Surface modification of inorganic materials with graphene oxide

From solution to high-temperature synthesis

SIMON TIDÉN
The use of graphene as an additive in materials is often challenging due to the agglomeration of the two-dimensional graphene sheets. An alternative additive is graphene oxide (GO), an oxidized form of graphene, which is easily dispersed in water. In this thesis, a method based on electrostatic interactions has been developed to coat powder particles with GO. The GO surface has a negative charge at most pH values, while most inorganic materials form a thin oxide surface layer with a pH-dependent surface charge. Below a certain pH, a powder surface can have a positively charged surface oxide, which can interact with the negatively charged GO sheets and form a coated particle. The pH range for a successful coating process can be predicted based on the ionic potential (z/r) of the surface oxides and the oxide stability regions seen in Pourbaix diagrams. In the thesis, GO-coatings were obtained on powders of Cu, Fe, 316L stainless steel, MnAl(C) and AlSi7Mg. The coated powders showed reduced reflectance, long-term oxidation stability and in most cases improved flowability.

The effect of the GO-coating on the processability of Cu, MnAl(C), 316L stainless steel and AlSi7Mg in laser powder bed fusion (L-PBF) was also investigated. For Cu, the reduced reflectance at the wavelength of the laser led to printing of fully dense parts compared to a 10 % porosity of the printed uncoated Cu powder using the same printing parameters. L-PBF printing of MnAl(C) has a problem with cracking but printing with the GO-coated powder resulted in a 35 % crack reduction. Fully dense parts could also be printed with GO-coated AlSi7Mg and 316L stainless steel powders. Significant changes in texture compared to the uncoated reference as well as moderately improved mechanical properties were observed.

TiB$_2$-SiC composites can be formed by reactive hot pressing of a TiC-Si-B$_4$C powder mixture. In agreement with predictions, it was very difficult to coat powders of Si and B$_4$C due to their acidic surface oxides. In the thesis, the influence of reduced GO (rGO) and carbon black (CB) on the microstructure and properties of the TiB$_2$-SiC composite was investigated using ball milled mixtures of the powders. After reactive hot pressing at 1850 °C, sheet-like structures could be observed at fractured surfaces suggesting that graphene-like sheets survive the high temperatures. The rGO containing samples showed increased thermal conductivity, hardness, and fracture toughness by 50 %, 16 % and 20 %, respectively. The improved properties were attributed to a good dispersion of the rGO additive, a change in the microstructure and a decreased oxygen content of the composite.

Keywords: Graphene, Graphene oxide, Coatings, Additive Manufacturing, Laser Powder Bed Fusion, Reactive Hot Pressing

Simon Tidén, Department of Chemistry - Ångström, Box 523, Uppsala University, SE-75120 Uppsala, Sweden.

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List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


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My contributions

I. I planned the study and conducted all the experimental work besides the flowability analysis. I led the discussions and wrote the main part of the manuscript.

II. I planned the study and conducted most of the experimental work. I led the discussions and wrote the main part of the manuscript.

III. I led the planning of the study and conducted or participated in all the experimental work. I participated in all the discussions and wrote the main part of the manuscript.

IV. I was involved in planning the study and conducted most of the characterization. I took part of the discussions and wrote part of the manuscript.

V. I planned the study and conducted all experimental work. I led the discussions and wrote the main part of the manuscript.

Other work the author has contributed to:

### Abbreviations

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<th>Abbreviation</th>
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<tr>
<td>GO</td>
<td>Graphene oxide</td>
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<td>rGO</td>
<td>Reduced graphene oxide</td>
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<td>AM</td>
<td>Additive manufacturing</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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<td>TEM</td>
<td>Transmission electron microscopy</td>
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<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
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<tr>
<td>L-PBF</td>
<td>Laser powder bed fusion</td>
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<td>EBSD</td>
<td>Electron back-scatter diffraction</td>
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<td>RHP</td>
<td>Reactive hot pressing</td>
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<tr>
<td>PZC</td>
<td>Point of zero charge</td>
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<td>IEP</td>
<td>Isoelectric point</td>
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<td>RPA</td>
<td>Revolution powder analyzer</td>
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1 Introduction

The idea of adding small amounts of a compound, an additive, to another material to change its properties or processing in a desirable way has been widely used in all fields of chemistry and materials synthesis. The effect of an additive can be classified into three general categories; enhancing processability, affecting microstructure or phases formed of the final material and lastly forming a composite with the additive as an additional phase. An additive could be used for one or several of these three categories. For example, in the pharmaceutical industry, powders are prone to agglomeration and therefore the additive magnesium stearate is used in small quantities to improve the flowability of the powders which makes them easier to process [1]. Additives can also influence microstructure, for example, by affecting the viscosity and therefore the solidification of a melt. Additives such as nanoparticles of similar unit cell dimensions as the bulk material can also act as nucleating sites which can create equiaxed and smaller grains which can improve the mechanical properties [2]. Composite materials consist of two or more separate phases with dissimilar chemical or physical properties that together form a material with new properties, such as wood, concrete and cemented carbides. When additives are used to create composite materials, the ratio between the amount of the additive and the matrix material can be very low and the addition of only a few percent of another phase can significantly change the properties of the composite material. For example, a few weight-percentage (wt. %) of carbon nanotubes added to a polymer matrix can more than double the Young’s modulus [3]. A general problem with additives, however, is to obtain an even distribution of the added component to secure homogeneous isotropic properties of the final material.

Graphene and graphene-derivatives are an interesting group of materials to use as additive due to their unique properties and aspect ratio (this will be further discussed in Chapter 3. Graphene has the potential to act as additive in all three categories outlined above. Firstly, a graphene-coated powder could exhibit completely different flowability and spreadability in e.g., additive manufacturing (AM) due to the weak interactions between the graphene sheets and graphene acting as solid lubricant between the particles [4]. Secondly, the graphene can affect the microstructure by inhibiting grain growth [5]. Finally, graphene may be added to form composites with improved properties [6, 7,
However, the use of graphene as additive has some associated challenges. For example, it may be hard to incorporate perfect single sheets of graphene into a bulk material without damaging the integrity of the 2D structure of graphene. Additionally, since the graphene sheets tend to agglomerate into multilayer structures via interactions of the \(\pi\)-orbitals, it is a challenge to disperse the graphene sheets evenly throughout a matrix material. Despite this, various graphene-type materials have successfully been incorporated to enhance the properties of various metals and alloys [7, 6].

A common way to add graphene to a powder of metals, alloys or ceramics is by mechanical mixing of the graphene-type material and the metal powder using ball milling. However, ball milling can cause damage to the graphene sheets [9, 10] and introduce changes in the metal powder morphology [11]. This can reduce the powder flowability, which is very important in e.g., powder-bed based additive manufacturing techniques. An alternative route is to mix the metal powder and graphene in solution. However, the hydrophobic pristine graphene sheets are not stable in water. They will agglomerate making it difficult to achieve a homogeneous distribution of the sheets. Another alternative is to use graphene oxide (GO) where oxygen-containing functional groups are attached to the graphene sheets. This will partly break up the perfect sp\(^3\)-bonded network but also form hydrophilic sheets which are stable in water. The oxygen functional groups can also be deprotonated which gives them a negative charge, thus repelling other GO sheets and prevent agglomeration (this discussed more in Chapter 3). An additional benefit with GO is that the charged functional groups on the sheets can interact with surfaces with an opposite charge through electrostatic attractive forces. The benefit of this approach is that it minimizes the agglomeration and maximizes the dispersion of GO since the sheets are repelled from each other and attracted to the net positively charged surfaces that have not yet been covered by GO sheets. This attractive electrostatic interaction has been used to attach oxide nanoparticles to GO sheets [12, 13]. GO has also been used to nucleate metal oxide particles, which subsequently have been reduced to metal particles and incorporated in a metal matrix composite [14]. Surfactants, such as (3-aminopropyl) triethoxysilane APTES [15] and cetyltrimethylammonium bromide (CTAB) [16], have been used on the surface of larger metal powders to create favorable electrostatic interactions. However, this requires an additional synthesis step and increases the risk of introducing more contaminants in the consolidated material later on.

In the present thesis, I have used an alternative method outlined in Fig. 1. Most materials have a thin native surface oxide. By tuning the pH, it may be possible to vary the surface charge of this native oxide from negative to positive. As will be discussed in Chapter 3, GO has a negative surface charge in a broad pH window. For many surface oxides, but not all, it should be possible to find
a pH window where negatively charged GO sheets can interact with positively charged surfaces due to protonation to enable coating of the powder surfaces with GO.

![Figure 1. Schematic illustration of the coating method. Electrostatic attractive forces between the negatively charged graphene oxide (GO) sheets and the positively charged particle surfaces result in the coating of the particle with GO.](image)

An important aim of this thesis is to develop methods to surface engineer different inorganic material powders with GO and determine when such surface modifications are possible and not. To do this, a number of different technologically relevant metals, alloys and ceramics with different surface charge properties have been investigated. The investigated powders are: Cu, Fe, 316L stainless steel, AlSiMg, MnAl, TiC, B₄C and Si. In the thesis, I also investigate how the GO-coating modification affects the powder properties and powder-based processes, such as additive manufacturing (AM) using laser powder bed fusion (L-PBF) and a reactive hot pressing (RHP) process. The effects of the graphene additive on the final properties, such electrical, thermal, mechanical of the consolidated materials have been investigated. In the thesis I have addressed a number of scientific questions. They are:

1. Can we use the electrostatic attractive forces approach to effectively coat metal powders with graphene oxide?
2. What are the limitations of the electrostatic attractive forces approach regarding which materials we can coat?
3. How will a graphene oxide coating affect powder characteristics such as reflectance and flowability relevant for powder-bed based additive manufacturing techniques?
4. How will the graphene oxide coating affect densification processes such as L-PBF and reactive hot pressing?
5. How will the graphene oxide coating influence the properties of the manufactured parts?
6. How will the graphene oxide coating influence the further oxidation and shelf-life of copper powder?
7. Can we control the oxide on the powder surface to improve the coating process?
2 Surface charges and zeta potentials of solid surfaces

When a solid inorganic material is placed in a liquid of dipolar molecules such as water, there will be a tendency for electric charges in the material to be distributed unevenly near the surface which creates a surface charge. The density of the surface charge is described in coulombs per square meter. Firstly, the surface charge of pure metal(hydr)oxides will be discussed and secondly how it translates to an oxide layer on a metal particle in Chapter 3. Generally, metal (hydr)oxides in water give rise to surface charge by protonation or deprotonation of oxygen atoms at the surface, and by leaching of species into solution [17]. The electric charge at the surface is referred to as a surface potential. The charged surface will attract ions of the opposite charge, which will decrease the electric potential further away from the surface. Various models have been used to describe how the ions affect the decay of electric potential away from a charged surface, also called the electrical double layer. One of them is the Helmholtz-Perrin model, which uses a fixed charged counter-ion layer with a linear decay of potential between the layers [18]. Another is the Guoy-Chapmann model, which also includes a diffuse layer of counter-ions ordered by electrostatic attraction but disordered by thermal molecular agitation and yielding an exponential decay of the surface potential into the solution [19, 20]. Stern further developed this model which gave the Stern model of a double layer (see Fig. 2) [21], with more strongly bonded ions adjacent to the charged surface (Stern layer) surrounded by a diffuse layer with counterions that interact more indirectly with the surface. The slipping plane is where the liquid (with ions) starts to be able to move in relation to the charged surface. The potential at the slipping plane is called zeta potential, while the potential at the Stern Layer is called the Stern potential.
In a water solution, OH\(^-\) and H\(^+\) are the most important ions that influence both the surface charge and zeta potential through protonation and deprotonation. They also affect the leaching of anions and cations into solution. Therefore, pH of the solution plays a determining role in water as it describes the concentration of H\(^+\) ions. For example, assume we have a particle with negative surface charge and therefore negative surface potential as shown in Fig. 2. Lowering the pH will increase the concentration of H\(^+\) ions, which will lead to a higher degree of protonation of the surface and a decrease in the negative surface potential. A further reduction in pH will eventually protonate the surface of the particle to such a degree that it will be positively charged, and the surface potential and zeta potential will then be positive. The pH where the surface charge density is zero is called point of zero charge (PZC), and the term is most often used when the results are obtained from the inflection point of acid-base titration curves. The zeta potential can be directly measured using electrokinetic methods and the pH where the zeta potential is zero is called the isoelectric point (IEP) [23]. It should be noted that when the surface charge is zero, the zeta potential is also zero. However, when measuring PZC and IEP they are not necessarily identical. They can differ due to specific adsorption
of other ions than H\(^+\) and OH\(^-\) such as ions dissolved from the surface or ions introduced when adjusting the pH [24]. This means that a material will generally have a positive surface charge (and therefore a positive surface- and zeta potential) at a low enough pH due to protonation of the surface. As the pH is increased, the surface charge (and therefore also the surface- and zeta potential) will eventually become negative as the IEP/PZC is crossed and more of the surface oxygen is deprotonated. Other counterions than OH\(^-\) and H\(^+\) can also affect the zeta potential. This must be taken into consideration at high ionic concentrations, for corroding systems where ion can leach into the solution or in the presence of other adsorbents such as surfactants or polymers.

