Fe–TiC metal matrix composite powder is manufactured applying vacuum inert gas atomization technique. The TiC reinforcement phase forms in situ within spraying of the Fe-based molten metal preliminary alloyed with 1 wt% [C] and 4 wt% [Ti]. Alloving strategy, homogenization time, and spraying temperature are varied for three conducted atomization experiments in this study. Medium particle size (d50) lies in a range of 41–55 μm for obtained spherical powders. Scanning electron microscopy (SEM) analysis and Energy-dispersive X-ray spectroscopy (EDX) mapping of powder cross-section samples reveal well-dispersed submicron TiC precipitates of two different morphologies—primary-blocky and eutectic-plate-shape carbides. The amount of precipitates and their morphology depend on the particle size. Namely, coarser powder particles tend to have more primary carbides that are presumably formed already in liquid droplets. Meanwhile, TiC precipitation in finer particles up to ≈25 μm is completely suppressed due to an extremely high cooling rate. Difficulties of the Fe–Ti–C melt atomization (e.g., formation of a semiliquid slag layer, loss of TiC forming elements, the presence of large precipitates in a powder) are discussed considering the thermodynamic analysis of this system and Fe–TiC remelting experiments conducted on a hot stage microscope.

1. Introduction

Metal matrix composites (MMCs) are materials that have a ductile matrix reinforced with a hard ceramic phase. This combination gives advanced mechanical and functional properties, such as high yield and tensile strength, modulus, and wear resistance.[11-41] Therefore, these materials are widely utilized in automotive, aerospace, medicine, and other high-tech industries. Traditionally, MMC materials are fabricated via the powder metallurgy route, where metal and ceramic powders are premixed and then sintered.[5] As the reinforcement phase, carbides, oxides, nitrides, and borides are normally implemented. Due to the rapid development of the additive manufacturing (AM) market, there is a demand for new materials that can be fabricated additively including MMCs. Moreover, MMCs are normally hard to machine adjusting a semiprocess to a final shape. Thus, manufacturing a near-net-shape MMC product is an attractive solution, which can further promote the introduction of AM techniques. Dadbakhsh et al.[6] reviewed several attempts of MMC manufacturing via laser powder bed fusion (L-PBF) dealing with Al-, Ti-, and steel-based materials. Specifically, Yuan et al.[7] produced AlSi10Mg–5.8 vol% TiC composite material finding the optimal parameters for the sufficient distribution of the TiC-phase during a L-PBF process. Gu et al.[8] fabricated the Ti/TiC composite revealing a dependence of the reinforcement phase shape and its distribution in the matrix on the L-PBF process parameters and TiC content (up to 22.5 wt%). AlMangour et al.[9] investigated 316 L/TiC MMC with varying reinforcement phase content from 2.5 to 15 vol%. These examples describe the ex situ addition of the reinforcement phase to the matrix by mixing metal and TiC powders prior to the printing process.

As an alternative, it is possible to fabricate the reinforcement phase in situ bringing needed elements in contact. Tjong et al.[10] summarized the benefits of in situ formation of the reinforce-ment phase: enhanced thermodynamic stability, strong interfacial bonding, sufficient reinforcement phase distribution, and refinement, which further improve the mechanical properties of MMC. In the recent years, the in situ approach for AM gained much attention among researchers.[11–25] For instance, Promakhov et al.[24] produced Inconel 625/TiB2 MMC material applying self-propagating high-temperature synthesis (SHS). Obtained blocks were grinded to a coarse powder and then plasma spheroidized yielding spherical particles with TiB2 reinforcements of 0.5–5 μm size. Thereby, this powder was successfully utilized for test samples fabrication by direct laser deposition technique (DLD). AlMangour et al.[12] utilized for L-PBF mechanically alloyed composite powder. For this experiment, 316L–Ti–graphite mixed powders were milled for 35 h
forming \( \approx 20 \) nm diameter TiC particles well distributed in the matrix.

