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MATERIALS SCIENCE

Incorporation of Graphene-based Materials in Modern Powder-based Processes

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Cover image: Representative SEM images illustrating the versatility of the molecular-level mixing method for depositing graphene oxide onto metallic powder particles with different compositions, sizes, and morphologies. a) Copper spherical. b) WC-Co-Cr porous. c) Inconel 939. d) Copper dendritic.

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Abstract

The incorporation of graphene-based materials into powder-based manufacturing processes offers opportunities to tailor material processing and performance. However, achieving controlled graphene characteristics, retaining its functionality during manufacturing, and developing scalable incorporation methods remain important challenges. This thesis investigates these aspects through graphene oxide (GO) deposition on metallic powders, the retention and tribological performance of graphene-based materials in thermal spraying, and the influence of GO on the laser powder bed fusion (PBF-LB) processing of pure copper.

A molecular-level mixing method was developed to deposit GO onto metallic powder particles using APTES as a coupling agent. Adjusting the APTES concentration and GO loading enabled control over coating characteristics and surface coverage. By adapting the mixing conditions and chemical parameters, the methodology was scaled from 20 to 500 g batches that were repeatedly used to produce 10 kg of GO-coated copper powder.

Graphene retention and tribological functionality were investigated in Al_2O_3 coatings containing graphene nanoplatelets (GNPs), produced by suspension plasma spraying, and GO-containing WC-Co-Cr coatings, produced by high-velocity air-fuel spraying. Graphene-based materials were retained after deposition in both systems but underwent progressive structural and chemical modification during sliding wear. Synchrotron X-ray spectromicroscopy revealed GNPs retention at the alumina tribosurface, accompanied by carbon redistribution and amorphization beneath the wear track. In WC-Co-Cr, GO incorporation reduced the average coefficient of friction, although the lubricating effect diminished with prolonged wear.

For PBF-LB of copper, GO coating reduced powder reflectance and modified the melting behavior. Operando X-ray radiography revealed shallower and less slender keyholes during laser processing. At the same time, complementary metallographic characterization of samples produced using a commercial PBF-LB process indicated a tendency toward wider melt pools, suggesting possible changes in the lateral spreading of molten Cu. GO-coated copper enabled thin-wall fabrication over a broader processing range and exhibited higher relative density than unmodified copper under the investigated conditions. Most of the additional carbon was removed during processing, accompanied by a substantial reduction in oxygen content, suggesting a possible sacrificial role of the GO coating in promoting the reduction of copper oxides, which may contribute to improved wetting and spreading of molten copper.

Overall, the findings demonstrate how controlled integration of graphene-based materials into powder feedstocks can influence manufacturing behavior and material performance, with the selected approach determining whether graphene is retained or its functionality is exploited during processing.

Keywords: Graphene; Graphene nanoplatelets; Graphene oxide; Molecular-level mixing; Powder feedstocks; Thermal spraying; Powder bed fusion - laser beam.

Preface

This doctoral thesis is based on research conducted at the Department of Mechanical Engineering (former Industrial and Materials Science), Chalmers University of Technology, between January 2022 and November 2026. The work was carried out under the supervision of Professor Uta Klement and Associate Professor Jinhua Sun, with Professor Eduard Hryha serving as examiner. This research was supported by Chalmers Foundation and the Centre for Additive Manufacture – Metal (CAM²).

In parts of the thesis, the English was improved using Google Translate and Copilot.

List of the appended papers:

PAPER A: Synchrotron X-ray Spectromicroscopy analysis of wear tested graphene-containing alumina coatings

Antonio Mulone, Plinio Fernandes Borges Silva, Hui Yuan, Karina Thånell, Adam Hitchcock, Uta Klement

Carbon, Volume 227, Article 119245, 2024

<https://doi.org/10.1016/j.carbon.2024.119245>

PAPER B: Controllable Coating Graphene Oxide and Silanes on Cu Particles as Dual Protection for Anticorrosion

Jinhua Sun, Kristoffer H. Martinsen, Uta Klement, Alessandro Kovtun, Zhenyuan Xia, Plinio Fernandes Borges Silva, Eduard Hryha, Lars Nyborg, and Vincenzo Palermo

ACS Applied Materials & Interfaces, Volume 15, Issue 32

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PAPER C: Feasibility study of GO-Coated WC-Co-Cr Porous Powder for Improved Wear Resistance in HVOF Coatings

Plinio Fernandes, Jinhua Sun, Eric Tam, Stefan Björklund, Antonin Riche, Shrikant Joshi, Uta Klement

<https://doi.org/10.1016/j.surf.2026.108721>

Surfaces and Interfaces, Volume 86, Article 108721

PAPER D: Operando X-ray Radiography Analysis of the PBF-LB Process of Graphene Oxide Coated Copper Powder

Plinio Fernandes, Gowtham Soundarapandiyan, William Hearn, Steven Van Petegem, Yunhui Chen, Federico Sket, Jinhua Sun, Eduard Hryha, Uta Klement

In manuscript

PAPER E: Enhancing the PBF-LB Processability of Pure Copper through Graphene Oxide Surface Coating

Plinio Fernandes, Gowtham Soundarapandiyan, Juha Ottelin, Jukka Simola, Jinhua Sun, Eduard Hryha, Uta Klement

In manuscript

Contribution to the appended papers

The author's contributions to the appended papers are described in this section. All the experimental work conducted by the author was planned in consultation with his supervisors and co-authors.

PAPER A: The author was part of the team that conducted the XANES synchrotron measurements at MAX IV. Following the measurements, the author performed the data analysis in collaboration with Antonio Mulone and Adam Hitchcock. The author contributed to the interpretation of the results and participated in the preparation and revision of the manuscript.

PAPER B: The author carried out experimental work related to the Raman measurements and assisted in reviewing and revising the article.

PAPER C: The author carried out experimental work on the GO coating of the WC-Co-Cr powder. The HVAF spraying was performed by Stefan Björklund, and ball-on-disk tests were performed by Antonin Riche. The author did the characterization work and data analysis and wrote the article in collaboration with the co-authors.

PAPER D: The author produced the graphene oxide coated copper powder and participated in the operando synchrotron X-ray imaging experiments together with Gowtham Soundarapandiyan, William Hearn, Steven Van Petegem, Yunhui Chen, Federico Sket, and Uta Klement. The melt pool tracking algorithm was developed by Thiemo Benthien in collaboration with Gowtham Soundarapandiyan and the author. The commercial PBF-LB samples were printed by Juha Ottelin at EOS GmbH facility in Turku, Finland. The author performed the complementary characterization and data analysis and prepared the initial manuscript draft, which was subsequently revised together with the co-authors.

PAPER E: The author produced the graphene oxide coated copper powder and developed the scale-up procedure, with scale-up activities performed by Gowtham Raj Sowrirajan under the author's supervision. The PBF-LB processing of pure copper and GO-coated copper powder was performed by Juha Ottelin at EOS GmbH facility in Turku, Finland. The author performed the complementary characterization and data analysis and prepared the initial manuscript draft, which was subsequently revised together with the co-authors.

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List of abbreviations

8YSZ	8 wt.% yttria-stabilized zirconia
Al ₂ O ₃	Aluminium oxide (alumina)
AM	Additive manufacturing
APS	Atmospheric plasma spraying
APTES	(3-Aminopropyl)triethoxysilane
BJT	Binder jetting
CAM ²	Centre for Additive Manufacture – Metal
CLS	Canadian Light Source
CoF	Coefficient of friction
Cu	Copper
DBC	Direct-bonded copper (power electronics substrates)
DSC	Differential scanning calorimetry
EBS	Electron backscatter diffraction
ESRF	European Synchrotron Radiation Facility
FEG-SEM	Field-emission gun scanning electron microscopy
FIB	Focused ion beam
GIC	Graphite intercalation compound
GNPs	Graphene nanoplatelets
GO	Graphene oxide
GO-Cu	Graphene oxide-coated copper
GO-Cu 1C	Graphene oxide-coated copper with one coating cycle
GO-Cu 3C	Graphene oxide-coated copper with three coating cycles
HVAF	High-velocity air-fuel
HVOF	High-velocity oxy-fuel
LST	Laser surface texturing
MgO	Magnesium oxide
NEXAFS	Near-edge X-ray absorption fine structure
OM	Optical microscopy
PBF	Powder bed fusion
PBF-EB	Powder bed fusion – electron beam
PBF-LB	Powder bed fusion – laser beam
PFIB	Plasma focused ion beam
PMMA	Poly(methyl methacrylate)
ppm	Parts per million
Pure-Cu	Unmodified copper reference
rGO	Reduced graphene oxide
S-HVOF	Suspension high-velocity oxy-fuel
SEM	Scanning electron microscopy
SPS	Suspension plasma spraying
STEM-EDS	Scanning transmission electron microscopy–energy-dispersive X-ray spectroscopy
STXM	Scanning transmission X-ray microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
vol.%	Volume percent
WC–Co–Cr	Tungsten carbide–cobalt–chromium
wt.%	Weight percent
XANES	X-ray absorption near-edge structure
XPS	X-ray photoelectron spectroscopy
YSZ	Yttria-stabilized zirconia

CHAPTER 1

Introduction

1.1 Motivation

Modern manufacturing technologies increasingly rely on tailored feedstock materials to improve processability and component performance [1]. As these technologies are often associated with significant production costs and stringent quality requirements, the development of optimized feedstock materials remains a continuous objective [2]. In this context, graphene-based materials have attracted significant attention due to their exceptional properties, including high tensile strength (~ 130 GPa) [3,4], Young's modulus (~ 1.0 TPa) [5,6], thermal conductivity (~ 5000 W/m.K) [4], and electron mobility ($\sim 2 \times 10^5$ cm²/V.s) [5]. These characteristics make graphene-based materials promising candidates for reinforcing and enhancing ceramics, polymers, and metals [7].

Despite their potential, graphene-based materials are not yet widely used in modern manufacturing processes. This is mainly due to the challenges associated with their incorporation into matrix materials [8]. Achieving homogeneous dispersion, strong interfacial interactions, retention of graphene during processing, and industrially relevant scalability remain difficult [9]. One promising strategy to overcome these limitations is the incorporation of graphene-based materials into powder feedstocks [10]. The high surface area of powder feedstocks provides numerous interaction sites for graphene, making powder particles well suited for its incorporation [11]. Furthermore, many modern manufacturing technologies rely on metallic, ceramic, or cermet powders as feedstock, creating an opportunity to introduce graphene during early stages of component or coating fabrication [12].

Of the available graphene incorporation strategies, achieving both precise process control and industrial scalability remains a major challenge [7]. While some approaches are suitable for processing larger quantities of material, maintaining control over graphene distribution and preserving its structural integrity remain important challenges. In contrast, methods capable of producing or incorporating high-

quality graphene under well-controlled conditions can be difficult to reproduce at larger production scales [13,14]. Therefore, scalable and controllable incorporation strategies are essential to adapt graphene-containing feedstock materials to the requirements of modern manufacturing processes [15].

One important application of graphene-containing powder feedstocks is thermal spraying for the production of wear-resistant coatings [16]. The potential of graphene to improve tribological properties has attracted considerable research interest [17]. However, the elevated temperatures and severe processing conditions inherent to thermal spraying can compromise graphene retention and functionality, underscoring the need for effective incorporation strategies to fully exploit its potential [18]. Another promising application of graphene-containing materials is in laser-based additive manufacturing, particularly for highly reflective metals such as copper [19]. The inherently low laser absorptivity of these materials compromises process stability and restricts the available processing window [20]. To overcome these challenges, surface modification with graphene oxide has been proposed as a means of enhancing laser/material interactions by increasing the absorptivity of the powder feedstock [21]. If successful, this approach could contribute to improved process stability and facilitate the fabrication of high-density copper components [22].

1.2 Research objectives

This thesis investigates the incorporation of graphene-based materials into modern powder-based processes. It addresses incorporation and retention challenges, develops and scales up a controllable graphene oxide coating method, and evaluates its effects on processing and material properties. Thermal spraying and powder bed fusion – laser beam (PBF-LB) are used to assess the method's capabilities and limitations.

1.3 Research questions

This work is based on the following research questions:

- **Q1. How can a controllable and scalable deposition of graphene oxide on metallic powder particles be achieved?**

A molecular-level mixing method was developed to achieve controlled graphene oxide deposition onto metal powders. Controllable deposition relies on tailoring the interactions between the powder surface, the coupling agent, and graphene oxide, enabling regulation of graphene adhesion, surface coverage, and coating characteristics. Beyond achieving control at laboratory scale, the methodology must preserve these characteristics as the powder batch size increases. This requires understanding the processing conditions that influence powder suspension, mixing, and the availability of the functionalizing agent during scale-up. These aspects are investigated through the development and understanding of the molecular-level mixing method in Paper B, followed by the systematic evaluation of the parameters governing its reproducibility and scalability to larger powder batches in Paper E.

- **Q2. To what extent do graphene-based materials remain intact during thermal spraying and subsequent wear, and how does their incorporation affect the tribological properties of the resulting materials?**

Graphene-based materials can enhance the tribological performance of thermal-sprayed materials by acting as a solid lubricant. Their layered structure facilitates sliding between adjacent layers and can reduce interaction between contacting surfaces during wear. Maintaining this functionality requires the graphene-based materials to remain within the material during thermal spraying and subsequent wear. In this thesis, two different graphene-containing thermal-sprayed coating systems are investigated, involving different graphene-based materials, coating matrices, and thermal spray processes. The investigation of these systems provides a broader understanding of graphene retention and tribological behavior in thermal-sprayed coatings, while also considering how graphene-based materials can be protected from degradation under the high-temperature conditions associated with thermal spraying. These aspects are investigated in Papers A and C.

- **Q3. How does coating copper powder with graphene oxide affect laser/powder interactions and the processability in PBF-LB?**

The developed GO coating methodology can modify the surface of the powder feedstock of PBF-LB and therefore influence the interaction between the powder particles and the incident laser energy. This interaction is particularly important for pure copper due to its high reflectivity at conventional near-infrared laser wavelengths and high thermal conductivity, which limit energy absorption and make stable processing challenging. In this thesis, the influence of graphene oxide coating is investigated by considering its effect on the optical response of the powder and its subsequent influence on keyhole behavior, melt pool geometry, and processability during PBF-LB. This enables the relationship between powder surface modification, laser/powder interaction, and copper processability to be evaluated, while also considering whether the benefits introduced at the powder stage are maintained throughout the manufacturing process. These aspects are investigated in Papers D and E, which together provide insight into the potential and limitations of graphene oxide surface modification as a strategy for improving the PBF-LB processability of copper.

The research questions presented in this thesis are addressed by the appended papers, as summarized in the table below:

	Q1	Q2	Q3
Paper A			
Paper B			
Paper C			
Paper D			
Paper E			

CHAPTER 2

Graphene-based Materials

2.1 Structure and properties of graphene

Graphene is a two-dimensional form of carbon material consisting of a single atomic layer arranged in a hexagonal honeycomb lattice. Its successful isolation in 2004 [23] represented a major milestone in carbon nanomaterial research and stimulated the rapid development of the broader field of two-dimensional materials [24,25]. Much of this interest originates from its unique atomic configuration, which gives rise to an exceptional combination of mechanical, electrical, and thermal properties.

The atomic structure of graphene is characterized by sp^2 -hybridized carbon atoms. Each carbon atom is covalently bonded to three neighboring atoms through strong σ -bonds within the two-dimensional plane. The remaining electron occupies a p_z orbital oriented perpendicular to the graphene plane, as illustrated in Figure 2.1. The overlap between adjacent p_z orbitals produces a delocalized π -electron system extending across the graphene sheet [26,27]. The strong in-plane covalent bonding provides graphene with exceptional mechanical stability, while the delocalized electronic structure enables highly efficient charge and heat transport [28,29].

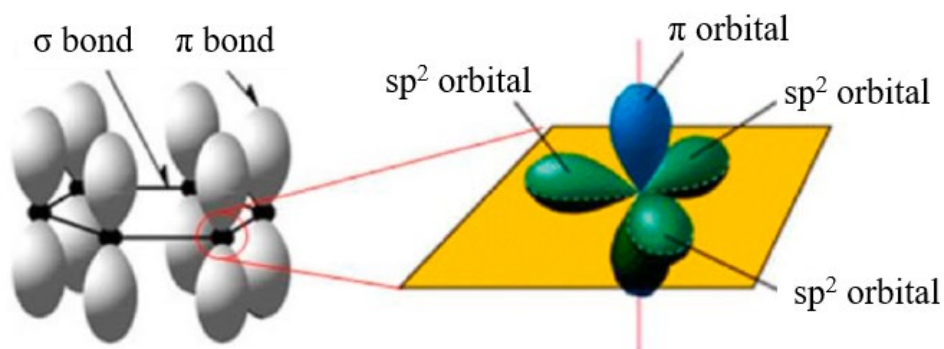


Figure 2.1: Schematic representation of sp^2 hybridization and bonding in graphene, showing the in-plane σ bonds and the perpendicular p_z orbitals involved in π bonding. Reprinted from Ghodrati and Ghomashchi [30] with permission from Elsevier.

These structural characteristics result in remarkable mechanical and transport properties. Defect-free monolayer graphene has an intrinsic strength of approximately 130 GPa and a Young's modulus of about 1 TPa [29]. Its electronic properties are similarly remarkable, with carrier mobilities exceeding $200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ reported for high-quality suspended graphene [31]. Suspended single-layer graphene also exhibits exceptionally high thermal conductivity, with near-room-temperature values of approximately $4,800\text{--}5,300 \text{ W m}^{-1} \text{ K}^{-1}$ [32]. The magnitude of these properties becomes particularly evident when compared with conventional engineering materials: the Young's modulus of steel is typically around 200 GPa [33], while highly conductive metals such as copper and silver exhibit room-temperature thermal conductivities of approximately $400 \text{ W m}^{-1} \text{ K}^{-1}$ [34]. Beyond its mechanical and transport properties, graphene possesses a theoretical specific surface area of $2,630 \text{ m}^2 \text{ g}^{-1}$ [35], can act as an ultrathin protective barrier against oxidation and corrosion of metallic surfaces [36,37], and, when defect-free, is effectively impermeable to most gases [38].

While these exceptional characteristics make graphene highly attractive for technological applications, they are strongly dependent on their structural quality. The properties of graphene can be significantly affected by defects, the number of layers, and the presence of functional groups or foreign atoms [39,40]. Pristine single-layer graphene provides properties closest to the theoretical limits, but its production at large scale and with consistently high quality remains challenging [41]. Consequently, other graphene-based materials have become potential alternatives for applications where large-scale production and processing are important. These materials can retain properties beneficial for composite applications while facilitating their processing and incorporation into other materials [42]. Graphene oxide (GO) and graphene nanoplatelets (GNPs) are two particularly relevant examples and are discussed in the following section.

2.2 Graphene oxide and graphene nanoplatelets

The term “graphene-based materials” encompasses a broad family of carbon nanomaterials structurally and chemically related to pristine single-layer graphene. These materials can differ in characteristics such as the number of layers, lateral dimensions, degree of oxidation, and surface chemistry [43]. Examples include few- and multi-layer graphene, graphene oxide (GO), reduced graphene oxide (rGO), and graphene nanoplatelets (GNPs). Figure 2.2 schematically illustrates single-layer graphene and some of the most common graphene-based materials.

