{A}} \frac{dP}{dh} \quad (5)$$

3. Results

For the production of MMNCs, an excellent homogenous coating of graphene platelets is crucial [17], resulting in well-dispersed graphene platelets before entering the PBF process. Therefore, the aim of this work is to obtain a set of parameters with beneficial graphene distribution. Attention will be given to the distribution of graphene layers without altering the particle shape of the host particles to maintain a good flowability. Consequently, different tip speeds and mixing times were compared in the high intensity mixer. For the evaluation of the process, the energy input related to the mass m_p of processed powders is calculated. The specific energy E_m for mixing a product mass m_p can be derived analogously to the one calculated in stirred media mills [62]. $P(t)$ is the power draw at time step t and P_0 is the no-load power draw of the rotor at a given tip speed.

$$E_m = \frac{\int_0^t P(t) - P_0 dt}{m_p} \quad (6)$$

3.1. Material structure

3.1.1. Model steel powder characteristics

The influence of the high intensity mixing at 30 m/s tip speed on the crystallographic structure of the steel is determined via XRD measurements. Fig. 3 shows the influence of specific energy input on the XRD diffraction pattern. The as-received powder exhibits the typical

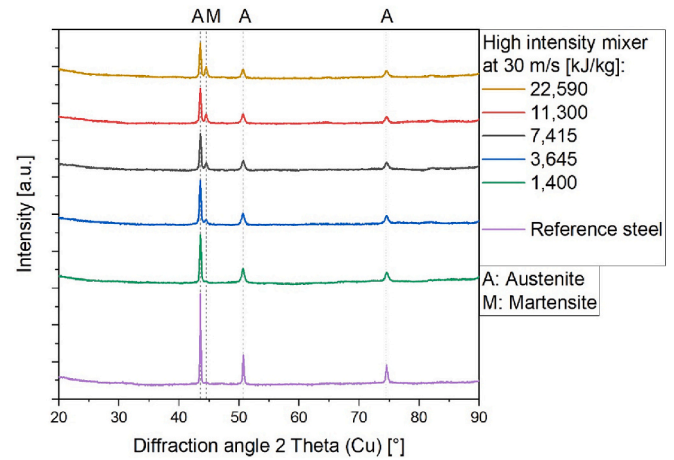


Fig. 3. XRD-Pattern of graphene-coated steel powder and the feed-stock material.

diffraction peaks reported for austenitic steels [63]. A second peak becomes apparent at 45° with increasing process time. The peak area increases with higher specific energies. According to [63], a transformation of an austenite to a martensite, so-called deformation-induced martensitic formation, is probably the reason for the peak. In general, martensitic transformations are diffusionless structural phase transformations. They occur when the structures of the educt and the product phase are transformed into each other by a shear-dominated lattice deformation [64]. Since the powder is molten in the PBF-LB/M process, these transformation should be negligible in terms of final part properties.

3.1.2. Graphene

The Raman spectra of the as-received graphene platelets and selected processed powders are shown in Fig. 4 (all spectra are provided in the supporting information in Fig. S5). The three characteristic peaks of graphitic material can be seen in the graphene platelets spectra. The G line is at around 1582 cm^{-1} , the D line in the region of 1350 cm^{-1} and the 2D line at 2700 cm^{-1} [65].

The Raman activity is provoked through the sp^2 type of the covalent bonds in the graphitic plane. Therefore, Raman spectroscopy is a tool to compare multiple graphene layers quantitatively and qualitatively [65]. According to Graf et al. [65], it is possible to relate the number of defects in a graphitic plane through the D line intensity. An absence of the D line stands for quasi-defect-free graphene sheets, whereas the occurrence of the D band indicates defects and disorder. Ferrari et al. [66] indicate that

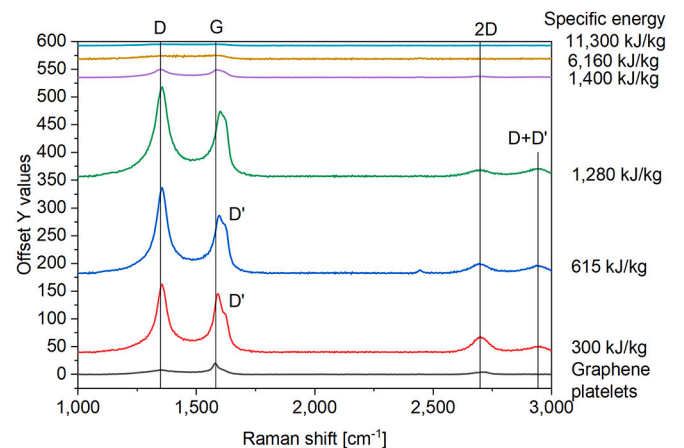


Fig. 4. Raman spectra of as-received graphene platelets and spectra on the metal particles at selected specific energies.

the presence of the D-band is assigned to the existence of sixfold aromatic rings. With increasing disorder, the ratio of $I(D)/I(G)$ increases and follows the Tuinstra and Koenig eq. (TK) [67] where $I(D)/I(G)$ is proportional to the reciprocal cluster diameter L_a . For even more disordered graphitic planes they state that cluster size and amount decrease, become more disordered, and finally unfurl. Here, $I(D)$ decreases in relation to $I(G)$, since $I(G)$ is solely related to the relative motion of $C sp^2$ atoms and the TK equation is not valid anymore. The D intensity is now proportional to finding a sixfold ring in the shrinking cluster (amount and size) [66]. With the opening up, the degree of amorphisation increases. This is called the trajectory of amorphisation [66]. Equally, Lucchese et al. [68] stated there are two competing mechanisms contributing to the Raman D band of graphene. One follows the TK equation for low defect densities, and the other for high defect densities is proportional to L_a to the power of 2. They gained a controlled amount of defects through ion-induced bombardment. In addition, Gokus et al. [69] find similar results with oxygen plasma treatment of single-layer graphene. The above-mentioned relations are achieved under extremely controlled conditions and ordered carbons. The defects are controlled in lab conditions and are controllable through different ion or plasma doses.