The current study focuses on the production of powder with Fe-based MMC structure for AM via gas atomization technique. TiC as reinforcement was chosen due to its advanced properties (high hardness [2859–3200 HV], high melting point [3067 °C], low density [4.93 g cm\(^{-3}\)], strong interfacial bonding, and semi-coherent lattice structure to iron.\(^{[16,26,27]}\) The gas atomization process is a common method for AM powder fabrication, which provides fine particle sizes (<100 \( \mu \)m), high sphericity, high flowability, and bulk density. During the atomization process, molten metal is sprayed by high-pressurized gas jets yielding metal droplets, which then solidify and form metal powder particles.\(^{[28]}\) In the current study, it is possible to implement MMC casting techniques for the melt prior to spraying. Specifically, the inductively heated melt can be alloyed with the reinforcement forming elements (C and Ti) in a tundish. Herewith, the uniform distribution of these elements is realized via high overheating above \( T_\text{i} \) and electromagnetic stirring. Afterward, the melt is released to the spraying area, where the TiC phase starts to form in situ during cooling. This approach is comparable to MMC casting techniques sufficiently described in the literature.\(^{[29–34]}\) For instance, Ni et al.\(^{[29]}\) manufactured a block with the stainless steel/5 vol % TiC structure by casting. According to the implemented procedure, preformed Fe–Ti–C mixtures were introduced into the melt at 1600–1650 °C, which induced an exothermic reaction in the melt gaining TiC particles. After the reaction was completed, the melt was casted to a sand mold. The resulting block contained well distributed TiC particles of 2–10 \( \mu \)m size. Terry et al.\(^{[30]}\) fabricated Fe/TiC composite adding graphite to the Fe–24 wt% Ti alloy at 1600 °C. Thereby, well-dispersed TiC particles of \( \approx 10 \mu \)m size were formed in the final block. Nevertheless, the casting of MMCs suffers from reinforcement segregation and coarsening due to density differences and insufficient cooling rate. In case of atomization, these negative effects take place in a tiny volume—in solidifying powder particles; and both segregation and coarsening of the reinforcement are additionally suppressed by extremely high cooling rates. Golod et al.\(^{[35]}\) reported that the cooling rate by the atomization process can reach \( 10^9–10^{10} \) K s\(^{-1}\) depending on the particle size. Pengjun et al.\(^{[36]}\) obtained slightly lower cooling rates for nitrogen atomized Ni-based super alloy ranging from \( 1.0 \times 10^7 \) K s\(^{-1}\) to \( 4.8 \times 10^8 \) K s\(^{-1}\) throughout an experiment. For this study, three atomization experiments were conducted at varying alloying elements introduction strategy, spraying temperature (molten metal temperature measured prior to release), and homogenization period (time between last elements addition and melt release). The charged material amount, spraying time, and thus spraying rate (charged amount divided by spraying time) were as well diverse for the conducted experiments. Table 1 shows this information for experiments Fe–TiC 1–3. As an initial material, premelted steel blocks with 1 wt% [C] and pure Ti plates were utilized. The vacuum induction furnace VIM 12 (ALD Vacuum Technologies GmbH) was used for steel premelting. Table 2 shows the chemical composition of the utilized steel. The spark forming

### Reinforcement Forming Materials

| Table 1: Chemical composition of the utilized steel | Table 2: Chemical composition of the utilized steel |
|-----------------------------------------------|-----------------------------------------------|
| Fe–TiC 1 | Fe–TiC 2 |
| Fe                  | 95.4 | Fe                  | 95.4 |
| C                  | 0.05 | C                  | 0.05 |
| Si                 | 0.3  | Si                 | 0.3  |
| Mn                 | 0.1  | Mn                 | 0.1  |
| Cr                 | 1.2  | Cr                 | 1.2  |
| Ni                 | 1.5  | Ni                 | 1.5  |
| Cu                 | 0.5  | Cu                 | 0.5  |
| Ti                 | 1.2  | Ti                 | 1.2  |
| Al                 | 0.2  | Al                 | 0.2  |
| Nb                 | 0.1  | Nb                 | 0.1  |
| Mo                 | 0.1  | Mo                 | 0.1  |
| Other             | 0.5  | Other             | 0.5  |