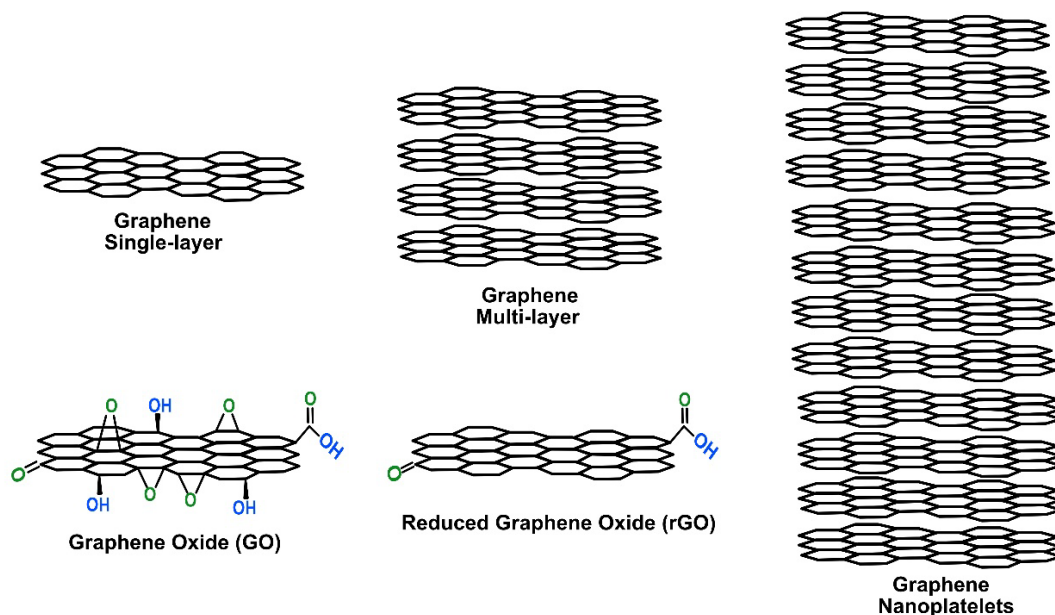


Figure 2.2: Graphene and its derivatives. Reprint from licentiate thesis [44].

Graphene nanoplatelets are carbon nanomaterials composed of multiple stacked graphene layers, resulting in a nanometer-scale thickness and lateral dimensions ranging from hundreds of nanometers to several micrometers [45]. Their structural configuration is not strictly defined, as their dimensions and number of layers can vary considerably depending on the production method. GNPs are predominantly composed of sp^2 -hybridized carbon and generally exhibit a relatively low defect content, allowing them to retain many of the outstanding properties of single-layer graphene, such as high mechanical strength and good thermal and electrical conductivity [46]. Although their intrinsic properties are generally lower than those of single-layer graphene, GNPs offer advantages in terms of production scalability, cost, and processability, making them attractive graphene-based materials for use in commercial composite products [47].

Despite their widespread use, the terminology associated with graphene nanoplatelets is not consistently defined throughout the literature. Terms such as graphene nanoplatelets, graphene platelets, graphene flakes, graphene nanosheets, few-layer graphene, and graphite nanoplatelets are sometimes used to describe materials with very similar characteristics [47]. This inconsistency can be partially attributed to variations in the number of layers and dimensions of these materials [43]. Nevertheless, graphene nanoplatelets, or GNPs, remains an established term in the literature and is used throughout this thesis to refer to platelet-like multilayer graphene materials and, specifically, to the material investigated in Paper A.

In contrast to GNPs, which mostly retain the graphene structure across stacked carbon layers, graphene oxide is a chemically modified graphene-based material characterized by the incorporation of oxygen functional groups into the carbon structure [48]. The oxidation of graphene partially breaks its continuous sp^2 -hybridized

network, introducing sp^3 -hybridized carbon while leaving regions of the original conjugated sp^2 structure intact [49]. Consequently, GO exhibits a chemically and structurally heterogeneous carbon framework rather than the predominantly sp^2 -hybridized structure characteristic of pristine graphene and GNPs [50].

Several structural models have been proposed to describe the arrangement of oxidized and non-oxidized regions in GO, including the types and locations of oxygen functional groups within its structure [51]. Among these, the Lerf–Klinowski model has become one of the most widely adopted descriptions of GO [52]. In this model, the carbon framework comprises aromatic sp^2 regions mixed with oxidized sp^3 domains containing different oxygen functionalities [52]. Hydroxyl and epoxy groups are predominantly associated with the basal plane, whereas carbonyl and carboxyl groups are generally located at the sheet edges [53]. The coexistence and non-uniform distribution of these functionalities contribute to the heterogeneous chemical structure characteristic of GO [50]. Figure 2.3 presents a schematic representation of a modern interpretation of the GO structure based on the Lerf–Klinowski model, incorporating structural features and oxygen functionalities proposed in subsequent studies.

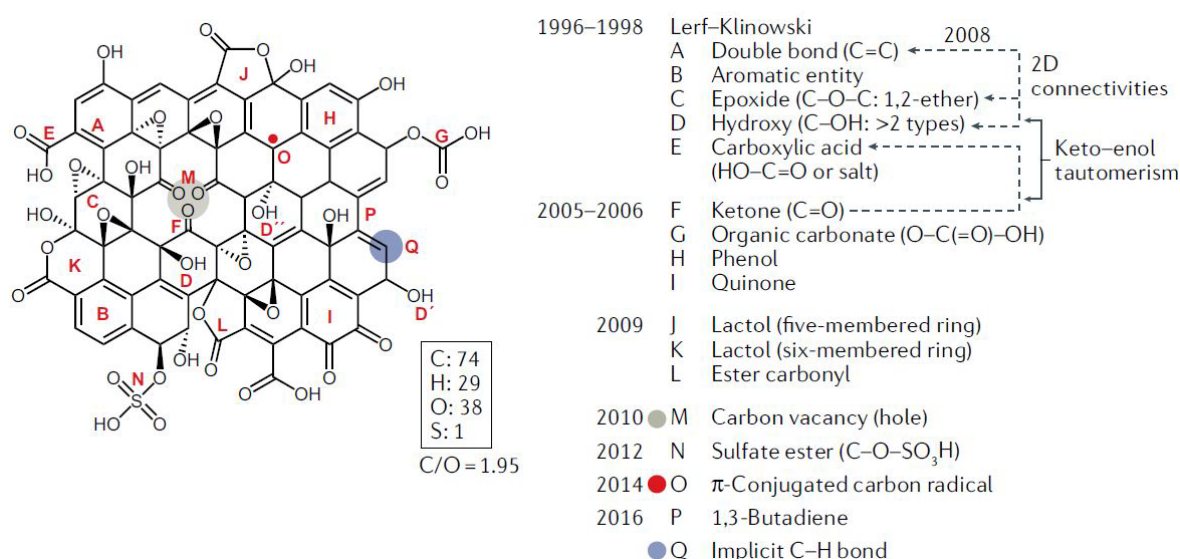


Figure 2.3: Schematic representation of a modern interpretation of the graphene oxide structure based on the Lerf–Klinowski model, incorporating structural features proposed in subsequent studies. Adapted from Guo et al. [53]. Reproduced with permission from Springer Nature.

The introduction of oxygen functionalities substantially alters the properties of graphene, creating a trade-off between intrinsic performance and chemical versatility [54]. Although oxidation disrupts the original graphene structure and reduces some of its exceptional properties, the resulting oxygen functional groups provide GO with characteristics that facilitate its processing, chemical modification, and incorporation into other materials [55]. This combination has contributed to the extensive investigation of GO for composite applications. Importantly, the structure and characteristics of GO, including its degree of oxidation, type and distribution of the oxygen functional groups, and lateral dimensions, are strongly influenced by the method and conditions used for its production [54]. Understanding the synthesis of GO

and other graphene-based materials is therefore essential for controlling their characteristics and suitability for different applications.

2.3 Synthesis routes for graphene-based materials

The synthesis of graphene-based materials can generally be classified into two main approaches: bottom-up and top-down methods [47]. Bottom-up methods involve the production of graphene from carbon-rich gaseous precursors, which are used to grow graphene on specific substrates or catalysts [56]. Graphene produced through bottom-up methods is typically of high quality, with a low defect density and reduced risk of contamination and oxidation due to the well-controlled growth environment. However, the large-scale application of these methods can be hindered by the need for precise control of the processing conditions and, in some cases, by the requirement for a subsequent step to transfer the graphene from the growth substrate, which can introduce defects into its structure [56]. In contrast, top-down methods rely on the isolation or exfoliation of graphene sheets from graphite [57]. These approaches offer advantages in terms of production cost and scalability. However, the characteristics and quality of the resulting graphene are strongly influenced by the conditions employed during the exfoliation process [58]. Figure 2.4 schematically illustrates these two synthesis approaches and one example of the principal routes considered to produce graphene, GNPs, and GO.

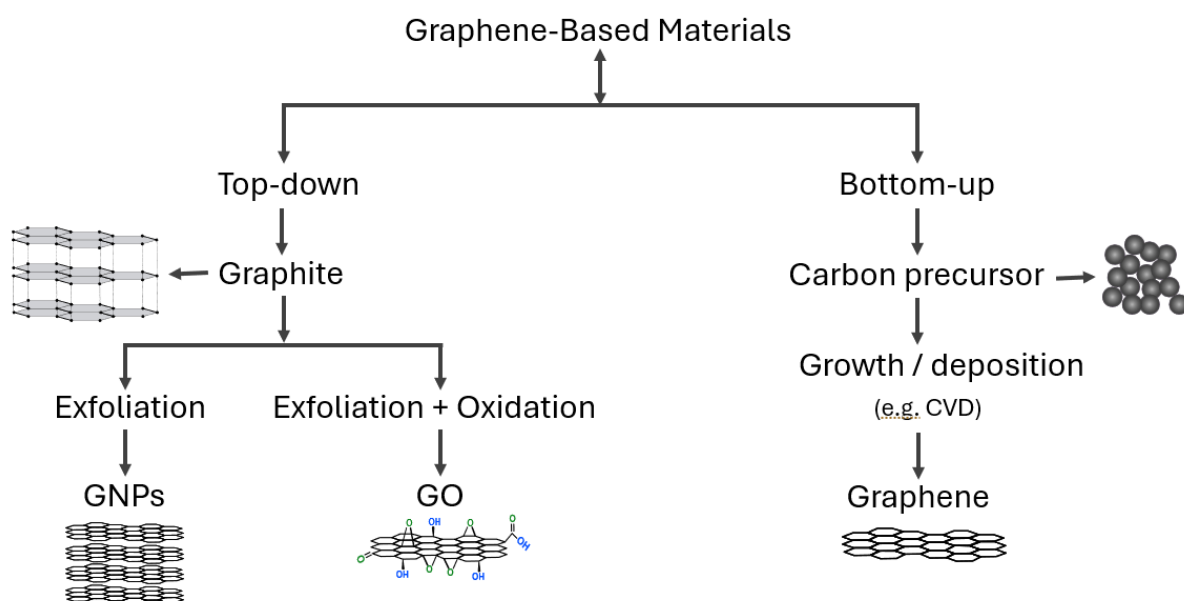


Figure 2.4: Schematic representation of the top-down and bottom-up synthesis routes for graphene-based materials, highlighting the production of graphene, graphene nanoplatelets (GNPs), and graphene oxide (GO).

Graphene nanoplatelets are mainly produced through top-down exfoliation of graphite, using mechanical, liquid-phase, chemical, thermal, or electrochemical approaches [57]. Among these, intercalation-assisted exfoliation represents an important route for large-scale GNPs production. In this approach, acids, ions, or organic molecules are introduced between the graphene layers of graphite to form graphite intercalation

compounds (GICs) [45]. Subsequent expansion of the intercalated species increases the separation between the graphite layers and facilitates their exfoliation into thinner platelets. For example, GNPs can be produced from commercial GICs through rapid thermal expansion followed by ultrasonication in a suitable solvent. During thermal treatment, the intercalated species generate gases that rapidly expand the graphite structure, while subsequent ultrasonication promotes further separation into individual nanoplatelets [46].

Graphene oxide is also a graphene-based material mainly produced by top-down methods involving the exfoliation of graphite but preceded by an oxidation step that is not typically involved in GNPs synthesis [59]. The most widely known process for GO production is the Hummers method, named after its developer, which consists of exposing graphite to a strongly acidic environment, followed by the introduction of strong oxidizing agents and mechanical treatment to promote the exfoliation of GO sheets [60]. Several modifications of the Hummers method, as well as other synthesis routes like the Brodie and Staudenmaier methods, have been developed to improve aspects such as reaction efficiency, safety, scalability, and environmental impact [50].

Although several modifications and improvements to GO synthesis routes have been developed, the main principles of the synthesis remain similar. In general, graphite is exposed to a strongly acidic environment that increases the separation between the graphitic layers, eventually forming a graphite intercalation compound (GIC) [61]. This expanded structure facilitates the penetration of oxidizing agents, which progressively oxidize the graphite from the edges towards its interior. The incorporation of oxygen functional groups further disrupts the interactions between the stacked graphitic layers, while subsequent vigorous stirring or ultrasonication promotes their separation into individual GO sheets [61]. As discussed previously, synthesis conditions also influence the oxidation degree, oxygen functional groups, defect concentration, and sheet dimensions [6]. The presence of oxygen functional groups is particularly important for the surface chemistry of GO, as it enables various chemical interactions and functionalization pathways, as discussed in the following section [53].

2.4 Functionalization and surface chemistry of graphene oxide

The oxidation processes described in the previous section not only facilitate the exfoliation of graphite into GO sheets but also introduce a variety of oxygen functional groups into the carbon structure [51]. The presence of these groups is one of the main advantages of GO since they significantly increase its chemical reactivity compared with pristine graphene by providing multiple sites for subsequent chemical interactions and functionalization [53,55].

The chemical reactivity of GO originates from the different oxygen functionalities distributed across its basal plane and edges. As discussed in Section 2.2, hydroxyl (C–OH) and epoxide groups (C–O–C) are predominantly located on the basal plane, whereas carbonyl (C=O) and carboxyl groups (–COOH) are more frequently

associated with the sheet edges [51,53,62]. However, these functional groups differ considerably in their chemical behavior and therefore provide different reaction pathways for the functionalization of GO [59]. The relative contribution of each functional group to interactions with other materials remains difficult to generalize, as it depends on both the surface chemistry of GO, which can vary considerably depending on the synthesis conditions, and the chemical characteristics of the interacting material [53].

One important functionalization pathway occurs through the reaction of nucleophilic species with epoxide groups on the GO basal plane [63]. As the epoxide ring introduces local strain into the carbon structure, its carbon atoms become more susceptible to nucleophilic attack [63,64]. Nucleophiles such as amines can attack one of these carbon atoms, resulting in the opening of the epoxide ring and the formation of a covalent bond between the nucleophile and the GO surface [65]. During this reaction, the oxygen originally present in the epoxide remains attached to the carbon structure as a hydroxyl group [63,65]. Figure 2.5 schematically illustrates this reaction mechanism, showing the nucleophilic attack of an amine on an epoxide group and the subsequent opening of the epoxide ring. This mechanism provides an effective route for introducing molecules containing nucleophilic functional groups onto GO or for binding GO to materials containing nucleophilic groups.

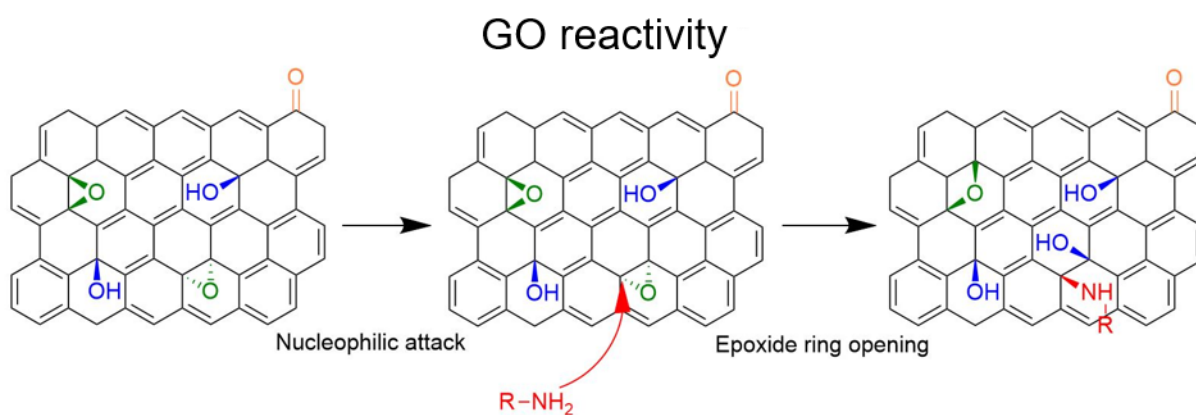


Figure 2.5: Schematic representation of the nucleophilic attack of an amine on an epoxide group on the GO basal plane, resulting in epoxide ring opening and covalent attachment of the amine-containing molecule to the GO surface. Reprint from licentiate thesis [44].

Hydroxyl groups on GO can also participate in functionalization reactions, particularly through condensation with hydrolyzed organosilanes [66]. Organosilanes containing hydrolyzable alkoxy groups can initially react with water to form silanol (Si–OH) groups. These silanol groups can interact with hydroxyl groups on the GO surface and then participate in condensation reactions, leading to the formation of covalent Si–O–C bonds between the organosilane and GO [66,67]. Figure 2.6 schematically illustrates this functionalization pathway, showing the hydrolysis of an organosilane followed by its reaction with hydroxyl groups on the GO surface. This reaction provides another pathway for the functionalization of GO, while the organic group of the organosilane remains available for further interactions. Importantly, the different

reactive sites present on GO allow multiple functionalization pathways to occur without necessarily being mutually exclusive. Reactions involving hydroxyl groups can occur simultaneously with nucleophilic reactions involving epoxide groups, further demonstrating the versatility of GO surface chemistry [68].

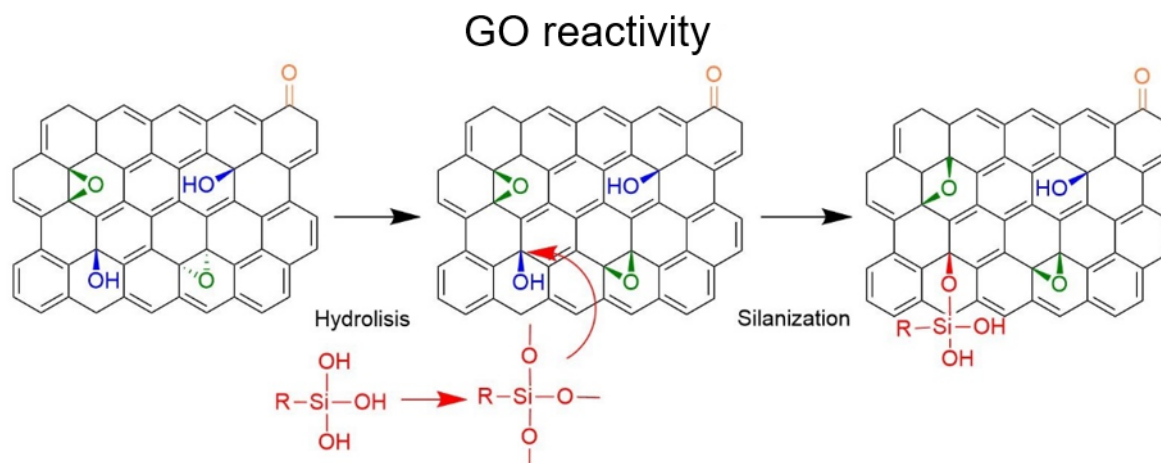


Figure 2.6: Schematic representation of GO functionalization with an organosilane through hydrolysis and subsequent reaction with hydroxyl groups on the GO surface. Reprint from licentiate thesis [44].

The coexistence of hydroxyl, epoxide, carbonyl, and carboxyl oxygen functional groups gives GO a chemically versatile surface that can participate in several types of interactions with other materials [53]. This represents an important advantage over pristine graphene for applications where surface reactivity and interfacial interactions are required [55]. However, the availability of reactive sites alone does not guarantee successful incorporation into a composite. The effectiveness of graphene-based materials as reinforcement or functional additive also depends on their distribution within the matrix, compatibility with the matrix material, and the resulting interfacial interactions [69,70]. These considerations establish the connection between the surface chemistry discussed here and the incorporation of graphene-based materials into composites, which is addressed in the following chapter.

CHAPTER 3

Graphene-Based Composite Materials

3.1 Graphene reinforcement in composite materials

Graphene-based materials have been extensively investigated as reinforcements and functional additives in composite materials due to their combination of mechanical, electrical, thermal, and tribological properties [54,71]. The possibility of combining these properties with the advantages offered by different matrix materials, such as polymers, ceramics, and metals, makes graphene-based composites an attractive approach for enhancing the performance of existing materials across a wide range of applications [71].