Additional factors that can affect the measured zeta potential of a specific material is the temperature of the solution [25], and even the crystallographic orientation of the facets exposed to the liquid. Increasing the salt concentration in the liquid will decrease the absolute value of the zeta potential because the electric double layer shrinks but it may only cause a minor shift to the IEP.

The zeta potential is important to determine if a dispersion of particles will be stable or if the particles will adhere to other particles and form larger and larger aggregates. Small particles that have a high enough zeta potential with the same sign will repel each other to such a degree that they can form a stable aqueous dispersion given that their density is somewhat similar to the dispersant and the particles do not sediment too quickly. This is widely used to create stable dispersions of various oxide (nano)particles in water. Powders with low absolute zeta potentials may undergo a process called flocculation, where particles adhere to one another and form larger aggregates. The aggregates may phase separate and settle as sediment. For the relatively large metal particles that will be used in this thesis, sedimentation is inevitable even if the particles would have a high surface charge. However, to demonstrate the surface charge of the native metal oxide, the smallest size fractions of Cu and Fe powders were used in Paper I. These powder particles were suspended in solution for long enough time to conduct zeta potential measurements.
3 The materials and their zeta potentials

The thesis includes studies with graphene oxide combined with different powders ranging from pure metals to alloys and ceramic materials. This chapter is a comprehensive summary of the used materials and general trends in their zeta potentials at different pH.

3.1 Graphene and graphene oxide

Graphene is single layer of graphite, consisting of a single layer of sp²-bonded carbon atoms in a hexagonal honeycomb lattice. The interest in graphene was sparked when Novoselov et al. [26] displayed the remarkable electric properties of free-standing graphene layers created by manual exfoliation of graphite. Thereafter, an immense amount of research has been done on this material to characterize its properties [27, 28] such as electron mobilities of $2.5 \times 10^5$ cm²V⁻¹s⁻¹ [29] and thermal conductivity of $\sim 4000$ Wm⁻¹K⁻¹ [30]. It also has excellent mechanical properties with a Young’s modulus of 1 TPa and intrinsic strength of 130 GPa [31] making it the strongest material ever measured. To produce large quantities of graphene for use as additives in other materials, various synthesis routes have been investigated. Instead of exfoliating graphite to create graphene or form graphene with a vapour deposition method, there are alternative methods to oxidize graphite and introduce functional groups which increase the interlayer distance. This facilitates exfoliation and makes it possible to produce large amounts of material [32, 33, 34]. The most commonly used method is the Hummer’s method where graphite is oxidized in a solution of sodium nitrate, potassium permanganate and sulfuric acid [33].

The sheets produced with chemical oxidation consist of a single layer of carbon atoms but with oxygen-containing functional groups such as hydroxyl, carboxyl, and epoxide groups [35, 36], and the material is then called graphene oxide (GO). The carboxyl groups are primarily attached to the edges of the GO sheets while the other functional groups are spread out over the basal planes. This will break up the sp²-bonded network which in turn removes some of the exceptional properties of graphene. However, GO can later be reduced chemically [37, 38] or thermally [39] to create reduced graphene oxide (rGO) which can remove most of the oxygen containing functional groups and partly
restore the sp²-bonded carbon network and its conductive properties [37]. The structural differences between graphene, GO and rGO are shown in Fig. 3.

Figure 3. Showing the structural differences between graphene, graphene oxide (GO) and reduced graphene oxide (rGO). Graphene is a single sheet of sp²-bonded carbon atoms, but when oxidized forms GO with various oxygen containing functional groups on the edges and the faces of the sheets. GO can be reduced to various degrees which removes the oxygen and partly restores the sp² network. Reprinted from ref. [40] with permission from Springer Nature.

3.2 Zeta potential of graphene oxide

The surface charge of GO and reduced GO (rGO) is due to their oxygen containing functional groups, which can be protonated or deprotonated similar to the surface oxygen atoms of metal (hydr)oxides. The functional groups will, for most pH values, be net negatively charged. This means that the surface charge and zeta potential of GO and various degrees of rGO are negative for a wide pH range [41], as shown in Fig. 4. Konkena et al. used titration experiments combined with IR-spectroscopy and identified three pKₐ values for GO [42]. The first two pKₐ values at 4.3 and 6.6 were attributed to deprotonation of different carboxylic groups, respectively. The third pKₐ value at 9.8 was attributed to phenolic OH-groups mostly on the faces of the sheets. The distribution around these pKₐ values were quite wide for GO. However, in rGO, the pKₐ value for the carboxyl groups was instead 7.9 and the distribution was much narrower. This can be explained by the more complex chemistry and variation in chemical bonding environments for GO compared to rGO. Additionally, the number of oxygen-containing functional groups can also increase the absolute value of the zeta potential [41, 42, 43]. As described in Section 3.1, carboxyl groups are generally formed on the edges of the GO sheets, while the basal planes of the GO sheets are dominated by OH-groups [44, 35]. Since the two functional groups deprotonate at different pH, the exact pH value could be important when considering GO interaction with other materials.
3.3 Surfaces of metals and alloys

In this thesis, the coating process outlined in Fig. 1 has been applied to a range of different metals and alloys including Cu, Fe, Al, MnAl, AlSiMg and 316L stainless steel. Most metals and alloys except gold form a native oxide layer in air, and when submerged in water, they can also form a stable oxide that might passivate the material. This means that the properties of the surface oxide at different pH will determine the interactions with GO. It is possible to predict the oxide formed using a Pourbaix diagram, which shows the different stability regions for an element at different pH and potentials [45]. The Pourbaix diagrams for Cu, Fe, Al, and Cr are shown in Fig. 5. The lines that separate two phases can be either vertical, horizontal or tilted. When a line is horizontal it means that the corresponding reaction between those phases is a redox reaction and dependent on the potential but not pH. An example of this is the redox reaction between Fe$^{2+}$ and Fe$^{3+}$ in Fig. 5c. A vertical line on the other hand corresponds to an acid-base reaction that is not dependent on the potential, such as the line between Fe$^{3+}$ and Fe$_2$O$_3$. A tilted line means that the reaction is dependent on both the potential and the pH. All the lines that involve reactions with different ions can shift depending on the concentration of the ion species involved in the reaction as it changes the equilibrium. The corrosion potential will determine the potential in the Pourbaix diagram unless an external potential is applied. For example, the Pourbaix diagram in Fig. 5a for

![Figure 4. Zeta potential of GO (red) and rGO (black) as a function of pH. Reprinted from ref. [42] with permission from the American Chemical Society.](image-url)
Cu shows that a (hydr)oxide for Cu should exist in the pH range is between ~4 and ~14 at a certain positive potential and depending on the ion concentration. The Pourbaix diagrams are important tools in the application of the coating process in Fig. 1 since they show the stability regions for oxides on the powder surface.

![Figure 5. Pourbaix diagram of a) Cu, b) Al, c) Fe and d) Cr at 25 °C. Reprinted with permission from [45].](image)

A major limitation with the Pourbaix diagram like all other phase diagrams is that they do not take into consideration if a phase actually forms or how long it takes due to kinetic reasons. Therefore, a surface oxide formed in air might be stable for long enough time to conduct experiments on when submerged in water even if that oxide is not stable according to the Pourbaix diagram. An (hydr)oxide phase that is stable in the Pourbaix diagram can be passivating,
which means that the oxide layer inhibits the growth of more oxide, but it can also continue to grow at the expense of the bulk metal. Additionally, the oxide may dissolve in the solution which means that new oxide has to form continuously, so that there is corrosion anyway. This is something to consider for the coating process as it might make it difficult to attach GO sheets to a dissolving oxide. These Pourbaix diagrams do not take into account the presence of other ions species which might significantly change what phases are stable at certain conditions. It is also hard to know the concentration of metal-ions in solution as it can change during the coating process.

The oxide formation for alloys is more complex since several different metals are present and can form surface oxides. However, often the top surface oxide is dominated by the most stable oxide. For example, in Paper III we have coated MnAl with GO. Here, the most stable oxide is expected to be Al₂O₃ in air which has also been confirmed experimentally [46]. According to the Pourbaix diagram in Fig. 5c this oxide should be stable between pH ~4 and ~9 for all Al-ion concentrations. Another example is stainless steels such as 316L, which gains its excellent corrosion resistance properties from the passive chromium oxide that forms on the surface. It is worth noting that small amounts of the other alloying elements also can exist in the surface oxide which could influence the zeta potential.

3.4 Trends for the isoelectric points of oxides on metals and alloys

In order to coat a powder particle with GO it is important to determine the isoelectric point (IEP). Several physical constants such as electronegativity and the hydrolysis constant \( K_{\text{hydrolysis}} \) can be used to explain trends in IEP [24]. However, a useful parameter to describe the IEP is the ionic potential \( (z/r) \), which is the ratio between the electrical charge of the cation and the cationic radius. The ratio \( z/R \) which also includes the anionic ion radius can also be used [21]. The ionic potential is a value of the charge density at the surface of the ion. High charge density indicates stronger attractive interactions with ions of the opposite charge and stronger repulsive interactions with ions of the same charge. High ionic potential means the cations adjacent to the surface oxygen atoms will polarize the electron cloud of the oxygen more towards the cation, weakening the O-H bond at the surface which facilitates deprotonation creating a negative charge at the surface. The opposite is true for oxides of low ionic potential. This means that the oxides can be divided into three categories: acidic oxides with high ionic potential, basic oxides with low ionic potential and amphoteric oxides which can act as both depending on the pH. The correlation between \( z/r \) and IEP is shown in Fig. 6 which clearly shows
that the IEP decreases with increasing z/r, i.e., acidity of the oxide. An outlier in Fig. 6 is Si, which behaves slightly different compared to the metals when measuring the surface charge at various ionic strengths, and the results are often reported as IEP below a certain value (i.e., < 2) due to extrapolation instead of interpolation.

Another aspect to consider is the hydration level of the compounds which is the ratio between oxygen and hydrogen atoms. For some metals, such as Co, Cu, Mg, Ni and Pb, the IEP of the (hydr)oxides increases with increasing hydration level by up to 1-2 [24]. However, for some other metals the effect is not significant (Al, Cr, Fe, Nd, Sn, Zr).

3.5 Trends for the isoelectric points of ceramic materials

Non-metallic elements and ceramic compounds that are not oxides, such as carbides, nitride, borides, and sulphides can also develop surface charges in aqueous solution. In many cases they may form a thin native oxide and the
IEP can then be estimated from Fig. 6. For example, Si used in Paper IV has a native oxide of amorphous SiO$_2$ and according to Fig. 6 we should expect a very low IEP suggesting a negative surface charge in a broad pH range. It should be noted, however, that an amorphous native oxide is not identical to a crystalline SiO$_2$ particle and that they can show a slightly different IEP value. Boron oxide is another oxide that may form on for example boron carbide (used in Paper IV) or boron nitride. Reports on IEP for boron oxide are very limited, but it has been shown that an oxide layer on BN [47] or B$_4$C [48] reduced the surface charging of the particles. However, the zeta potential was negative for all measured pH.

Carbides generally show negative zeta potential at most pH [49, 50, 51, 52] with IEP < 3 and with limited positive zeta potential at lower pH. The surfaces also display a complex phenomenon involving dissolved CO$_2$ which increase the negative value of the zeta potential. The surfaces can be cleaned but the zeta potential still only approaches zero even at very low pH [49]. Similar problems also exist for carbonates. Complex surface reactions for nitrides and sulphides, such as hydration and oxidation, mean that their surface potentials depend on the degassing of the water, aging time of the solvent or particles and the cleaning protocols. There are especially many IEP reported for the technologically relevant materials Si$_3$N$_4$, CaCO$_3$ and apatites, but the results are scattered. Additionally, for some salts such as silver halides, other ions than OH$^-$ and H$^+$ govern the zeta potential, thus making it is quite insensitive to changes in the pH [53].