### Experimental Section

Atomization experiments were conducted on the atomization unit VIGA 1B (ALD Vacuum Technologies GmbH), which is schematically shown in Figure 1. VIGA 1B is a close-coupled gas atomizer with a bottom release system. A double thermocouple placed inside a stopper rod allows controlling the melt temperature throughout an experiment. For this study, three atomization experiments were conducted at varying alloying elements introduction strategy, spraying temperature (molten metal temperature measured prior to release), and homogenization period (time between last elements addition and melt release). The charged material amount, spraying time, and thus spraying rate (charged amount divided by spraying time) were as well diverse for the conducted experiments. Table 1 shows this information for experiments Fe–TiC 1–3. As an initial material, premelted steel blocks with 1 wt% [C] and pure Ti plates were utilized. The vacuum induction furnace VIM 12 (ALD Vacuum Technologies GmbH) was used for steel premelting. Table 2 shows the chemical composition of the utilized steel. The spark forming

![Figure 1. Scheme of atomization unit VIGA 1B.](image-url)
spectrometer Foundry-Master UV (Oxford Instruments) provided a general analysis of the chemical composition, meanwhile \([\text{C}] / [\text{S}]\) and \([\text{O}] / [\text{N}]\) values were determined by Bruker G4 Ikarus and Bruker G8 Galileo combustion analyzers, respectively.

In situ formation of the TiC phase was accomplished by the addition of pure Ti plates to the molten metal targeting 4 wt% [Ti]. Two introduction strategies were utilized for conducted experiments. For the Fe–TiC 1 experiment, half of the Ti plates were placed initially to the tundish along with steel blocks. As steel started to melt, the formed liquid pool dissolved the Ti plates, and consequently, an exothermic reaction was observed. Afterward, the second half of Ti plates was added to the molten metal in a steel box, which was also accompanied by a well-observable exothermic reaction. For the other two experiments (Fe–TiC 2–3), Ti plates were introduced into the melt in two steel box batches. Herewith, the spraying temperature was increased, and the homogenization period was shortened (see Table 1).

The extracted powder was sieved to fractions 0–25, 25–63, 63–100, and 100–200 μm. Furthermore, powder size distribution and median particle size were assessed by laser diffractometer Horiba (LA-960). Chemical composition of powder was determined applying X-ray fluorescence spectrometer S8 Tiger (Fa. Bruker AXS) for most of the elements including [Ti] value; Bruker G4 Ikarus and Bruker G8 Galileo combustion analyzers were applied for [C] and [N] values, respectively. Morphology, chemical composition, and microstructure of powder particles including characterization of TiC inclusions were investigated by scanning electron microscopy (SEM) analysis and energy-dispersive X-ray spectroscopy (EDX) mapping (Ultra55, Zeiss NTS GmbH). The open source software GIMP v.2.10 and ImageJ bundled with 64-bit Java 1.8.0_112 were implemented for calculation of TiC area on cross-section samples. Thereby, initial SEM images were sharpened by GIMP, and then processed by ImageJ applying the “threshold” filter and the “analyze particles” procedure. Figure 2 shows an example of this image analysis.

Thermodynamic assessment of the system Fe–Ti–C was done by ThermoCalc software applying the TCFE-7 database. In addition, influence of [N] on thermodynamic stability of TiCN was considered. Thereby, a phase diagram for 4 wt% [Ti], 0–50 ppm [N], and a phase development diagram in dependence on temperature for 1 wt% [C], 4 wt% [Ti], and 0–50 ppm [N] were calculated (see Figure 3).

Formation of a slag layer was observed for all conducted atomization experiments. To investigate this issue, two remelting experiments were conducted on the hot stage microscope. Here, a sample of ≈3 g was placed on an alumina substrate and remelted inside a heating graphite tube under Ar protective atmosphere. The Fe–5 wt% TiC alloy was utilized as initial material. Table 2 shows the chemical composition of this alloy. Due to spark spectrometer limitation, there is no accurate [Ti] value provided; nevertheless, it is expected to have ≈4 wt% according to alloyed quantity. Melting procedure was observed with a CCD camera. A thermocouple type B placed under the alumina substrate controlled the temperature. Table 3 shows heating and cooling rates, as well as homogenization periods for conducted experiments. Microstructure of the remelted samples with a focus on TiC phase was investigated by SEM and EDX mapping.