Different graphene-based materials can be selected as reinforcements or functional additives depending on the intended application [47]. As shown in Table 3.1, graphene oxide and graphene nanoplatelets differ from pristine graphene in their mechanical, electrical, thermal, and surface properties [72–75]. The reported values should therefore be considered representative, especially for GO and GNPs, because their structure and properties can vary substantially with synthesis conditions, number of layers, defect density, and surface chemistry [55]. Although some intrinsic properties may be lower than those of pristine single-layer graphene, their scalability, cost, processability, and chemical functionality can make them better suited to specific applications while still enabling significant composite-property improvements at relatively low additions [54,71].

Table 3.1: Representative properties of pristine graphene, graphene oxide (GO), and graphene nanoplatelets (GNPs).

Property	Pristine Graphene [74]	GO [72,73]	GNPs [75]
Electrical Conductivity	10^8 S/m	10^{-3} - 10^3 S/m	$\sim 10^5$ - 10^6 S/m
Tensile Strength	130 GPa	21 - 54 GPa	80 - 130 GPa
Young's Modulus	1000 GPa	274 - 542 GPa	800 - 1000 GPa
Thermal conductivity	4800-5300 W.m ⁻¹ .K ⁻¹	8.8 - 42 W.m ⁻¹ .K ⁻¹	~ 3000 – 5000 W.m ⁻¹ .K ⁻¹
Surface Area	2630 m ² /g	890 m ² /g	500 - 700 m ² /g

However, the processing conditions and, particularly, the interactions established between the reinforcement and the matrix strongly influence the properties of the resulting composite [45]. A homogeneous distribution of graphene throughout the matrix is important for effectively exploiting its high surface area and avoiding localized agglomeration, while suitable interfacial interactions are required to promote adhesion and transfer mechanical or functional effects between the two constituents [46]. Poor graphene distribution and weak interfacial interactions can therefore hinder the expected improvements and, in some cases, negatively affect the properties of the composite [46]. In this context, the higher chemical reactivity of GO provides an additional advantage, since its oxygen functional groups offer possibilities for modifying and tailoring the interaction with different matrix materials [55].

Achieving the desired distribution and interaction between graphene-based materials and the matrix depends strongly on the selected incorporation approach [71,76]. The relative importance of these requirements depends on the graphene-based material, matrix, and intended application, meaning that no single incorporation approach is universally optimal [71,77]. The selection and implementation of the incorporation method are therefore important steps in determining the characteristics and performance of graphene-based composites. The following sections discuss the main incorporation strategies, with a focus on ceramic and metallic matrices.

3.2 Graphene incorporation strategies

A wide range of strategies have been developed for incorporating graphene-based materials into composite matrices [70]. These approaches aim to promote suitable distribution and interaction between the constituents while also considering practical aspects such as cost-effectiveness and scalability. Although individual techniques can involve overlapping mechanisms, incorporation strategies can broadly be grouped into mechanical methods, solution-based methods, chemically assisted methods, and in-situ growth methods [78,79]. Their suitability depends on the graphene-based material, matrix material, and intended application.

Mechanical incorporation methods rely on the application of mechanical forces to distribute graphene-based materials within the matrix. Among the most commonly used approaches are mechanical stirring, ultrasonication, and ball milling [78,80]. Mechanical stirring promotes dispersion through the movement and circulation of the constituents, while ultrasonication uses acoustic cavitation to generate localized forces that can separate stacked graphene sheets or break existing agglomerates. Ball milling provides more intensive mechanical mixing through repeated collisions between the milling media, graphene-based material, and matrix, which can promote a more homogeneous distribution and stronger physical interaction between the constituents [70,79]. These methods are generally attractive due to their simplicity, relatively low cost, and potential scalability. However, the mechanical forces involved, particularly during high-energy ball milling and prolonged ultrasonication, can introduce structural defects, reduce the lateral dimensions of graphene-based materials, or modify their surface chemistry [80,81]. Therefore, the processing intensity

and duration must be carefully controlled to balance improved distribution with preservation of the reinforcement characteristics.

Solution-based incorporation methods rely on the dispersion of graphene-based materials and one or more composite constituents in a liquid medium to promote their mixing and distribution [82]. Common approaches include solution mixing, colloidal processing, and solvothermal methods. In solution mixing, the constituents are dispersed or dissolved in a suitable solvent and mixed before the liquid medium is removed, while colloidal processing relies on stable suspensions, sometimes assisted by surfactants or dispersants to prevent agglomeration and sedimentation [78,82]. Solvothermal methods additionally employ elevated temperature and pressure to promote reactions or the formation of the matrix material in the presence of graphene-based materials [83]. These approaches can facilitate homogeneous distribution while reducing the need for intensive mechanical processing. However, their effectiveness depends strongly on the stability and compatibility of the constituents in the selected liquid medium, while additional steps such as solvent removal, washing, and drying can increase process complexity, cost, and limit scalability [79,82].

In-situ growth provides an alternative incorporation strategy in which graphene is directly formed on or within the matrix material rather than being separately produced and subsequently mixed with it [4]. Typically, a carbon precursor is introduced in contact with the matrix and converted into graphene under controlled processing conditions, commonly at elevated temperatures. This approach can promote homogeneous distribution and intimate contact between graphene and the matrix while reducing the mechanical damage associated with conventional mixing processes [84]. However, the characteristics of the resulting graphene depend strongly on parameters such as the carbon precursor, growth temperature, growth time, and matrix material, which can increase process complexity and restrict the range of suitable material combinations [85].

Chemically assisted incorporation methods exploit the surface chemistry of graphene-based materials and the matrix to promote their distribution and interaction. Surface functionalization can be applied to one or both constituents to establish interactions that would otherwise be limited [4,78]. Graphene-based materials can, for example, be modified by introducing specific functional groups or heteroatoms to facilitate their interaction with the matrix [55,78]. Alternatively, the matrix or its precursors can be functionalized with ions or chemical groups, while changes in the pH of the surrounding medium can be used to modify their surface charge [4,86]. Coupling agents provide another approach by forming chemical bridges between different surfaces, while electrostatic interactions can also promote their assembly [4,86]. These chemically assisted interactions promote the association of the constituents through a molecular-level mixing approach that relies on interactions established at their surfaces [4]. GO is particularly suitable for chemically assisted approaches due to the presence of numerous oxygen-containing functional groups, as discussed in Section 2.4 [55].

Within molecular-level mixing approaches, organosilanes such as (3-aminopropyl)-triethoxysilane (APTES) can be used as coupling agents to promote the attachment of graphene-based materials to surfaces such as those of metallic powders. APTES contains three hydrolysable ethoxy groups and an aminopropyl group terminated by a primary amine, providing two chemically distinct functionalities [87,88]. Hydrolysis converts the ethoxy groups into silanol groups (Si–OH), which can subsequently undergo condensation with hydroxyl groups associated with oxide/hydroxide surfaces, resulting in surface–O–Si bonds and attachment of APTES [87,89]. The terminal amine group remains available for subsequent interaction with GO, while condensation between neighboring surface-associated APTES molecules can also form Si–O–Si bonds within the silane layer [87,89].

The availability of water plays an important role in controlling APTES hydrolysis and condensation [87,88]. Limited water availability can result in incomplete hydrolysis, while increasing water availability promotes more extensive hydrolysis and increases the possibility of condensation between neighboring APTES molecules [87]. Although Si–O–Si bonding can contribute to the formation of the functionalized surface layer, extensive self-condensation can result in APTES polymerization and agglomeration [87,88]. Consequently, the reaction medium and water availability are important considerations for controlling APTES functionalization.

Covalent interactions can further contribute to GO attachment. The primary amine group of APTES can react with epoxy groups on GO through nucleophilic ring opening, forming a C–N bond [65,89]. Condensation between residual silanol groups of APTES and hydroxyl groups associated with GO provides another possible interaction [89]. APTES functionalization can therefore promote GO attachment through a combination of electrostatic and covalent interactions. Figure 3.1 schematically illustrates the functionalization of a metallic powder surface with APTES and examples of possible interactions between GO and the APTES-functionalized surface.

The different incorporation strategies provide distinct routes for promoting the distribution and interaction of graphene-based materials with a matrix [4,78]. Mechanical methods can be suitable when the constituents can withstand the applied forces, and some modification of the graphene-based material can be tolerated. Solution-based methods can be advantageous for constituents that are sensitive to intensive mechanical processing or can be processed in a liquid medium before subsequent solidification or consolidation [79,82]. Chemically assisted methods are particularly relevant when limited compatibility requires modification of the constituent surfaces [78,79], while in-situ growth can promote intimate contact and distribution when the matrix and processing conditions are suitable for graphene formation [85]. Therefore, the following section focuses on the application of these incorporation strategies to the preparation of powder feedstocks for advanced manufacturing.

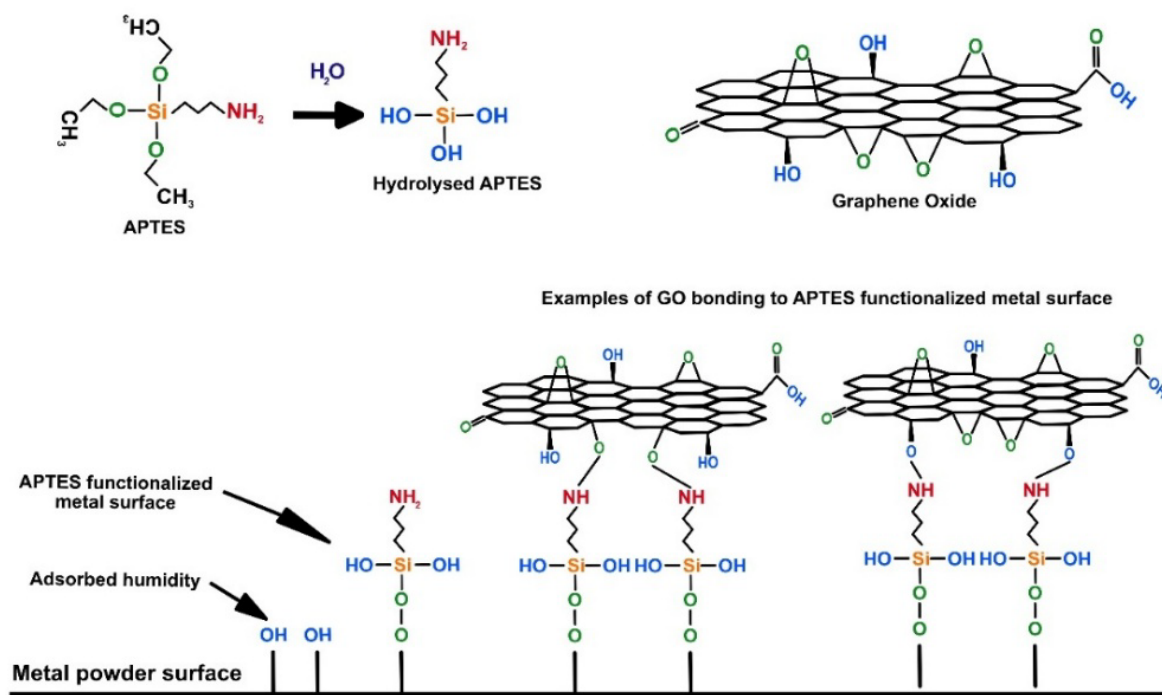


Figure 3.1: Schematic representation of APTES functionalization of a metallic powder surface and possible interactions between GO and the APTES-functionalized surface. Reprint from licentiate thesis [44].

The different incorporation strategies provide distinct routes for promoting the distribution and interaction of graphene-based materials with a matrix [4,78]. Mechanical methods can be suitable when the constituents can withstand the applied forces, and some modification of the graphene-based material can be tolerated. Solution-based methods can be advantageous for constituents that are sensitive to intensive mechanical processing or can be processed in a liquid medium before subsequent solidification or consolidation [79,82]. Chemically assisted methods are particularly relevant when limited compatibility requires modification of the constituent surfaces [78,79], while in-situ growth can promote intimate contact and distribution when the matrix and processing conditions are suitable for graphene formation [85]. Therefore, the following section focuses on the application of these incorporation strategies to the preparation of powder feedstocks for advanced manufacturing.

3.3 Preparation of graphene-containing powder feedstocks

Powder feedstocks provide an attractive route for the incorporation of graphene-based materials into composite matrices, as their high surface area enables the reinforcement to be distributed between or directly associated with individual powder particles [79]. However, the preparation of graphene-containing powder feedstocks requires not only homogeneous graphene distribution and suitable interfacial interactions, but also consideration of the characteristics of the powder required for subsequent processing [15]. The incorporation method can influence the morphology, particle size, surface condition, and distribution of the resulting composite powder,

which can consequently affect its suitability for further consolidation or manufacturing processes [86]. Among the graphene incorporation strategies discussed in the previous section, specific methodologies can be applied to the preparation of powder feedstocks, as discussed in the following examples.

Among these approaches, ball milling can promote the distribution and attachment of graphene-based materials onto metallic powder particles by breaking up agglomerates through mechanical forces [90,91]. However, the resulting powder characteristics depend strongly on parameters such as milling speed, time, and ball-to-powder ratio [90]. Phuong et al. [91], for example, incorporated 2 vol.% functionalized graphene into Cu powder by high-energy ball milling at 200 rpm using a ball-to-powder ratio of 10:1, followed by reduction in H_2 at 300 °C for 3 h to remove metal oxide components. Figure 3.2 schematically illustrates the high-energy ball milling and subsequent reduction process used to produce a graphene/Cu composite powder. The process successfully distributed graphene over the Cu particles, although some graphene clusters remained after milling and the original Cu powder morphology was considerably deformed. These results highlight an important limitation of ball milling, as the mechanical forces used to improve graphene distribution can simultaneously modify the matrix powder and damage the graphene structure [90,91].

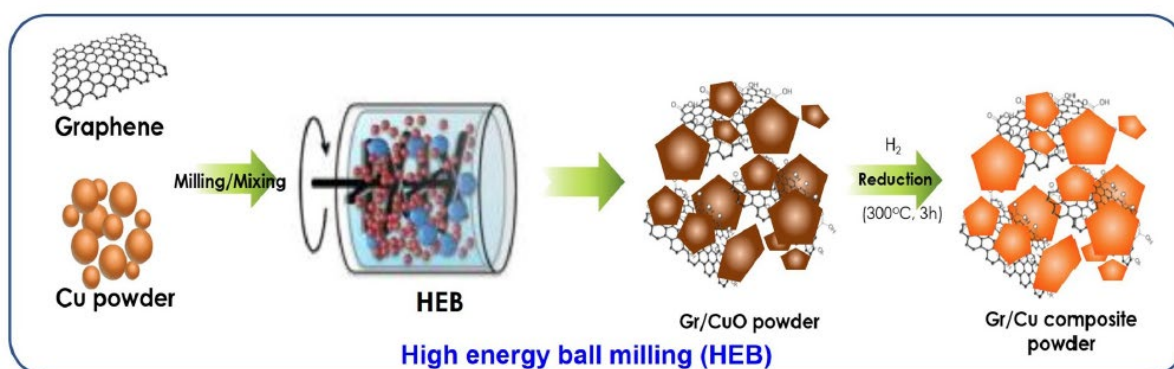


Figure 3.2: Schematic representation of the high-energy ball milling and subsequent reduction process used to incorporate graphene into Cu powder. Reprint from Phuong et al. [91] under Creative Commons license.

Solution-assisted mixing provides an alternative approach for incorporating graphene-based materials into metallic powder feedstock without the intensive mechanical forces associated with ball milling. The graphene-based material is dispersed in a suitable liquid medium, mixed with the matrix powder, and subsequently dried to obtain the composite powder [1,79]. Souza et al. [92] investigated four solution-assisted routes for depositing GO into Cu powder using mechanical stirring, ultrasound, rotary evaporation, and ultrasound followed by mechanical stirring, while maintaining the subsequent processing conditions constant among the different routes. Figure 3.3 schematically illustrates one of the solution-assisted routes investigated, combining ultrasound and mechanical stirring for the incorporation of GO into Cu powder. In all cases, GO was initially dispersed in acetone before mixing with the Cu powder. The combination of ultrasound and mechanical stirring provided the most homogeneous

GO distribution, with fewer agglomerated regions and improved properties after consolidation [92]. These results demonstrate the importance of controlling both the initial dispersion and subsequent mixing with the matrix powder. In addition, the selection of the solvent can significantly influence the dispersion and attachment of graphene-based materials onto the matrix powder [93]. However, solution-assisted methods require additional solvent removal and drying steps, increasing process complexity and potentially limiting scalability [1].



Figure 3.3: Schematic representation of the solution-assisted incorporation of GO into Cu powder using ultrasound followed by mechanical stirring. Reprint from Souza et al. [92] under Creative Commons license.

Chemically assisted surface modification provides greater control over the attachment of graphene-based materials to individual powder particles by deliberately modifying the interactions between their surfaces. Coupling agents can be introduced to create chemical interactions between otherwise poorly interacting constituents, promoting both graphene attachment and interfacial bonding [79]. Zhang et al. [94], for example, used aminopropyl triethoxysilane (APS) as a coupling agent to produce GO-coated Al powders. APS was first preferentially adsorbed onto the oxide surface of the Al powder, after which its remaining functional groups reacted with GO. This promoted the self-assembly of GO onto the powder surface. Figure 3.4 schematically illustrates this chemically assisted route for the preparation of GO-coated Al powders using APS as a coupling agent. This approach increased GO attachment compared with physical adsorption without APS and enabled a uniform GO coating with contents up to 1.0 wt.% [94]. However, the reaction sequence required careful control, as excessive cross-linking between GO sheets could instead promote their agglomeration [94].

Chemically assisted attachment can also be achieved without coupling agents. Tidén et al. [86] controlled the pH to generate opposite surface charges between negatively charged GO and the passive oxide layers of metallic powders, enabling electrostatic

attachment of GO onto Cu, and 316L stainless-steel powders. Such approaches can therefore provide controlled attachment of graphene-based materials to powder surfaces while avoiding intensive mechanical processing. However, the effectiveness of these approaches depends strongly on the surface chemistry of the constituents and the processing conditions. In addition, increasing the powder quantity can make it more difficult to maintain uniform surface functionalization and GO coating [79,94].

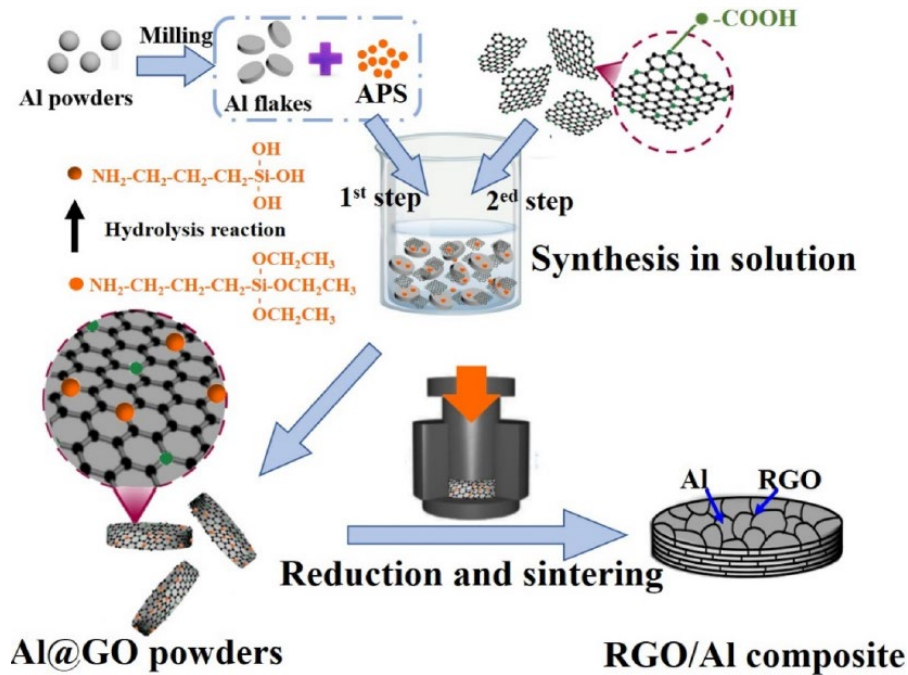


Figure 3.4: Schematic representation of the chemically assisted preparation of GO-coated Al powders using APS as a coupling agent, followed by reduction and consolidation to produce an rGO/Al composite. Reprinted from Zhang et al. [95] with permission from Elsevier.