When referring to the Raman spectra of the high intensity mixed graphene-metal composite particles, there are additional influencing factors on the formation of defects in the graphene platelets. Due to possible interaction with the metallic surface and shear forces, bigger defects can occur. No controlled stress events between metal particles with different stress intensities are present. Nevertheless, equal trends to controlled laboratory conditions can be observed in Fig. 5a. With increasing specific energy input, the $I(D)/I(G)$ ratio rises, implying that defects in the graphene plane increase and crystal sizes decrease. Even the ascent of the curve follows the proportionality of the power of 2. At a specific energy input of around 600 kJ/kg, the curve reaches its maximum and descends thereafter. Following the literature, this decrease in the $I(D)/I(G)$ ratio shows an increasing amorphisation, where the number of ordered rings decreases and so does the $I(D)$ intensity. The graphene planes are at this point dominated by the induced structurally disordered areas [68]. The proportionality of the power of -1 also fits in this stage. For higher specific energies above 2000 kJ/kg, the $I(D)/I(G)$ ratio fluctuates around 1. We explain this behaviour by different possible hysteresis effects, which can occur due to the nature of uncontrolled defects induced in the high intensity mixing process.

With increasing specific energies, the D' peak, known as second disorder-induced peak at around 1620 cm^{-1} [70], becomes apparent (see Fig. 4). The D' peak merges into the G peak at high specific energies due to the broadening effect induced by defects [69].

The 2D peak is evident as well as the $D + D'$ peak at higher specific energy, which is known to be around 2950 cm^{-1} [69] (cf. Fig. 4). Analogous, the scattering due to defects broadens the second-order modes. This results in increasing the width of 2D peaks. For ideal few-layer graphene, researchers could assign the width of the 2D line and

the ratio of $I(G)/I(2D)$ to the layer number or thickness of graphene platelets [65,71]. Consequently, the ratio of $I(G)$ to (2D) line can be utilized to compare different flake thicknesses and stressing conditions of graphene flakes. In our case, the stressing condition is complex and the proof of exact thicknesses by AFM is not feasible on the metal particles. That is why we consider just the width of the 2D peak, which monotonically increases with the specific energy (see Fig. 5b). This broadening can be assigned to the increase in defects, as shown by [72]. This finding coincides with the previously demonstrated evolution of $I(D)$ and $I(G)$. The parameter set at 30 m/s and 1400 kJ/kg exhibits a narrower width (see Fig. 5b). This is assignable to the short mixing time of 2 min, where not all graphene platelets are stressed equally. At specific energy inputs above 2000 kJ/kg, defined second-order peaks are not present anymore (see Fig. 4 and Fig. S5). The behaviour mentioned beforehand is in accordance with the amorphisation trajectory proposed by Ferrari et al. [66], indicating the amorphisation of the graphene platelets. Furthermore, Childres et al. [69,72] report a corresponding behaviour at high defect densities.

In summary, Raman measurements helped to understand the processes involved with graphene platelet evolution. For specific energies under 2000 kJ/kg, the high intensity induced defects into the graphene platelet sheets and a gradual change in amorphisation could be observed above 2000 kJ/kg.

3.2. Particle surface properties

To further determine the process, the parameter set with the highest specific energy input is used for additional investigation. At 30 m/s, a change in surface appearance, surface roughness, specific surface area and lattice conformation can be observed with increasing process time.

In the first time step from 0 to 1400 kJ/kg, a dispersion of graphene on the host particle surface occurs. Graphene platelets are visible in the SEM pictures (see Fig. 6a) and Raman measurement revealed characteristic graphene platelet peaks. Simultaneously, the surface roughness decreases from 47 to 32 nm and the specific surface area decreases relatively in the same way (see Fig. 8).

With further processing to 7415 kJ/kg, graphene agglomerates are no longer visible on the host particle surface (see Fig. 6b and f). The surface appears very smooth, the surface roughness decreases to 0.5 nm, and Raman measurements do not reveal a 2D peak. Together with the C-content measured via combustion, which does not change significantly with the processing time (see Fig. 7), the results indicate that the graphene on the surface changed into an amorphous carbon layer.

For the specific energy increase from 7414 kJ/kg to 11,299 kJ/kg (Fig. 6c and g), the surface roughness increases again to 7 nm. A closer look at the surface shows more valleys and defects on the metal particle surface. Plastic deformation of material on the particle surface takes place. Moreover, the specific surface area and surface roughness increase again (see Fig. 8). No carbonous material is lost in this deformation step, as the C-content measurement shows (see Fig. 7). At the

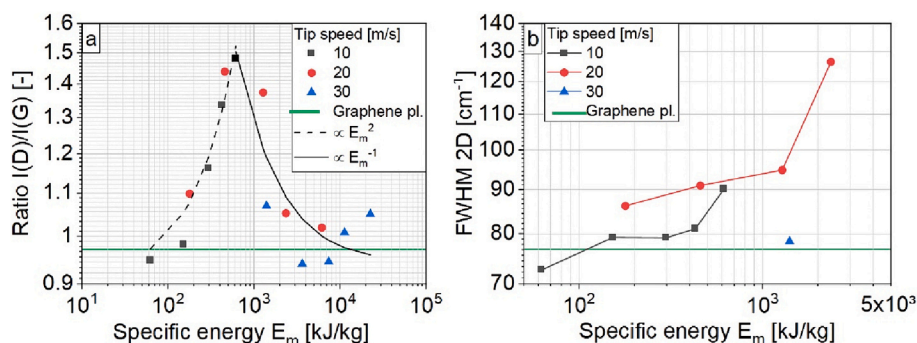


Fig. 5. Evolution of the $I(D)/I(G)$ ratio concerning the specific energy at different tip speeds (a), Full Width at Half Maximum (FWHM) of the 2D-peak in relation to the specific energy at different tip speeds (b).