### 3.6 Predicting suitable coating parameters

Based on the discussions in Sections 3.2-3.5 it is now possible to predict suitable coating parameters starting with GO. Here, a high absolute zeta potential is favourable since it prevents GO from aggregating and the sheets can stay separated as a dispersion in water. Usually, this requires zeta potentials above +30 mV or below -30 mV. Since GO and rGO have negative zeta potentials at most pH, we need a pH where the potential is below -30 mV, this is marked with a dotted line in Fig. 4. This means that we need a pH higher than about 4 and 8 for GO and rGO, respectively. For GO it is generally best if the pH is kept as high as possible to increase the amount of hydroxyl groups on the basal planes that are deprotonated. This will increase the attractive forces of the whole sheet to a positively charged particle which promotes a good contact and minimizes wrinkling/folding of the GO sheets. However, an important aspect is to consider the ion/salt concentration during the adjustment of the pH. As it can not only lead to changes of the surface charge properties, such as decreased absolute value of zeta potential but also introduce more contaminations in the final material.
Mixing materials with different surface charges can cause either attractive interactions if they are oppositely charged, or repulsive forces if they have the same sign of the zeta potential. Since GO has a negative zeta potential at most pH, it is expected that particles with surfaces that have a large positive zeta potential will show attractive interactions with the GO making it possible to coat a powder particle. However, if the absolute value of the zeta potential is not large enough the particles will have more limited interactions with other particles. Therefore, it is not only important to consider the sign of the surface charge, i.e., if its below or above the IEP, but also the absolute value of the zeta potential. For elements and compounds that have a negative zeta potential for the majority of pH values, repulsive interactions will take place with GO, and it will not be possible to use electrostatic forces to create intimately mixed materials. This will likely be the case for acidic oxides such as SiO₂, boron oxide, and silicates [53].

To coat a surface with GO, a suitable pH range can be predicted based on the properties of the material to achieve attractive electrostatic forces. This pH range can be determined from a zeta potential versus pH plot combined with information from the Pourbaix diagram as is shown in Fig. 7. For the material (in this case a metal), it needs to have a stable surface phase (usually an oxide) at the pH used in the coating process. For Cu it would be above pH ~4 based on the Pourbaix diagram in Fig. 5a. In addition to this, the zeta potential should also be as high as possible. A pH region with high positive zeta potential for a stable oxide phase is shown in green in Fig. 7. In this pH range, coating of the metal oxide with GO is possible due to attractive electrostatic forces. If the zeta potential is not positive enough, the attractive electrostatic forces might be too small to coat the surface with GO considering other forces during, for example, agitation of the mixture. Therefore, a pH very close to the IEP should preferably not be used and is shown with orange colour in Fig. 7. At pH values well above the IEP, electrostatic repulsion will occur between the metal oxide surface and GO, and coating will not be possible. Although a high positive zeta potential can be obtained at certain pH, it is advised to not operate too close to any phase boundaries in the Pourbaix diagram as the exact position will depend on the concentration of the metal ions in solution. As will be shown in Chapter 5 and in Papers I-III, there are process windows for coating Fe, Cu, Al, and alloys with these elements with GO. The coated powder can then be used to e.g., improve the printing process in an additive manufacturing process.
Figure 7. Schematic figure showing the zeta potential plotted versus pH for graphene oxide (GO) and a metal oxide. At low pH, the metal oxide will be unstable and at too high pH there will be a negative surface charge causing electrostatic repulsion with the GO sheets (red areas). Near the isoelectric point (IEP) of the metal oxide the interactions will be weak since the absolute surface potential is low (orange area). For a certain pH (green area) there will be electrostatic attraction between metal oxide surfaces with a positive zeta potential and GO sheets with a negative zeta potential.

As will be shown later, there is a need to optimize the coating process parameters with respect to e.g., time. The added benefit with the electrostatic assembly is that the repulsive forces between GO sheets and the attractive forces between uncoated material surfaces should promote excellent dispersion given enough time for the material and GO to mix since GO will prefer to attach to surfaces that are not yet covered by other GO sheets. Therefore, the time of mixing is an important parameter in the coating process. The materials need to have long enough time to mix well but it is also advised to keep the time as low as possible to decrease the oxidation for non-bulk-oxide materials such as metals. Another important aspect to consider for the coating process is the subsequent drying, as the elevated temperatures can influence the surface charge and increase the oxidation of the material. Furthermore, the native oxide that forms in air might not be the oxide that is stable in water. It can also take time to form the oxide in the Pourbaix diagram when submerged in water. This means that the initial oxide that is stable in air could be kinetically stable for long enough to last during the coating experiment. Therefore, the IEP for
other oxide phases of that metal/element could be considered from the literature. If the different oxide phases display vastly different IEP values, practical tests would have to be conducted to identify best process pH.
4 Materials and methods

In this chapter, the method used for the coating of the powders with graphene oxide (GO) is described together with the techniques used to characterize the coated powder. The two methods used to synthesize the materials, laser powder bed fusion (L-PBF) and reactive hot pressing (RHP), are also briefly described. Finally, the most important analytical techniques used in the thesis are summarized.

4.1 Materials

In this thesis several different metal powders and GO have been used as starting materials. Details of all powders and graphene-related materials are summarized in Table 1.

As shown in Fig. 8, the powders in Table 1 have different sizes and shapes depending on their use in the thesis. Powder particles made by gas atomization are very spherical and are suitable when good powder flowability is important. They are suitable for AM with L-PBF and are usually sieved to the size range between 15-63 µm. An example is the Cu powder from Metalpine (Fig. 8a) used in Paper V. The Fe powder (Fig. 8b) particles are much smaller compared to the those in Fig 8a. These powders can be seen to adhere a lot to each other and were, for example, used in Paper I to investigate the effects of GO-coating on the flowability. The TiC, B₄C and Si powder particles (Fig. 8c) used in Paper IV were made by a carbo-thermal reduction process of oxides and then reduced in size and mixed by ball milling. Due to the ball milling process they have irregular shapes, and some particles are smaller than 1 µm in size.
Table 1. Summary of the starting materials used in the thesis. The Cu from Alfa Aesar and Heraeus were named (A) and (B), respectively, as they are both discussed in Paper I.

<table>
<thead>
<tr>
<th>Material</th>
<th>Manufacturer</th>
<th>Method</th>
<th>Shape and particle size</th>
<th>Use in thesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Sandvik/Osprey</td>
<td>Gas atomization</td>
<td>Spherical 15-45 µm</td>
<td>Paper II</td>
</tr>
<tr>
<td>Cu</td>
<td>Metalpine</td>
<td>Gas atomization</td>
<td>Spherical 15-45 µm</td>
<td>Paper V</td>
</tr>
<tr>
<td>Cu (A)</td>
<td>Alfa Aesar</td>
<td>Gas atomization</td>
<td>Spherical 10 µm</td>
<td>Paper V</td>
</tr>
<tr>
<td>Cu (B)</td>
<td>Heraeus</td>
<td>Gas atomization</td>
<td>Spherical 15-53 µm</td>
<td>Paper I</td>
</tr>
<tr>
<td>Fe</td>
<td>Alfa Aesar</td>
<td>Reduced</td>
<td>Irregular &lt; 10 µm</td>
<td>Paper I</td>
</tr>
<tr>
<td>316 L</td>
<td>Sandvik/Osprey</td>
<td>Gas atomization</td>
<td>Spherical 90% &lt; 22 µm</td>
<td>Paper I</td>
</tr>
<tr>
<td>316 L</td>
<td>Sandvik/Osprey</td>
<td>Gas atomization</td>
<td>Spherical 15-45 µm</td>
<td>Thesis summary</td>
</tr>
<tr>
<td>AlSi7Mg</td>
<td>Sandvik/Osprey</td>
<td>Gas atomization</td>
<td>Spherical 15-53 µm</td>
<td>Thesis summary</td>
</tr>
<tr>
<td>MnAl</td>
<td>Höganäs</td>
<td>Gas atomization</td>
<td>Spherical &lt; 63 µm</td>
<td>Paper III</td>
</tr>
<tr>
<td>TiC</td>
<td>DRF*</td>
<td>Carbo-thermal reduction</td>
<td>~0.4-5 µm**</td>
<td>Paper IV</td>
</tr>
<tr>
<td>BaC</td>
<td>DRF*</td>
<td>Carbo-thermal reduction</td>
<td>~0.4-5 µm**</td>
<td>Paper IV</td>
</tr>
<tr>
<td>Si</td>
<td>DRF*</td>
<td>Carbo-thermal reduction</td>
<td>~0.4-5 µm**</td>
<td>Paper IV</td>
</tr>
<tr>
<td>GO</td>
<td>Graphenea</td>
<td>Hummer’s</td>
<td>~6-33 µm***</td>
<td>Paper I</td>
</tr>
<tr>
<td>GO</td>
<td>LayerOne</td>
<td>Hummer’s</td>
<td>&gt;10 µm***</td>
<td>Paper I, II, III, V</td>
</tr>
<tr>
<td>Aros Graphene rGO [54]</td>
<td>Graphmatech</td>
<td>Hummer’s, chemical and thermal reduction</td>
<td>-</td>
<td>Paper IV</td>
</tr>
<tr>
<td>Carbon black</td>
<td>Sigma Aldrich</td>
<td>Thermal decomposition</td>
<td>-</td>
<td>Paper IV</td>
</tr>
</tbody>
</table>

*Donetsk Reactive Factory, Ukraine
**After ball-milling, estimated from SEM micrographs
***Before ultrasonication
Figure 8. SEM micrographs of different types of powders showing a) very spherical Cu powder (Metalpine) with particles in the 15-45 µm range, b) smaller and more irregularly shaped Fe powder (Alfa Aesar) < 10 µm and c) a mix of ball milled Si, B₄C and TiC powder. These powder particles are not spherical at all and some particles are below 1 µm in size. Adapted from a) Paper V, b) I and c) IV.

The electrostatic coating process outlined in Fig. 1 is based on the fact that all powders in the thesis have a native surface oxide. This oxide can in some cases be a problem if it becomes too thick. GO can here be used as a protective coating to decrease the degree of oxidation. This was investigated in Paper V. Here the amount of copper oxides on the Cu powder surface was studied after treatment with oxalic acid (Fluka Analytical, > 99.9%). The oxalic acid treatments of Cu powders were done by exposing the powders to 3 wt. % oxalic acid dissolved in ethanol for 20 min.

Two different types of graphene oxide (GO) and one type of reduced graphene (rGO) were also used in the thesis. GO and rGO do not have well-defined structures. This is because their structure depends on the oxidation, exfoliation and reduction processes that can result in different types and amounts of functional groups. Additionally, the lateral sizes of the sheets and the number of layers that are stacked together can vary. Both types of GO seen in Table 1 were made with a modified Hummer’s method (described in Section 3.1) but used as-received. The GO types were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy, shown in Fig. 9.
The two GO have different morphologies, seen in the SEM micrographs in Fig. 9a and b. The Raman spectra look similar but the GO from Graphenea has slightly larger spacing between stacked sheets seen from the shift to lower 2θ in the X-ray diffractograms. This could indicate that the GO from Graphenea has slightly more functional groups on the faces of the sheets. The Aros Graphene rGO was supplied by Graphmatech [54]. It was produced by a modified Hummer’s method followed by both chemical and thermal reduction [54].

4.2 Powder characterization
All starting materials were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM) and in some cases Raman spectroscopy. These techniques are briefly described in Section 4.4. However, in Paper I, a more detailed powder characterization was carried out for the Cu and Fe powders to determine the zeta potential, flowability and absorbance.
4.2.1 Zeta potential measurements

To coat the powders with GO they must have a suitable zeta potential (see the discussion in Chapters 2 and 3). The zeta potential can be measured with electrophoretic light scattering. It uses an alternating electric field applied over a dispersion of particles. Depending on the surface charge of the particles their response to the electric field will be different. As a consequence, the laser going through the dispersion will have frequency shift compared to a reference beam (see Fig. 10). This frequency shift depends on the movement of the particles and can be related to properties of the particles in the suspension such as the zeta potential. This can be done for multiple pH values to study the pH-dependence of the zeta potential. In this study a Zetasizer Nano ZS from Malvern Panalytical was used to measure the zeta potentials of the powders and GO at various pH values after 60 s sedimentation.

![Figure 10. Schematic illustration of electrophoretic light scattering used for zeta potential measurements. Reprinted from ref. [55] with permission from Elsevier.](image)

4.2.2 Powder flowability

Powder flowability describes how well a powder flows and how powder particles interact with each other when not in a liquid. Factors that influence the powder flowability include the shape and size of the powders, the porosity, density, electrostatic behavior, humidity and the oxide surface layer, especially for metal powders. The flowability can be measured in a number of ways, but in this thesis a revolution powder analyzer (RPA) from Mercury Scientific was used. The technique uses a rotating drum half-filled with powder with a light source that can shine through the container. The silhouette of the powder is then recorded by a camera on the other side making it possible to measure the angles before and after the powder creates avalanches as the drum is slowly rotated. The surface fractal, which is how even the powder surface is, was also recorded. The rotational speed was 0.5 rpm and values for 100 avalanches were recorded and averaged.
4.2.3 Absorbance and reflectance measurements

Additive manufacturing with L-PBF requires that the powder can absorb the laser light. As will be discussed below, some metals such as Cu and Ag have a very low absorption for the wavelengths (1060-1070 nm) typically used in L-PBF. The absorbance can be improved by a GO-coating. Determining how much a material absorbs, reflects, or transmits light at various wavelengths can be done in a number of ways. In this thesis, the reflectance of dry powders was measured by covering a tape with powder followed by measurements in a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer. The powder coverage of the tapes was inspected afterwards using light optical microscopy. It did not matter if a white or black tape was used, which also indicates good coverage. Absorbance measurements were done on GO-water dispersions after coating experiments to qualitatively compare how much GO was remaining after mixing with metal powders at various pH. For this an Ocean Optics spectrometer and the Spectrasuite software with a Mikropack DH-2000-BAL deuterium and halogen lamp as light source were used.