In-situ growth provides another approach in which graphene is directly synthesized on the surface of the matrix powder from a carbon precursor, promoting uniform distribution and strong interfacial interaction without requiring the incorporation of pre-produced graphene-based materials [96]. Wang et al. [97], for example, used PMMA as a solid carbon source to grow graphene directly onto Cu powder at 800 °C, obtaining graphene coverage of the powder particles. Figure 3.5 schematically illustrates the in-situ growth route used, including the preparation of the Cu/PMMA/MgO powder mixture, graphene growth, and subsequent consolidation of the graphene/Cu composite. However, the high temperatures required for graphene growth can promote sintering and neck formation between Cu particles, making the addition of MgO as a dispersant necessary to prevent particle agglomeration [97]. Therefore, although in-situ growth can provide high-quality interfaces and direct graphene coverage, its applicability is strongly dependent on the matrix material and the temperature and conditions required for graphene formation [85,96].



Figure 3.5: Schematic representation of the in-situ growth of graphene on Cu powder using PMMA as a carbon source and MgO as a dispersant. Reprint from Wang et al. [97] *under Creative Commons license*.

Therefore, for the preparation of graphene-containing powder feedstocks, the selection of an incorporation strategy should consider factors such as graphene distribution, interfacial interactions, preservation of powder characteristics, process complexity, scalability, and compatibility with subsequent manufacturing processes [15,79]. The following chapter discusses potential applications of graphene-containing powder feedstocks in modern manufacturing processes.

CHAPTER 4

Graphene-Based Materials in Modern Powder-Based Processes

4.1 Thermal spraying techniques

4.1.1 Process fundamentals

Thermal spraying is a group of technologies used to deposit feedstock material onto a substrate to form a coating. During the process, the feedstock material is heated and accelerated towards the substrate. Depending on the technology, the feedstock can be supplied as powder, wire, rod, or suspension and can reach the substrate in a molten, semi-molten, or solid state [98,99]. Upon impact, the particles deform and adhere to the substrate or previously deposited material, forming splats that progressively build the coating through successive depositions [98]. Consequently, the properties of the resulting coating depend strongly on the temperature and velocity of the sprayed particles during deposition [100].

The main differences between thermal spray processes lie in the heating energy source, operating temperature, and velocity of the sprayed particles. Among the principal techniques are flame or combustion spraying, arc spraying, plasma spraying, high-velocity oxy-fuel (HVOF), high-velocity air-fuel (HVOF), and cold spraying [99,101]. Flame and high-velocity processes rely on combustion, while arc and plasma spraying use electrical energy to generate the heat required for deposition [98,101]. In these conventional thermal spray processes, the sprayed particles generally reach the substrate in a molten or semi-molten state. In contrast, cold spraying differs because the particles remain predominantly in the solid state, and deposition relies mainly on their high kinetic energy [98]. Consequently, these technologies cover a broad range of operating conditions, from the high temperatures characteristic of plasma spraying to the high particle velocities and comparatively lower thermal input associated with processes such as HVOF and cold spraying, as illustrated in Figure 4.1 [99,101,102].

Plasma spraying is particularly suitable for ceramic and ceramic-based composite coatings due to the high temperatures generated during processing, enabling the deposition of high-melting-point materials [108]. Consequently, it is widely employed for thermal barrier coatings and wear- and corrosion-resistant coatings, particularly in aerospace and energy applications [107,108]. However, the characteristics and performance of plasma-sprayed coatings are strongly influenced by processing parameters such as plasma power, gas composition, feed rate, and stand-off distance, which determine the thermal and kinetic conditions experienced by the sprayed particles [108]. Inadequate processing conditions can result in incomplete particle melting, increased porosity, microcracking, or phase transformations, making process control important for obtaining the desired coating properties [108].

Conventional APS generally produces a lamellar structure through the successive deposition and solidification of flattened splats [109]. In suspension plasma spraying (SPS), where finer particles are fed in a liquid suspension, columnar structures can form instead if low-momentum particles are deflected near the substrate and strike the surface at shallow angles; this leads to a shadowing effect and preferential columnar growth [109,110]. The gaps between these columns provide strain tolerance and can accommodate stresses arising from thermal-expansion mismatch, making such structures particularly attractive for thermal barrier coatings [109,111]. Depending on the processing conditions, SPS can also produce more porous, lamellar, or vertically cracked structures [109,110].

HVOF and HVAF are well suited for producing dense metallic and cermet coatings that protect against wear, erosion, corrosion, and oxidation [105,107]. They are widely applied to components exposed to demanding service conditions in aerospace, energy, oil and gas, and marine sectors [105,107]. The high particle velocities characteristic of these processes promote strong deformation upon impact and the formation of thin, closely packed splats, improving intersplat contact and limiting porosity [112]. The resulting dense and well-bonded structures are particularly advantageous for wear and corrosion protection, where pores and weak intersplat regions can facilitate material removal or provide pathways for corrosive species [107,112]. Cermets such as WC-CoCr are especially compatible with high-velocity spraying because the processes combine high particle velocities with relatively moderate thermal input [105]. However, coating properties remain strongly affected by feedstock particle size and spraying parameters, and excessive heat can promote oxidation or degradation of temperature-sensitive constituents [105,113]. In this regard, HVAF can reduce oxidation and degradation compared with HVOF because of its lower thermal input, while still providing the particle velocities needed to form dense coatings [113].

4.1.3 Graphene-based materials for tribological applications

Graphene-based materials are promising additives for tribological coatings because they combine strong mechanical properties with solid-lubricating behavior [114]. Their layered structure enables sliding between adjacent carbon layers, while graphene at the contact region can reduce interactions between opposing surfaces and support the formation of lubricating layers during wear [115]. Figure 4.2 schematically illustrates this mechanism in a graphene-containing coating, showing graphene within the coating and its transfer to the contact region during sliding wear. These properties have encouraged the use of graphene-based materials in thermally sprayed ceramic and cermet coatings, with the aim of combining matrix-based wear resistance with the friction-reducing and lubricating effects of graphene [75].

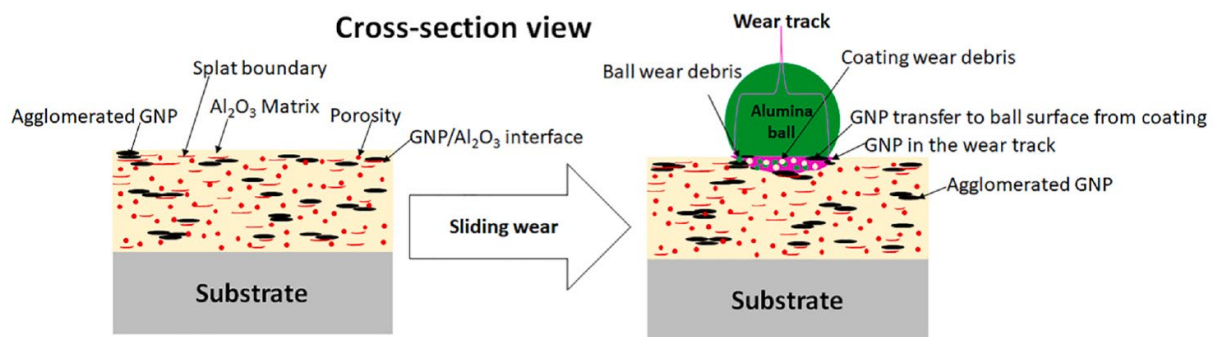


Figure 4.2: Schematic representation of GNPs distribution in an Al_2O_3 coating and the proposed transfer of GNPs to the contact region during sliding wear. Reprint from [116] with permission from Elsevier.

For plasma spraying, suspension plasma spraying (SPS) has been explored as a route for incorporating graphene-based materials into ceramic coatings. In SPS, fine particles are dispersed in a liquid carrier, typically water or alcohol, allowing submicron and low-density materials that are difficult to feed as conventional dry powders to be processed [112]. The evaporation of the liquid carrier consumes part of the thermal energy supplied by plasma, which can reduce the thermal exposure of the suspended material during the initial stages of flight [112,117]. These characteristics make SPS particularly attractive for incorporating graphene-based materials. Ganvir et al. [117] demonstrated an early application of this approach by depositing 8 wt.% yttria-stabilized zirconia (8YSZ) coatings containing graphene from a mixed 8YSZ–GO suspension. Graphenaceous material was retained within the ceramic matrix, although its retention decreased with increasing plasma power, illustrating the need to balance sufficient thermal input for ceramic deposition with the preservation of the graphene-based material [117].

Similarly, Mahade et al. [118] incorporated GNPs into an alumina coating using a mixed water-based Al_2O_3 -GNPs suspension processed by suspension plasma spraying. Raman analysis confirmed that GNPs were retained after spraying, and the composite coating exhibited a 36% lower coefficient of friction and a 69% lower

specific wear rate than the monolithic alumina coating. The improvement was attributed to the lubricating effect of the retained GNPs as well as their contribution to crack deflection and arrest within the ceramic matrix [118].

Graphene nanoplatelets agglomerates were observed within the as-deposited alumina matrix and attributed to π – π interactions and strong van der Waals forces, highlighting a challenge in controlling GNPs dispersion during processing [118]. Alternatively, co-spraying approaches can be considered, in which a graphene-containing suspension is introduced together with a conventional powder feedstock. The graphene suspension can also be injected radially downstream into the plasma jet, shortening its exposure to the high-temperature environment, while independent feeding provides greater flexibility in controlling the incorporation of graphene into the thermal spray coating [117].

Graphene-based materials have also been deposited using high-velocity processes such as suspension HVOF (S-HVOF). Derelizade et al. [119] deposited GNPs directly onto stainless steel using S-HVOF by axially injecting a water-based GNPs suspension into the combustion chamber. The GNPs structure was largely retained during spraying, even though increasing the flame power from 25 to 50 kW substantially reduced the GNPs surface coverage, which the authors attributed to increased combustion and removal of GNPs at the higher flame power. Despite the non-uniform distribution of GNPs on the substrate surface, the deposited GNPs substantially reduced the coefficient of friction through the formation of a tribofilm. During continued sliding wear, however, the GNPs underwent oxidation and progressive structural degradation, eventually transforming toward amorphous carbon and losing their lubricating ability, as shown in Figure 4.3 [119].

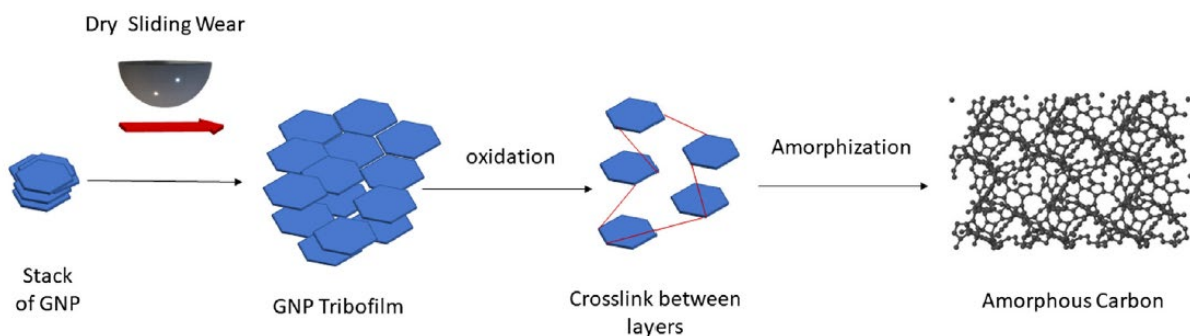


Figure 4.3: Schematic illustration of GNP amorphization during dry sliding wear. Reprint from [119] under Creative Commons license.

In a subsequent study, Derelizade et al. [120] investigated GNPs addition to WC–Co coatings using a hybrid HVOF process, in which conventional WC–Co powder was injected axially while a water-based GNPs suspension was injected radially downstream of the nozzle, allowing the two feedstocks to mix *in situ* during spraying. This approach avoided premixing the micron-sized WC–Co powder and submicron GNPs before spraying. Although promising overall wear performance was obtained, a clear lubricating effect or tribofilm formation was not observed. Furthermore, the

GNPs-containing coatings exhibited increased porosity because GNPs positioned between successive WC–Co splats hindered their bonding, while one of the investigated GNPs-containing coatings also showed reduced hardness [120].

In contrast, Kumar et al. [121] incorporated GNPs into WC–10Co–4Cr coatings by blending the GNPs and WC–10Co–4Cr powders before conventional HVOF spraying. Prior to deposition, laser surface texturing (LST) was applied to the substrate to generate a controlled surface roughness and enhance mechanical interlocking between coating and substrate [121]. The resulting GNPs-containing coating exhibited a denser structure with lower porosity, which the authors attributed to GNPs filling voids within the WC–10Co–4Cr coating, together with higher microhardness than the reference coating. The authors also reported improved abrasion resistance, which was attributed to the denser coating structure and the lubricating effect of the incorporated GNPs.

Overall, the studies discussed above demonstrate that different approaches can be used to incorporate graphene-based materials into plasma- and high-velocity thermal-sprayed coatings, with several studies reporting improvements in friction and wear performance [75,112,117,118,120,121]. However, the results also highlight challenges associated with retaining graphene during deposition and controlling its distribution within the resulting coating. Agglomeration of GNPs was observed in suspension plasma-sprayed coatings, whereas the incorporation of graphene into hybrid HVOF coatings was associated with increased porosity, as GNPs can be positioned between successive splats, thereby impairing their bonding [118,120]. Furthermore, prolonged or severe sliding conditions can lead to structural degradation or amorphization of graphene-based materials, potentially limiting their long-term lubricating effectiveness [119].

4.2 Powder bed fusion - laser beam

4.2.1 Process fundamentals

Powder bed fusion–laser beam (PBF-LB) is a processing technology within additive manufacturing (AM), a group of manufacturing technologies in which 3D components are produced layer by layer. These technologies use three-dimensional digital models to define the geometry of the components, enabling the fabrication of complex shapes that can be difficult to achieve using conventional manufacturing methods [122]. Among the different AM technologies, several processes use powder materials as feedstock, including binder jetting (BJT) and powder bed fusion (PBF) [122,123]. In BJT, a liquid binder is selectively deposited onto successive powder layers to produce a green component that requires subsequent densification, typically through sintering [123]. In contrast, PBF processes use a concentrated energy source to selectively fuse areas of the powder bed; they can be classified according to the energy source employed, with electron beam powder bed fusion (PBF-EB) and laser powder bed fusion being the main technologies used for metallic materials [19].

In PBF-LB, a thin layer of metallic powder is distributed over the build platform and selectively irradiated by a focused laser according to the geometry defined by the sliced digital model [123]. The absorbed energy from the laser heats and melts the powder, forming a localized melt pool that can also partially remelt the previously solidified material, promoting bonding between successive layers [122]. The melt pool subsequently solidifies, consolidating the material and progressively forming the component. After each layer is completed, the build platform is lowered and a new powder layer is deposited, with this sequence repeated until the component is produced [124]. The main elements involved in this layer-by-layer process are schematically illustrated in Figure 4.4. The characteristics of the process are strongly influenced by parameters such as laser power, scan speed, hatch distance, layer thickness, and scanning strategy, which affect the energy delivered to the material, melt-pool behavior, and the resulting microstructure of the printed component [122,124].

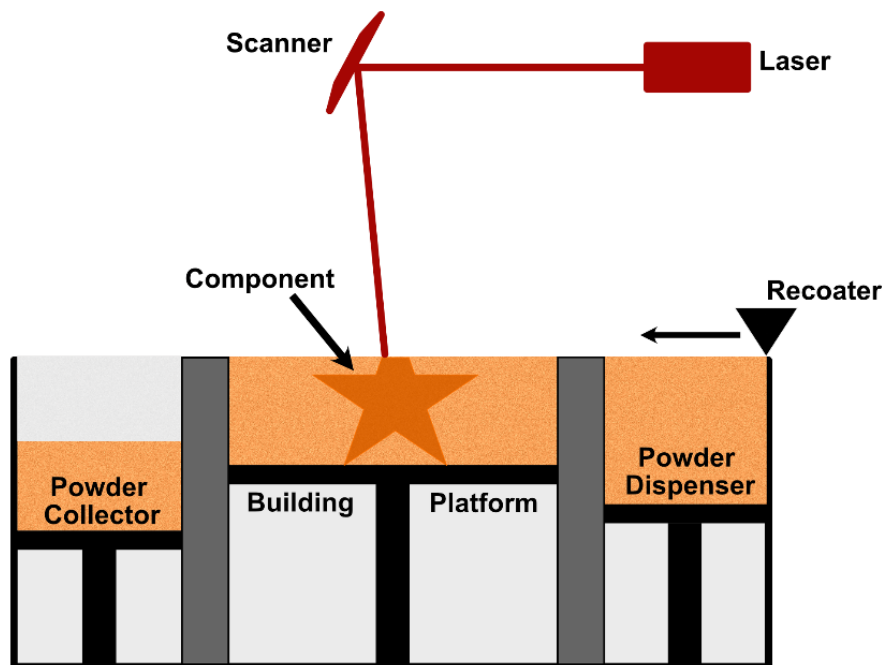


Figure 4.4: Schematic representation of the PBF-LB process.

PBF-LB provides several advantages for the production of metallic components, including high geometrical freedom, reduced material waste, and the possibility of producing complex internal features [19]. However, successful processing depends heavily on both the properties of the starting powder and the properties of the material being processed [19,122]. Powder characteristics such as particle size distribution, morphology, flowability, and surface condition influence powder spreading and packing behavior, while the optical and thermophysical properties of the material influence its interaction with the laser and the resulting melt-pool behavior [122,125]. PBF-LB has successfully established itself for several metallic materials, including 316L stainless steel, Ti-6Al-4V, Inconel 718, and AlSi10Mg [124,126]. Nevertheless, some metallic materials remain particularly challenging to process, with pure copper representing an

important example due to its high thermal conductivity and high reflectivity at conventional near-infrared laser wavelengths (around 1080 nm) [19,125].

4.2.2 Applications and processing challenges of pure copper in PBF-LB

Pure copper is attractive for PBF-LB because of its high electrical and thermal conductivity and corrosion resistance [19,122], making it suitable for heat exchangers, heat sinks, cooling systems, electrical contacts, induction coils, and power electronics [19,127,128]. Furthermore, the high geometrical freedom and resolution of the PBF-LB process enable the fabrication of complex, small-scale Cu structures that are difficult to realize using conventional manufacturing methods, creating opportunities for applications in microelectronics and other miniaturized functional devices [129,130].

The processing of pure copper by PBF-LB is particularly challenging when conventional near-infrared laser sources are employed. At wavelengths around 1070 nm, Cu exhibits high reflectivity and consequently absorbs only a limited fraction of the incident laser energy [19,125]. In addition, the high thermal conductivity of Cu promotes rapid heat dissipation from the irradiated region, further increasing the energy required to establish and maintain a stable melt pool [19,129]. The combination of low laser absorption and rapid heat dissipation can result in insufficient melting and remelting between adjacent tracks and successive layers, promoting lack-of-fusion defects and reducing the density of the produced components [131]. Increasing the energy input can improve melting and densification, but excessive energy input can promote keyhole formation, melt-pool instabilities, spattering, and keyhole-induced porosity [131,132]. These processing challenges can also lead to macroscopic build failures, including buckling and delamination, as illustrated in Figure 4.5 for copper alloys [19]. Consequently, achieving stable processing of pure Cu using conventional near-infrared PBF-LB requires careful optimization of the processing parameters within a relatively narrow processing window [131].