Initial material for the remelting experiments was fabricated in a Cold Crucible Inductive Melting KIT unit (Linn High Therm GmbH). According to the experimental procedure, ≈300 g of 1 wt% [C] steel (see Table 2) was melted in an alumina crucible placed inside of a graphite heating crucible. After melting, titanium plates placed in a steel box were added in the ratio 4:1 to carbon producing exothermic reaction by Ti dissolution. Resulted melt was heated up to 1630 °C with a rate of ≈50 K min⁻¹, homogenized for 5 min, and cooled down with

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**Table 1.** Varied parameters for conducted atomization experiments.

|               | Fe–TiC 1 | Fe–TiC 2 | Fe–TiC 3 |
|---------------|----------|----------|----------|
| Spraying temperature [°C] | 1575     | 1575     | 1625     |
| Alloying strategy | The first half of Ti plates is placed by initial material; the second is introduced to the melt in a steel box | Both batches are introduced to the melt in a steel box | Both batches are introduced to the melt in a steel box |
| Temperature by first Ti plates batch [°C] | 1465     | 1630     | 1650     |
| Temperature by second Ti plates batch [°C] | 1570     | 1590     | 1640     |
| Homogenization time between first and second batches [min] | ≈90      | 5        | 1        |
| Homogenization time between second batch and spraying [min] | 15       | 10       | 5        |
| Charged material [g] | 4998.5 steel + 200 Ti | 4798 steel + 191.5 Ti | 6750 steel + 270 Ti |
| Spraying time [s] | 70       | 50       | 116      |
| Spraying rate [g s⁻¹] | 74.3     | 99.8     | 60.3     |

**Table 2.** Chemical composition of utilized steel prior to Ti alloying for further atomization (A), and of steel utilized in remelting experiments (B), wt%.

|      | C   | Ti  | Si  | Mn  | Cr  | Ni  | P   | S   | N   | O   | Fe  |   |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|---|
| (A)  | 0.998 | 0.004 | <0.005 | 0.089 | 0.016 | 0.009 | 0.009 | 0.0083 | 0.0007 | 0.0013 | Rest |
| (B)  | 1.06 | >1.9 | 0.091 | 0.042 | 0.010 | 0.001 | <0.010 | <0.010 | 0.012 | –   | Rest |
the furnace. Pyrometer thermocamera was utilized for the temperature control.

3. Results

3.1. Powder Size Distribution and Particles Morphology

Powder particles with a composite microstructure were successfully manufactured in all conducted atomization experiments. Table 4 shows powder size distribution (PSD) measurements comparing characterization values (d10, d50, and d90) for fabricated powders. Thereby, the Fe–TiC 1 powder has slightly higher PSD than Fe–TiC 2–3, which can be related to alloying procedure, spraying rate, and spraying temperature (see Table 1). Surface observation of fabricated powders reveals spherical particles, which is common for all fabricated powders in this study.
Table 3. Varied parameters for conducted remelting experiments.

|                      | EM1          | EM2          |
|----------------------|--------------|--------------|
| Semiliquid state temperature [°C] | 1570         | 1508         |
| Liquid state temperature [°C]     | Not achieved | 1660         |
| Max temperature [°C]             | 1680         | 1680         |
| Heating rate [K min⁻¹]            | 60           | 5            |
| Time from melting to liquid state [min] | -    | 32           |
| Time from melting to cooling [min] | 23           | 71           |
| Cooling rate [K s⁻¹]              | 5            | 5            |

*See Figure 11.