4.3 Coating of powder with GO

For all powders, experiments were carried out to evaluate if GO could be coated using electrostatic interactions as described in Fig. 1. Suitable pH ranges for coating were determined based on experiments, IEP values in literature and Pourbaix diagrams. The experiments to determine suitable coating pH values were carried out in a beaker with magnetic stirring or in a vial mixed with a vortex plate. The coating of GO could be seen from the solution changing from yellowish brown to clear. Additionally, the presence of GO on the powder surface was confirmed with SEM and Raman spectroscopy.

When a suitable pH window had been established, the coating process for larger powder batches used in L-PBF was carried out in a rotary evaporator, see Fig. 11. The rotary evaporator uses a rotating round bottom flask partially submerged in a heated water bath, connected to a vacuum pump and condenser to evaporate the liquid, and to mix the GO dispersion and metal powder. Since all liquid is evaporated it is possible to determine the GO concentration in the coated powder based on the GO concentration of the liquid and the weight of the liquid and metal powder. In this thesis, the concentration was generally kept between 0.1-0.5 wt. % GO compared to metal. After coating, the powder was dried in a vacuum oven at 60 °C overnight.
4.4 Material synthesis

The coated powders were used to print Cu and MnAl(C) with L-PBF in Papers II and III. Some preliminary but not published results on printing with other powders such as 316L stainless steel and AlSi7Mg are also described in Chapter 5. As will be shown below, however, it was very difficult to coat TiC, B₄C and Si in Paper IV and the composite powders were instead mixed by ball milling. Since coating by electrostatic forces was not possible, there was no need to use a graphene material with many oxygen-containing functional groups. Therefore, rGO was used instead of GO in Paper IV. The composite was made by a RHP process. The two methods are briefly described below.

4.4.1 Laser powder bed fusion

Laser powder bed fusion (L-PBF) is an AM technique. It is also often referred as selective laser melting (SLM). L-PBF is a bottom-up synthesis method that starts with a feedstock powder. The geometry of the print is created digitally and divided into layers of the desired thickness. The powder is spread out over a build plate with the chosen layer thickness using a blade, brush, or roller. Therefore, powder flowability is important as the applied powder layer has to be smooth and dense. The powder is subsequently melted/fused by a laser in the pattern of that specific layer using a scanning mirror. After this, the build plate is lowered with the same distance as the layer thickness and a new
powder layer is applied from the powder feed supply and melted again [57]. This process is repeated until the part is completely solidified as shown in Fig. 12.

Since the powder has to absorb the energy of the laser to be melted, the reflectance of the powders, and wavelength of the laser are of great importance. The most common wavelength used for commercial L-PBF printers is around ~1060 nm (marked with the red line in Fig. 13). This is also the wavelength used in this thesis. The absorbances of powder beds are much higher than that of a polished surface of the same material. This is because most of the photons are not reflected back immediately but can instead be reflected multiple times as the light is scattered into the powder bed. For each reflection, a portion of the photons are absorbed [59, 60]. Fig. 13 shows the absorbance in the 330-1150 nm range for a number of metal and alloy powders. As can be seen, the absorbance of Cu is relatively low at 1060 nm, making it difficult to print with this type of lasers. For oxidized and aged metal powders, generally the absorbance becomes slightly lower in the visible-near infrared (VIS-NIR) range and higher in the ultraviolet (UV) range [61]. This can have a negative impact on the L-PBF process using 1060 nm wavelength lasers which is in the NIR. Printing of materials with a low absorbance can be a challenge and a modification of the powder surface can be done to improve the printing process. In Paper II, the Cu powder has been coated with GO to significantly increase the absorbance.
Figure 13. Absorbance of different metal and alloy powder beds. Reprinted from ref. [61] with permission from Elsevier.

The build chamber is most often kept in inert atmosphere to avoid oxidation during melting. In this thesis argon was used for all prints. In addition to the layer thickness, there are a number of parameters associated with the laser that greatly affect the L-PBF process both productivity-wise but also the density and microstructure of the part. However, the main parameters that are investigated in this thesis are: laser power \( P \), scanning speed \( v \), hatch distance \( h \) and the aforementioned layer thickness \( t \). The laser power is the power of the laser, and the scanning speed is the speed by which the laser moves across the powder bed. The hatch distance is the distance between two adjacent laser scans as it is scanned in a raster pattern to melt a larger area. These four parameters can be combined to estimate the volumetric energy density (VED) from the laser using the equation (1) usually given in the unit J/mm\(^3\).

\[
E = \frac{P}{v \cdot h \cdot t} \tag{1}
\]

In this thesis, laser powers and scanning speeds ranging between 50-500 W and 100-1000 mm/s, respectively, have been investigated depending on the material. Additionally, a 0.07 mm hatch distance and layer thicknesses of 0.02 or 0.03 mm have been used. For melting even larger areas they can be segmented in different ways. In Papers II and III, a stripe pattern was used with a width of 5 mm and the scanning patterns were rotated 67° for each new layer. The raster pattern together with the stripe segmenting is illustrated in Fig. 14. Two different printers have been used, an AconityMIDI equipped with 500 W
fiber laser for the Cu powder and an EOS 100 M equipped with a 200 W fiber laser for the Al-alloys.

![Schematic illustration showing a cylinder being melted](image)

*Figure 14. Schematic illustration showing a cylinder being melted. Adapted from the supplementary information to Paper III.*

The high heating and cooling rates of several thousand degrees per second [62], as well as partly re-melting or annealing of previous layers give the parts produced by L-PBF a very unique microstructure. The parts can have anisotropic properties and form metastable phases. Additionally, new type of defects arise that are not common in traditional metallurgical processes. These have to be addressed to minimize their negative influence on the properties of the printed part and the printing process itself [57]. Some of these are lack of fusing pores, keyhole pores, spatter, balling, delamination, and evaporation of low boiling point elements. A serious problem may be cracking in the build, which will be detrimental to the mechanical properties. Cracking in L-PBF can be caused by stresses from the thermal cycling of the material during the print process. Additionally, they can also be caused by solidification cracking (also known as hot-cracking) that occur at the final stage of solidification of the melt [63]. An example, where cracking is a problem is L-PBF of MnAl(C) [64, 65], a potential magnetic material [66]. In Paper III, MnAl(C) powder coated with GO is used to decrease the degree of cracking.
4.4.2 Reactive hot pressing

Reactive hot pressing (RHP) is a type of consolidation technique often used for ceramic materials. It uses chemical reactions together with high applied pressure to consolidate powders into larger parts [67]. Because of the chemical reaction, the consolidation can often occur in a single step and the temperature can be below the normal sintering temperature. It is also much quicker than normal sintering processes. In this thesis TiC, B₄C and Si powders were RHP into TiB₂-SiC composites according to the chemical reaction:

\[ 2\text{TiC}_{0.8} + \text{B}_4\text{C} + 2.5\text{Si} \to 2\text{TiB}_2 + 2.5\text{SiC} + 0.1\text{C} \]

The slight carbon excess in the reaction was used to minimize the reaction of the carbon additives with the ceramic matrix during the process. Prior to RHP the starting powders was ball milled in a zirconia jar with 10 mm zirconia balls (10:1 ball to powder ratio) at 600 rpm for 3 h. The powders were mixed with the carbon additives using a polyvinylpyrrolidone (PVP) solution employing sonication, and subsequently ball milled using 4 mm zirconia balls at 300 rpm for 30 min. RHP was done at 1850 °C and 30 MPa for 4 min in a graphite die and argon atmosphere. After preheating at 500 °C for 10 min a heating rate of ~100 °C/min was used to reach 1850 °C.

4.5 Materials analysis

4.5.1 Electron microscopy

Electron microscopy techniques are a group of imaging methods that use an electron beam instead of photons. The electrons can be focused with magnetic lenses and accelerated to controlled wavelengths. Scanning electron microscopy (SEM) uses a focused electron beam in the range of 2-20 kV which raster an area of the sample. Electrons undergo inelastic and elastic scattering with the sample in the interaction volume and the electrons that are emitted from the sample are detected, counted, and assigned as an intensity to a pixel. The atomic numbers from different elements and topologies give contrast to the image. In this thesis, SEM was used to characterize the powder morphologies before and after coating of GO. Additionally, it was used to characterize the microstructure and presence of GO in the polished cross-sections and fractured surfaces of consolidated samples. Three different SEM microscopes have been used in this thesis, a Zeiss Merlin, a Zeiss LEO 1530, and a Zeiss LEO 1550.

Higher resolution can be achieved in transmission electron microscopy (TEM), where electrons are accelerated to 200-300 kV and probe the sample in the transmission mode. This means that the detector is on the other side of
the sample compared to the electron source. Because of this, the samples have to be thin and were therefore prepared using a Zeiss Focused Ion Beam (FIB) SEM Crossbeam 550 with a Ga ion-sculptor gun and an Omniprobe 200 to ion mill a thin lamella of the sample. The TEM can both use a focused and parallel beam and various detectors to create different contrasts. In this thesis a FEI Titan Themis 200 TEM with probe corrector was used to investigate potential carbon sheets in the grain boundaries of the printed and RHP materials.

In both SEM and TEM, the incoming electron beam can excite electrons in the material that in turn create characteristic X-rays. These can be detected using an energy dispersive X-ray detector (EDS) and this can be used to analyse the elemental composition of the sample. This was used in the thesis to compare the oxygen contents and elemental compositions for different samples. In the SEM a X-Max 80 mm² silicon drift detector was used and, in the TEM, a SuperX EDS detector was used.

4.5.2 Diffraction

Diffraction techniques are non-destructive and are used to analyse phases, crystal sizes, crystal orientations and textures. X-ray diffraction (XRD) uses the interference that occurs between the photon waves and the periodic ordering of atoms in a crystal structure. This occurs when the distance between atomic planes is similar to the wavelengths of the X-rays. At specific angles depending on the distance between parallel atomic planes, constructive interference will occur based on Bragg’s law, which can be detected as peaks in the diffractogram. The position of the peaks and their amplitudes relative towards each other give information about the crystal structure and potentially preferential orientation of the grains. In this study, a Bruker TwinTwin and D8 Powder X-ray diffractometer were operated in Bragg-Brentano focusing geometry to do θ-2θ measurements of atomic planes parallel to the substrate. The diffractometers were operated at 40 kV and 40 mA while using Cu Kα (1.5406 Å wavelength) radiation for all measurements. X-ray diffraction was used in this study to characterize the crystal phases of powders, consolidated parts, and texture of L-PFB printed samples.

More localized diffraction information can be achieved using an electron beam in the SEM with an electron back-scatter detector (EBSD) since the interaction volume is much smaller for electrons compared to X-rays. It uses the backscattering of electrons that are diffracted from atomic planes in the material that give rise to so-called Kikuchi patterns. Adding the known crystal phases to the software makes it possible to assign a crystal phase and orientation to every pixel. Therefore, maps of the distribution and orientation of the grains for all the phases in the material can be constructed. In this thesis, a
Nordlys Max EBSD detector was used in combination with Aztec HKL software. To enhance the signal, the samples were tilted 70° with respect to the incoming electron beam. A final polishing with colloidal silica was done after diamond suspension polishing to achieve a surface with minimal deformation to improve the quality of the Kikuchi patterns.

4.5.3 Raman spectroscopy

Raman spectroscopy is a non-destructive analysis technique that gives information about the vibrational modes of different type of bonds that are Raman-active in the material. The type of bonds that are Raman active are those that change the polarizability. Raman uses a monochromatic light from a laser to irradiate the sample. Most of the photons are elastically scattered (Rayleigh scattering) and do not change wavelength. However, a few of the photons interact with vibrational modes of the material and the energy of the photons are shifted to lower (Stokes lines) or higher energies (anti-Stokes lines). This shift can be detected and gives information about the material. Raman spectroscopy is commonly used to characterize carbon materials and especially different graphene-derivatives [68]. In this thesis a InVia Raman microscope from Renishaw, was used to detect GO on the metal powders, map the distribution of the GO sheets on the powders and investigate changes in the GO and rGO that occurred during the coating, L-PBF and RHP processes. A laser wavelength of 532 nm and low enough power not to cause observable changes in the Raman spectra during the measurements were used.