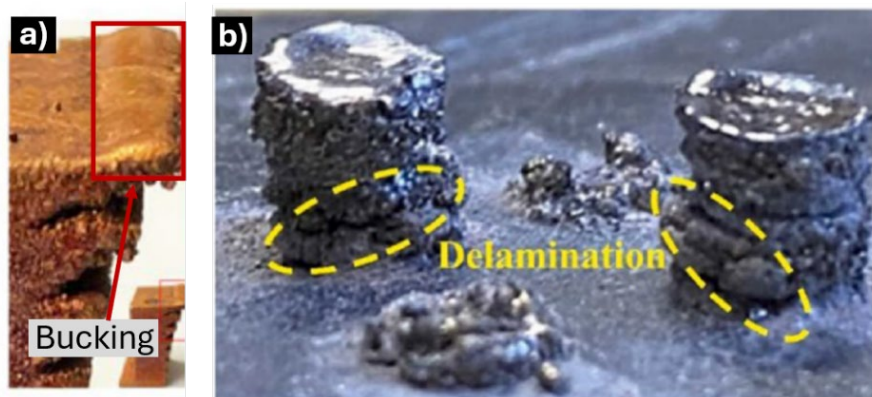


Figure 4.5: Examples of macroscopic build failures during PBF-LB processing of copper alloys: (a) buckling of CuCrZr and (b) delamination of Cu–Al–Ni–Mn. Adapted from [19] under Creative Commons license.

Several strategies have been investigated to address the challenges associated with PBF-LB processing of pure Cu. When using conventional near-infrared lasers, higher laser powers and optimized processing parameters can increase the energy transferred to the material and improve densification [129]. Alternatively, green and blue laser sources, operating at shorter wavelengths, can substantially increase the laser absorption of Cu and enable stable processing at lower laser powers [133]. Material-based approaches have also been explored, including alloying and modification of the powder feedstock [19,134]. Although alloying can improve processability, the addition of alloying elements can reduce the high electrical and thermal conductivity that makes pure Cu attractive for many applications [135]. Surface modification of Cu powders with materials exhibiting higher laser absorption represents another alternative strategy to improve laser/powder interaction while limiting changes to the bulk composition of Cu [136]. In this context, graphene-based materials have been investigated as surface modifiers to enhance the laser absorption and PBF-LB processability of Cu powders, as discussed in the following section.

4.2.3 Graphene-based materials for improved laser absorption of copper powder

The high reflectivity of Cu at the wavelength of conventional near-infrared lasers limits the fraction of incident laser energy absorbed by the powder during the PBF-LB process, making the production of dense Cu components difficult [136]. Graphene-based materials have therefore been investigated as a means of increasing the laser absorption of Cu powder feedstocks. Different approaches have been explored, including mixing graphene flakes with Cu powder and coating individual Cu powder particles with GO [86,137]. These approaches can substantially alter the optical response of the feedstock even at relatively low graphene contents; however, the resulting PBF-LB behavior depends on how the graphene-based material is introduced, its concentration, and its influence on the powder and melt behavior during processing [22,86,137–139].

Tertuliano et al. [137] investigated multilayer graphene flakes as an additive for improving the PBF-LB processability of Cu. For the printing experiments, graphene microflakes were mechanically mixed with gas-atomized Cu powder at a concentration of 0.1 wt.%, with the graphene flakes located between the Cu powder particles. The addition of graphene increased the absorptivity of the powder during laser scanning and resulted in higher relative densities over the investigated processing range, with a maximum relative density of 99.2%. The graphene-containing powder also exhibited a wider processing range for producing high-density material compared with unmodified Cu. However, lack-of-fusion defects were still observed under several of the investigated processing conditions, and the authors noted that retained graphitic material could potentially influence the electrical, thermal, and mechanical properties of the printed component [137].

Tidén et al. [86] developed an alternative approach for coating individual Cu powder particles with GO using a wet-chemical method that relies on pH-dependent electrostatic interactions between negatively charged GO sheets and the oxide-covered surface of Cu particles. Following investigation of the pH-dependent interaction, a rotary evaporator was used to mix the powder and GO suspension while gradually removing the solvent, bringing the GO sheets into contact with the Cu powder particles and promoting their deposition onto the particle surfaces. Raman mapping confirmed the presence of GO across the powder, while a 0.1 wt.% GO coating reduced the reflectance of Cu powder at 1070 nm from approximately 61% to 28% [86]. The same wet-chemical coating approach was subsequently used by Graphmatech AB to treat Cu powders with 0.1 and 0.3 wt.% GO, which were further evaluated by Tidén et al. [22] during PBF-LB. The reduced reflectivity improved Cu processability, and a relative density of 99.8% was obtained using the 0.1 wt.% GO-treated powder. However, increasing the GO content to 0.3 wt.% did not further improve processability and instead promoted greater spattering and lower density. The authors also observed a tendency toward balling at insufficient energy input and over-melting at excessive energy input, demonstrating the importance of optimizing both the processing parameters and GO content for PBF-LB of GO-treated Cu powder [22].

In contrast to the improved processability reported by previously described approaches, Calignano et al. [139] investigated Cu-GNPs feedstocks produced by mechanically mixing gas-atomized Cu powder with varying GNPs contents in a low-energy jar mill for a period of 24 to 72 hours. Even small GNPs additions deteriorated powder flowability and spreadability, while GNPs contents above 1.5 wt.% promoted agglomeration. Based on the powder characterization, 0.5 wt.% GNPs was identified as the most suitable of the compositions investigated. Nevertheless, PBF-LB of the Cu-GNPs mixtures resulted in poorer processability than pure Cu. Ball formation, spattering and keyhole-related defects were observed, and dense Cu-GNPs samples could not be obtained under processing conditions that successfully consolidated pure Cu [139]. The authors suggested that the presence of GNPs may interfere with heat transfer between Cu particles, limiting their melting and consolidation.

More recently, Günther et al. [138] investigated GO-coated Cu powder supplied by Graphmatech AB using PBF-LB with a green laser, comparing unmodified Cu with powders containing 0.1 and 0.3 wt.% GO. Small Cu functional structures for power-electronics applications were manufactured directly onto a direct bonded copper (DBC) substrate, consisting of an electrically insulating Al_2O_3 ceramic core with Cu metallization on both sides. This approach enables the Cu structures to be manufactured and joined directly to the substrate in a single processing step. However, sufficient bonding between the deposited Cu and the surface metallization must be achieved while limiting the thermal loading of the underlying ceramic, which is susceptible to cracking.

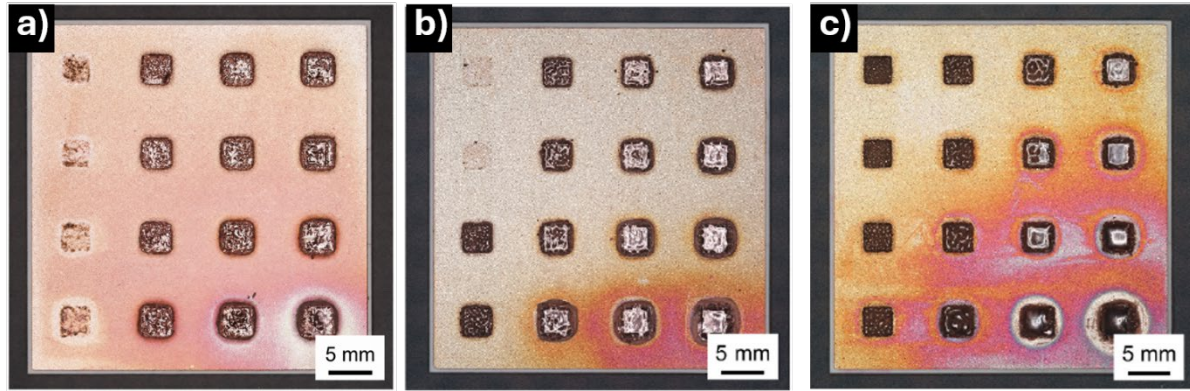


Figure 4.6: PBF-LB samples produced on DBC substrates using (a) pure Cu, (b) 0.1 wt.% GO-coated Cu, and (c) 0.3 wt.% GO-coated Cu, illustrating the expansion of the processing window with GO addition. Reprint from Günther et al. [138] under Creative Commons license.

The GO coating shifted the processing window toward lower energy input, enabling fully bonded structures at lower laser powers than pure Cu, as illustrated in Figure 4.6. Increasing the GO content to 0.3 wt.% further expanded the range of conditions producing fully bonded structures, although 0.1 wt.% GO provided a more favorable processing window for achieving high-density samples [138]. However, the GO-containing samples exhibited gas porosity and pronounced ball formation, reducing density and surface quality. The authors associated the gas pores with possible combustion of GO during PBF-LB and discussed the increased oxygen content, retained carbon, and reduced melt-pool wetting as possible contributors to the observed balling behavior [138].

These studies demonstrate that graphene-based materials can substantially increase the laser absorption of Cu powder feedstocks, but this does not necessarily translate into improved PBF-LB processability. The method used to introduce the graphene-based material and its concentration influence not only the optical properties of the feedstock but also powder flowability and spreadability, melt-pool stability, spattering, ball formation, and porosity [22,86,137–139]. While the controlled coating of Cu powder with GO has enabled the production of high-density material within wider processing windows, excessive GO content can promote process instability, whereas mechanically mixed Cu-GNPs feedstocks have shown difficulties associated with agglomeration, powder spreading, and consolidation [22,138,139]. Furthermore, the behavior of the graphene-based material during PBF-LB can influence both the processing behavior and properties of the resulting material, as residual carbonaceous constituents, oxidation, and the potential combustion of GO have been reported or proposed to affect these outcomes [22,137,138]. These findings highlight the importance of developing a controlled approach for adding GO to Cu powder feedstocks, allowing the GO content to be adjusted to promote increased laser absorption while limiting detrimental effects on powder and PBF-LB processability.

CHAPTER 5

Experimental Work

5.1 Materials and processing methods

The experimental work presented in this thesis involved different powder feedstocks and graphene-based materials depending on the manufacturing process investigated. This section presents the materials, their preparation, and the corresponding processing methods used in Papers A–E. A central part of the experimental work described in Papers B–E was the development and application of a molecular-level mixing method for coating metallic powder feedstocks with GO. This process, including its subsequent adaptation and scaling for processing larger powder quantities, is therefore described in a dedicated section before its application in thermal spraying and PBF-LB is addressed.

5.1.1 Suspension plasma spraying of Al_2O_3

The Al_2O_3 –GNP coatings investigated in Paper A were produced by suspension plasma spraying (SPS). The Al_2O_3 feedstock was supplied by Treibacher Industrie AG (Austria) as a water-based suspension containing 40% solid load. The GNPs were supplied by 2D Fab AB (Sweden) as a water-based suspension containing 10 wt.% GNP. The GNPs consisted of multilayer flakes with at least four graphene layers and an average flake length of approximately 50 μm .

As discussed in Section 4.1.3, using a suspension allows fine ceramic particles and low-density graphene-based materials, which are both difficult to feed and spray as dry powders, to be processed. The suspension not only improves material feeding but also provides temporary thermal protection. Evaporation of the liquid carrier absorbs part of the thermal energy during the initial stages of flight, reducing the GNPs direct exposure of the GNPs to the high-temperature plasma. This protection was particularly important for the Al_2O_3 –GNP system investigated in Paper A, where retaining the graphene-based material during plasma spraying was essential to its subsequent tribological function.

A homogeneous suspension was prepared by mixing the water-based Al_2O_3 and GNPs suspensions in proportions calculated to achieve a graphene nanoplatelet content equivalent to 5 wt.% relative to the Al_2O_3 powder content. The combined suspension was continuously agitated overnight using a roller mixer to enhance dispersion and promote a uniform distribution of Al_2O_3 particles and graphene nanoplatelets throughout the mixture. This preparation represents a solution-based mixing approach, as discussed in Section 3.2. Coating deposition was performed using an Axial III plasma torch coupled with a Nanofeed 350 suspension feeding system (Northwest Mettech Corporation, Canada), with the suspension fed axially into the torch. The same processing conditions were used for the monolithic Al_2O_3 and Al_2O_3 –GNPs coatings, as displayed in detail in Table 1 by Mahade et al. [118].

5.1.2 GO coating of metallic powder feedstocks

The GO coating process used in Papers B–E employed graphene oxide (GO), (3-aminopropyl)triethoxysilane (APTES), and toluene as the main ingredients. The Cu powder used for the development and scale-up of the coating process was supplied by Carpenter Additive (UltraFine Copper-MIM CCP 3123 270M + 15 μm), with measured particle size values of $D_{50} = 37 \mu\text{m}$ and $D_{90} = 57 \mu\text{m}$. GO was supplied by LayerOne as a de-acidified aqueous paste with a concentration of 10 wt.% and consisted of sheets with 3–5 layers and lateral dimensions ranging from 2 to 20 μm . According to the supplier, the GO had a C/O atomic ratio of approximately 3.1. The coupling agent used for powder surface functionalization step was (3-aminopropyl)-triethoxysilane (APTES, 99%, Sigma-Aldrich), while toluene (Supelco) was used as the organic solvent during this step. APTES is an organosilane molecule containing three hydrolysable ethoxy groups and a terminal amine group, enabling the functionalization of the powder surface and facilitating the subsequent attachment of GO during the coating process.

The GO coating process consists of three main stages: surface functionalization of the powder, GO deposition, and drying. During the first stage, the metallic powder is dispersed in toluene and vigorously mixed with APTES, which acts as the coupling agent. Toluene is used as the reaction medium due to its low water content, which allows greater control over APTES hydrolysis and surface reaction, as discussed in Section 3.2. The extent of powder functionalization is governed by several processing parameters, including the amount of powder, the volume of toluene, the APTES concentration, and the mixing time. These parameters influence the amount and distribution of APTES on the particle surface and consequently affect the coverage and thickness of the subsequently deposited GO layer. After functionalization, the powder is first washed with toluene to remove excess and unreacted APTES and then rinsed with deionized water to remove residual toluene.

The second stage begins with the preparation of a dilute GO suspension from the commercial 10 wt.% aqueous GO paste. The paste is diluted with deionized water to a concentration of 0.2 g/L and mechanically stirred to promote homogeneous dispersion. Due to the slightly acidic character of the starting GO suspension, its pH is adjusted to approximately 7 by gradually adding a small amount of 1 M ammonium

hydroxide, typically 0.5–1 mL. After approximately 1 h of stirring, the functionalized powder, previously dispersed in deionized water, is combined with the GO suspension. The resulting mixture is vigorously stirred for a short period to promote uniform contact between the GO sheets and the functionalized particle surfaces. After coating, the excess liquid is removed, and the GO-coated powder is dried in air at 40 °C for 12 h. A full description of the GO coating process, including a schematic representation of the complete coating process, is provided in Paper B.

The coating procedure was progressively adapted to process larger quantities of copper powder, starting from the initial 20 g batches produced using magnetic stirring. As the powder quantity increased, maintaining the dense Cu particles in suspension became increasingly important, and magnetic stirring was replaced by a mechanical stirring system to provide stronger agitation and improve powder circulation throughout the vessel. Two impeller configurations producing predominantly radial and axial flow were evaluated. Radial flow provided stronger local mixing but more limited circulation, whereas axial flow promoted vertical recirculation through a larger volume of the suspension, as illustrated in Figure 5.1. Based on its improved ability to maintain the Cu powder in suspension, the axial-flow configuration was selected for the subsequent scaling experiments.

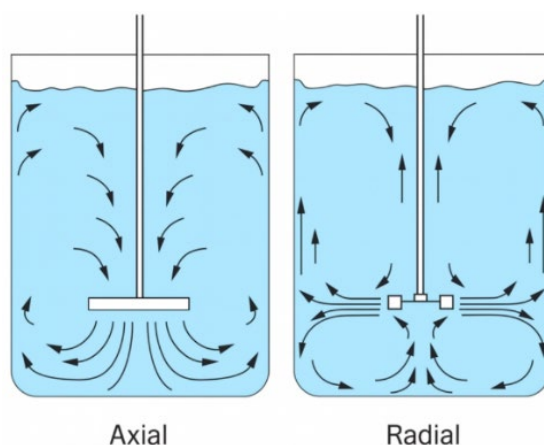


Figure 5.1: Schematic representation of the axial and radial flow patterns generated by the mechanical stirring configurations evaluated during scale-up of the GO coating process.

Following the selection of the axial-flow configuration, the coating process was then applied to batches of 200, 300, and 500 g, with the volumes of toluene and APTES adjusted according to the amount of powder being processed. The remaining coating conditions, including preparation of the GO suspension, pH adjustment, coating time, and drying conditions, were maintained according to the procedure described above. Further details regarding the development of the scale-up process and its effect on the resulting GO-coated powder are provided in Paper E.

A recoating strategy was also investigated to increase the amount of GO deposited on the powder surface. In this approach, the dried GO-coated powder obtained after the initial coating process was subjected to additional molecular-level mixing cycles using the same coating procedure. After each cycle, the powder was dried before being

subjected to the subsequent recoating step, allowing the amount of deposited GO and the surface coverage to be progressively increased without changing the established coating conditions. Up to two additional recoating cycles were investigated, resulting in powders subjected to one, two, and three consecutive coating cycles. Further details on the recoating procedure and the resulting powder characteristics are provided in Paper D.

5.1.3 HVOF spraying of GO-containing and virgin WC-Co-Cr powders

In Paper C, HVOF spraying was employed to process both virgin and GO-containing WC-Co-Cr powders. A porous WC-Co-Cr powder (grade 558.444), supplied by Höganäs AB (Sweden), was selected to improve the retention of GO during thermal spraying. The open porous structure enabled the molecular-level mixing process described in Section 5.1.2 to deposit GO not only on the external particle surfaces but also within the internal pore surfaces, as showed in Figure 5.2b. This internal deposition was intended to shield the GO from the high thermal exposure encountered during the HVOF process. Both the virgin and GO-containing powders were deposited onto Domex steel substrates using an M3 HVOF gun (Uniquecoat Technologies LLC, Oilville, USA) under identical spraying conditions. The main processing parameters are summarized in Table 1 in Paper C.

5.1.4 PBF-LB processing of pure and GO-coated Cu powders

PBF-LB was used in Papers D and E to process pure and GO-coated Cu powders and investigate the influence of the GO coating on the processability of pure copper. The Cu powder used in both studies was EOS CuCp, supplied by EOS GmbH, with a purity of 99.95% and a particle size distribution of 15–53 μm . The powder was processed either in its virgin condition or after GO coating using the methodology described in Section 5.1.2. GO-coated Cu powder prepared using a single coating cycle was used for the experiments conducted on a commercial EOS M 290 1 kW system, whereas the recoating strategy described in Section 5.1.2 was applied to the GO-Cu powder used for the operando MiniSLM experiments. In this case, the powder was subjected to three consecutive coating cycles to increase the amount of deposited GO and enhance its influence on laser absorption. Two PBF-LB systems were employed: a commercial EOS M 290 1 kW system for sample fabrication and processability studies, and the MiniSLM system for operando investigation of the laser/powder interaction using synchrotron X-ray radiography.

Commercial PBF-LB processing was performed using an EOS M 290 1 kW system (EOS GmbH) equipped with a Yb-fiber laser with a maximum power of 1000 W and a nominal focus diameter of approximately 90 μm . The high-power system was chosen to assess the effect of the GO coating within the context of an established PBF-LB process capable of processing pure copper. In Paper E, the processability study was

initially performed using a design of experiments (DoE) based on thin-wall structures. Four samples were fabricated using GO-coated Cu powder, each consisting of a dense outer structure containing 15 thin walls, resulting in a total of 60 walls. The thin walls were produced by vertically stacking parallel laser tracks layer by layer, with different combinations of laser power and scan speed. Laser power was varied from 300 to 800 W and scan speed from 300 to 1200 mm/s, while the layer thickness was maintained at 40 μm . The thin-wall structures were produced exclusively using the GO-coated Cu powder, as the same geometries could not be successfully fabricated from pure Cu under the investigated conditions. This experimental design therefore enabled the processability of the GO-coated Cu powder to be evaluated over a broad range of processing conditions.

Based on the processing conditions investigated in the thin-wall experiments, 16 cubic samples were subsequently produced from both pure Cu and GO-coated Cu powders to directly compare their processability and relative density. The same cubes were also used for combustion analysis in Paper E. One processing condition was then selected for ex-situ melt pool characterization in Paper D, allowing the melt pool behavior observed using the commercial EOS M 290 system to be compared with the operando MiniSLM observations. For this analysis, the corresponding Pure-Cu and GO-Cu cubes were sectioned perpendicularly to the scan direction of the final layer while preserving the top surface, enabling the melt pool geometry to be evaluated relative to the original surface. Further details of the EOS M 290 processing conditions and sample characterization are provided in Papers D and E.

