



UNIVERSITAT DE
BARCELONA

Deposition Strategies for New Applications of Cold Spray Additive Manufacturing

Andrea Garfias Bulnes

ADVERTIMENT. La consulta d'aquesta tesi queda condicionada a l'acceptació de les següents condicions d'ús: La difusió d'aquesta tesi per mitjà del servei TDX (www.tdx.cat) i a través del Dipòsit Digital de la UB (diposit.ub.edu) ha estat autoritzada pels titulars dels drets de propietat intel·lectual únicament per a usos privats emmarcats en activitats d'investigació i docència. No s'autoritza la seva reproducció amb finalitats de lucre ni la seva difusió i posada a disposició des d'un lloc aliè al servei TDX ni al Dipòsit Digital de la UB. No s'autoritza la presentació del seu contingut en una finestra o marc aliè a TDX o al Dipòsit Digital de la UB (framing). Aquesta reserva de drets afecta tant al resum de presentació de la tesi com als seus continguts. En la utilització o cita de parts de la tesi és obligat indicar el nom de la persona autora.

ADVERTENCIA. La consulta de esta tesis queda condicionada a la aceptación de las siguientes condiciones de uso: La difusión de esta tesis por medio del servicio TDR (www.tdx.cat) y a través del Repositorio Digital de la UB (diposit.ub.edu) ha sido autorizada por los titulares de los derechos de propiedad intelectual únicamente para usos privados enmarcados en actividades de investigación y docencia. No se autoriza su reproducción con finalidades de lucro ni su difusión y puesta a disposición desde un sitio ajeno al servicio TDR o al Repositorio Digital de la UB. No se autoriza la presentación de su contenido en una ventana o marco ajeno a TDR o al Repositorio Digital de la UB (framing). Esta reserva de derechos afecta tanto al resumen de presentación de la tesis como a sus contenidos. En la utilización o cita de partes de la tesis es obligado indicar el nombre de la persona autora.

WARNING. On having consulted this thesis you're accepting the following use conditions: Spreading this thesis by the TDX (www.tdx.cat) service and by the UB Digital Repository (diposit.ub.edu) has been authorized by the titular of the intellectual property rights only for private uses placed in investigation and teaching activities. Reproduction with lucrative aims is not authorized nor its spreading and availability from a site foreign to the TDX service or to the UB Digital Repository. Introducing its content in a window or frame foreign to the TDX service or to the UB Digital Repository is not authorized (framing). Those rights affect to the presentation summary of the thesis as well as to its contents. In the using or citation of parts of the thesis it's obliged to indicate the name of the author.

DEPOSITION STRATEGIES FOR NEW APPLICATIONS OF COLD SPRAY ADDITIVE MANUFACTURING

Andrea Garfias Bulnes



**UNIVERSITAT_{DE}
BARCELONA**



UNIVERSITAT DE
BARCELONA

Faculty of Chemistry

Doctoral program: Engineering and Applied Sciences 2024

DEPOSITION STRATEGIES FOR NEW APPLICATIONS OF COLD SPRAY ADDITIVE MANUFACTURING

PhD Thesis

Andrea Garfias Bulnes

Supervisors

Dr. Vicente Albaladejo Fuentes

Professor Universitat de Barcelona

*Department of Materials Science and
Physical Chemistry*

Dr. Irene García Cano

Professor Universitat de Barcelona

*Department of Materials Science and
Physical Chemistry*

Tutor

Dr. Irene García Cano

Professor Universitat de Barcelona

*Department of Materials Science and
Physical Chemistry*

*Dejamos fragmentos de nosotros en
todo aquello que hacemos con amor.*

Agradecimientos/Acknowledgements

Muchas veces me visualicé en este momento, escribiendo estas palabras. Una visión que en los momentos duros me impulsaba a seguir, mientras que en los momentos alegres me llenaba de orgullo. No es fácil cuando una etapa tan importante llega a su fin, especialmente una que ha sido tan retadora como expansiva. Hoy puedo asegurar que un doctorado es mucho más que un grado académico; es un proceso de vida que, sobre todo, me enseñó a enfrentarme a mí misma.