4.5.4 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) uses monochromatic photons to ionize the material and excite photoelectrons that are ejected from the sample. The energy of the photoelectrons is measured and based on the difference in energy compared to the photons and the work function, their ionization energies can be calculated. Based on the chemical environment of the specific atom, there will be small shifts in the ionization energy depending on the chemical environment of that specific atom e.g., if it is an oxide, carbide, or pure metal. The mean free paths of the generated photoelectrons are very short and therefore this technique only probes a depth of a few nm of the surface. The XPS measurements in this thesis were done with a Ulvac-PHI Quantera II scanning XPS microprobe, using Al Kα radiation. XPS was mainly used to characterize the surface oxide of metal powders in the presence and absence of a GO-coating. Sputter profiles using Ar+ ions were done for heavily oxidized surfaces. To analyse powders in the XPS they were first pressed into an indium foil.
5 Results and discussion

5.1 Evaluation of the GO-coating process

To evaluate the GO-coating process outlined in Figs. 1 and 7, detailed coating experiments were performed on the pure Cu and Fe metal powders. Additionally, some examples of successful GO-coating on alloys (316L, MnAl(C) AlSi7Mg) and unsuccessful coatings experiments for a mixture of TiC, B4C and Si powders will be presented. In Sections 5.1-5.3, the powders referred to as Cu (A) and Cu (B) are those from Alfa Aesar and Metalpine (see Table 1), respectively.

5.1.1 GO-coatings on metal powders

Zeta potential measurements were done on the fine Cu (A) powders in solutions between pH 4.2 and 11.3 (Fig. 15). A majority of the larger Cu powder particles sedimented too fast to allow measurements. Therefore, only the smallest particles from this powder contributed to the zeta potential measurement. As can be seen in Fig. 15, the Cu powder has a positive zeta potential below about pH 9. For pH values above the IEP, the zeta potential is negative. This is similar behavior as for the general metal oxide depicted in Fig. 7 (Section 3.6).

Figure 15. Zeta potential measurements for graphene oxide (Graphenea) and Cu (A) powder from Alfa Aesar. Adapted from Paper I.
An IEP between pH 9 and 10 for the native Cu oxide on metal particles agrees with previously reported values for copper (hydr)oxides [24]. The result indicates that it should indeed be possible to use the native oxide of Cu metal powder particles to create electrostatic interactions with GO sheets for pH values below about 9. In Fig. 15 it can also be seen that GO has a negative zeta potential for all measured pH values, as expected. In order to investigate the interactions between Cu powder and GO sheets, a series of mixing experiments were done, shown in Fig. 16. GO dispersions of 0.01 wt.% GO were adjusted to different pH values. From the Pourbaix diagram in Fig. 5a, it can be seen, that CuO has a stable region in the pH range of about pH 4 to pH 12-13 (depending on the ion concentration). All mixing experiments were therefore carried out between pH 4.2 and pH 11.3 using 10 g GO solution and 5 g Cu powder. Before addition of the Cu powder (top row), the GO dispersions in Figs. 16 are clearly darker at higher pH values. In a second step, Cu powder was added and mixed for 1 min (middle row in Fig. 16). After mixing, the powder has sedimented. The water phase (bottom row) is now transparent for pH values between pH 4.2 and 8. This suggests that most of the GO in this pH range is present in the sedimented Cu powder. Meanwhile, some GO is still found in the water phase between pH 8.9 and 9.5, while the water solutions look similar to before the addition of powder for pH 10.3 and 11.3 suggesting that GO remains in solution. This was confirmed by absorbance measurements of the solutions seen in Fig. 16b and c.
Figure 16. a) Coating experiments at pH values between 4.2 and 11.3 showing GO dispersions before (top row) and after (middle row) mixing with Cu powder. The bottom row in a) shows the solutions after mixing. Absorbance measurements of the remaining liquid are shown in b). The pH-dependent absorbance at wavelength 250 nm is shown in c). Adapted from Paper I.

SEM micrographs of the Cu powders after mixing at pH 4.2, 6.5 and 11.3 are shown in Fig. 17. For the Cu powder particles mixed at pH 4.2 (Fig. 17a, b), GO sheets can be observed that are tightly adhered to the surface (shown with red arrows). Between these sheets small particles on the surface can be observed that are attributed to formation of oxides. The powder coated at pH 6.5 (Fig. 17c, d) also shows GO sheets on the surface of the Cu powders (shown with red arrows). Since the GO sheets are not sticking out from the surface, the presence of GO can mostly be seen from wrinkles on the sheets. However, for the powder coated at pH 11.3 (Fig. 17e, f), which is above the IEP, no GO sheets could be observed on the surface of the powders. This is agreement with the predictions based on Fig 15 and the coating experiments in Fig. 16.
Similar coating experiments to those on Cu in Fig. 16 were also done using Fe powders. The zeta potential for the Fe powder could not be measured because the powder sedimented too fast. Literature data, however, report IEP values between pH 8.3-9.5 for hematite (see Fig. 6) and 6.4-8.0 for magnetite [24]. This suggests that GO coating should be possible for pH below these values. Based on the Pourbaix diagram in Fig. 5c, we should expect an oxide phase to be stable down to around pH 4-5 depending on the ion concentration and corrosion potential. The coating experiments were carried out in the pH range from 4.2 to 11.3 and the results are shown in Fig. 18. At pH values lower than 8.9, the solution becomes more transparent after mixing. This means that the GO sheets have attached to Fe particles and sedimented with them to the bottom of the vials. The results show that GO-coated Fe powder particles can be obtained for a pH below the IEP [12].
At pH 8.9 and above, the color of the GO dispersion is similar before and after mixing. This means that the GO sheets remain in dispersion even after mixing with the Fe powder. This can also be observed as a volume increase for the Fe powder when comparing the samples at pH 11.3 and pH 4.2-8 (Fig. 18a). The volume increase after GO-coating is more apparent for the Fe powder compared to the Cu powder. This can be due different powder particle sizes and densities of the metals. Another notable difference between Fe and Cu is that more of the GO has attached at pH 8.9 and pH 9.5 which can be seen in the absorbance measurements comparing Fig. 16b,c and Fig. 18b,c. An explanation for this could be that the IEP of the native Fe oxide is slightly lower than that of the native Cu oxide. This is in agreement with previous reported results of iron (hydr)oxides [24]. SEM micrographs of the Fe powder mixed with GO at pH 4.2 and pH 11.3 are shown in Fig. 19. Similar to the Cu powder, GO sheets can be observed on the Fe powder surface mixed at pH 4.2 (shown with
red arrows in Fig. 19b). GO sheets could not be observed on the Fe powders mixed at pH 11.3. This agrees with the color changes of the GO dispersion and the absorbance measurements in Fig. 18.

Figure 19. SEM micrographs of Fe powders after mixing in GO dispersion at pH a,b) 4.2, and c,d) 11.3. The GO sheets are shown with red arrows in b). Adapted from the supplementary information to Paper I.

As can be seen in Fig. 16c and 18c, the absorbance does not become zero after mixing (except at pH 4.2). This suggests that some GO sheets remain in solution without interactions with the powder surfaces. In order to investigate the effect of the powder to GO ratio a series of tests were carried out with different amounts of Fe and Cu powders (Fig. 20). For Cu 10, 5, 3.33 and 2 g powder was mixed with 0.01 wt.% GO dispersion at pH 7.3. This corresponds to GO/metal concentrations of 0.01, 0.02, 0.03 and 0.05 wt %, respectively. After mixing for 1 min, we can see that the solution becomes increasingly more transparent with more metal powder (Fig. 20a). This behavior could also be observed for the Fe powder (Fig. 20b). The results suggest that the GO sheets primarily attach to uncoated metal surfaces. When most of the powder surface area is covered with GO, additional bonding of GO sheets is inhibited or at least slowed down significantly. This further strengthens the concept of coating through electrostatic forces outlined in Fig. 1.
To demonstrate that GO sheets are present on the metal powder surface, Raman spectroscopy was carried out on Cu and Fe powders mixed with GO at pH 4.2, 6.5 and 11.3. As can be seen in Fig. 21, no peaks can be observed for the uncoated Cu reference powder. For the coated Cu powders mixed at pH 4.2 and pH 6.5, the broad peaks at around $\sim1353\text{ cm}^{-1}$ (D-band) and $\sim1600\text{ cm}^{-1}$ (G-band) as well as overtone bands in the $\sim2600$-$3200\text{ cm}^{-1}$ region can be attributed to the presence of GO sheets on the surface [43]. For the Cu powder mixed at pH 11.3 no peaks from GO can be observed in agreement with the results above. Peaks from copper oxides can also be seen in the Raman spectra. The peak around $\sim299\text{ cm}^{-1}$ can be attributed to CuO, while the peaks at $\sim149\text{ cm}^{-1}$, $\sim217\text{ cm}^{-1}$ and $\sim540\text{ cm}^{-1}$ originate from Cu$_2$O [69]. The broad peak around $\sim627\text{ cm}^{-1}$ could be attributed to both CuO and Cu$_2$O. The powder mixed at pH 11.3 show mostly peaks for CuO while the samples coated with GO at pH 4.2 and 6.5 have reduced peaks from CuO but peaks for Cu$_2$O also appear. For the Fe powder in Fig. 21b, similar results are obtained regarding the presence of GO peaks at pH 4.2 and 6.5, while no GO is present on the powder mixed at pH 11.3. The peaks at around $\sim665\text{ cm}^{-1}$ can be attributed to iron (hydr)oxides [70]. XRD of the Cu and Fe powder after coatings shows additional peaks from crystalline oxides (see supplementary information to Paper I). In summary, the results above show that Cu and Fe particles can be coated with GO by a tuning of the pH below the IEP. Most likely, similar results can be obtained on most metals with a thin surface oxide.
5.1.2 GO-coating of alloy powders

The concept involving electrostatic GO-coating on powder surfaces was also investigated together with a few alloys including 316L stainless steel, MnAl(C) and AlSi7Mg. The 316L stainless steel forms a native oxide mainly consisting of chromium oxide. Based on Fig. 6, it can be predicted that the IEP for this powder is found about pH 8, slightly lower than for Fe. Furthermore, the Pourbaix diagram for Cr in Fig. 5d suggests that a chromium oxide should be stable between pH 4 and 14. However, these pH values can shift some depending on Cr-ion concentrations and the corrosion potential. Initial test showed that it was indeed possible to coat 316L stainless steel in the pH 5-6 range. Detailed coating experiments outside this range was not conducted but highlights the predictive power of this model using the literature values for IEP and Pourbaix diagrams.

GO-coating of MnAl(C) powders was also investigated in Paper III. Here we expect that the native surface oxide should be Al-rich both in air [46] and water. As can be seen in Fig. 6, aluminium oxide has similar IEP as Cu and Fe around pH 9. Additionally, the Pourbaix diagram in Fig. 5b show that Al₂O₃ should be stable between pH 4 and 9. Therefore, initial coating experiments were done between pH 6 and 9. The powders were able to be coated at these pH values indicating that the surface oxide is indeed Al-rich (since Mn show an IEP of around pH 5). EDS measurements showed that the oxygen concentration was lowest for pH 7.7. Therefore, this pH was used to coat the powder used in in the L-PBF study in Section 5.4.2. Finally, we investigated if GO-coatings can be applied to an Al-based alloy (AlSi7Mg). Here we also expect the surface oxide to be Al-rich, and similar observations were made as for the MnAl alloy with successful coating of GO at pH 7.7. The coating experiments suggest that many, potentially most alloys can be coated with GO
but that the optimal pH values for the coating will depend on the composition of the outermost surface oxide layer.

5.1.3 GO-coating of ceramic powders

GO-coating experiments were also conducted with a mixture of ball milled TiC, Si and B₄C ceramic powders. Here, Si is expected to have a surface oxide of SiO₂, which according to Fig. 6 should have an IEP at about pH 2. This means that the surface is negatively charged for most pH values. B₄C and TiC are carbides, which as described in Section 3.5 have a negative surface charge for most pH (IEP<3). B₄C may have a native boron oxide surface but also this oxide is negatively charged at most pH. TiC may have a thin titanium oxide layer with an expected IEP at pH of about 6. In summary, from the discussion in Chapter 3, we should expect it to be very difficult, or impossible to coat these materials with GO at most pH values. This was investigated by a coating experiment at pH 6 (see Fig. 22a). Before mixing with the powder, the GO solution has a yellowish-brown colour. After mixing the dispersion become very dark due to the presence of ceramic powder particles. Since the powder particles were so small and of lower density than the previously studied metal powders, the sedimentation process was much slower. However, after one week the solution was still yellowish-brown from the GO. This shows that the GO is not coated on this powder mixture as predicted above. The dried powders after mixing were also inspected in SEM (Fig. 22b), but no GO sheets could be detected on the surface of the particles. The results suggest that coatings on ceramic materials can be a challenge as many native surface oxides are acidic with low IEP values.