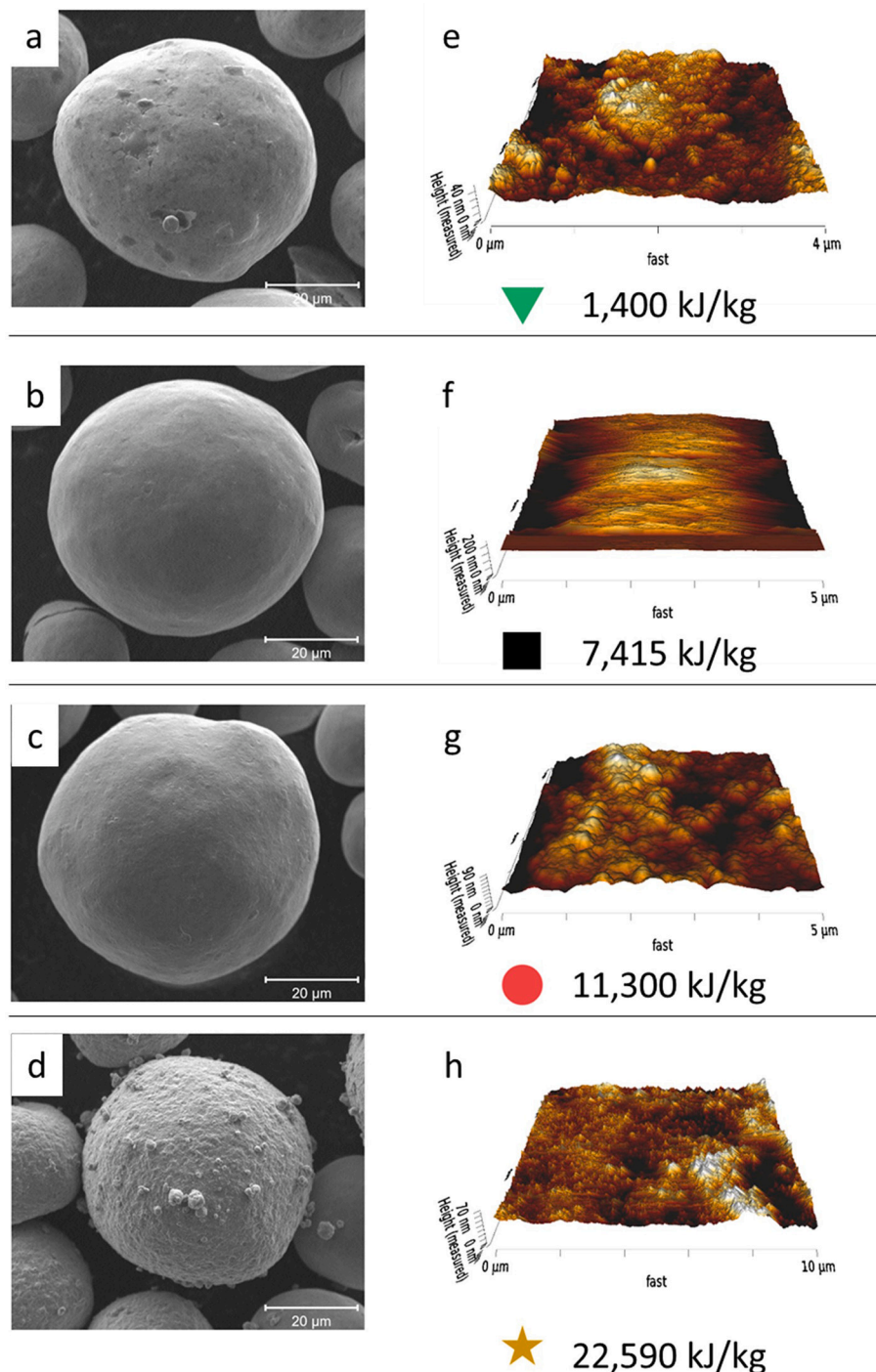


Fig. 6. SEM- pictures of high intensity mixing at 30 m/s tip speed (left row), corresponding AFM-topographs (right row) at different specific energy inputs.

highest specific energy of 22,590 kJ/kg, the surface starts to detach and form ball-like structures (see Fig. 6d and h), which are one order of a magnitude smaller than the host particles. Selective EDX point measurements of the ball-like structure, compared to the as received feed-stock material show the presence of a significant carbon peak (see Fig. S6). Consequently, carbonous as well as metal material accumulates in these ball structures. Due to the high specific power input of 22,590 kJ/kg, excessive degradation of the surface, and different surface structure (ball-formation), this parameter set behaves differently than the other produced powders at 30 m/s and is not suitable for powder bed fusion applications. In the following this parameter set will be discussed separately. As a result, it is possible to attach graphene platelets to the

host particle surfaces and alter the properties of the graphene to higher amorphous proportions at higher specific energies. Here, the specific energy input into the system plays a predominant role.

The comparison of SEM images and the measured surface roughness show a clear connection between the surface appearance and the surface roughness. Since the surface roughness measurement with AFM is very time-consuming and the statistical relevance is unfavourable, the specific surface area of the powder processed at 30 m/s was measured. Here, a complete bulk of powder is analysed with the BET method. As shown in Fig. 8b, the surface roughness measured via AFM correlates very well with the specific surface area except for very high specific energies. This supports the findings achieved via AFM. For processing

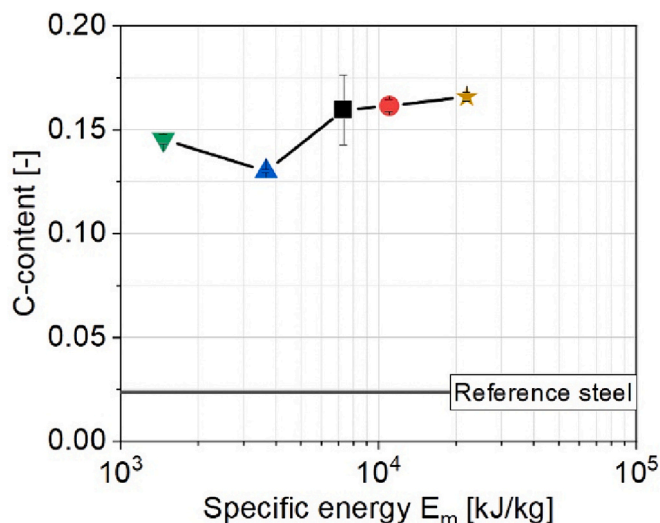


Fig. 7. C-Content in relation to the specific energy for mixing at 30 m/s. The horizontal line represents the C-Content of the feedstock reference material.

times of 30 min (22,590 kJ/kg), material is detached from the surface and is no longer captured by the AFM measurements, in contrast to the BET measurement, where the complete surface area is measured. Therefore, AFM results decrease at very long processing times, whereas BET results increase further.