Todo este trabajo fue posible gracias a muchas personas que me guiaron y me acompañaron. Primero que nada, quiero agradecer a mis directores. A Irene por abrirme las puertas, confiar en mí y ser siempre un apoyo. A Vicente, que no me alcanzarían las líneas para agradecerle todo, por la paciencia, la guía, las risas y los consejos de vida. Muchas gracias también al resto de mis compañeros del CPT por las largas pláticas, las palabras de aliento y las incontables carcajadas; nos sobran historias que contar.

Diese Arbeit wurde ebenfalls am Fraunhofer IGCV durchgeführt. Ein besonderer Dank gilt Ismail, der mich in sein Team aufgenommen hat, sowie Philipp, Martin und dem restlichen Team der Additiven Fertigung für ihre Anleitung und dafür, dass sie mich so herzlich aufgenommen haben.

Agradezco profundamente a mi familia. A mi hermano por estar siempre. A mi madre, por creer en mí más que yo misma, ser mi mayor apoyo y no dejarme nunca alejarme del camino. A los Bulnes, donde estén ustedes, estará mi hogar.

Gracias a Isabel, mi traductora de vida, por ponerme los pies en la realidad y apuntar siempre hacia mi evolución. Somos equipo.

No puedo cerrar sin agradecer a mis amigos. A aquellos que siempre han estado. A aquellos que han llegado para quedarse. Y a aquellos que han sido estrellas fugaces que me han inspirado en su paso. Ustedes son mi familia elegida.

Me llevo en el corazón infinidad de recuerdos con una sonrisa.

Financial support

This work was done with the financial support received from grant 2021 FISDU 00300 by the Agència de Gestió d'Ajuts Universitaris i de Recerca (AGAUR) funded by the Generalitat de Catalunya.



**Generalitat
de Catalunya**

Abstract

The potential of CSAM has attracted the attention from the scientific community due to its advantages over other heat-focused AM methods, such as solid-state deposition, high deposition rates, ability to deposit temperature-sensitive materials, and reduction of tensile residual stresses, among others.

Therefore, the efforts of the researchers in the CSAM field are focused on developing this technology beyond its inherent challenges. To do so, state-of-the-art deposition strategies are currently being investigated. These new deposition strategies include optimizing the robotic path trajectories or employing masks to overcome constraints to manufacture objects with a more complex shape; introducing advanced strategies during spraying or process modifications, such as substrate preheating; and implementing post-process methods such as heat treatments or machining that help to enhance microstructure densification and surface finish, respectively.

This thesis focuses on the development of CSAM as a metal AM technology by understanding the CSAM process variables and deposition strategies for its further development and application as an additive manufacturing technology.

Two robot path trajectories, a traditional (T) toolpath, and a novel strategy called Metal Knitting (MK), were used for the reconstruction of CSAM parts from various metallic materials: Cu, Al, Ti, and Ti6Al4V. The final geometry, microstructure, and mechanical properties of the obtained parts were assessed and compared. It was found that the novel MK robot path trajectory enabled a precise control over the geometry of the reconstructed parts. However, the deposition angle reduced the plastic deformation of the particles, increasing porosity within the microstructure and hindering adhesion with the substrate. To address this, the effects of annealing on the components' microstructure and its influence on adhesion, resistance to erosion, and abrasive wear were also evaluated. In this sense annealing was found to be an effective deposition strategy for reducing porosity, and improving cohesion between particles and adhesion with the substrate. It was concluded that spraying with the MK toolpath, followed by annealing, enabled the reconstruction of Cu and Al parts with

mechanical properties comparable to other bulk production methods. Nevertheless, alternative deposition strategies are needed for the CSAM reconstruction of dense parts from less ductile materials such as Ti and Ti6Al4V.