Figure 22. a) TiC, Si and B₄C mixed in GO dispersion and b) SEM micrographs of powders after mixing and drying. Unpublished work.
5.2 Coating with a rotary evaporator

The coating experiments in Section 5.1 above are based on mixing of powder and GO in vials where the solution was decanted and filtered to remove uncoated GO sheets. For a more controlled process, a coating system with a rotary evaporator was constructed (see Fig. 11). SEM micrographs of Cu (A) and Cu (B) powders after coating in this evaporator with 0.1 wt. % GO can be seen in Fig. 23.

![SEM micrographs of Cu (A) and Cu (B) powders coated with 0.1 wt. % GO in the rotary evaporator. GO sheets are shown with red arrows.](image)

Comparing the morphologies of these powder and those in Fig. 17, the GO sheets are now more easily observed in Fig. 23 (shown with red arrows). The GO sheets can be seen sticking out from the surface, as wrinkles on the surface, or completely wrapping the powder particles. Mapping of the GO-coated Cu (A) powders using Raman spectroscopy are shown in Fig. 24. The map shows the intensity of the peaks between 1000-1800 cm$^{-1}$ which includes the D- and the G-band of GO. It can be seen that even on the low intensity region there is still signal from GO. This means that most of the Cu particles are coated with GO using the rotary evaporator system.
Other metals and alloys, such as AlSi7Mg, MnAl and 316L stainless steel, were also successfully coated with GO in the rotary evaporator. SEM micrographs of GO-coated powder surfaces are shown in Fig. 25. The micrographs show the presence of GO (some shown with red arrows) on the powder particles. These powders and Cu were processed in L-PBF (results shown in Section 5.4).

The GO-coating process described above has been patented by Graphmatech AB [71]. A coating system based on the results in the thesis has been constructed at Graphmatech AB for a more large-scale production of powder. The coated powders used in Papers II and III were obtained from Graphmatech AB.
5.3 Properties of GO-coated powder

Coating of a powder with GO will change some important powder properties. Metals such as Cu and Ag with high reflectance will most likely absorb more light when coated with GO. This may enable a more efficient additive manufacturing of Cu using L-PBF. Furthermore, a GO-coating may change the rheology of the powder and influence, for example, flowability and spreadability. Finally, graphene-related materials are known to be strong diffusion barriers. GO-coated powder may therefore be more oxidation resistant with a longer shelf-life than uncoated powder.

5.3.1 Reduced reflectance of GO-coated Cu powder

Cu has a high reflectance and is therefore difficult to process in L-PBF, as displayed in Fig. 13. Therefore, the effect of GO on the reflectance of the powders was investigated, as shown in Fig. 26. Both the uncoated reference Cu(A) powder and Cu(B) powder showed around ~61% reflectance at 1070 nm which is similar to the absorbance of 30-40% shown in the Fig. 13 (as there is no transmittance).

Coating the powders with GO decreases the reflectance. The reflectance at 1070 nm as a function of GO concentration is shown in Fig. 26a. As can be seen, the reflectance decreases with increasing GO concentration. At 1.5 wt.% GO the reflectance has been decreased by 66 %. The reflectance for wavelengths between 300 and 1200 nm is shown for the Cu(B) powder in Fig. 26b. This powder has a much larger particle size than Cu(A), which means that the surface to volume ratio is smaller. Therefore, a 0.1 wt.% GO-coating was enough to decrease the reflectance from 61.3 % to 27.6 %.

![Figure 26. Reflectance measurements of powders showing a) reflectance at 1070 nm as a function of GO concentration for Cu(A) and b) reflectance as a function of wavelength for Cu(B) for uncoated reference and 0.1 wt. % GO-coated powder. Adapted from Paper I.](image-url)
5.3.2 Influence of GO-coatings on flowability

Another important powder property is the flowability of the powders. GO sheets have weak interactions and GO-coated powders may therefore exhibit completely different flowability compared to uncoated powder. In the thesis, the Cu, MnAl and AlSi7Mg powders showed a good flowability. In contrast, a poor flowability was observed for the Fe powder and the 316L stainless steel powder for metal-injection moulding (90 % < 20 µm). The flowability was evaluated with a revolution powder analyzer (RPA) and the results are summarized in Fig. 27. Major improvements to the flowability could be seen for the 316L stainless steel powder, while only small improvements were observed for the Fe powder. For the 316L powder both the angles at which avalanches occur and the rest angle afterwards are lower for the coated powder, which indicate improved flowability. The surface fractal is a measure of how uneven the surface is. For a perfectly even surface the surface fractal would be one. A significant reduction of the surface fractal from 6.64 of the reference to 2.81 was observed for the coated 316L powder. This also shows that the coated powders have significantly better flowability. In contrast, the Fe powder in Fig. 27b only showed minimal improvements in flowability and the surface fractal was only decreased from 4.31 to 4.11 while the avalanche angle was very similar. The coated powder had slightly lower rest angle, which may explain the increased avalanche energy.

![Figure 27](image)

*Figure 27. Flowability measurements using revolution powder analyzer (RPA) for reference and GO-coated a) 316L stainless steel and b) Fe powders showing changes in the surface fractal, avalanche/rest angles and break/avalanche energies. Adapted from Paper I.*

5.3.3 Oxidation of GO-coated Cu powder

The formation of surface oxides may be a problem in some processes such as L-PBF where clean and oxygen-free components are needed for optimal properties. An example is Cu, where oxygen can have a detrimental effect on electrical and thermal conductivity [72]. Potentially, a GO-coating can decrease the oxidation rate and prolong the shelf-life of the powder. This was
investigated in Paper V together with the possibility to reduce the oxide thickness by etching with oxalic acid. The results show that etching of the powder with 3 wt. % oxalic acid in ethanol indeed decreased the thickness of the surface oxides, but it was difficult to clean off web-like remains on the powder originating from the oxalic acid (shown in SEM micrographs in Paper IV). Furthermore, the etching of oxalic acid prior to GO-coating resulted in worse adhesion of the GO sheets leaving some areas uncoated.

For the oxidation study, GO-coated Cu powder together with a combination of the oxalic acid treatment (OX) and GO was used, either with the GO-coating first (GO-OX) or the oxalic acid treatment first (OX-GO). The oxygen contents in these three powders were analysed with SEM and EDS after 9 months storage in air using polyethylene bottles without desiccants. After 9 months, the surface of the uncoated reference powder was very rough due to oxidation, while the surface of the GO-coated powder seemed to be unaffected (see SEM images in Paper V). The OX-GO powder showed areas with rough oxidized appearance, which can be attributed to the problems to coat a surface with oxalic acid residues. In Fig. 28, average oxygen contents from the EDS analysis of coated powders are compared with an uncoated reference (Ref) and an uncoated oxalic acid etched powder (OX). As can be seen the oxygen content in the GO-coated powder is significantly lower compared to for the untreated reference and the OX treated powders. However, it should be noted that remains of oxalic acid could be observed on the surface of the OX-treated powder which can contribute to the oxygen content, and all oxygen in Fig. 28 is therefore not necessarily originating from copper oxides.

![Figure 28](image.png)

*Figure 28. Oxygen content measured with energy dispersive X-ray spectra (EDS) for Cu powders 9 months after different treatments. Ten measurements on different particles were made for each powder batch. The average oxygen content is shown together with error bars showing the standard deviation. The powders were stored without desiccants in polyethylene bottles and air atmosphere. Adapted from Paper V.*
In addition to the EDS analysis, the powders were also investigated with XPS to analyse the surface chemistry. XPS spectra from sputter profiles of the powders showing the Cu 2p\(_{3/2}\) peak can be seen in Fig. 29. The uncoated reference powder has the main peak around 932.6 eV which can be attributed to either metallic or monovalent Cu. A shoulder to the left of this peak can be seen at 934.2 eV which is from divalent Cu in the form of CuO and Cu(OH)\(_2\). Shake-up peaks originating from the divalent Cu can also be observed in the 939-945 eV range. With increased sputter time the peak at 934.2 eV and the shake-up peaks decrease in intensity indicating removal of a CuO/Cu(OH)\(_2\) layer (which should be the outer copper oxide [73]). As can be seen for the powders treated with GO, the shoulder at 934.2 eV and shake-up peaks are much smaller and immediately disappear when sputtering for only 30 seconds, indicating a thinner oxide layer. The peak at 930.2 eV can be explained by the presence of Cu oxalates [74, 75]. The results from Fig. 28 and 29 show that the GO-coating can be used to protect powders from long term oxidation in air and therefore increase the shelf-life. The oxalic acid etching decreases the oxide thickness, but residual oxalic acid is detrimental for the coating process. A more efficient cleaning process is therefore needed.
Figure 29. XPS depth analysis of Cu powders after 9 months of storage without desiccant in polyethylene bottles and air atmosphere. The Cu 2p$_{3/2}$ peak with corresponding shake-up peaks for a) reference powder, b) OX powder, c) GO powder, d) GO-OX powder and e) OX-GO are shown with sputter times using 500 V Ar-ions for 0, 30, 90, 270 and 630 seconds. Adapted from Paper V.

5.4 Additive manufacturing with GO-coated powder

The GO-coated metal and alloy powders described in Sections 5.1-5.3 were used as feedstock in AM with L-PBF. The most important results in Papers II and III are presented in this section. The Cu powder was printed using an AcornityMIDI printer and the 316L stainless steel was printed using a GE Concept Laser MLAB printer. The MnAl and AlSi7Mg powders were printed using an EOS 100 M printer.
5.4.1 L-PBF of Cu

A problem with L-PBF of Cu is the low absorbance of this material at the wavelength used in most printers today. This leads to a low energy density during printing and incomplete melting of the powder. This problem is only enhanced by the high thermal conductivity of copper making it even more difficult to form a stable melt pool [76]. To investigate how the decreased reflectance of the GO-coated Cu powder affects the L-PBF printing of Cu, three different powders (0, 0.1 and 0.3 wt. % GO) were used in Paper II. The prints were made with Cu powder from Sandvik Osprey, but they showed similar decreases in reflectance when coated as those from Heraeus due to similar particle sizes. The prints were made with a laser power of 200-500 W. SEM micrographs of polished cross-sections of a print with uncoated powder and 0.1 wt. % GO powder are shown in Fig. 30. Both samples were printed using the same parameters: 500 W, 660 mm/s scanning speed, 0.07 hatch distance and 0.02 mm layer thickness. As can clearly be seen, the print with uncoated powder (Fig. 30a) displays a lot of darker features attributed to lack-of-fusion pores. However, the build with the Cu powder coated with 0.1 wt. % GO show almost a completely dense microstructure. Using the program ImageJ, the density of the print with uncoated powder was estimated to 89.0 % and for the GO-coated powder 99.8 %. Increasing the GO concentration to 0.3 wt. % GO did not improve densification further due to an increased amount of spattering (discussed later in Section 5.4). It was not possible to significantly increase the density of the print with uncoated powder with other printing parameters.

![Figure 30. SEM micrographs showing polished cross-sections of L-PBF printed samples using a) uncoated Cu powder and b) 0.1 wt.% GO-coated Cu powder. Using image analysis, the density was estimated to a) 89.0 % and b) 99.8 %. Both samples were printed using 500 W, 660 mm/s scanning speed, 0.07 mm hatch distance and 0.02 mm layer thickness. Adapted from Paper II.](image)

Further investigations were made to investigate the effects of the GO-coating on the texture using XRD and EBSD, as shown in Fig. 31. Both EBSD and XRD were carried out on the plane orthogonal to the build direction. The X-ray diffractograms in Fig. 31d clearly show a difference in texture for the different feedstocks. The build with uncoated Cu powder shows a diffractogram
you would expect for a random orientation of the grains. The 0.1 wt. % GO sample on the other hand shows a stronger <110> texture along the build direction. Finally, with 0.3 wt. % GO, the printed sample shows a stronger <100> texture.

Figure 31. Diffraction results from L-PBF printed Cu samples. EBSD orientation maps (print direction out of plane) are shown for a) uncoated reference, b) 0.1 wt. % GO and c) 0.3 wt. % GO samples. Scalebars are 200 µm. X-ray diffractograms of the three samples are also shown in d). Adapted from Paper II.

These observations were also confirmed in the EBSD maps (Fig. 31a-c). The build printed with uncoated reference powder shows small grains that are randomly distributed in the solidified parts of the sample and there are large pores (black) in the sample. This indicates incomplete melting. In contrast, the EBSD map from the 0.1 wt. % sample is practically free from pores with many large grains with a clear <110> texture. For the 0.3 wt. % GO build, more grains with the <001> orientation can be observed in agreement with the XRD results.