In Paper D, the MiniSLM system was used to investigate the PBF-LB process by operando synchrotron X-ray radiography. The MiniSLM is a custom-built miniature PBF-LB machine specifically designed for integration into synchrotron beamlines, allowing direct observation of the laser/powder interaction and melt pool evolution during processing [140,141]. For each powder condition, Pure-Cu and GO-coated Cu, three thin walls approximately 3 mm long, 2 mm high, and 0.5 mm thick were initially fabricated on a copper baseplate using identical processing conditions and a laser power of 350 W. A groove containing loose powder was subsequently prepared at the top of each wall by melting the outer tracks while leaving the middle track unmelted, followed by recoating process to fill in the groove with powder for the operando experiment. A single laser track was then scanned through the loose powder while being recorded by X-ray radiography. For these recorded scans, the laser power varied between 210, 280, and 350 W, while the remaining processing parameters were kept constant, allowing the influence of laser power and the GO coating on the laser/powder interaction to be investigated. Further details of the experimental setup, together with a schematic of the MiniSLM system, are provided in Paper D.

5.2 Materials characterization

5.2.1 Scanning electron microscopy

Scanning electron microscopy (SEM) was extensively used throughout this thesis for high-resolution characterization of powder surfaces and processed samples. SEM generates images by scanning a focused electron beam across the sample and detecting signals produced by the interaction between the electrons and the material. The analyses were performed using LEO-1550 Gemini and Zeiss Gemini 450 field emission scanning electron microscopes (FEG-SEM). For GO-coated metallic powders, an inlens SE detector was used at a low acceleration voltage of 5 kV and a short working distance, typically below 5 mm, to increase surface sensitivity and facilitate visualization of the thin GO layers. Representative SEM images showing GO-coated powders with different particle morphologies are shown in Figure 5.2.

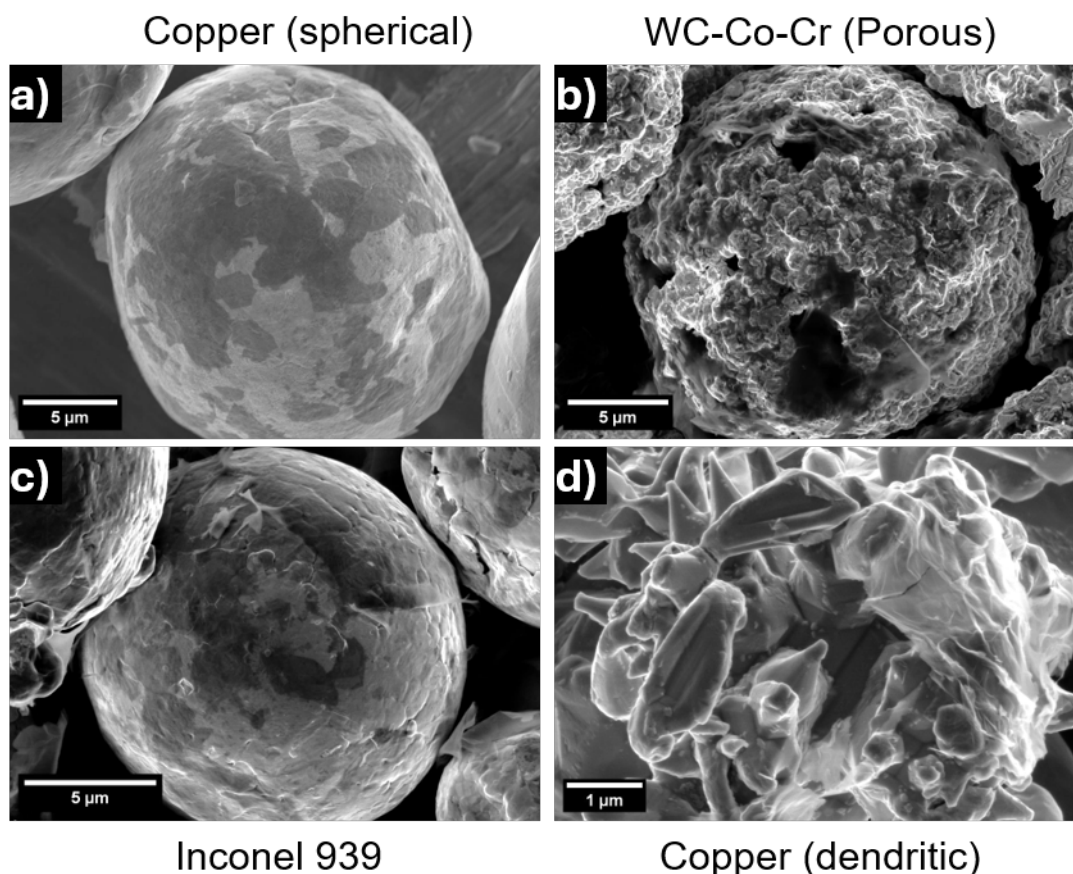


Figure 5.2: Representative SEM images of GO-coated powders: a) Spherical copper powder, b) Porous WC-Co-Cr, c) Dendritic copper, d) Inconel 939

SEM was a key technique for evaluating the GO coating during the development and scaling of the molecular-level mixing process in Papers B and E, enabling direct observation of GO coverage and distribution on individual powder particles. It was also used to characterize processed materials in Papers A, C, and D, including thermal-

sprayed coatings and wear-tested surfaces in Papers A and C, as well as the top-surface morphology of the MiniSLM samples in Paper D.

5.2.2 Raman spectroscopy

Raman spectroscopy was central to the identification and characterization of graphene-based materials in this thesis. The technique relies on the inelastic scattering of monochromatic light, where shifts in the energy of the scattered photons reveal information about the vibrational modes of the analyzed material. For graphene-based materials, the characteristic D and G bands, located at approximately 1350 and 1580 cm^{-1} , respectively, were used to confirm the presence of GO and GNPs and to assess their structural characteristics. Raman analyses were performed using a WITec Alpha 300R Raman microscope, employing either individual spectra or Raman mapping depending on the material under investigation.

Raman spectroscopy was among the main techniques used to evaluate the GO coating during the development and scale-up of the molecular-level mixing process in Papers B and E. In particular, Raman mapping provided spatially resolved information on the presence and distribution of GO within individual powder particles. The technique was also applied to graphene-based materials after processing in Papers A, C, and D, where it was used to assess their presence and structural integrity following thermal spraying, wear testing, and PBF-LB processing. Figure 5.3 shows an example of Raman mapping performed on a GO-containing WC-Co-Cr powder particle.

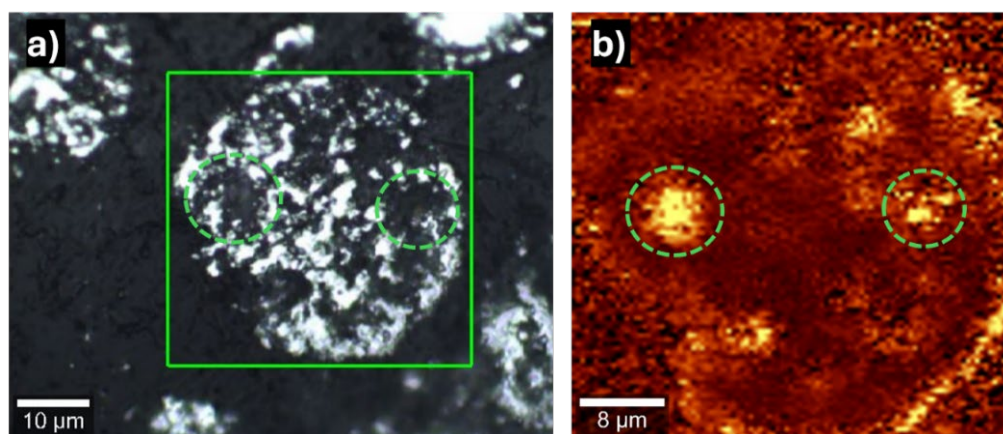


Figure 5.3: Investigation of a cross-sectioned GO-coated WC-Co-Cr powder particle. a) Optical micrograph showing the analyzed region and b) corresponding Raman map showing the distribution of graphene-based material within the particle. Reprint from paper C [12] under Creative Commons license.

5.2.3 Optical microscopy

Optical microscopy (OM) was used to characterize processed samples by providing images over relatively large areas through the interaction of visible light with the sample surface. In Paper C, OM was primarily used to examine cross-sections of the thermal-sprayed coatings and determine their relative density through image analysis.

In Papers D and E, OM was used to characterize PBF-LB samples, including relative density measurements and the assessment of melt pool geometry after metallographic preparation and etching. The resulting images enabled measurements of melt pool depth and width, allowing the melting behavior of pure Cu and GO-coated Cu to be compared under different processing conditions. Representative cross-sections of the pure Cu and GO-coated Cu cubes used for relative density analysis are shown in Figure 5.4.

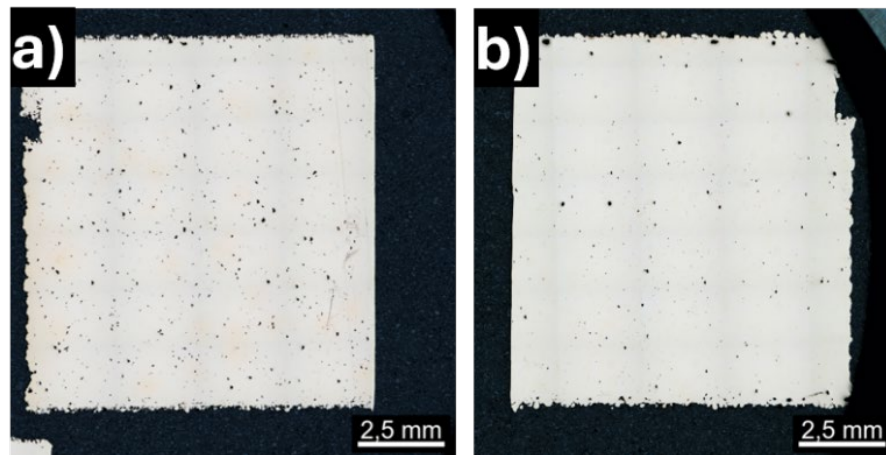


Figure 5.4: OM images of cross-sections of PBF-LB processed Cu cubes used for relative density analysis. Both samples were produced using identical processing parameters. a) Pure copper b) GO-coated copper.

5.2.4 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to examine the surface chemistry and chemical composition of selected materials in Papers B and C. The technique is based on the photoelectric effect, where X-ray irradiation induces the emission of core-level electrons with binding energies characteristic of their chemical environment. Analysis of the resulting spectra therefore provides information on both the elements present and the corresponding chemical states. In Paper B, XPS was applied to Cu powder during functionalization and GO coating, providing evidence for the formation of the silane layer and subsequent attachment of GO. In Paper C, XPS was performed on wear-tested WC-Co-Cr coatings to investigate their surface chemistry and further confirm the presence of graphene-based material after thermal spraying and wear testing.

5.2.5 Electron backscatter diffraction

Electron backscatter diffraction (EBSD) was used in Paper E to characterize the crystallographic structure of the PBF-LB processed Cu samples. The technique is performed in an SEM by directing the electron beam onto a 70°-tilted crystalline sample and detecting the resulting diffraction patterns, known as Kikuchi patterns. Indexing these patterns across a scanned area enables crystallographic orientation at individual points to be determined and orientation maps to be generated. These maps can then be used to evaluate microstructural features such as grain size, grain

morphology, and crystallographic texture. EBSD analysis was performed in a Zeiss Gemini 450 FEG-SEM equipped with an Oxford Instruments CMOS Symmetry detector. In Paper E, EBSD was applied to pure Cu and GO-coated Cu samples, which were produced under identical PBF-LB conditions, to assess whether the GO coating influenced the grain size distribution and morphology of the printed material.

5.2.6 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was applied in Paper C to assess the thermal stability of the GO coating and its effect on the oxidation behavior of the WC-Co-Cr powder. The technique monitors changes in sample mass as a function of temperature under a controlled atmosphere, enabling thermal reactions associated with mass gain or loss to be identified. Measurements were performed in a Mettler TGA/DSC 3+ in air from room temperature to 900 °C at different heating rates. These heating conditions were selected to evaluate the behavior of GO-coated powder during rapid heating, reflecting conditions relevant to high-temperature manufacturing processes such as thermal spraying.

5.2.7 Elemental composition analysis

Carbon and oxygen analyses were performed in Paper E to assess compositional changes associated with the GO coating and subsequent PBF-LB processing. The measurements were performed using Bruker elemental analyzers, with a G4 ICARUS system used for carbon determination by combustion and a G8 GALILEO system for oxygen determination by inert gas fusion. These instruments are intended for the analysis of carbon, sulfur, oxygen, nitrogen, and hydrogen, respectively. Pure Cu and GO-coated Cu powders, together with their corresponding PBF-LB processed samples, were analyzed under identical conditions to compare their carbon and oxygen concentrations. The results were used to evaluate the compositional changes introduced by the GO coating and to determine whether GO-derived carbon was retained after PBF-LB processing. Further details of the measurement procedure and results are provided in Paper E.

5.2.8 Dry sliding wear testing

Dry sliding wear tests were conducted to evaluate the tribological behavior of the thermally sprayed coatings investigated in Papers A and C. In both cases, tests were carried out using a TRB3 ball-on-disc tribometer (Anton Paar) with an alumina ball as the counter-body. During the test, the ball was pressed against the rotating coating surface under controlled conditions, while the coefficient of friction was continuously recorded throughout the sliding process. In Paper C, the method was used to evaluate the effect of GO incorporation on the tribological performance and wear resistance of the WC-Co-Cr coatings, with the specific testing parameters and wear-rate calculations described in the paper. In Paper A, wear-tested Al_2O_3 -GNP coatings were analyzed using STXM to investigate wear-induced structural and chemical changes in the GNPs and the surrounding alumina matrix.

5.2.9 Synchrotron-based characterization

5.2.9.1 Scanning transmission X-ray microscopy

Scanning transmission X-ray microscopy (STXM) was the central characterization technique in Paper A, combining spatially resolved X-ray imaging with X-ray absorption spectroscopy. In STXM, a focused monochromatic X-ray beam is scanned across a thin, X-ray-transparent sample while the transmitted intensity is recorded. Images are acquired over a sequence of photon energies across a selected elemental absorption edge, generating a series of energy-dependent images commonly referred to as an image stack. The spectral features observed close to the absorption edge provide X-ray absorption near-edge structure (XANES) spectra, also referred to as near-edge X-ray absorption fine structure (NEXAFS). While STXM provides the spatially resolved imaging capability, XANES/NEXAFS provides information about the local chemical state, bonding environment, and structural organization of the investigated element [142].

Thin electron-transparent lamellae for the STXM measurements were prepared by focused ion beam (FIB) milling. In FIB preparation, a focused ion beam is used to progressively remove material from a selected region until a sufficiently thin section is obtained for X-ray transmission. Samples analyzed at the Al K-edge were prepared using an FEI Versa 3D Ga⁺ FIB-SEM. For the C K-edge measurements, a Thermo Scientific Helios 5 PFIB UXe equipped with a Xe⁺ plasma ion source was applied.

In Paper A, STXM was used to investigate the structural and chemical changes occurring in the GNPs-containing Al₂O₃ coating following thermal spraying and wear testing. Measurements were performed at the SoftiMAX beamline at MAX IV and the SpectroMicroscopy beamline (10ID1) at the Canadian Light Source (CLS). Analysis at the Al K-edge was used to distinguish and spatially map different alumina phases, whereas measurements at the C K-edge were employed to assess the presence, structural state, and orientation of the GNPs. By combining spatial mapping with XANES analysis, changes in both the alumina matrix and the GNPs could be examined before and after wear, including GNPs orientation and structural modifications within the wear-affected region. Figure 5.5 shows an example of the spatial identification of alumina phases based on Al K-edge STXM data.

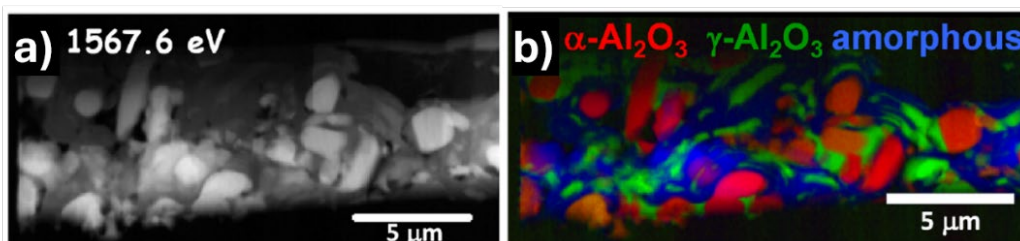


Figure 5.5: STXM analysis at the Al K-edge. a) STXM image of the Al₂O₃ FIB sample b) corresponding XANES-derived component map showing the spatial distribution of α-Al₂O₃, γ-Al₂O₃, and amorphous alumina. Adapted from paper A [142] under Creative Commons license.

5.2.9.2 Operando X-ray radiography

Operando synchrotron X-ray radiography was used in Paper D to observe the laser/powder interactions and the evolution of keyhole-associated features during PBF-LB processing. The technique relies on the transmission of high-energy X-rays through the sample, enabling dynamic changes within the material to be visualized during laser scanning. The experiments were conducted at beamline ID19 of the European Synchrotron Radiation Facility (ESRF), using the MiniSLM system described in Section 5.1.4. A white X-ray beam with a peak energy of 35 keV was transmitted through the processing region, converted into visible light by a scintillator, and recorded using a high-speed camera at 40,000 images/s with a spatial resolution of 2.2 $\mu\text{m}/\text{pixel}$. This setup enabled real-time observation of the laser-induced changes during processing of Pure-Cu and GO-Cu-3C powders.

The main objective of the operando analysis was to examine how the GO coating affects the laser/powder interaction and keyhole behavior under identical processing conditions. In the radiographs, the keyhole-associated features were identified from local contrast changes during laser scanning. The radiographs were converted to 8-bit images and processed using a melt pool tracking algorithm that detected changes in the laser-affected region between consecutive frames and generated binary masks of the tracked features. The vertical dimension of the bounding rectangle surrounding each mask was defined as the apparent laser penetration extent. This parameter was used to quantitatively compare the radiographically observed features for Pure-Cu and GO-Cu-3C, without it reflected the actual melt pool depth. Further details of the experimental configuration, image processing, and tracking procedure are provided in Paper D. A representative radiographic frame and the corresponding tracked feature are shown in Figure 5.6.

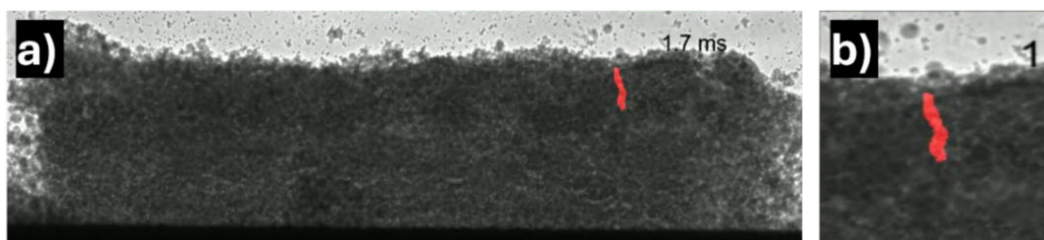


Figure 5.6: Representative operando X-ray radiograph acquired during PBF-LB processing of pure Cu. a) Radiographic frame showing the thin-wall sample during laser scanning b) Magnified view of the laser-affected region highlighting the tracked keyhole-associated feature.

CHAPTER 6

Results and Summary of Appended Papers

This chapter summarizes and discusses the main findings of the appended papers, which collectively address the research questions presented in Section 1.3. The discussion is organized into three main sections. Section 6.1 summarizes the findings from Papers B and E on the development and scale-up of the GO coating methodology, addressing RQ1. Section 6.2 discusses the findings from Papers A and C on the retention of graphene-based materials during thermal spraying and subsequent wear, together with their influence on tribological properties, addressing RQ2. Finally, Section 6.3 discusses the findings from Papers D and E on the influence of GO coating on laser/powder interaction and the processability of copper in PBF-LB, addressing RQ3. The main findings discussed in this chapter provide the basis for addressing the research questions in Chapter 7.