Moreover, the effects of substrate preheating on high-strength materials with low particle plasticity was investigated. Since the interest in repairing IN718 damaged parts with CSAM has increased in the last years, the effect of IN718 substrate preheating on the CSAM IN718 deposit microstructure and thickness, as well as the adhesion mechanisms and strength at room and preheating temperatures of 250 C and 400 °C was evaluated. The results showed that the substrate preheating improved the bonding strength, adhesion, and cohesion of CS IN718 deposits by softening the substrate, which improved the materials' plasticity during deposition. It was concluded that increasing the preheating temperature and the deposit thickness improved the deposit density, reaching values comparable to an IN718 bulk reference, > 99.9%.

Finally, the fabrication of 3D patterned parts with a desired pattern based on a bottom-up approach using a masked CSAM deposition strategy was investigated for fabricating new Ti bipolar plates (BPPs) for Proton Exchange Membrane (PEM) electrolyzers. The dimensional and microstructural characteristics of pin fins fabricated with spherical and irregular Ti powders were assessed. The results demonstrated that the masked CSAM technology allowed precise control and customization of the dimensions of the 3D-printed pin fins. Additionally, the performance of both Ti parts for its application in PEM electrolyzers was evaluated in terms of corrosion resistance and interfacial contact resistance (ICR). The results suggest that the masked CSAM technology shows great potential for the fabrication of Ti BPPs.

Table of contents

Table of contents

Agradecimientos/Acknowledgements.....	i
Financial support	ii
Abstract	iii
Thesis structure	4
Chapter 1: Introduction	8
1.1 General introduction	8
1.1.1 Additive Manufacturing	8
1.1.2 Cold Spray Overview.....	11
1.2 Fundamentals of Cold Spray	13
1.2.1 CS nozzle design	15
1.2.2 Cold spray deposition & adhesion mechanisms	17
1.3 Cold spray process variables.....	23
1.3.1 Feedstock powder	24
1.3.2 Cold spray operating process parameters.....	26
1.3.3 Robotic parameters	27
1.3.4 Substrate characteristics	30
1.3 Cold Spray Additive Manufacturing.....	32
1.3.1 Properties of CSAM deposits	34
1.3.2 Applications of CSAM.....	41
1.3.3 Challenges in CSAM	46
1.3.4 CSAM deposition strategies	50
1.4 References	64
Chapter 2: Scope of work.....	78
Chapter 3: Materials and Methods	82
3.1 Raw materials	82
3.2 CSAM equipment and process parameters	83
3.3 CSAM deposition strategies.....	84
3.3.1 Robot path trajectories	84
3.3.2 Heat treatments.....	84
3.3.3 Substrate preheating	85
3.3.4 CSAM masking process	85
3.4 Characterization techniques	86

3.4.1 Feedstock powders characterization	86
3.4.2 CSAM parts characterization.....	87
3.5 References	95
Chapters 4-6 Results & Discussion	96
Chapter 4: Geometry and Microstructure Control of Remanufactured Metallic Parts by Cold Spray Additive Manufacturing	98
4.1 Introduction	98
4.2 Materials and Methods.....	101
4.2.1 Feedstock Powder Characterization.....	101
4.2.2 CSAM Spraying Parameters	102
4.2.3 Heat Treatment of CSAM Deposits	102
4.2.4 Characterization and Mechanical Properties	102
4.2.5 Resistance to Erosion and Abrasive Wear	103
4.3 Results and Discussion.....	104
4.3.1 Feedstock Powder Characterization.....	104
4.3.2 Geometry Analysis of the Reconstructed Metallic Parts.....	105
4.3.3 Microstructure Characterization and Physical Properties of the CS Deposits	107
4.3.4 Effect of Heat Treatment on the Microstructure of CSAM Deposits	109
4.3.5 Adhesion Strength of the Reconstructed Part to the Substrate	112
4.3.6 Erosive and Abrasive Wear Resistance	115
4.4 Conclusions	119
4.5 Acknowledgements.....	120
4.6 References	121
Chapter 5: Repair of Inconel 718 parts by Cold Spray Additive Manufacturing: the effect of substrate preheating on thick coatings properties	130
5.1 Introduction	130
5.2 Materials and Methods.....	132
5.2.1 Feedstock powder	132
5.2.2 CSAM parameters and substrate preheating conditions	133
5.2.3 Microstructural characterization	134
5.2.4 Adhesion mechanisms & evaluation.....	135
5.3 Results and Discussion.....	135
5.3.1 Microstructural characterization	135