Vickers hardness and electrical conductivity were measured for the L-PBF printed samples and are shown in Fig. 32. The electrical conductivity is given as percent when compared to the International Annealed Copper Standard (IACS) of 58 MS/m. As expected, the low density of the reference printed
with uncoated powder resulted in low Vickers hardness and poor electrical conductivity. Both printed GO samples showed significantly higher hardness of 75.7 HV and 70.8 HV for the 0.1 and 0.3 wt. % samples, respectively. This is mainly attributed to the increase in density. The electrical conductivities were 75.1 % and 77.8 compared to the IACS for the 0.1 wt. % sample and 0.3 wt. % GO sample, respectively. The increase compared to reference is expected to mainly be due to the higher density and larger grain size. It is important to note that the samples were measured in the as-printed state. Annealing of the samples is expected to increase the conductivity further.

The carbon and oxygen contents of the printed samples were determined with LECO combustion analysis and shown in Table 2. As can be seen, the carbon content is the same for the reference and the 0.1 wt. % GO sample, but the oxygen concentration is significantly reduced for the latter. However, the 0.3 wt. % GO printed sample showed a higher carbon content of 0.018 wt. % and the oxygen content was decreased further down to 0.010 wt. %. This shows that with low concentrations, most of the GO will be removed during processing with a high-power laser. The decreased oxygen content can be explained by a chemical reaction between GO and oxygen in Cu under the formation of CO₂. However, if the GO concentration is increased to at least 0.3 wt. % some of the carbon will remain in the printed parts while still providing a significant reduction in oxygen content.
Table 2. Carbon content from L-PBF printed Cu samples using 500 W laser. Measured using LECO combustion analysis. Adapted from Paper II.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon (wt. %)</th>
<th>Oxygen (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Cu</td>
<td>0.005</td>
<td>0.075</td>
</tr>
<tr>
<td>0.1 wt. % GO</td>
<td>0.005</td>
<td>0.017</td>
</tr>
<tr>
<td>0.3 wt. % GO</td>
<td>0.018</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Cu forms no carbides and the interstitial solubility of carbon in Cu is in the ~8 ppm range just below the melting point. Furthermore, the solubility decreases with decreasing temperature [77]. This means that carbon dissolved in the melt pool during printing should diffuse out to the grain boundaries or top surface during cooling. This carbon could potentially form graphene in the grain boundaries during the cooling process. In fact, graphene formation on Cu surfaces from a hydrocarbon source is a well-known process [78]. A Cu-graphene composite may be a superior material for applications where high electrical and thermal conductivities are required. For this reason, the 0.3 wt. % sample in Table 2 with the highest carbon content was investigated with TEM and SEM to identify any remaining GO or any graphene formed in the grain boundaries. In Fig. 33a,c, SEM micrographs of a fractured cross-section from the 0.3 wt. % GO sample are shown. In the fractured surface a few pores can be seen with sheet-like structures (marked with red arrows).
EDS mapping of these areas (Fig. 33b) shows that they are indeed carbon-rich (green colour) with a significantly lower oxygen content compared to the GO used in the powder coatings. This indicates that some of the sheets can survive the L-PBF process and that they are reduced during processing. This was confirmed with Raman spectroscopy (see Fig. 33d) of a pore region in the fractured cross-section of a build printed with 0.3wt. % GO (“Printed 0.3G”). Compared to as-received GO or the GO-coated Cu powders, the Raman spectrum of the sheets inside the printed material shows a significantly more pronounced peak in the 2D region around ~2700 cm\(^{-1}\), additionally the intensity ratio between the D and the G-band has been reduced and the peaks width have decreased. It has been shown before that GO can be reduced by lasers with a similar wavelength, but the power of the laser was than lower by several orders of magnitude [79]. TEM was also used to investigate the carbon inside the material. As can be seen in Fig. 34, carbon-filled inclusions in the size range of 10 nm to several hundred nm, consisting of partly layered structure could be observed in the material. However, no carbon or any indication of graphene in the grain boundaries could be discovered.
5.4.2 L-PBF of MnAl(C)

MnAl is an interesting material for potential magnetic applications due to its good ferromagnetic properties. [66]. The magnetic properties stem from the metastable tetragonal \( \tau \)-phase which is formed after annealing and quenching of the alloy. Up to \( \sim 1 \) wt. % carbon is often added to this material to stabilize the \( \tau \)-phase [80]. Additive manufacturing is an interesting method to produce components of magnetic materials since the texture and microstructure can be controlled [81, 82, 83]. However, cracking has been reported as major problem when MnAl(C) is printed with L-PBF [65, 64]. This is due to a mix of thermal stresses, cracks originating from lack-of-fusion defects and stresses due to the presence of secondary phases.

A GO-coated powder will change the laser absorbance and also the thermal history during the printing process. This may have beneficial influence on the crack formation. This was investigated in Paper III, where the effect of the GO-coating on the printability, microstructure and magnetic properties was studied. In general, the GO-coated feedstock resulted in prints with more porosity (shown in Figure 35b). This can be mainly attributed to increased amount of spattering. However, a significant reduction in crack density was
observed in the GO-coated prints. The crack reduction was estimated to 35 % using image analysis of the polished cross-sections.

The cracks seemed to pass through some features (shown with red arrows) in Fig. 35c, d. Higher magnification of the features can be seen in Fig. 35 e, f). Based on the XRD and EBSD results of the as-printed samples, the features can be attributed to a mixture of two phases: $\gamma_2$-phase and $\varepsilon$-phase surrounded by a matrix of the $\varepsilon$-phase (see Paper III for details). The phase diagram (shown in supplementary information to Paper III) suggests that the two-phase features can be formed during direct solidification from the MnAl melt. The amount of the $\gamma_2$-$\varepsilon$ features is similar in both samples but the size, morphology, and distribution of them are different. The print with uncoated powder has a
larger number of smaller features than the print with the GO coated powder. This can be explained by the increased heat absorption provided by the GO-coating leading to a higher temperature in the melt pool and a different cooling rate. The presence of these $\gamma_2$-$\epsilon$ features can induce stresses during thermal cycling in the print process and promote cracking in the printed material.

As can be seen in the SEM micrographs in Fig. 36, a GO-coated powder resulted in a different microstructure compared to uncoated powder. Etching with Keller’s agent (described in Paper III) revealed a cellular microstructure and melt pool boundaries (marked with red arrows). The width of the cells for the reference sample printed with uncoated powder was calculated to $0.43 \pm 0.07 \, \mu m$ while the coated sample showed a much larger cell width of $0.71 \pm 0.12 \, \mu m$ which can be attributed to faster cooling rates in the uncoated material. The cells also seem to grow towards the middle of the melt pool.

![Figure 36. SEM micrographs of etched cross-sections of as-printed MnAl(C) a) reference and b) 0.2 wt. % GO samples revealing the cellular microstructure. Melt pool boundaries are shown with red arrows. The build direction (BD) is up in the images. Adapted from Paper III.](image)

After heat-treatment at 560 °C for 5 min followed by quenching, XRD analysis (see Paper III) shows that the texture difference of the as-printed parts is removed and both prints form the metastable ferromagnetic $\tau$-phase in addition to some minority phases. The magnetic properties of the heat-treated printed parts were measured using vibrating sample magnetometry (VSM) and the hysteresis curves are shown in Fig. 37 for measurements along the build direction. The sample printed with uncoated powder showed a coercivity of 139 kA/m and remanence of 33 Am²/kg while the GO-coated sample showed a coercivity of 130 kA/m and remanence of 30 Am²/kg. The difference could be attributed to slight increased amount of the ferromagnetic $\tau$-phase.
5.4.3 L-PBF of 316L

GO-coated 316L stainless steel powder was also used to print builds in L-PBF. Printing with a GE concept MLAB printer and tensile tests (sample geometry 4C20 according to ASTM E8M standard) was done at Sandvik contracted by Graphmatech AB. As described in 5.3.2, a GO-coating improves the flowability of a 316L powder, but the uncoated powder used in this study had a flowability good enough for printing. No major issues with spattering were observed for the coated powder. Two concentrations of 0.05 wt. % and 0.2 wt. % GO were investigated in the printing experiments. They resulted in miniscule improvements in density but even the uncoated 316L powder produced builds with >99.9 % density. X-ray diffractograms of the printed parts with the diffraction vector parallel to the building direction are shown in Fig. 38a. All prints showed the presence of a single austenitic phase but a stronger <110> texture could be observed for GO-coated powders compared to the uncoated powder. A SEM micrograph from a cross-section of a sample printed with 0.2 wt% GO is shown Fig 38b. The microstructure shows the typical cellular features usually observed in L-PBF of 316L [84, 82]. No difference in cell width was observed between prints from uncoated and coated powders.
Tensile tests were performed on samples built either parallel or perpendicular to the build direction. The mechanical properties such as yield strength, ultimate yield strength, elongation and Young's modulus are shown in Table 1. As can be seen, the samples are more ductile when built vertically but have higher yield strength and ultimate tensile strength when built horizontally. This is also commonly observed in literature and is due to the elongated grains along the build direction [85]. With GO-coated powder, the yield strength and ultimate tensile strength increased by up to ~12% with a slight increase in Young’s modulus. The ductility was, however, reduced with increasing GO concentration. LECO combustion analysis of the samples showed 0.013, 0.025 and 0.075 wt. % carbon in the uncoated reference, 0.05 wt. % and 0.2 wt. % GO samples, respectively. This increase in carbon content was larger than for Cu (see Table 2). A possible explanation for this could be the increased solid solubility in the austenite phase and presence of carbide forming elements in the 316L stainless steel.
Table 3. Mechanical properties of printed 316L stainless steel reference (uncoated), 0.05 wt. % and 0.2 wt. % GO samples obtained from tensile tests. Tensile tests were done by Sandvik contracted by Graphmatech AB with sample geometry 4C20 according to ASTM E8M standard. Unpublished work.

<table>
<thead>
<tr>
<th>Material</th>
<th>Orientation</th>
<th>$\sigma_f$ (MPa)</th>
<th>$\sigma_u$ (MPa)</th>
<th>$\varepsilon$ (%)</th>
<th>$E$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref</td>
<td>Horizontal</td>
<td>602 ± 2</td>
<td>691 ± 3</td>
<td>34 ± 0</td>
<td>185 ± 7</td>
</tr>
<tr>
<td></td>
<td>Vertical</td>
<td>546 ± 3</td>
<td>616 ± 1</td>
<td>40 ± 1</td>
<td>185 ± 13</td>
</tr>
<tr>
<td>0.05 wt.%</td>
<td>Horizontal</td>
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<td>711 ± 6</td>
<td>33 ± 1</td>
<td>196 ± 3</td>
</tr>
<tr>
<td></td>
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<td>566 ± 1</td>
<td>631 ± 2</td>
<td>37 ± 1</td>
<td>193 ± 4</td>
</tr>
<tr>
<td>0.2 wt.%</td>
<td>Horizontal</td>
<td>673 ± 4</td>
<td>759 ± 7</td>
<td>31 ± 0</td>
<td>198 ± 3</td>
</tr>
<tr>
<td></td>
<td>Vertical</td>
<td>598 ± 4</td>
<td>665 ± 2</td>
<td>35 ± 1</td>
<td>196 ± 6</td>
</tr>
</tbody>
</table>

5.4.4 L-PBF of AlSi7Mg

Some preliminary studies were also carried out on GO-coated AlSi7Mg powders to determine their printability. In general, the powders behaved similar to uncoated reference, but an increased spattering could be observed with the GO-coated powder for very high scanning speeds, i.e., above 1000 mm/s. In general, 99 % densities and higher could be achieved for GO-coated powders similar to uncoated AlSi7Mg powder. In Fig. 39a, images of some L-PBF printed cylinders from 0.2 wt. % GO-coated AlSi7Mg powder are shown. Fig. 39b show a light optical microscopy image of a polished cross-section of sample with 99 % density printed with 100 W laser power, 400 mm/s scanning speed, 0.05 mm hatch distance and 0.02 mm layer thickness.

Figure 39. a) Photo of printed parts from 0.2 wt. % GO-coated AlSi7Mg powder. b) Light optical microscopy image of polished cross-section of sample with 99 % density, marker with red arrow. Unpublished work.
Scanning TEM micrograph and corresponding EDS maps are shown in Fig. 41. They show that the printed AlSi7Mg coated with 0.2 wt. % GO has a cellular structure with Si enriched in the cell boundaries. However, no carbon enrichment in the boundaries could be observed. The uncoated reference showed similar cellular structure. This microstructure is also observed in the literature for similar Al-Si-Mg alloys [86, 87].