6.1 Controllable and Scalable GO coating of metal powders

6.1.1 Control of GO surface modification

The molecular-level mixing method developed and described in Paper B uses APTES as a coupling agent to promote GO attachment to the Cu powder surface. As shown in Figure 2 of Paper B, increasing the APTES concentration transformed the GO coating from partial coverage at 0.05% to complete coverage at 0.2%. Further increases produced thicker and more wrinkled GO coatings, with an excessively thick APTES layer at 1.5%. GO was also successfully deposited on both larger spherical and smaller irregular Cu particles, demonstrating that the method is applicable across particle sizes and morphologies.

In addition to APTES concentration, the amount of GO introduced during deposition provided a second parameter for controlling the coating characteristics. As shown in Figure 6.1, increasing the GO loading resulted in progressively greater GO coverage of the powder particles, as indicated by the Raman maps and spectra. At lower GO loadings, the coating appeared more localized, while higher GO loadings were

associated with a more widespread GO distribution and stronger Raman signals. At the highest GO loading, the observations suggested the formation of thicker GO deposits in some regions

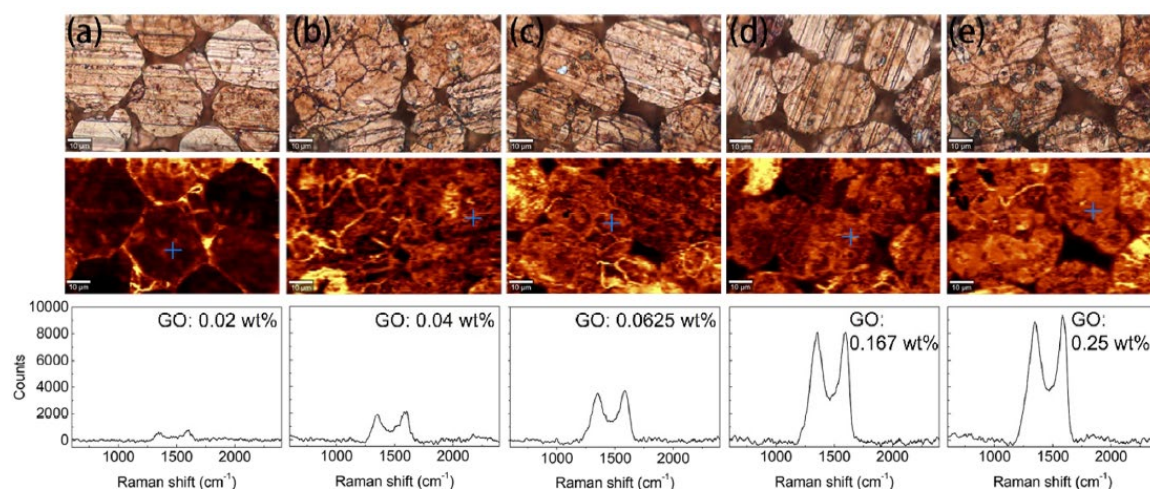


Figure 6.1: Optical images, Raman spectra, and Raman maps of GO-coated Cu powders prepared with different GO loadings, illustrating the influence of GO loading on the amount and surface distribution of GO. Reprint from Paper B [143] under Creative Commons license.

Together, these results demonstrate that control of the GO coating depends on both the surface functionalization of the powder and the amount of GO available during deposition. Surface functionalization is particularly important because it controls the attachment of GO to the powder surface. APTES hydrolysis enables its interaction with the powder surface, while the amino groups promote the subsequent attachment of GO. Controlling this step is crucial for tailoring surface chemistry and, consequently, the extent of GO coverage, while the amount of GO available provides an additional level of control over the coating characteristics. Importantly, this control was transferable beyond Cu, as demonstrated in Paper C for WC–Co–Cr powder, where partial GO coverage was intentionally targeted and achieved primarily by adjusting the APTES functionalization step. These findings demonstrate that the molecular-level mixing method provides a route to tailor GO coating characteristics according to the requirements of the powder feedstock and its intended application.

6.1.2 Upscaling the coating process

During the initial scale-up, the batch size was increased from 20 to 100 g while keeping the concentrations of APTES and Cu powder constant. As shown in Figure 6.2, although GO deposition was maintained, the 100 g batch exhibited a less uniform coating, featuring localized darker areas and line-like GO structures. This demonstrated that maintaining identical chemical conditions was insufficient to reproduce the coating characteristics at larger batch sizes and that the mixing conditions also required adjustments during the scale-up process.

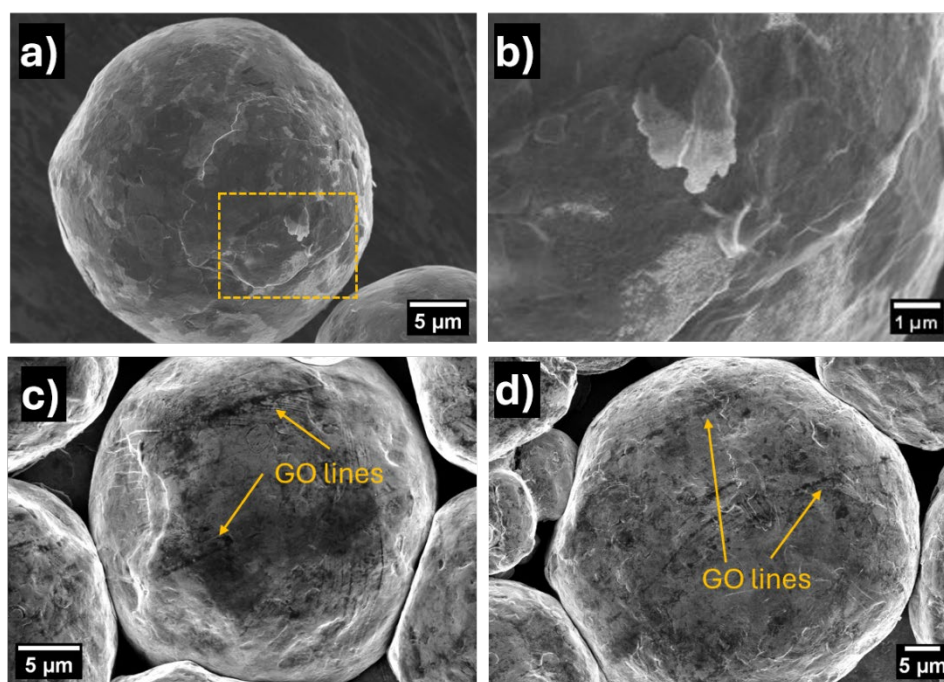


Figure 6.2: SEM images of GO-coated Cu powder produced at different batch sizes: a,b) 20 g and c,d) 100 g, showing differences in GO coating distribution.

Raman mapping confirmed that GO remained distributed over most of the analyzed particles when increasing the batch size from 20 to 100 g, despite the local coating irregularities observed by SEM. The intentionally partial coating resulted in areas with low or undetectable Raman signals, while GO-covered regions were detected across the majority of the analyzed particles. The corresponding optical microscopy images and Raman maps are presented in Figure 5 of Paper E.

Further scale-up to 500 g required adjustments to the mixing conditions, APTES-to-powder ratio, and solvent volume. As the amount of Cu powder increased, magnetic stirring became insufficient to maintain the powder in suspension and was replaced by mechanical stirring. Axial-flow agitation provided better powder suspension and circulation than radial-flow stirring. Inadequate conditions during the intermediate scale-up steps resulted in coating irregularities, including localized GO agglomeration, line-like features, and irregular GO distribution on individual Cu particles (Figure 6.3). These observations guided the adjustment of mixing, APTES availability, and solvent volume required to maintain adequate powder circulation, functionalization, wetting, and GO deposition at larger batch sizes.

With the processing conditions adjusted, the molecular-level mixing method was successfully scaled from 20 to 500 g while maintaining the targeted GO coating and was subsequently used to produce 10 kg of GO-coated Cu powder for the PBF-LB experiments in Paper E. Successive coating cycles also provided an additional means of increasing the amount and coverage of GO without changing the fundamental coating method and were used to produce the triple-coated powder investigated in Paper D.

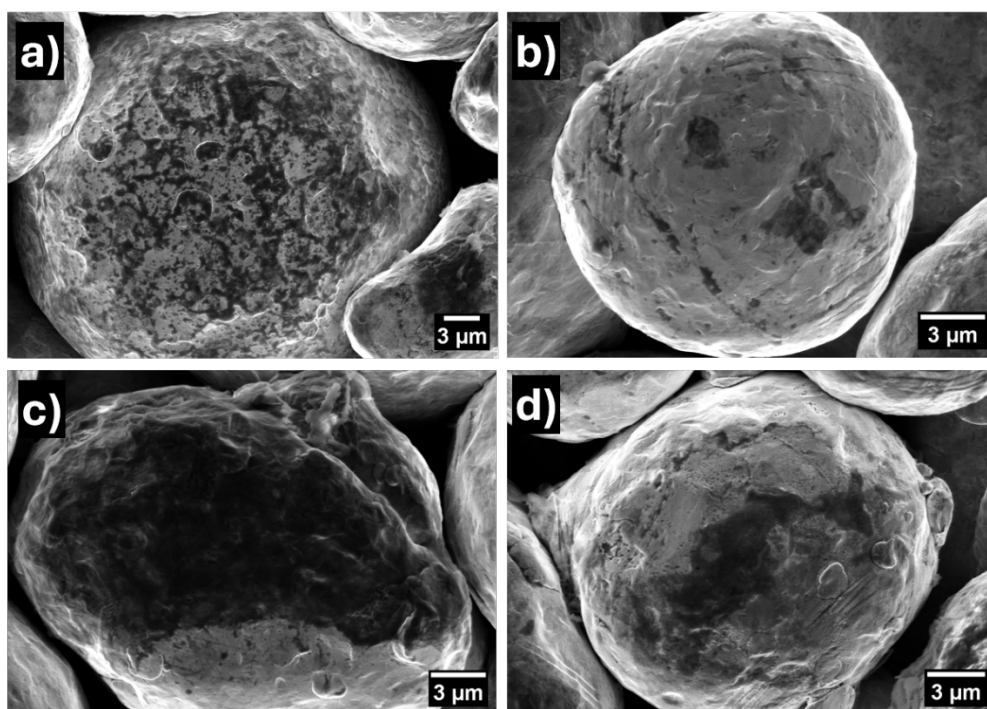


Figure 6.3: SEM images showing representative GO coating irregularities observed during scale-up: a,b) localized GO agglomeration and line-like features; c,d) irregular GO distribution on Cu particles.

The scale-up therefore added an important aspect to the understanding of the molecular-level mixing method. Paper B established surface chemistry, particularly APTES functionalization and GO availability, as the basis for controlling GO deposition. At larger batch sizes, however, these chemical conditions could only be maintained if the dense metallic powder was effectively suspended and circulated throughout the solution. Sufficient solvent and APTES also had to be available to promote wetting and functionalization of the increased amount of powder. Therefore, scalable GO deposition is governed by surface chemistry but also regulated by the mixing conditions: the chemistry controls GO attachment at the particle surface, while powder suspension, circulation, and reagent availability determine whether these conditions can be reproduced throughout a larger powder batch.

6.2 Graphene retention and tribological behavior in thermal spraying

6.2.1 Retention during thermal spraying

A fundamental challenge in incorporating graphene-based materials into thermally sprayed coatings is retaining a sufficient amount of the material during the high-temperature deposition process. In Paper C, porous WC-Co-Cr powder was coated with GO prior to HVAF spraying, allowing the GO to deposit on the particle surface as well as within the internal pores, where the surrounding material provided some protection during the spraying process. Further details of the feedstock preparation and characterization are provided in Paper C. After HVAF spraying, SEM observations identified graphene-like flakes within the deposited coating, while Raman mapping

confirmed GO-related signals on the surface of the as-sprayed coating (Figure 6.4). These observations demonstrate that at least a portion of the GO was preserved during HVOF processing, thereby supporting the use of the porous feedstock as a strategy to protect the GO during thermal spraying.

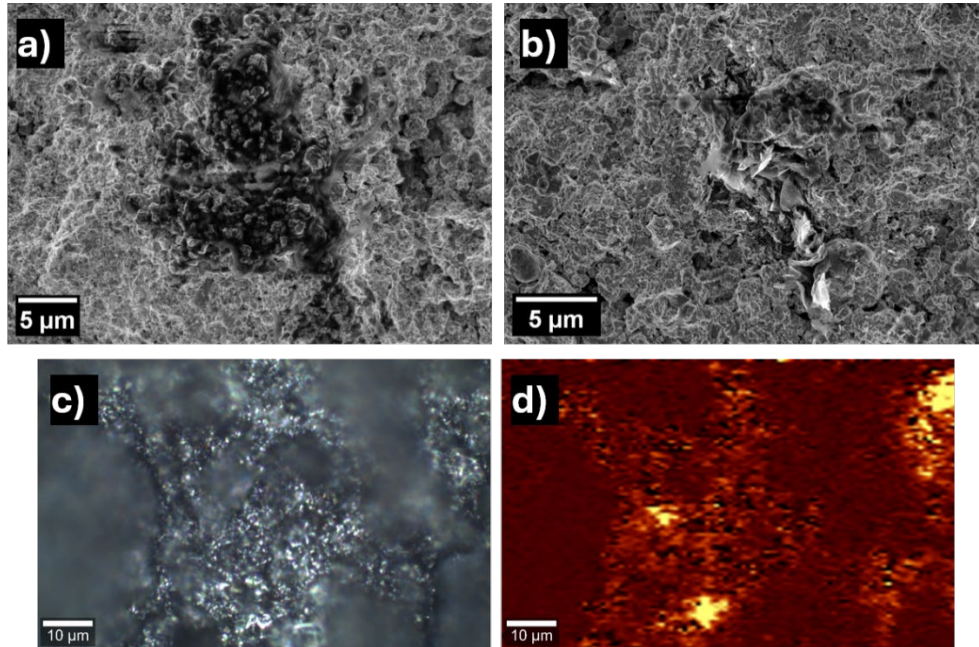


Figure 6.4: SEM, optical microscopy, and Raman characterization of the GO-containing WC-Co-Cr coating after HVOF spraying. Adapted from Paper C [12] under Creative Commons license.

A similar approach was investigated for the Al_2O_3 -GNPs system in Paper A, where GNPs were deposited by SPS using a water-based suspension. Evaporation of the liquid during spraying can reduce the thermal exposure of the GNPs, contributing to their retention. C K-edge STXM analysis of the as-sprayed coating confirmed that GNPs were retained within the Al_2O_3 matrix (Figure 6.5), while linear dichroism showed that they were preferentially oriented parallel to the coating surface.

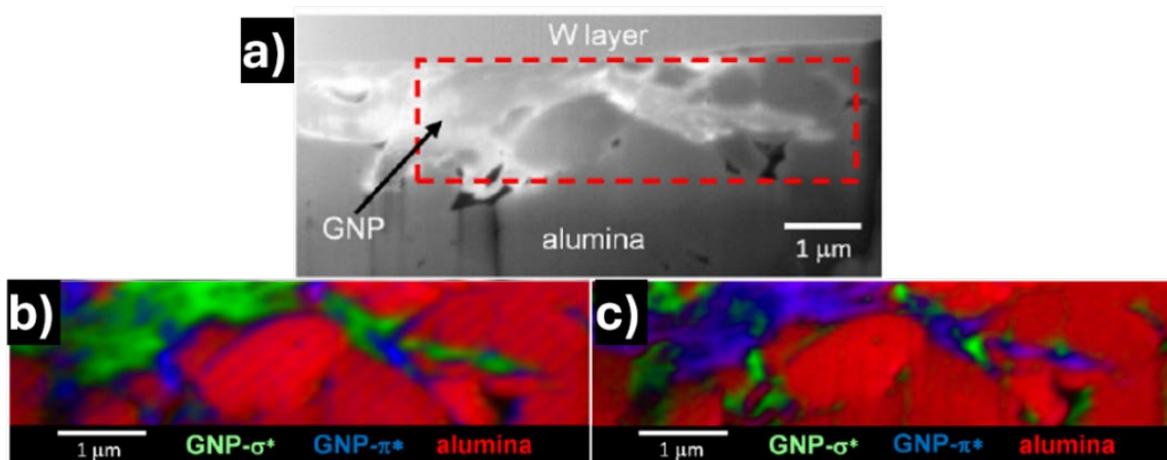


Figure 6.5: C K-edge STXM analysis of GNPs retained in the as-sprayed Al_2O_3 -GNPs coating. Adapted from Paper A [142] under Creative Commons license.

When considering both systems, the results demonstrate that the retention of graphene-based materials during thermal spraying depends on both the incorporation method and the spraying process. In SPS, the liquid carrier reduces the thermal exposure of the GNP through solvent evaporation, while in the WC–Co–Cr system, the porous feedstock provides physical protection by shielding part of the GO within the powder particles. In addition, the lower operating temperature and short particle residence time of HVOF further limit GO exposure during spraying. Therefore, successful retention may require a combination of an incorporation method that can protect the graphene-based material and a spraying process that limits its temperature and exposure time.

6.2.2 Retention during sliding wear

In addition to withstanding the thermal spraying process, graphene-based materials must retain their tribological functionality under subsequent wear stress. Paper A investigated this by comparing the as-sprayed and wear-tested Al_2O_3 -GNPs coatings. While well-preserved GNP were detected in the as-sprayed coating, C K-edge STXM measurements on the wear-tested material revealed that the GNP predominantly remained at the tribosurface (Figure 6.6), whereas amorphous carbon was distributed beneath the wear track. This redistribution and amorphization of carbon was accompanied by amorphization of the Al_2O_3 matrix, as demonstrated by the Al K-edge analysis presented in Paper A.

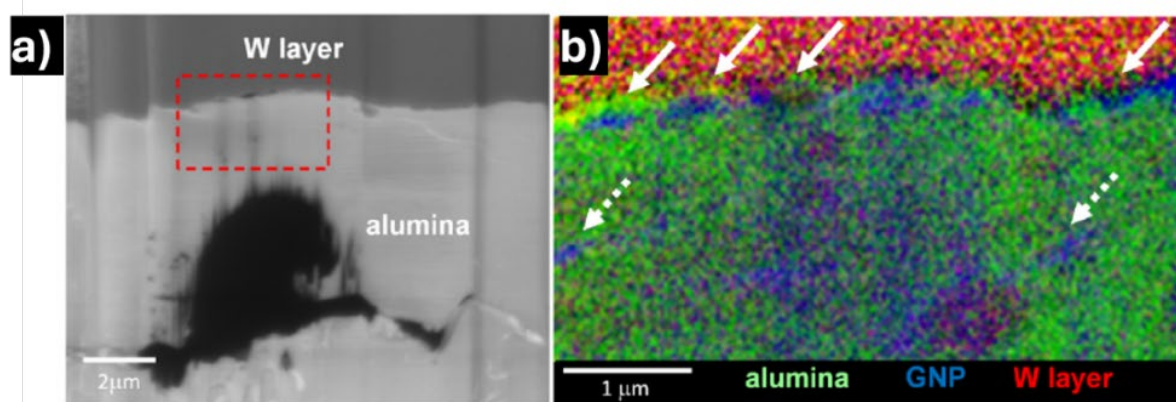


Figure 6.6: C K-edge STXM analysis of GNPs in the wear-tested Al_2O_3 -GNPs coating. a) STXM image with scale bar at $2\mu\text{m}$. b) XANES color composite map. Adapted from Paper A [142] under Creative Commons license.

The degradation of the GNPs during wear was further supported by STEM-EDS. The TEM micrograph presented in Figure 7a of Paper A shows amorphous and crystalline Al_2O_3 regions beneath the wear track, while the corresponding STEM-EDS analysis in Table 6.1 reveals, in addition to the respective oxygen contents, a carbon content approximately four times higher in the amorphous region (region 1) compared with the crystalline region (region 2). Although some carbon contamination of the lamella could not be ruled out, the higher carbon content in the amorphous region led to the conclusion that carbon from the GNPs was incorporated into the alumina during wear.

Table 6.1: STEM-EDS composition of amorphous and crystalline regions in the wear-tested Al_2O_3 -GNPs coating. Adapted from Paper A .