Reflectance measured via DRIFTS at 1064 nm wavelength is depicted in Fig. 9. An explicit linear relation of the reflectivity to the specific energy of the high intensity mixer at 30 m/s is apparent. As shown before, the higher the specific energy, the better the distribution of graphene platelets and the higher the amorphisation degree of the coating.

3.3. Powder properties

The different parameter sets (10, 20 and 30 m/s) are compared regarding their flowability (ff_c) (see Fig. 10s) and dynamic angle of repose at 10 rpm drum velocity (see Fig. 10b). With increasing specific energy, the flowability ff_c increases with the specific energy following a power function (linear in log-log scale) and the dynamic angle of repose decreases following an e-function (linear in log scale). At elevated specific energies (> 2000 kJ/kg) the curve shows a drop to a lower dynamic angle of repose but maintains the same slope as in the region before. Similarly, the ff_c value raises above 10 for such high specific energies. The reason for this drop can be explained by a change in the amorphisation degree of the graphene platelets, which is discussed in section 3.1.2. As a result, higher specific energy inputs lead to a better

flowability in the quasi-static (ring shear tester) and the dynamic range (rotating drum). In the supporting information, an estimation of the dimensionless mixing time is provided. This dimensionless mixing time is proportional to the number of stress events (stress number) for a given geometry and constant particle sizes. Plotting the flowability (Fig. S7 dyn. Angle of repose, Fig. S8 ff_c) in relation to the dimensionless mixing time results in similar curve progressions, indicating that the main driver for the change in flowability is the number of stresses in the mixer and not the energy of stresses.

There must be a favorable graphene platelet distribution and surface roughness at higher specific energies leading to enhanced flowabilities. The particle size of the produced powder is not altered through the processing in the high intensity mixer for all specific energies (see supporting information Fig. S3). In addition, the particle shape is maintained (see Fig. 6 for 30 m/s and Fig. S4 for 10 and 20 m/s). This implies no excessive deformation of the host metal particles and no stripped away graphene platelets, as they adhere to the host particles firmly. For one parameter set at the highest specific energy at 30 m/s, ball-like structures formed on the surface (see Fig. 6d), which however were not detected by the particle size measurement. As a result, we conclude that these small particles adhere to the surface.

Considering the bulk density of the produced powders, differences can be seen between 10 m/s and higher tip speeds (see Fig. 11). The lower bulk densities of the 10 m/s speed are likely to be caused by

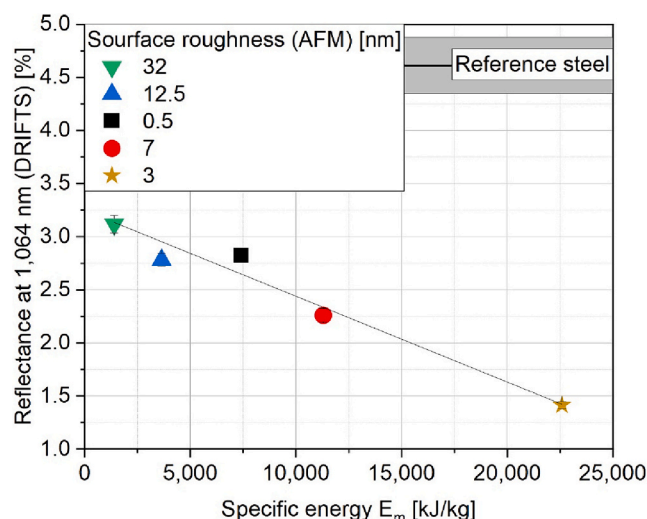


Fig. 9. Reflectivity measured at a wavelength of 1064 nm in relation to the specific energy at 30 m/s processing in the high intensity mixer. The horizontal line and grey box represent the average and standard deviation of the feedstock reference powder, respectively.

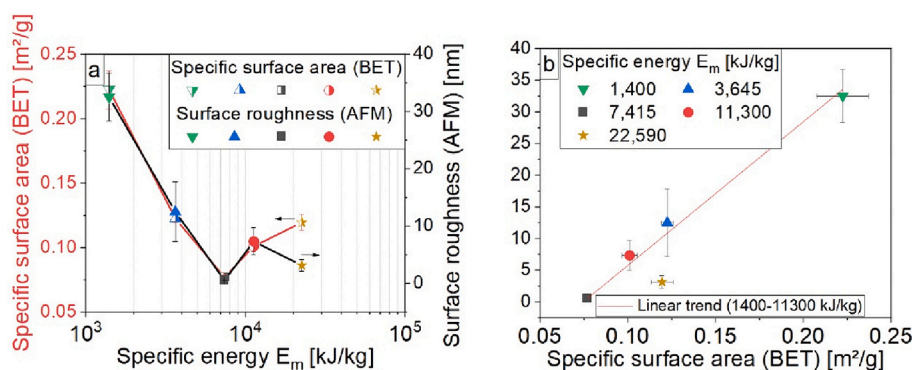


Fig. 8. Specific surface area (BET) and surface roughness (AFM) as function of the specific energy for mixing at 30 m/s, arrows indicate the related axis (a). Correlation of surface roughness (AFM) with the specific surface area (BET), point at 22590 kJ/kg is excluded from the linear trend because of ball structures (b).