5.3.2 Adhesion mechanisms and strength	141
5.4 Conclusions	146
5.5 Acknowledgements	147
5.6 References	148
Chapter 6: Manufacturing and properties characterization of Ti patterned coatings for water electrolyzers by masked CSAM.....	154
6.1 Introduction	154
6.2 Materials and Methods.....	157
6.2.1 Feedstock powder characterization.....	157
6.2.2 Bipolar plates manufacturing and process parameters	158
6.2.3 Microstructure, mechanical properties & adhesion.....	159
6.2.4 Bipolar plates profile & 3D topography	159
6.2.5 Electrochemical experiments	160
6.2.6 Interfacial contact resistance	160
6.3 Results and Discussion.....	161
6.3.1 Feedstock powder	161
6.3.2 Bipolar plates profile & 3D topography	162
6.3.3 Microstructure, mechanical properties & adhesion.....	166
6.3.4 Electrochemical experiments	168
6.3.5 Interfacial contact resistance	171
6.4 Conclusions	173
6.5 Acknowledgements.....	174
6.6 References	175
Chapter 7: Global Discussions	182
7.2 References	188
Chapter 8: General Conclusions	192
Appendix	198
Publications and scientific activities	198

Thesis structure

Thesis structure

This thesis has been structured in several chapters, summarized as follows:

Chapter 1 introduces the background of the CSAM technology by describing an overview of the additive manufacturing technology and briefly introduces the general basics of the CS process. In addition, it compiles state-of-the art research related to the CSAM technology, where the fundamentals are described in depth and the existing gaps in the field are identified and discussed.

Chapter 2 outlines the scope of work and objectives for this thesis, which are established based on the knowledge gaps and challenges identified in Chapter 1.

Chapter 3 describes the materials and methods used in this thesis. It lists the feedstock materials and the CSAM process parameters utilized in this research. Additionally, it details the implemented CSAM deposition strategies, including robot path trajectories, heat treatments, substrate preheating and masking process. Finally, the chapter describes in detail the methodology used throughout this thesis and explains the fundamentals of the experimental procedures for the CSAM parts characterization.

Chapters 4 to 6 are dedicated to the presentation and discussion of the experimental results obtained. Each chapter includes an introduction and an experimental section to ensure they can be read independently.

Chapter 4 investigates two robot path trajectories for the reconstruction of CSAM parts from various metallic materials. The final geometry, microstructure, and mechanical properties of the obtained parts were assessed and compared. Additionally, the effects of heat treatment annealing on the components' microstructure and its influence on adhesion, resistance to erosion, and abrasive wear were also evaluated.

The results from this chapter have led to the following publication:

- **A. Garfias**, R. Vaz, V. Albaladejo, J. Sánchez, I. García-Cano. Geometry and microstructure control of remanufactured metallic parts by Cold Spray Additive Manufacturing. *Materials*. 2023, 16(13), 4735. <https://doi.org/10.3390/ma16134735>. **SJR (2023): 0.56. Impact Factor 3.1 – Q2 (2023)**

Chapter 5 investigates the effect of substrate preheating on the deposition of high strength materials, such as IN718. The deposits' microstructure and thickness, as well as the adhesion mechanisms and strength at room and preheating temperatures of 250 and 400 °C were evaluated.