Table 4. Powder size distribution values for conducted atomization experiments, μm. Standard deviation out of three measurements.

|        | d10     | d50     | d90     |
|--------|---------|---------|---------|
| Fe–TiC 1 | 16.6 ± 0.3 | 54.2 ± 0.3 | 117.0 ± 2.3 |
| Fe–TiC 2 | 13.4 ± 0.3 | 42.2 ± 0.7 | 99.0 ± 2.8  |
| Fe–TiC 3 | 13.9 ± 0.2 | 41.1 ± 0.3 | 93.2 ± 2.6  |

3.2. Powder Chemical Composition

The distribution of TiC forming elements was investigated examining [Ti] and [C] values for fabricated powders by fractions (see Table 5). In addition, [N] value for powder fractions is considered. Here, [Ti] values of Fe–TiC 1 for fractions 0–25, 25–63, 63–100, and 0–200 μm are slightly lower than those ones of Fe–TiC 2–3. However, the obtained [Ti] values are close to each other and can be assumed as equal considering accuracy of the X-ray fluorescence spectrometry. Meanwhile, [C] values by Fe–TiC 1 are slightly higher than Fe–TiC 2–3 under consideration of the combustion analysis accuracy. The [N] value for all fabricated powders does not exceed 100 ppm. Moreover, three samples from the experiment Fe–TiC 3 taken from different positions in the powder container demonstrate homogeneous distribution of the TiC forming elements (see Supporting Information). This result was achieved despite the lowest homogenization time by the Fe–TiC 3 experiment. Nevertheless, all obtained [C] and [Ti] values deviate from target ones, which was induced by formation of a slag layer. Detected elements by EDX analysis of this layer (see Figure 5) correspond to the formation of TiO₂, TiC, and TiC(N).

3.3. Powder Microstructure. Morphology of Precipitates

Investigating the cross-section samples of Fe–TiC 1–3 powders exposed formation of well-distributed submicron precipitates. Herewith, number and morphology of these precipitates depend on the particle size. Finer particles tend to have less precipitates than coarser ones, which is shown in Figure 6. The EDX mapping shown in Figure 7a demonstrates enhanced concentrations of Ti for both blocky and plate-like precipitates. According to chemical analysis of fabricated powders, detected precipitates are most likely TiC. However, TiC(N) and TiN precipitates can be present as well in a limited quantity. Figure 8 shows TiC precipitates of both discussed morphologies with higher magnification.

Assuming that all detected precipitates are TiC, image analysis was implemented to several SEM images from the experiment Fe–TiC 2 (see Figure 2). As a result, Figure 9 shows a dependence of the TiC area on the powder particle size. Specifically, precipitation was almost completely suppressed up to ≈25 μm and then it intensified for coarser particles. In addition to observed precipitates, there was a limited number of large precipitates that were detected by SEM investigations of all analyzed powder cross-section samples. Figure 10 shows an example of a large TiC precipitate detected on a Fe–TiC 1 particle.

3.4. Remelting Experiments in Hot Stage Microscope

Remelting experiments confirmed formation of a slag layer on top of a sample. Moreover, semiliquid state of the sample was observed for both conducted experiments. According to Table 3, the experiment EM2 has lower heating rate than EM1, which ensured enough time for TiC dissolution. Thereby, the EM2 sample achieved fully molten condition at 1660 °C; meanwhile, the EM1 specimen did not obtain sufficient time even being treated at higher temperature of 1680 °C. Figure 11 shows a melting process of the EM2 specimen. Here, the specimen first spreads uncommonly by the substrate and then slowly starts to form a droplet covered with a slag layer; afterward, this layer dissolves by further heating. SEM analysis and EDX mapping of the EM2 cross-section sample are shown in Figure 7b. Analyzed TiC precipitates have similar morphology to the ones detected in powder particles, while their size is much bigger.