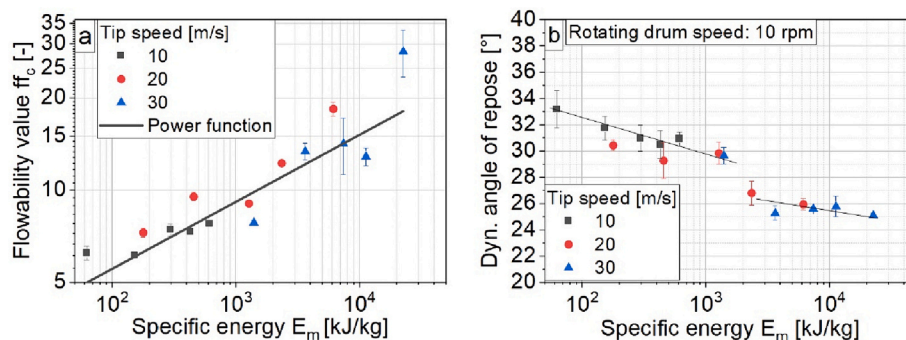


Fig. 10. Flowability value ff_c measured with the ring shear tester at a pre shear stress of 3 kPa in relation to the specific energy for different tip speeds of the high intensity mixer (a), Dynamic angle of repose measured with the rotating drum in relation to the specific energy for different tip speeds of the high intensity mixer. Lines are guides to the eye (b).

graphene platelets, which increase the distance between host metal particles. This finding can be confirmed with SEM results (see Fig. S4) and Raman measurements (see Fig. 5). The bulk densities of 20 m/s and 30 m/s show the same trend with increasing specific energy. Here, also a rapid increase in bulk density can be observed at 2000 kJ/kg. For a specific energy above 7500 kJ/kg, a drop of the bulk density is apparent. In Section 3.2, the surface roughness of the powders processed with 30 m/s is determined. The specific energy with the smoothest metal particle surface appears at 7415 kJ/kg, exactly where the highest bulk densities are present.

In Fig. 12 powder properties (flowability ff_c , reflectance and bulk density) of powder processed at 30 m/s are depicted as a function of the surface roughness. As mentioned before, the parameter with the highest specific energy input of 22,590 kJ/kg (marked as stars) is excluded from the line graphs and the overall considerations, because of the completely different surface properties due to the ball-like structures and the deviation from the real surface roughness. However, this parameter exhibits the highest flowability and lowest reflection (see Fig. 12 (stars)). Due to the ball-like structures, multiple scattering of laser light is provoked and the reflection decreases.

By comparing the surface roughness and flowability in Fig. 12, it becomes evident that a high flowability (ff_c of 11) could be reached in the surface roughness region of 10–20 nm (see Fig. 12a). This finding is in line with the theoretical calculations of the van der Waals forces published earlier [1]. Here, the calculated minimum of van der Waals forces due to induced nano roughnesses is also in the region of 10–20 nm (see Fig. 1). According to the mechanism proposed by Rumpf [73], the additional nano roughness acts as a spacer, reducing the van der Waals

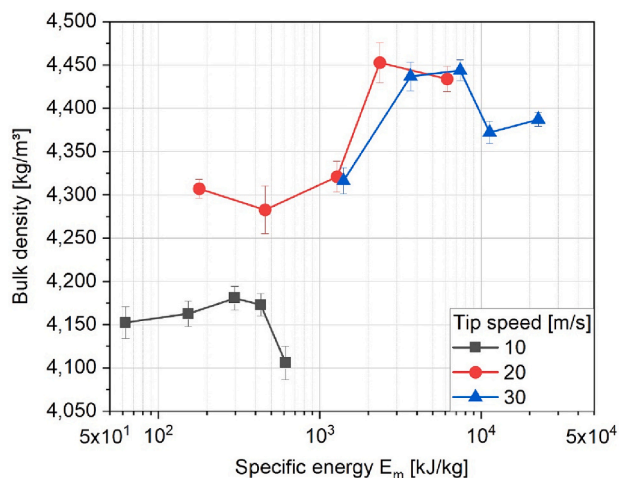


Fig. 11. Bulk densities in relation to the specific energy for different tip speeds of the high intensity mixer.

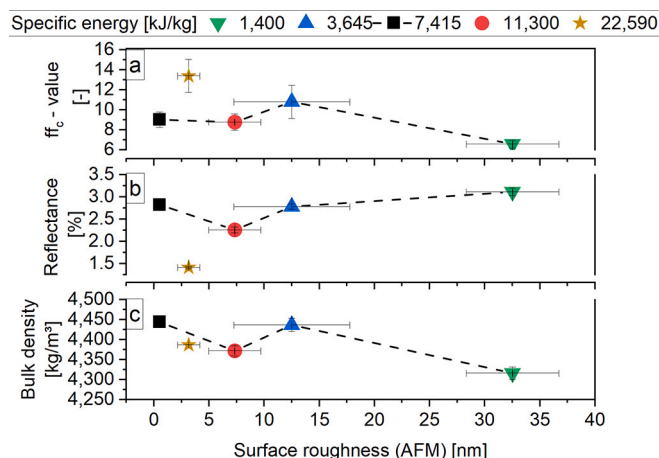


Fig. 12. Powder properties for processing at 30 m/s in the high intensity mixer in relation to the surface roughness measured with the AFM. ff_c -value (a), reflection of laser light at 1064 nm measured with DRIFTS (b) and, bulk density in relation to the surface roughness (c). Stars correspond to values obtained at the highest specific energy.

forces between the host particles. Smoother surfaces (< 10 nm, left side of the minimum) decrease the distance between host particles, so that the van der Waals forces between the host particles progressively become predominant. As a result, also the flowability decreases to a ff_c -value of 8–9. With rougher surfaces (> 20 nm, right side of the minimum), the distance between the host particle increases further, simultaneously the attraction between the nano elevations increases and becomes predominant so that an increase in van der Waals forces results. Accordingly, the flowability value decreases to 6.5. For a minimum reflectivity, a roughness of about 7.5 nm seems to be beneficial (see Fig. 12b). In contrast, the reflectivity is more dependent on the specific energy during processing (see Fig. 9), as stated before. The higher the specific energy, the lower the reflection. It is well known, that the light reflectivity of a metallic powder can correlate with the specific surface area of the powder, as shown in [74], and therefore indirectly with the surface roughness for powders processed in the high intensity mixer at 30 m/s from 1400 to 11,300 kJ/kg. According to Boley et al. [75] the absorption of laser light depends also on multiple scattering of rays in the powder and therefore on the surface roughness, as well as on the packing of the powder bed. Additionally, Liu et al. [76] state that, with an increasing degree of amorphisation (higher content of sp^3 orbitals) of a-C films, the reflectivity of these films increases. In this study, the presented reflectivity does not depend highly on the bulk density or the surface roughness (see Fig. 12b and c). As a result, the change in the carbon structure of processed powders in the high intensity mixer, which

is provoked through the specific energy, has a bigger influence on the reflectance of the powder.

The bulk density of powders processed at 30 m/s increases tendentially with smoother surfaces (see Fig. 12c). This is mainly because of smaller distances between the metal particles and thus a decreased void fraction.