This study was conducted as part of a doctoral stay at the Fraunhofer IGCV research institute in Augsburg, Germany, from July 20th, 2023, to October 20th, 2023. This enables this thesis to qualify for an International Doctorate mention.

The results from this chapter have led to the following publication:

- **A. Garfias**, P. Kindermann, M. Wunderer, R.F. Vaz, V. Albaladejo-Fuentes, J. Sánchez, I. Ünsal, G. Schlick, I.G. Cano. Repairing alloy 718 parts by cold spray additive manufacturing: the effect of substrate preheating on the deposit properties. *Journal of Manufacturing Processes*. ***Submitted on Sep 2024. SJR (2023): 1.39. Impact Factor 6.2 – Q1**

Chapter 6 evaluates the fabrication of Ti patterned parts using a masked CSAM deposition strategy for their application as bipolar plates (BPPs) for Proton Exchange Membrane (PEM) electrolyzers. The dimensional and microstructural characteristics of pin fins were assessed. Additionally, the performance of both Ti parts for its application in PEM electrolyzers was evaluated in terms of corrosion resistance and interfacial contact resistance (ICR).

The results from this chapter have led to the following publication:

- **A. Garfias**, M. Sarret, J. Sánchez, I. García-Cano, V. Albaladejo, Andreu, T. (2023). Manufacturing and properties characterization of Ti patterned coatings for water electrolyzers by CSAM. *Applied Surface Science Advances*. ***In revision on Sep 2024. SJR (2023): 1.16. Impact Factor 7.5 – Q1**

Chapter 7 summarizes the results obtained throughout this thesis and discusses the contributions of Chapters 4-6 in addressing the challenges previously identified in Chapter 2.

Chapter 8 enlists the general conclusions derived in the studies presented this thesis.

In the **Appendix**, the scientific contributions of the PhD candidate are listed, including published articles, doctoral stays and works presented in congresses.

Chapter 1: Introduction

This chapter introduces the background of the CSAM technology by providing a general introduction that describes the overview of the additive manufacturing technology and briefly introduces the general basics of the CS process. In addition, it compiles state-of-the art research related to the CSAM technology, where the fundamentals of this technology are described in depth and the existing gaps in the field are identified and discussed.

Chapter 1: Introduction

1.1 General introduction

1.1.1 Additive Manufacturing

Additive manufacturing (AM) or 3D printing is the process of building an object layer-by-layer based on a digital design. AM allows to manufacture complex-shaped objects from a bottom-up approach in a continuous process, contrary to traditional top-down methods where the final object is obtained by cutting a block of material. In this process of building components, the 3D printed object is first digitally designed using a computer aided design (CAD) system. The digital model of the object is layered and interpreted by the AM machine that deposits material one layer at a time. Each layer of added material corresponds to a thin cross-section of the final printed object, allowing to produce components with complex geometries that would be impossible to obtain with conventional machining processes [1,2].

In the 1980s, AM was developed as a rapid prototyping technology, which was based on quickly creating prototypes or models that eventually would end up as products. In later years, as the technology was further developed, the printing of final functional parts with AM became a more reliable method. Nowadays, a wide range of materials, including metals or polymers, can be processed with the different AM technologies to obtain reliable dense parts for various industries. Therefore, the AM technology has undergone extensive investigation, resulting in a fast-paced development of this manufacturing process [1].

In general, its main advantages include the reduction of manufacturing costs, production time and material waste, in addition to a precise control of the final object's shape [3,4]. Moreover, it enables the metal 3D printing of near-net-shape parts, making it a valuable technology with many applications in various sectors; allowing to print tool components and finished parts for the aerospace, marine and automotive industries, medical implants for knees or hips, supplies for the military industry, cooling channels for electronic devices, and so on.

The classification of AM technologies is based on factors such as material feedstock, energy source, layer formation process, and shape of the final product.