Figure 4. Surface observation of Fe–TiC 3 powder.
Table 5. Comparison of [Ti], [C], and [N] values for conducted atomization experiments in dependence on size fraction.

|        | 0–25 µm | 25–63 µm | 63–100 µm | 100–200 µm | 0–200 µm |
|--------|---------|----------|-----------|------------|----------|
| [Ti] a) [wt%] | Fe–TiC 1 | 3.45 | 3.51 | 3.55 | 3.64 | 3.49 |
|        | Fe–TiC 2 | 3.67 | 3.66 | 3.63 | 3.62 | 3.57 |
|        | Fe–TiC 3 | 3.68 | 3.60 | 3.64 | 3.68 | 3.67 |
| [C] b) [wt%] | Fe–TiC 1 | 0.841 ± 0.013 | 0.860 ± 0.005 | 0.882 ± 0.003 | 0.887 ± 0.003 | 0.887 ± 0.008 |
|        | Fe–TiC 2 | 0.826 ± 0.002 | 0.827 ± 0.009 | 0.827 ± 0.007 | 0.820 ± 0.007 | 0.830 ± 0.002 |
|        | Fe–TiC 3 | 0.819 ± 0.008 | 0.816 ± 0.002 | 0.821 ± 0.004 | 0.812 ± 0.009 | 0.811 ± 0.014 |
| [N] c) [ppm] | Fe–TiC 1 | 32 ± 2 | 20 ± 3 | 19 ± 5 | 17 ± 3 | 38 ± 3 |
|        | Fe–TiC 2 | 38 ± 8 | 60 ± 6 | 59 ± 4 | 58 ± 4 | 54 ± 5 |
|        | Fe–TiC 3 | 47 ± 4 | 67 ± 5 | 69 ± 4 | 73 ± 7 | 61 ± 4 |

a) Standard error of applied X-ray fluorescence spectrometer is 0.26 wt%; b) Standard deviation out of three measurements.

Figure 5. SEM/EDX analysis of slag layer formed within Fe–TiC 1 experiment. EDX data are collected from the whole image.

Figure 6. SEM images of powder particles from Fe–TiC 2 experiment. Sizes of powder particles: a) 16 µm; b) 32 µm; c) 54 µm; and d) 115 µm.
Figure 7. a) EDX mapping of Fe–TiC 1 powder particle, and b) EM2 sample.
4. Discussion

4.1. Powder Size Distribution and Particles Morphology

Examining obtained PSD values, manufactured powders remain in a range of typical values for this atomization unit under comparison to previously published works. Korobeinikov et al. reported that d50 decreases by enhancing of the spraying temperature and decrease in the spraying rate. Nevertheless, these tendencies are not fully realized in the current study. Namely, the Fe–TiC 1 powder has the coarsest PSD despite the middle spraying rate and the same spraying temperature as the Fe–TiC 2 powder; the Fe–TiC 3 powder has only slightly finer PSD than Fe–TiC 2 despite the lowest spraying rate and the elevated spraying temperature. Herewith, a slag layer and the presence of solid TiC precipitates can possibly have affected the PSD values. Further investigation is required.

4.2. Powder Chemical Composition

Formation of the TiC phase after Ti plates addition in molten metal is an exothermic reaction, which is depicted in Equation (1).

$$\text{Ti} + \text{C} \rightarrow \text{TiC}, \Delta H = -180.3 \text{ KJ mol}^{-1}$$

The formed TiC phase has a melting point of 3067°C and thus can be only dissolved by the melt. As demonstrated in the remelting experiments, the dissolution takes a considerable amount of time. The presence of a slag layer and respective loss of Ti is related to the thermodynamic stability of TiC at spraying temperatures, as well as its incompletely dissolution by the melt. This phenomenon is further strengthened due to a presence of nitrogen in the melt, which increases the thermodynamic stability of TiC(N) at higher temperatures (see Figure 3). Further improvement of the Ti absorption coefficient is possible by increasing the spraying temperature, e.g., to 1660°C, at which the dissolution of a slag layer was observed in the remelting experiment (see Figure 11), and by reduction of dissolved [N] in the melt. Increasing in the spraying temperature was limited due to reduced inductive heating efficiency by Ti addition, and by the alumina tundish maximum temperature. Meanwhile, dividing the added amount of Ti plates into more batches or utilizing a wire alloying strategy can further improve a TiC dissolution efficiency.