In Fig. 13 the thermal diffusivity of the feedstock powder and powders processed in the high intensity mixer at 30 m/s in relation to the specific energy is depicted. With increasing specific energy the thermal diffusivity increases until it reaches a maximum at 7415 kJ/kg. Thereafter, a decrease in thermal diffusivity is visible. As shown beforehand, the powder processed with 7415 kJ/kg exhibits the smoothest surface (see Fig. 6) and the highest bulk density (see Fig. 11). Regarding the feedstock powder, a relative increase in thermal diffusivity of 21.8% could be achieved with this parameter set. In general, it can be observed, that powders processed at 30 m/s in the high intensity mixer with a higher surface area and lower bulk density exhibit a lower thermal diffusivity. Since the heat capacity and density of processed powders are not expected to change significantly (same amount of graphene platelet addition), a relative comparison between the processed powders concerning the heat conduction in correlation with the thermal conductivity is feasible. It is known that smaller particles and reduced bulk densities lead to decreased heat conductivities [77,78]. According to Sangros et al. [79] the heat conductivity of particles is mainly determined by the number of contacts of particles and the contact area of these particle-particle contacts whereas they relate the bulk density to the contact number, and the particle size to the contact area. For this study, the aforementioned consideration leads to the following assumptions for powders processed in the high intensity mixer at 30 m/s. A higher amount of induced nano roughness

- increases the distance between the metal host particles and decreases the bulk density and
- decreases the contact area between the metal particles

leading to a decreased thermal diffusivity and conductivity, respectively.

The influence of the graphene platelets on the thermophysical properties is assumed to be marginal for the investigated powders, because of the increasing amount of amorphisation (see Section 3.1.2.). In addition, the extraordinary high thermal conductivities reported for graphene [30] are in the direction of the sheet planes, and not tangential or rather vertical to the planes as it is the case for graphene platelets

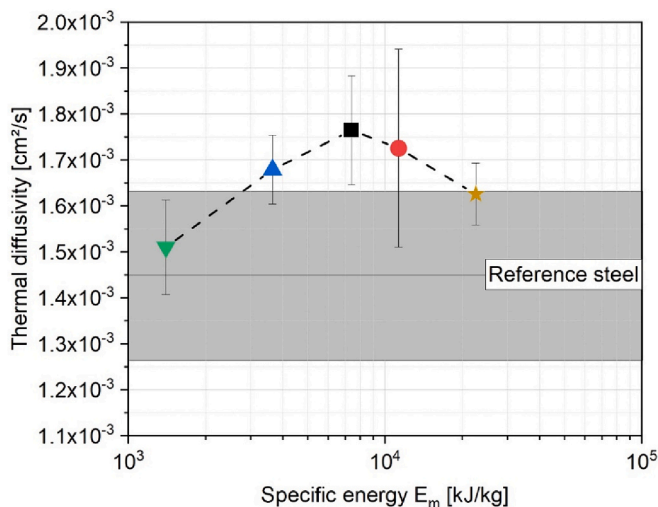


Fig. 13. Thermal diffusivity of powders processed in the high intensity mixer at 30 m/s. The horizontal line and grey box represent the average and standard deviation of the feedstock reference powder, respectively.

coated on metal particle surfaces.

3.4. PBF-LB/M process parameters and final part properties

Fig. 14 shows the relative density of the PBF-LB/M samples manufactured using the powders processed at 30 m/s and the uncoated powder feedstock. The same specimen orientation and assignment of process parameters to the specimens were used for all build processes. In general, high component densities were achieved, especially compared to Das et al. [44], who achieved a maximum relative density of 94.7% for 0.2 wt% graphene/stainless steel powder. Compared to the powders processed at 1400 and 7415 kJ/kg, the relative density of the uncoated samples is lower than that of the coated samples, especially at higher scanning speeds. Considering all parameter combinations, the densest PBF-LB/M samples were produced using the powder processed at 1400 kJ/kg (2 min processing time in high intensity mixer at 30 m/s). In this powder, the graphene platelets are still present and not amorphous. The positive effect of this powder could be due to the effects that graphene enables in the PBF process, such as increased thermal conductivity [39,80] and reduced thermal expansion of composites [29,80]. PBF-LB/M samples produced using the powder processed at 7415 kJ/kg (10 min high-intensity mixing) achieve overall the second highest density. This powder shows a smooth particle surface and increased bulk density. According to Spierings et al. [24] and Liu et al. [23], the bulk density of the powder, the density of the powder bed and the final part density are likely to be linked. The samples manufactured using the powders processed at 1400 kJ/kg and 7415 kJ/kg show the least effect of changing the PBF-LB/M process parameters on the part density. Each of the parameter combinations used results in a relative density > 99.93% using these powders. The lower influence of a change in the process parameters means a larger parameter window in which dense samples can be produced and thus better processability by PBF-LB/M.

The PBF-LB/M samples made using the powders processed at 11,300 kJ/kg (15 min) show lower relative densities, which could be explained by the lower bulk density (see Fig. 11) and the higher surface roughness (see Fig. 8). Decreasing relative densities can be observed especially at volumetric energy densities < 100 J/mm³ (see Fig. 15). Interestingly, the PBF-LB/M samples manufactured using the powder processed at 22,590 kJ/kg show the lowest relative densities regardless of the laser reading at high scanning speeds, despite being the powder with the lowest reflectivity (1.4%) and the best flowability (ffc 13.4; dynamic angle of repose 25.1). One possible explanation is that the small ball-like structures (see Fig. 6) allow multiple scattering of the laser beam and reduce van der Waals forces on the one hand, but also reduce the contact areas between the particles and hinder heat conduction in the powder (see Fig. 13).

At a low scanning speed of 600 mm/s and a low laser power of 150 W at 22,590 kJ/kg, parts with a relative density of 99.98% were obtained (see Fig. 16a). At higher volumetric energy densities, a clear tendency towards denser parts can be observed (see Fig. 15). Above a volumetric energy density of 100 J/mm³, high-quality and dense specimens could be obtained for all powders. Micrographs of powders processed at 22,590 kJ/kg at lower volumetric energy densities show irregular defects (see Fig. 16b), suggesting areas with lack of fusion. As a result, the reduced densities at higher scan speeds could be attributed to a lower solid-liquid volumetric fraction, as shown in [81,82].