The ASTM ISO/ASTM52900 [5] categorizes the AM technologies into eight categories: Binder Jetting (BJ), Directed Energy Deposition (DED), Material Extrusion (ME), Material Jetting (MJ), Powder Bed Fusion (PBF), Sheet Lamination (SL), VAT Photopolymerization, and Solid-State AM. These AM technologies included in the ASTM ISO/ASTM52900 are summarized in Table 1.1.

Table 1.1. Main characteristics of the AM technologies according to ASTM-ISO/ASTM52900.

AM group	Main characteristics according to ASTM-ISO/ASTM52900
Binder Jetting	A liquid bonding agent acts as an adhesive between powder layers to create an object.
Directed Energy Deposition	A focused energy (laser, electron beam or plasma arc) is used to melt a material deposited by a nozzle.
Material Extrusion	A continuous filament of material is selectively deposited through a nozzle.
Material Jetting	Droplets of liquid resin are selectively fused by a printhead.
Powder Bed Fusion	A focused heat source selectively melts areas of a powder bed.
Sheet Lamination	Sheets of material are adhered to create a component.
VAT Photopolymerization	A photopolymer liquid resin is cures with light waves.
Solid-State	Powder feedstock is deposited into a substrate at high kinetic energies to build up a deposit.

Each type of AM technology offers specific benefits according to its intended applications (such as repair or reconstruction), size of the part fabrication, and material characteristics. From all these AM categories, only a few can fabricate metallic parts that meet the requirements necessary for industrial applications; Figure 1.1 shows schematically the classification of the metal AM processes [6].

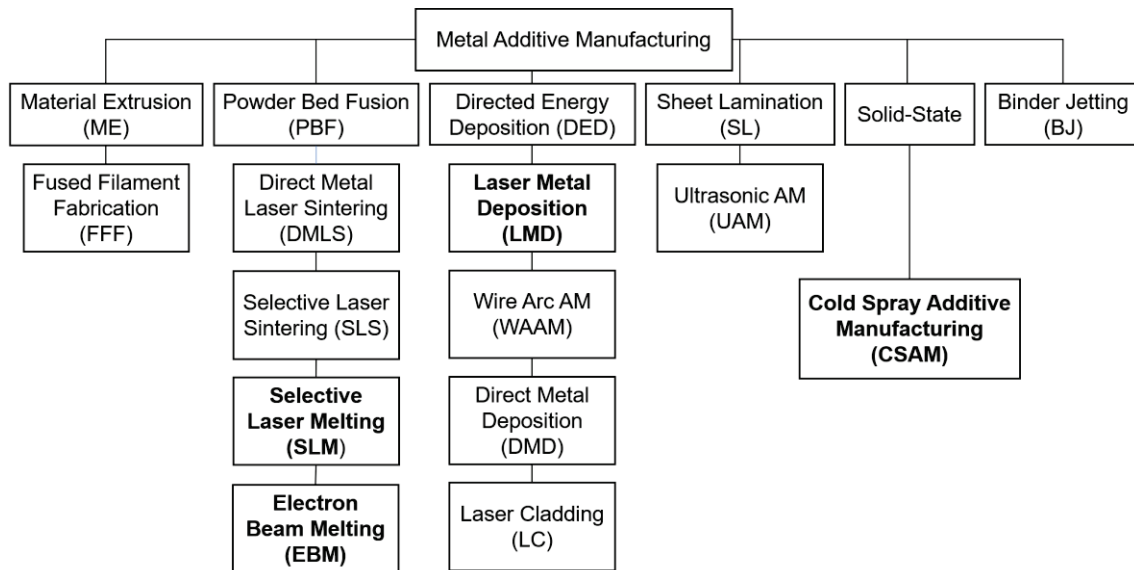


Figure 1.1. Metal AM technologies classification.

The most widely used AM techniques for the 3D printing of metals are the Powder Bed Fusion (PBF) and the Directed Energy Deposition (DED) processes.