Point	Al (wt.%)	O (wt.%)	C (wt.%)
1	27 ± 2	19 ± 2	54 ± 2
2	53 ± 4	34 ± 2	13 ± 2

A similar trend was observed for the GO-containing WC–Co–Cr coating in Paper C. XPS confirmed the presence of graphene-related states after HVAF spraying, while analysis following wear testing revealed increased oxidation and changes in the relative sp^2 and sp^3 fractions, indicating progressive degradation of the GO structure. Further details regarding the XPS analysis are provided in Paper C.

Together, these results show that retaining graphene-based materials during thermal spraying does not ensure that their structure will remain unchanged during subsequent wear. Under prolonged and severe sliding conditions, contact forces and frictional heat can promote oxidation and progressively increase structural disorder, eventually leading to amorphization. This behavior was observed for the Al_2O_3 -GNPs system in Paper A and is consistent with previous studies discussed in that paper. Paper C showed a similar progression through the oxidation and structural degradation of GO during wear, although complete amorphization was not directly demonstrated. Therefore, severe wear represents an important limitation for the preservation of graphene-based materials, as progressive oxidation and structural damage can increase disorder and eventually lead to amorphization, which may ultimately be detrimental to their tribological performance.

6.2.3 Influence on tribological performance

The relationship between the structural modification of graphene and its lubricating effect was particularly evident in the WC-Co-Cr system. In the as-sprayed condition, GO incorporation reduced the average CoF from 0.68 to 0.58 (Figure 6.7a). Although the CoF of both coatings progressively increased during sliding, the GO-containing coating maintained a lower CoF than the virgin WC-Co-Cr coating throughout the test, indicating that the lubricating effect associated with GO persisted during wear testing.

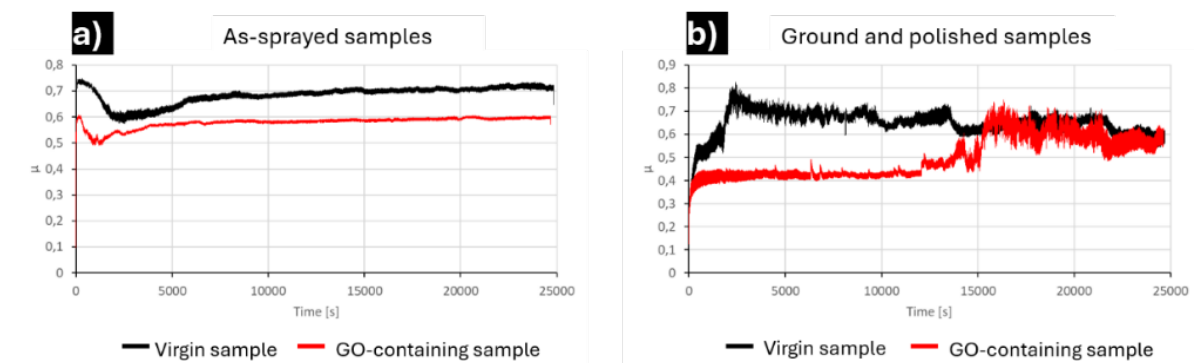


Figure 6.7: CoF evolution of virgin and GO-containing WC-Co-Cr coatings in the a) as-sprayed and b) ground and polished conditions. Adapted from Paper C [12] under Creative Commons license.

After grinding and polishing (Figure 6.7b), both coatings exhibited lower initial CoF values, with the GO-containing coating maintaining a CoF of approximately 0.4 for around 15,000 s. Beyond this stage, the GO-containing sample presented an increase in CoF to approximately 0.6, approaching the value measured for the virgin WC-Co-Cr coating. Paper C associated this evolution with progressive damage to the incorporated GO during surface preparation and wear. This behavior is consistent with the results of Paper A, where severe sliding resulted in the transformation of GNPs into amorphous carbon, and with previous studies discussed in Papers A and C reporting progressive damage to graphene-based materials during sliding wear. These observations indicate that preservation of the graphitic structure is important for maintaining its lubricating effect.

The GO-containing sample also exhibited lower porosity than the virgin WC-Co-Cr coating, as illustrated in Figure 6.8, with the measured porosity decreasing from approximately 13% to 9%. In Paper C, this is partly attributed to the influence of GO on heat transfer during spraying: the high thermal conductivity of graphene-based material was proposed to promote a more uniform temperature distribution and improve bonding and densification during deposition.

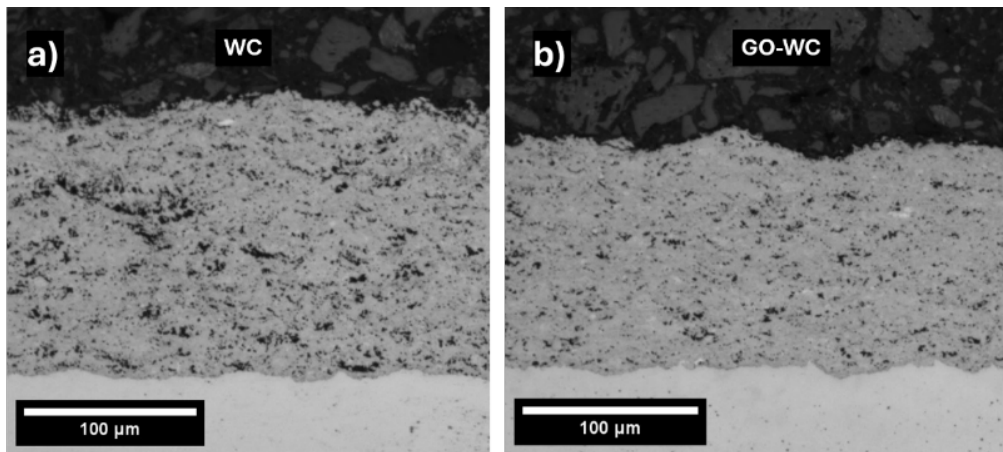


Figure 6.8: Cross-sectional optical microscopy images of a) virgin and b) GO-containing WC-Co-Cr coatings. Adapted from Paper C [12] under Creative Commons license.

The results from the two thermal-spray systems show that graphene-based materials can be retained through thermal spraying and provide a lubricating effect. However, as discussed in Section 6.2.2, prolonged and severe wear can progressively oxidize and damage their structure, eventually leading to amorphization and a reduction in their lubricating effect. Therefore, graphene-based materials show potential as solid lubricants in thermally sprayed coatings, but their effectiveness is strongly dependent on the wear conditions and their ability to preserve the graphitic structure during service. For applications involving prolonged or severe wear, this progressive degradation represents an important limitation to their long-term tribological performance.

6.3 Influence of GO on PBF-LB processing of copper

6.3.1 Laser/powder interaction and melt pool behavior

The first effect of the GO coating on PBF-LB processing was the modification of the optical response of the Cu powder. As shown in Figure 6 of Paper D, GO reduced the reflectance at the near-infrared laser wavelength of approximately 1070 nm from around 77% for Pure-Cu to 71% and 69% after one and three coating cycles, respectively. The relatively small difference between the single- and triple-coated powders indicates that most of the change in optical response was already achieved after the first coating cycle. This confirms that even a relatively small amount of GO distributed on the Cu particle surface can modify the initial laser/powder interaction.

Operando X-ray radiography demonstrated that this change in laser/powder interaction was accompanied by a clear modification in keyhole behavior. At 350 W, Pure-Cu predominantly exhibited deep and slender keyhole geometries, whereas GO-Cu-3C showed shallower and less slender keyholes, suggesting a shift toward transitional melting conditions (Figure 6.9).

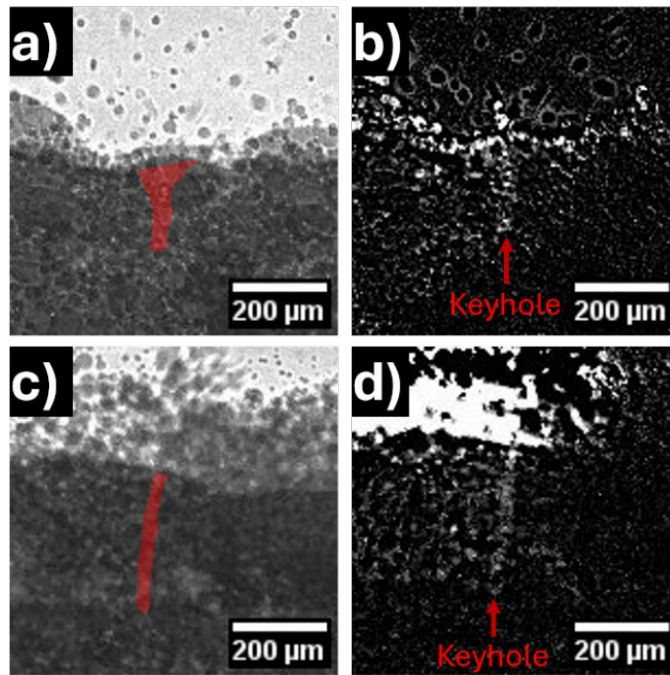


Figure 6.9: Representative operando X-ray radiographs and corresponding segmented keyhole-associated features for a,b) GO-Cu and c,d) Pure-Cu at 350 W.

Analysis of more than 170 radiographic masks for each condition revealed a lower mean apparent laser penetration extent for GO-Cu (68 μm) than for Pure-Cu (140 μm), as summarized in Table 6.2. These results are consistent with the shallower keyhole geometries observed in the radiographic sequences and indicate that the increased initial laser absorption associated with the GO coating did not result in a greater apparent laser penetration extent under the investigated conditions. Instead, the changes in keyhole geometry suggest a modification of the melting behavior,

potentially involving differences in energy distribution and melt pool dynamics. Further details of the operando analysis are provided in Paper D.

Table 6.2: Apparent laser penetration extent of GO-Cu and Pure-Cu determined from operando X-ray radiography at 350 W. Values are presented as mean $\pm$ standard deviation.

Sample	Apparent laser penetration extent (μm)
Pure-Cu	140 ± 56
GO-Cu	68 ± 40

The operando observations were complemented by metallographic characterization of samples produced using a commercial PBF-LB system. As summarized in Table 6.3, GO-Cu exhibited a lower average melt-pool depth and a higher average width than Pure-Cu. Although the differences were relatively small, the tendency toward shallower and wider melt pools was consistent with the operando observations. Together with the more uniform melting observed across the powder-filled groove in Figure 9 in Paper D, these findings suggest that GO modification may promote lateral spreading of molten Cu. However, the different processing configurations and GO coating cycles prevent a direct quantitative comparison, and further investigation is required to confirm the mechanisms responsible for this behavior.

Table 6.3: Melt-pool depth and width measured for Pure-Cu and GO-Cu samples produced using a commercial PBF-LB system.

Sample	Depth (μm)	Width (μm)
Pure-Cu	279.9 ± 33.9	173.1 ± 10.8
GO-Cu	231.1 ± 23.1	183.7 ± 13.5

Together, these findings show that the influence of GO on PBF-LB processing extends beyond the expected increase in laser absorption. If increased absorption were the dominant effect, greater energy coupling could be expected to increase apparent laser penetration. Instead, GO-Cu showed a shift from keyhole-like toward transition- and conduction-like melting, with reduced penetration and indications of increased lateral spreading. This unexpected behavior demonstrates that the influence of GO on the melting process is more complex than initially anticipated and suggests that additional mechanisms, potentially involving the wetting of molten Cu, contribute to the observed response. Further investigation is required to confirm these mechanisms, but these results highlight important aspects of GO-modified Cu that should be more extensively investigated.

6.3.2 Processability and consolidation of copper

The changes in laser/powder interaction and melt-pool behavior translated into a clear improvement in the PBF-LB processability of Cu. As shown in Figure 9 of Paper E, GO-Cu enabled the fabrication of thin-wall structures over a broad range of laser powers and scan speeds, whereas equivalent structures could not be successfully produced from Pure-Cu under the investigated conditions. The variation in wall thickness with increasing scan speed further demonstrates that the benefit of GO

depends on the applied processing conditions, particularly as the available energy and laser/material interaction time decrease at higher scan speeds.

The improved processability observed for the thin-wall structures also translated into improved consolidation of bulk samples. As shown in Figure 6.10, GO-Cu exhibited a higher relative density than Pure-Cu under all 16 paired processing conditions, with the lowest relative density obtained for GO-Cu remaining higher than the highest value measured for Pure-Cu. These results demonstrate that the effect of the GO coating was not limited to enabling the fabrication of thin structures, but also improved the consolidation of bulk Cu samples across the investigated PBF-LB conditions.

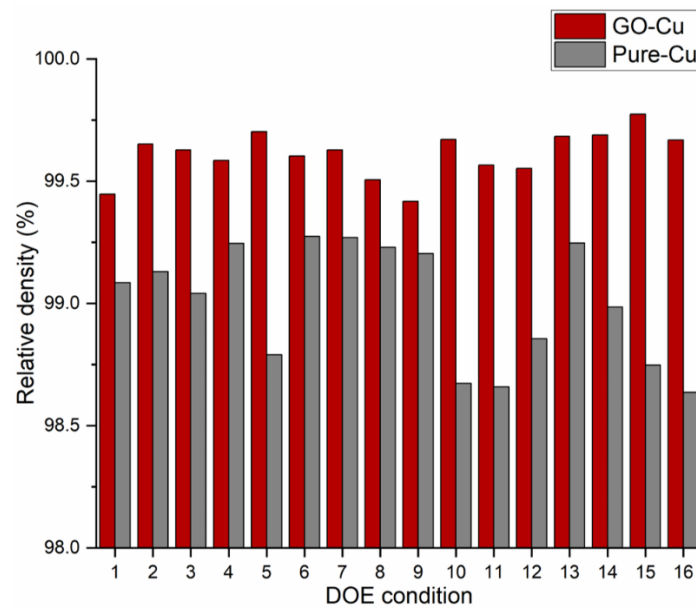


Figure 6.10: Relative density of GO-Cu and Pure-Cu samples produced under 16 paired PBF-LB processing conditions. GO-Cu exhibited a higher relative density than Pure-Cu under all investigated conditions.

Beyond improving laser absorption, the GO coating showed an additional function during PBF-LB through its consumption during processing. As shown in table 6.4, GO-Cu initially contained higher carbon and oxygen concentrations than Pure-Cu due to the coating. After PBF-LB, however, most of the additional carbon was removed, while the oxygen concentration decreased from 552 to 104 ppm. In comparison, the oxygen content of Pure-Cu decreased only from 345 to 309 ppm. This simultaneous reduction in carbon and oxygen supports the mechanism proposed in Paper E, in which carbon from the GO coating may contribute to the reduction of Cu surface oxides during processing.

Table 6.4: Carbon and Oxygen content of the samples in powder and after PBF-LB process (print). Values are the average of three measurements along with the $\pm$ standard deviation.

Sample	Carbon (ppm)	Oxygen (ppm)
Pure-Cu (powder)	4 ± 2	345 ± 10
GO-Cu (powder)	134 ± 3	552 ± 2
Pure-Cu (print)	35 ± 2	309 ± 14
GO-Cu (print)	29 ± 3	104 ± 16

The processability results complement the operando X-ray observations while also providing further insight into the mechanisms involved. The successful fabrication of thin structures and the higher relative density of GO-coated copper under all investigated bulk processing conditions demonstrate that the changes in laser/material interaction and melt-pool behavior observed by operando radiography translated into improved process stability and consolidation. In addition, the chemical analysis provided another important piece of evidence for understanding this behavior. The substantial decrease in oxygen content observed for GO-Cu after processing suggests that the influence of the coating extends beyond its optical effect and may involve the reduction of Cu surface oxides. The possible removal of these oxides can contribute to improved wetting and spreading of molten Cu, providing a potential explanation for the lateral spreading observed in Paper D. Therefore, the improved PBF-LB processability of GO-Cu may result from the combined influence of enhanced laser absorption, modified melt-pool behavior, and possible changes in the chemical condition of the molten material. These findings highlight the complexity of the mechanisms in which GO influences Cu processing in PBF-LB and the need for further investigation to determine their individual contributions to the improved processability.

Conclusion and Future Work

7.1 Conclusions

This thesis investigated the incorporation of graphene-based materials into powder feedstocks, focusing on controllable and scalable GO deposition, graphene retention and tribological functionality during thermal spraying and wear, and the influence of GO on the PBF-LB processing of Cu. The main conclusions are presented below in relation to the research questions introduced in Section 1.3.

Q1. How can a controllable and scalable deposition of graphene oxide on metallic powder particles be achieved?

- The molecular-level mixing methodology demonstrated that controllable GO deposition requires control of both the powder surface functionalization and the amount of GO available for deposition. APTES concentration and GO loading therefore provide complementary means of tailoring GO amount and surface coverage.
- Scale-up requires control of both surface chemistry and mixing conditions. As batch size increases, effective powder suspension and circulation, together with sufficient coupling-agent and solvent availability, are necessary to reproduce homogeneous functionalization and GO deposition throughout the powder batch.
- The successful scale-up enabled the production of 10 kg of GO-coated Cu powder and, together with its application to WC–Co–Cr powder, demonstrates that molecular-level mixing provides a controllable and adaptable route for GO coating of metallic powder feedstocks.

Q2. To what extent do graphene-based materials remain intact during thermal spraying and subsequent wear, and how does their incorporation affect the tribological properties of the resulting materials?

- Graphene-based materials can survive thermal spraying, but their retention depends strongly on how they are incorporated and protected during processing. The two investigated systems demonstrated different protection mechanisms: reduced thermal exposure associated with suspension-based processing and physical shielding of GO within porous feedstock particles.
- Both systems showed degradation of graphene-based materials during sliding wear. In the Al_2O_3 –GNP coating, some GNPs remained at the tribosurface, while carbon was also redistributed into amorphous alumina beneath the wear track. In the GO-containing WC-Co-Cr coating, XPS revealed progressive oxidation and changes in the carbon bonding structure, indicating degradation of GO during wear.
- GO incorporation reduced the coefficient of friction of the WC-Co-Cr coating, demonstrating its lubricating effect. However, this effect diminished as the GO structure progressively degraded during prolonged wear. These results indicate that graphene-based materials can improve the tribological performance of thermally sprayed coatings, although the duration of their lubricating effect depends on the wear conditions and the preservation of their graphitic structure.

Q3. How does coating copper powder with graphene oxide affect laser/powder interactions and the processability in PBF-LB?

- GO surface modification improved the interaction of Cu powder with the near-infrared laser, but its influence extended beyond increased laser absorption. Instead of increasing penetration, GO shifted the melting behavior from deep keyhole-like geometries toward shallower and more laterally spread morphologies, revealing a more complex influence on the melting process.
- These changes translated into improved PBF-LB processability in both thin and bulk geometries, demonstrating that modification introduced at the powder surface can influence the stability of the subsequent melting and consolidation.
- The removal of most of the additional carbon together with the pronounced decrease in oxygen after processing indicates that the influence of GO extends beyond its optical effect. The improved processability of GO-Cu therefore cannot be attributed to increased laser absorption alone.

7.2 Future work

The results of this thesis identify several directions for further development of graphene-based powder feedstocks. For the GO coating methodology, future work should focus on quantitatively determining coating thickness and surface coverage, as well as evaluating batch-to-batch reproducibility at the 500 g and kilogram scales. This would help establish manufacturing tolerances for further scale-up. Alternative coupling agents and functionalization chemistries should also be investigated to extend the methodology to other metallic powder surfaces and coating requirements.

For thermal spraying, a more direct relationship between graphene degradation and tribological performance should be established. Interrupted wear experiments combined with structural and chemical characterization could help determine when degradation of the graphene-based material begins. For GO-containing WC–Co–Cr coatings, future work should also explore alternative incorporation methods capable of introducing more material into the pores of the powder particles, aiming to increase the amount of GO protected within the porous structure and potentially prolong its lubricating effect.

Finally, the proposed influence of GO on wetting and spreading during PBF-LB should be further investigated through dedicated experiments, including in situ observations of molten Cu behavior. In addition, the potential oxygen-removal capability of GO could be evaluated using Cu powders with different oxygen contents and other oxidation-sensitive metallic powders to assess whether the proposed sacrificial behavior extends beyond the GO-Cu system.

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Plinio Fernandes Borges Silva

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