The hardness and Young's modulus of manufactured specimens of processed powder in the high intensity mixer at 30 m/s at a laser power of 150 W and 600 mm/s are depicted in Fig. 17. In general, the hardness of the manufactured specimen of processed powders in the high intensity mixer is higher than that of specimens manufactured out of the feedstock reference powder. The measured Young's modulus of the specimen produced with the processed powders is lower than the reference without graphene addition, except for the parameter at 7415 kJ/kg. Here the hardness increased by 7% and the Young's modulus by 17.6% compared to the feedstock reference powder. This is the powder

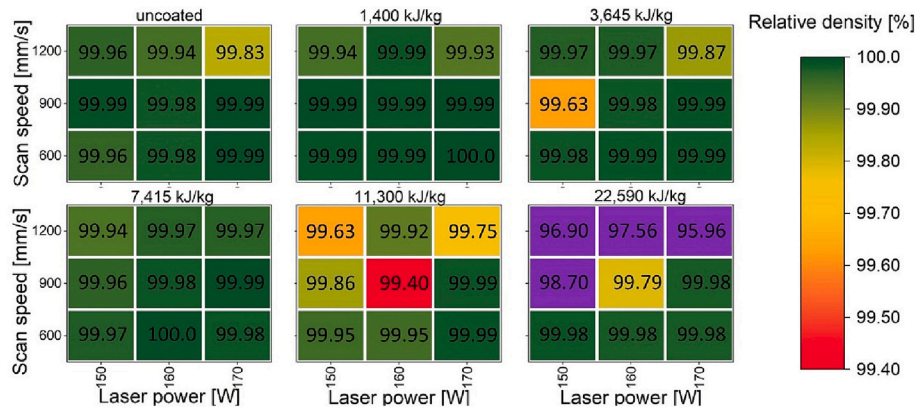


Fig. 14. Final part density of additively manufactured reference metal powder and graphene-coated metal powder at 30 m/s in the high intensity mixer at different specific energies. Variation of laser power and scan speed. Purple fields correspondent to relative densities lower than 99.4%. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

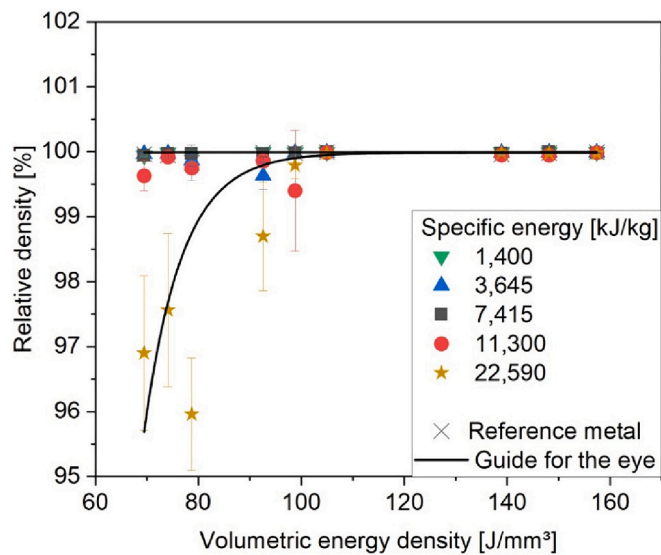


Fig. 15. Relative density as function of the volumetric energy density of reference metal powder and powder processed at 30 m/s in the high intensity mixer.

with the smoothest surface, the highest bulk density and the highest thermal diffusivity. The lowest hardness and Young's modulus can be observed for parts manufactured with powder processed with specific energies of 1400 kJ/kg and 11,300 kJ/kg. These are the samples with the lowest bulk densities. The same relative tendencies between the powders processed in the high intensity mixer described for 150 W and 600 mm/s can be seen for scan speeds of 900 mm/s and 1200 mm/s at 150 W laser power in the supporting information (see Fig. S10). The increase in hardness could be caused by a higher amount of dissolved carbon in the steel [64], precipitation of carbides, grain refinement or the presence of graphene nanoplatelets in the manufactured specimens [40]. However, back-scattered electron SEM images of specimens made of modified powder (1400 kJ/kg and 7415 kJ/kg) exhibit no significant changes in the solidified structure compared to the reference material (see supporting information Fig. S11).

Since the main focus of this research is to show the influence of high intensity mixing, these topics will be addressed in further work.

4. Conclusion

Within this study, graphene-coated metal powders were produced

with 0.75 vol% graphene platelets by high intensity mixing at different mixing times and rotational speeds, resulting in different specific energy inputs into the mixing process. The resulting powder properties are mainly dependent on the specific energy. The higher the specific energy, the better the flowability and the lower the reflectivity of the laser light. Interestingly, the flowability in the quasi-static regime (ring shear measurements) as well as the flowability in a more dynamic regime (rotating drum measurements) increase with the specific energy input. Considering the bulk densities of powder produced with low tip speeds, decreased values can be observed due to graphene platelets, which are loosely attached to the metal powder surface. This increases the porosity of the powder. At higher tip speeds, the bulk densities show a relation to the surface roughness of the powder: The smoother the surface, the higher the bulk density. Raman measurements reveal increasing defects in the graphene platelets with increasing specific energy. Above a specific energy input of 2000 kJ/kg, the amorphisation of graphene occurs. This leads to a volatile increase in flowability.

It could be shown, that theoretically calculated van der Waals forces correlate well with the flowability measured in the ring shear tester. In the roughness region where minimum van der Waals forces were predicted, the highest flowability (ff_c -value) occurs. Whereas, the reflectivity of processed powder is linearly dependent on the specific energy and not necessarily related to the surface roughness of powder processed in the high intensity mixer. This is because of the interaction from the laser beam with the whole powder in general. The porosity of the powder bulk, but in particular the amorphisation state of the graphene, plays an important role.