PBF technologies stand as the most established methods in the metal AM industry. In this process, a layer of powder is distributed across the surface of a designated work area. Subsequently, the powder undergoes melting or sintering through the application of a focused heat source, such as a laser beam or electron beam, that selectively scans the predetermined area and melts the powder. The repetition of this process leads to the fabrication of an object with the desired shape, where each layer aligns with a cross-section of the 3D object.

Moreover, in DED technologies, the feedstock, which can be in the form of wire or powder, flows through a nozzle following programmed 3D path. The material is melted by a focused heat source that directly bonds metallurgically with the substrate. The molten powder subsequently solidifies to constitute a cross-sectional layer of the intended object; this process is iterated until several deposited layers build the desired 3D component [4,7].

Up to date, some of the most relevant techniques for the 3D printing of metals are Selective Laser Melting (SLM), Laser Metal Deposition (LMD) and Electron Beam Melting (EBM). Each one of these technologies offers distinct advantages used in particular applications, for example, SLM specializes in the fabrication of metallic objects with high precision, usually for aerospace and

medical applications. In contrast, LMD, excels at repairing applications or to fabricate near-net-shape components. EBM operates in high vacuum environments, and finds its advantages in producing components with high superior material performance.

Thus, AM is a technology that has revolutionized the manufacturing industry with distinguishable advantages that include a sustainable fast production of complex shaped parts with high quality and consistency, at a more economic price than other methods. However, there are still some limitations with the metal 3D printing techniques that are based on a focused heat source. AM based on thermal methods can produce defects within the microstructure of the part that are not beneficial for its final application, such as undesired phase changes, oxidation, and formation of residual stresses. Therefore, from a materials engineering perspective, there is a need for the further investigation and development of different AM technologies that address these drawbacks [4].

1.1.2 Cold Spray Overview

Thermal Spraying (TS) is a group of technologies known for the production of metallic and non-metallic coatings, in which, in general terms, the material feedstock (powder or wire) is heated by a hot mixture of gases and accelerated towards a substrate. The combination of high particle temperature (in molten or semi-molten state) and the high velocity to which the particles are accelerated promotes the formation of splats on the surface of the substrate at the point of impact, where the particles remain adhered and produce a dense coating. TS comprises several coating formation processes that are classified according to the energy source supplied to the equipment, driven by electric discharge, combustion of gases or kinetic energy, such as plasma and arc spraying, flame spraying and HVOF/HVAF, and cold gas spraying, respectively. Figure 1.2 shows the process temperature and velocity range for the different thermal spray technologies.

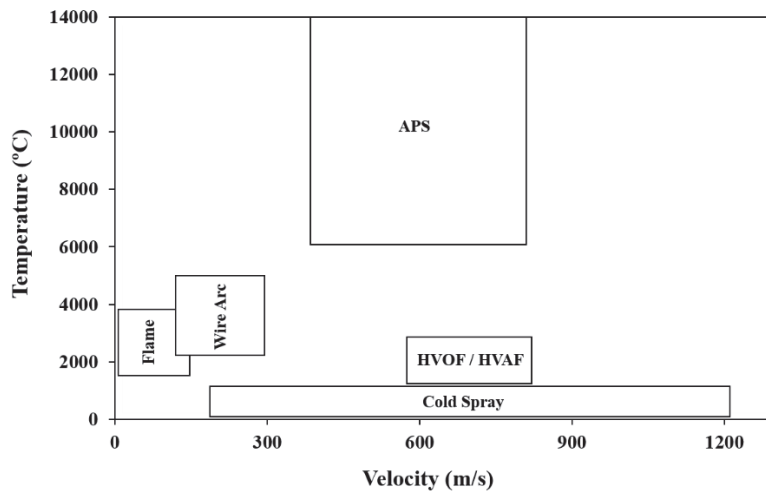


Figure 1.2. Gas temperatures and velocities of different thermal spray techniques.