In addition, Ti losses are induced by reactions with the chamber atmosphere and the tundish refractory, forming TiO₂ and TiC(N) (see Figure 5). All atomization experiments were conducted under Ar protective atmosphere (99.999 Ar purity), which eliminates almost completely the first factor. The possible reaction of the melt with a tundish was estimated in the thermodynamic analysis in FactSage v.7.2 utilizing databases FToxid, FSstel, and FactPS. Specifically, equilibrium calculation was implemented for the Fe–4 wt% [Ti]–1 wt%[C] melt and the Al₂O₃ solid phase. For a rough estimation, there are following assumptions applied: 4950 g Fe, 50 g C, and 200 g Ti are taken to simulate the melt, which is similar to the experiment Fe–TiC 1; melt density is assumed to be 7 g cm⁻³. The contact area of the melt with the tundish is evaluated considering the tundish geometry and a calculated melt volume. The tundish reaction layer is calculated as the contact area multiplied by 1 mm depth. The tundish density equals to pure Al₂O₃ (3.987 g cm⁻³). Consequently, the reaction layer mass is equated to 150 g. As a result, a series of calculations with these initial conditions demonstrated an exponential growth of a 1 mm tundish

![Figure 8. Morphology of TiC precipitates; 50 μm Fe–TiC 1 powder particle.](image)

![Figure 9. TiC area detected on Fe–TiC 2 SEM images in dependence on particle size.](image)

![Figure 10. SEM/EDX analysis of large TiC precipitate detected on 31 μm Fe–TiC 1 particle.](image)
layer dissolution by increasing in the melt temperature, which is presented in Supporting Information to this study. This phenomenon prohibits further elevation of a spraying temperature for currently applied tundish material and utilized [Ti] content. Possible tundish material alternatives (e.g., ZrO2, Y2O3, BN, and so on) for [Ti]-containing alloys were reviewed by Fashu et al.\textsuperscript{[47]} Herewith, the longest homogenization period of the Fe–TiC 1 experiment most likely induced elevated oxidation of Ti and thus a loss reduction of C in the powder (see Table 5). Therefore, the homogenization period after Ti addition prior to spraying should be maximally shortened as in the experiment Fe–TiC 3.

4.3. Powder Microstructure. Morphology of Precipitates

SEM analysis and EDX mapping of cross-section samples demonstrated well-dispersed submicron TiC precipitates of blocky and plate shapes (see Figure 7 and 8). This morphology effect corresponds to the formation of primary and eutectic titanium carbides, respectively.\textsuperscript{[16,48]} Borkar et al.\textsuperscript{[48]} investigated Ni-based MMCs fabricated by laser engineered net shaping (LENS). Specifically, Ni–10Ti–10C and Ni–3Ti–20C compositions were utilized. Herewith, specific 3D microstructure analysis based on the focused ion beam (FIB) serial sectioning methodology revealed TiC precipitates of cuboidal (primary carbides), needle-like, and plate-like (eutectic) morphologies. Moreover, detected precipitates were interconnected forming a 3D network. The thermodynamic analysis made in this study assumes the formation of half of TiC as primary carbides (see Figure 3b). In fact, the morphology of precipitates depends on the solidification rate, which varies in accordance with particle size. The larger particles tend to have a higher fraction of primary carbides (see Figure 6) due to lower cooling rate. The formation of primary TiC starts already in molten metal droplets. Meanwhile, finer particles undergo higher cooling rates than coarser ones, thus formation of primary TiC can be suppressed. Thereby, the moderate size particles of 30–50 μm show reduced amount of primary-blocky precipitates, while finer powder particles demonstrate an absence of primary carbides. Dissolved nitrogen in a melt favors formation of primary precipitates; nevertheless, this effect is negligible owing to Ar protective atmosphere throughout all conducted experiments and thus low [N] value. In addition, coarse precipitates as the one shown in Figure 10 can form already in the tundish and then be transferred to melt droplets, which leads to the formation of large coarse TiC precipitates of micron size. This negative effect can be reduced utilizing higher spraying temperatures or lower TiC concentrations. Formation of eutectic carbides was also in dependence on a cooling rate leading to a compete suppression of any precipitates for extremely fine particles.