Produced specimens at different laser scan speeds and laser power show dense parts above 99.98% relative density for all powders. The highest densities for all laser parameters could be reached with the powder processed in the high intensity mixer at 1400 kJ/kg. Here graphene platelets could be observed on the metal particles' surface and a high bulk density was apparent. The process window seems to be broadened, and even at the lowest volumetric energy density, dense specimens could be produced. The smoothest powder produced at a specific energy of 7415 kJ/kg, exhibits the highest bulk density and the highest thermal diffusivity. This results in a high relative density for all laser parameters. In comparison to the pure model feedstock powder an increased indentation hardness of 7% and an increased Young's modulus of 17.6% at a laser power of 150 W and a laser scan speed of 600 mm/s results.

The powder processed at the highest specific energy input of 22,590 kJ/kg exhibits the highest flowability and lowest laser reflectivity, but due to the small ball-like structures on the surface, the bulk density and thermal diffusivity are decreased, leading to lack of fusion defects. This shows that an excellent flowability and reflectivity of powder alone are

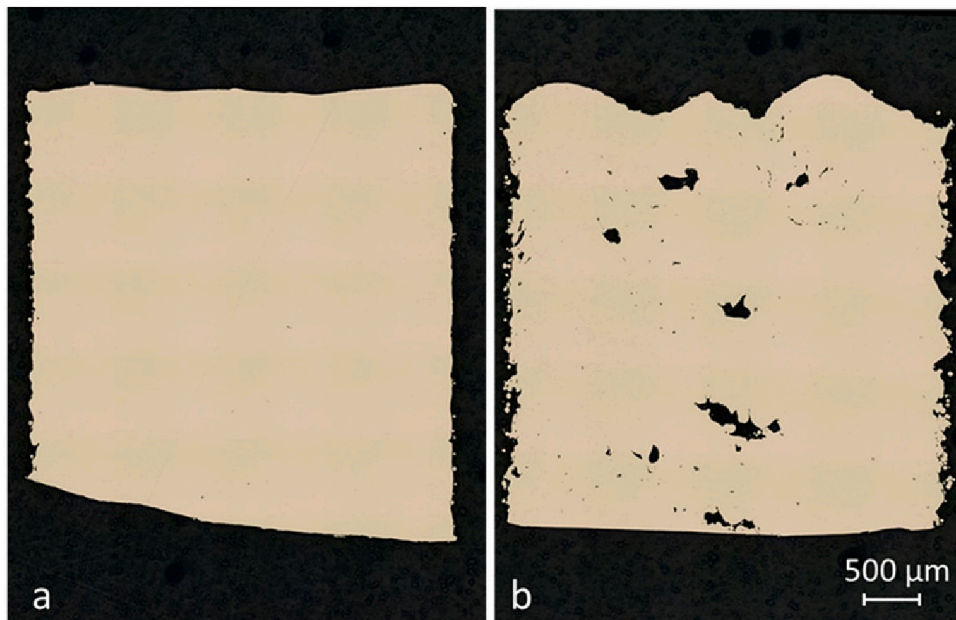


Fig. 16. Micrographs of samples produced with powder processed at 22590 kJ/kg in the high intensity mixer. Nearly fully dense specimen at 150 W and 600 mm/s (a), specimen at 170 W and 900 mm/s (b).

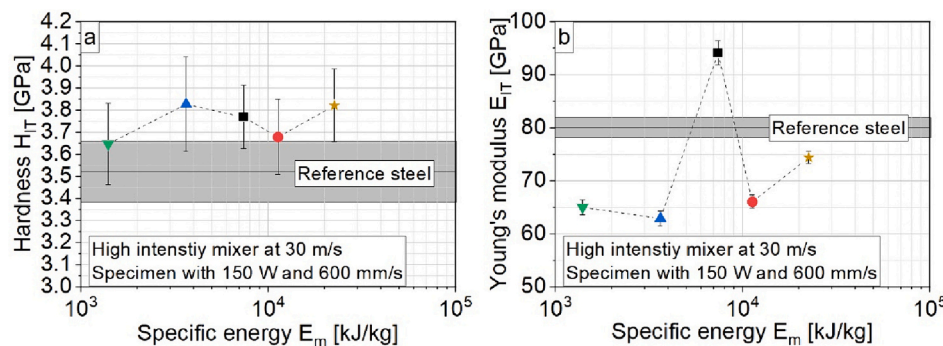


Fig. 17. Hardness (a) and Young's modulus (b) of manufactured parts at 150 W and 600 mm/s for powders processed in the high intensity mixer at 30 m/s. The horizontal line and grey box represent the average and standard deviation of the feedstock reference powder, respectively.

not decisive for a reliable Powder Bed Fusion (PBF) application.

In summary, the high intensity mixing is a suitable process to enhance metal feedstock materials for the PBF application with graphene platelets. With an understanding of the high intensity mixing processes, it is possible to adjust the roughness of the coated metal powder surface to a degree which is beneficial for the PBF process. The specific energy defines the surface roughness and reflectivity of powders, which has a major influence on flowability, bulk density, and laser absorption. Also, the heat diffusivity of powders, hardness and elasticity of manufactured specimens are changing. The particle processing in the high intensity mixer with the model material is easily transferable to other metal materials, such as tool steel or even aluminum or copper, where a possible carbide precipitation is precluded. As a result, it is possible to generate tailored particles for the demands of the PBF process.

In the future, extended characterisations are planned to evaluate the presence of graphene platelets in the manufactured specimen. The question of whether the carbon is dissolved in the steel precipitated as carbides or dispersed as nano-flakes will be addressed. In addition, chemical analysis to track the oxygen content will be conducted. Further analysis will be carried out to investigate the heat distribution in the AM process. For instance, in-situ thermography will be used to reveal the

effect of processed powders. In addition, an in-situ evaluation of the powder porosity after spreading with a test rig in a μ CT is planned to determine the influence of the powder properties on the real spreading behaviour.

CRediT authorship contribution statement

A. Lüddecke: Writing – original draft, Visualization, Methodology, Conceptualization. **H. Zetzener:** Writing – review & editing. **N. Hantke:** Writing – original draft, Data curation. **A. Berger:** Writing – review & editing, Data curation. **M.L. Scheck:** Data curation. **S. Weber:** Writing – review & editing. **J.T. Sehr:** Writing – review & editing, Funding acquisition. **A. Kwade:** Writing – review & editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors report there are no competing interests to declare.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.powtec.2024.119790>.

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