X-ray diffractograms of L-PBF printed reference and GO-coated AlSi7Mg samples are shown in Fig. 41. The presence of an Al phase and a Si phase can be observed. The uncoated reference sample display a much stronger <111> texture and the GO-coated sample show a stronger <100> texture. Since the samples diffractograms were normalized against highest intensity. The Si peaks appear to be of lower intensity for the uncoated sample, but this is just because the <111> peak of this sample is so strong while the coated samples have higher intensity on all other Al-peaks.
5.4.5 Influence of GO-coatings on spattering and texture – some general observations

A general observation for all the printing experiments was increased spattering and/or denudation with the GO powders compared to the uncoated feedstock. This was especially apparent at higher GO concentrations, where a lot of particles could be observed to be flying away from focused the laser spot and melt. This problem also generally increased with increasing scanning speeds. This was not necessarily a problem for the powders that could easily be fully densified such as 316L stainless steel or the AlSi7Mg alloy. However, for MnAl(C) which already had a problem with spattering with uncoated powder, this problem became worse with GO-coated powder. This resulted in lower density prints for the few print parameters that were investigated (see Fig 35b). The exact reason for the increased spattering is unclear but a hypothesis is that the coated powder particles form a “core-shell” structure, which absorbs more energy than an uncoated particle. When the powder melts, some of the GO sheets in the shell may crack giving rise to a directed release of melt resulting in spattering of the powder particle. Additional print strategies to reduce the amount of spattering needs to be done to achieve higher density parts of MnAl(C) printed from GO-coated powders.

It is also apparent that the GO has a significant impact on the energy absorption and melting behaviour. As a result, it affects the texture of the printed parts. This texture differences could be observed for all metals and alloys...
studied above. The GO is also reduced to some degree by the laser, and many GO sheets are also destroyed. The formation of gases could be a contributing factor to the hypothesis about spatter in the paragraph above. Increasing the laser power will inherently cause more damage to the GO sheets and less of the carbon material will remain inside the printed materials. As the GO is destroyed it can also react with oxides and reduce the overall oxide content inside the printed materials under the formation of CO$_2$.

5.5 Reactive hot pressing of TiB$_2$-SiC composites with rGO

TiB$_2$-SiC composites are interesting materials in the group of ultra-high-temperature-ceramics due to their high toughness at elevated temperatures and can for example be used for thermal protection in hypersonic vehicles and in propulsion systems [88]. A TiB$_2$-SiC composite can be manufactured by reactive hot pressing (RHP) of a TiC-Si-B$_4$C powder mixture. An interesting question is then if the presence of a graphene-related additive can affect the high temperature consolidation process. This was investigated in Paper IV. As described in Section 5.1.3, it was not possible to coat a ball milled mixture of TiC, Si and B$_4$C. Since oxygen-containing functional groups were not needed for the electrostatic interactions, reduced graphene oxide (rGO) was used in Paper IV instead of GO. An advantage with rGO is that it contains less oxygen-containing functional groups which can produce gaseous CO$_2$ during hot pressing. rGO may also give a lower oxygen content in the final product compared to GO. Carbon black was also studied in an attempt to separate the effects of added carbon and rGO sheets. Concentrations in the range of 0 to 7.4 wt. % of the additives were investigated.

After RHP at 1850 °C the main two phases were TiB$_2$ and SiC for all samples (diffractograms shown in Paper IV). A peak attributed to agglomerated carbon could be observed at 20 around ~26° for the 3.8 wt. % carbon black samples but not for the 3.8 wt. % rGO samples. SEM images and EDS maps of the RHP composites are shown in Fig. 42. The light grey phase in the SEM images is attributed to TiB$_2$ while the darker grey phase is SiC. The black regions in Fig. 42c are agglomerated carbon. A large number of white particles can also be seen in the SEM image in Fig. 41a (yellow in the EDS map in Fig. 42d). They can be attributed to zirconium oxide particles from the ball milling process. The samples with rGO or carbon black contain almost no zirconium oxide. Additionally, the reference without carbon additives showed the presence of SiO$_2$. This shows that the carbon additives can help to reduce oxides in the material. Fig. 42 shows that the sample sintered with rGO had a much coarser microstructure. The thermal conductivity of the composite is dependent on the
amount of grain boundaries in the sintered sample. An image analysis shows that the carbon black and reference sample had 36 % and 19 % more TiB2-SiC boundaries, respectively, compared to the rGO sample.

Figure 42. SEM micrographs (top row) and corresponding EDS maps (bottom) for a,d) reference, b,e) rGO and c,f) carbon black reactively hot pressed TiB2-SiC composites. Red arrow in a) indicates zirconium oxide particle. Red arrow in c) and white arrow in f) indicates agglomerated carbon. White arrow in d) show an area with increased oxygen concentration. Adapted from Paper IV.

SEM micrographs of fractured surfaces (shown in Paper IV) indicated a morphology difference between the three samples. Sheet-like structures in the fracture surfaces of both rGO and carbon black samples could be observed. This shows that at least some of the carbon additive has survived the consolidation process. Thermal conductivities of the RHP composites are shown in Fig. 43. Carbon black did not significantly improve the thermal conductivity at any concentrations. For the rGO however, a 50 % increase in thermal conductivity could be observed at 3.8 wt. % rGO. Further increasing the rGO content decreased the thermal conductivity and the samples became more similar to those of carbon black. The fracture toughness and the hardness of the composites are shown in Fig. 44. Similar trends as seen for the thermal conductivity could be observed. Carbon black did not improve the properties significantly at any concentration. However, for moderate amounts of rGO the hardness and fracture toughness could be improved by up to 20 %.
Figure 43. Thermal conductivity of the TiB$_2$-SiC composites as a functional of added carbon content. Adapted from Paper IV.

Figure 44. Mechanical properties of the TiB$_2$-SiC composites as a function of added carbon content for rGO (graphene) and carbon black. Adapted from Paper IV.
Similar to the tests in L-PBF, the results from the RHP study show that rGO can be used to reduce the oxide phases in the material. It seems that significant parts of the added rGO can survive the high temperatures and the RHP process. A clear difference was observed between carbon black and rGO regarding their influence on the thermal and mechanical properties of the TiB₂-SiC composites. As can be seen in Fig. 42, carbon black formed larger agglomerates, while this was not observed for the rGO sample at 3.8 wt. %. This is likely a major reason for the difference in mechanical properties and thermal conductivity. As the rGO content is increased it starts to agglomerate which results in worse dispersion and worse mechanical- and thermal properties. This highlights the important of good distribution of the additive inside a composite material.
6 Conclusions and outlook

The results in this thesis show that it is possible to use the native metal oxide on selected metal and alloy powder particles to coat them with graphene oxide (GO) sheets using electrostatic forces in aqueous dispersions. It was also possible to use Pourbaix diagrams and zeta potential trends to predict suitable coating parameters for other metals and alloys. Materials with negative zeta potentials for most pH such as TiC, Si and B4C could not be coated with GO using electrostatic forces. Instead, other techniques like ball milling had to be used to disperse reduced GO in a powder mixture. Coatings with controlled GO concentrations could be achieved with a rotary evaporator.

The GO-coating could improve the flowability of the powder, but the effect seemed to differ for various metals, alloys, and powder size distributions. The GO-coating can also protect powders from oxidation and prolong the shelf-life. This was demonstrated for GO-coated Cu, which was stored for 9 months in air without significant oxidation compared to uncoated powder which showed higher oxygen content. Oxalic acid was able to dissolve the surface oxides on Cu, but the acid was difficult to remove from the powder surface which resulted in less good GO-coatings. The GO-coated powders also showed reduced reflectance. When processing the GO-coated Cu powders in L-PBF, the reduced reflectance made it possible to print fully dense parts using merely a 500 W laser. This is a significant difference compared to L-PBF printing of the uncoated powder which resulted in approximately ~10 % porosity using the same printing parameters. For other materials in L-PBF, the GO-coating led to significantly different solidification behaviour and texture. For the MnAl(C) alloy the GO coating could reduce detrimental cracking during L-PBF printing by 35 %. Some of the GO could be observed in the L-PBF printed material as sheets which had been reduced to rGO, but other carbon inclusions of different shapes could also be observed. The carbon content in the printed parts indicates that most of the GO had been destroyed and not incorporated in the printed parts. The carbon content was lower when higher laser power was used. The carbon in the GO could also be seen to reduce some of the oxides inside the material which decreased the overall oxygen content after printing.
When reactively hot-pressing the TiC, Si and B₄C powders at 1850 °C to form TiB₂-SiC composites, the added carbon additives also decreased the amount of oxides in the final product. The hardness, fracture toughness and thermal conductivity could be improved for samples containing 3.8 wt. % rGO but decreased or was unchanged when using a carbon black additive or 7.4 wt. % rGO. This highlights the importance of the dispersion of the additive but also the properties of the additives themselves.

The results presented in this thesis give rise to new research questions that should be investigated to further understand the behaviour of and expand the application areas of this type of GO-coated powders. Some examples are:

- **Systematic studies of the flowability when using different particle size distributions and GO concentrations for the same material**
  The flowability of the GO-coated powders could be significantly improved. However, more systematic studies using different particle size distributions and various GO concentrations for the same material are needed to further understand the reasons for the improved flowability.

- **Detailed study of the laser and GO interactions during L-PBF**
  The GO-coated powders had increased absorption but the interactions with a high-power laser in L-PBF need to be studied further to develop process parameters optimized for GO-coated powders and to reduce e.g., spattering. This could be done by high-speed-imaging of the printing process and monitoring the local temperature during the printing.

- **Investigations of reducing the GO after the coating process**
  It was shown that rGO could be used to significantly improve the mechanical properties and thermal conductivity. At the same time, GO was shown to increase spattering in L-PBF. Investigations on reducing the GO to rGO after being coated on the powders should be made to study the effect on the adhesion of the sheets to the particle surface and the effects the subsequent synthesis processes such as L-PBF.

- **Further studies using GO coated MnAl(C) powders to increase the density of the printed parts**
  The GO-coated powders were shown to be able to decrease the detrimental cracking in MnAl(C). However, further studies using different process parameters should be done to improve the density of L-PBF printed parts of this promising magnetic material.
Sammanfattning på svenska


Ett annat intressant material på grund av dess magnetiska egenskaper är en legering (blandning av metaller) av mangan och aluminium (MnAl), eftersom denna legering inte innehåller sällsynta jordartsmetaller. Genom att tillverka dessa med L-PBF kan man finjustera de magnetiska egenskaperna på ett väl-digt kontrollerat sätt. Dessutom kan man skapa delar med komplexa geometrier som kan förstärka de magnetiska egenskaperna. Ett problem med L-PBF av MnAl är att det lätt bildas sprickor vilket är mycket dåligt för de mekaniska egenskaperna vilket förhindrar användningen i olika applikationer. Beläggningen av grafenoxid på pulverpartiklarna gjorde att smålt- och stel-ningsförloppet i L-PBF påverkades så att sprickbildningen minskade med upp till 35%. Grafenoxidbeläggningen användes också på rostfritt stål (316L) samt en annan aluminiumlegering innehållande kisel och magnesium (AlSi7Mg) och printades sedan med L-PBF vilket bland annat gav förbättrade mekaniska egenskaperna för de printade delarna.

För material som inte har en positiv ytladdning vid några pH, såsom Si och B₄C, måste andra metoder att blanda in grafen som ett additiv användas. Ett sätt är att mekaniskt blanda dem vilket ofta kan leda till att pulverpartiklarna deformeras. Detta görs redan för vissa keramiska pulver för att minska deras
storlek innan de sammanfogas till större komponenter. Ett keramiskt kompositmaterial som är intressant då det kan klara mekaniska påfrestningar vid höga temperaturer är en blandning av titanborid (TiB\(_2\)) och kiselkarbid (SiC). Det är av intresse att öka den termiska ledningsförmågan vilket minskar risken för sprickbildning. I denna avhandling har jag studerat tillverkning av TiB\(_2\)-SiC komposit från en blandning av TiC, B\(_4\)C och Si. För att öka den termiska ledningsförmågan har reducerad grafenoxid (rGO) och s.k. carbon black (CB) tillsatts till pulverbländningen. Resultaten visade att endast några få viktsprocent av rGO förbättrade värmeledningsförmågan med 50 %, hårdheten med 16 % och brottseghet med 20 % för detta material. Samtidigt minskade tillsatsen av rGO mängden av föroreningar genom att reducera keramiska oxider vilket är oönskat i det här fallet. Detta bidrog också till de förbättrade egenskaperna.

Sammanfattningsvis handlar denna avhandling om hur olika grafenbaserade material kan fördelas genom att belägga pulverpartiklar och hur detta påverkar de efterföljande tillverkningsprocesserna. Egenskaper för belagda pulver och tillverkade delar har också analyserats. Resultaten som presenteras är baserade på de fem ingående publikationerna och en del opublicerade forskningsresul-
tat.
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9 References


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