Area fraction analysis of the Fe–TiC 2 powder shown in Figure 9 demonstrates values up to 6.6 area% for the 115 μm particle. Meanwhile, thermodynamic assessment of vol% for the measured Fe–TiC 2 composition (3.57 wt% [Ti], 0.830 wt% [C]; see Table 5) made by ThermoCalc software reveals 7 vol% of TiC phase at 20 °C. The area fraction of TiC precipitates in this study can be roughly equated to the volume fraction considering their morphology.\textsuperscript{[48]} Thereby, large, coarse powder particles tend to approach a precipitation limit owing to a high affinity of titanium to carbon.

4.4. Remelting Experiments in Hot Stage Microscope

Transition of a sample to a semiliquid state during remelting experiments demonstrates thermodynamic stability of a carbides’ network at atomization temperatures. Moreover, dissolution of TiC requires significant time even at thermodynamically sufficient temperatures. This phenomenon should be considered in further implementation of the Fe–TiC composite powder in additive manufacturing (e.g., laser powder bed fusion, electron beam powder bed fusion, and direct laser deposition techniques), where remelting is required.

5. Conclusions

Fe–TiC composite spherical powder was successfully fabricated in all three experiments applying the vacuum inert gas atomization technique. The TiC reinforcement phase was formed in situ within spraying of the [Ti], [C]-containing Fe-based molten metal. Titanium plates divided into two batches were introduced into a carbon-containing melt prior to spraying depending on the applied alloying strategy (see Table 1). In addition, two remelting
experiments in the hot stage microscope were conducted. The following main observations were done in this study: 1) Among conducted experiments, the Fe–TiC 3 has the finest powder size distribution presumably due to increased spraying temperature. Nevertheless, influence of other factors (e.g., spraying rate, introdcution strategy, slag formation, the presence of solid TiC particles in the sprayed molten metal) is controversial and thus should be further investigated in a future work. 2) Fabricated powders are similar in composition and demonstrate homogeneous distribution of TiC forming elements. The Fe–TiC 1 powder has slightly lower [Ti] value and slightly higher [C] value than Fe–TiC 2–3 ones, which is presumably induced by the implemented alloying strategy (i.e., the longest homogenization period after Ti addition). 3) Chemical composition of all fabricated powders deviates from target values of 1 wt% [C], and 4 wt% [Ti] due to formation of a Ti-rich slag layer. SEM/EDX analysis of this slag corresponds to formation of TiO₂, Ti₂C, and Ti₃C(N). Further improvement of the Ti absorption coefficient is possible at enhanced atomization temperatures, by utilization of another tundish materials that superiorly tolerate Ti-containing melts, and by alloying strategy optimization (e.g., shortening the homogenization period after Ti-addition). 4) SEM analysis of powder cross-section samples revealed homogeneously distributed submicron TiC precipitates. There are two types of morphology detected: blocky and plate-shaped precipitates, which are primary and eutectic TiC, respectively. 5) According to thermodynamic analysis and obtained chemical composition, fabricated powders can have up to approximately 7 vol% TiC. In fact, the volume fraction of TiC precipitates as well as its morphology depends on the cooling rate and thus on the powder particle size despite similar chemical composition for coarser and finer powder fractions. Due to extremely high cooling rate, precipitation in particles up to ≈25 μm is suppressed almost completely. Coarser powder particles tend to have more primary precipitates than finer ones. 6) Several particles in cross-section samples have large, coarse TiC precipitates that are presumably formed already in the tundish prior to spraying. Formation of these precipitates is induced by thermodynamic stability of TiC phase at spraying temperatures, which is in accord with a thermodynamic analysis of the Fe–Ti–C system and conducted remelting experiments. The presence of dissolved N in a melt can favor this negative effect. 7) High thermodynamic stability of TiC and its long dissolution time in the Fe-based melt allows assuming that additively manufactured parts out of the MMC powder fabricated in this study will keep similar morphology and size of TiC reinforcement phase.

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Conflict of Interest

The authors declare no conflict of interest.
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