Particularly, Cold Spray (CS) is a solid-state process that consists in accelerating a powder feedstock inside a gun with a preheated, compressed, supersonic gas (generally N_2 or He) to high velocities (300 – 1200 m/s) through a convergent-divergent (de Laval) nozzle. When the accelerated powder is sprayed towards a substrate with enough kinetic energy, plastic deformation occurs at the point of impact, promoting the formation of a well-bonded coating or part layer by layer. Although the CS process does not reach enough temperature to melt the particles, it is still considered part of the thermal spray methods.

In recent years, the capabilities of CS as an AM technology have aroused the attention from the scientific community due to its advantages over other AM methods, such as high deposition rates, ability to deposit temperature-sensitive materials, and reduction of tensile residual stresses. Since CS is a solid-state process, it can overcome the limitations of the thermal metal AM technologies (SLM, LMD, and EBM). However, it also presents some challenges to be studied; including an unprecise control over the geometrical shape of the deposits, inferior mechanical properties in comparison with bulk materials, delamination between deposit-substrate caused by excessive residual stresses, and difficult deposition of hard materials, among others [8,9].

To address these challenges, critical deposition strategies need to be further investigated to reach the full potential of the CSAM technology [10]. These new deposition strategies can include improvements in the current deposition

process, implementing post-process methods to tailor the characteristics of the final objects, or investing in supplementary equipment to upgrade the CSAM process. Some examples of deposition strategies include optimizing the robotic path trajectories or employing masks to overcome constraints to manufacture objects with a more complex shape; introducing advanced strategies during spraying or process modifications, such as substrate preheating or in-situ shot peening to tailor the deposits characteristics; incorporating the laser-assisted cold spray (LACS) equipment to broaden the CSAM processing capability; and implementing post-process methods such as heat treatments or machining that help to enhance microstructure densification and surface finish, respectively.

1.2 Fundamentals of Cold Spray

The cold spray (CS) process was developed in the mid-1980s in the Soviet Union by the scientist Anatolii Papyrin, who was studying the two-phase flow of gas and solid particles in a wind tunnel. He found out that when in-flight particles impacted a substrate with velocities higher than a critical value (intrinsic to each material), they would remain adhered and stacked together. This discovery set the basis of CS, a new technology for the production of a broad range of material coatings, including pure metals, metal alloys, composite materials, and so on, that could be successfully deposited into different substrates. The CS technology relies on gas dynamics to accelerate and spray solid particles at high velocities towards a substrate. Upon impact, the particles deform and bond together, building up layers of material. This technology quickly showed a high potential in several engineering applications as a solid-state manufacturing process, since its most notable characteristic is its relatively low process temperature. CS expanded the family of thermal spray technologies with distinct benefits such as preservation of materials properties, low oxidation and degradation during the manufacturing process, high deposition rates, versatility in material deposition, and production of well bonded thick coatings [11].

In CS, a gas (either compressed air, nitrogen, helium or a mixture) is introduced inside a gun and accelerated to supersonic velocities (between 300 – 1200 m/s) with a convergent-divergent de Laval nozzle. Depending on the CS equipment, this gas can be introduced at room temperature or preheated to temperatures up to 1100°C. At the same time, feedstock powder is injected into

the gun and it is propelled towards the substrate by the supersonic jet of compressed gas. As the gas flows through the divergent part of the nozzle it expands and rapidly cools down. Thus, the residence time of the particles that are in contact with the hot gas is brief. Accordingly, they achieve high velocities and still remain in solid state throughout the process, promoting the formation of good-quality, dense coatings [12,13].

In general, CS can be classified in two main categories based on the gas pressure applied to the propellant gas: low-pressure cold spray (LPCS) and high-pressure cold spray (HPCS). Figure 1.3 shows the schematic of the cold spray processes, while Table 1.2 describes and compares their operating conditions.

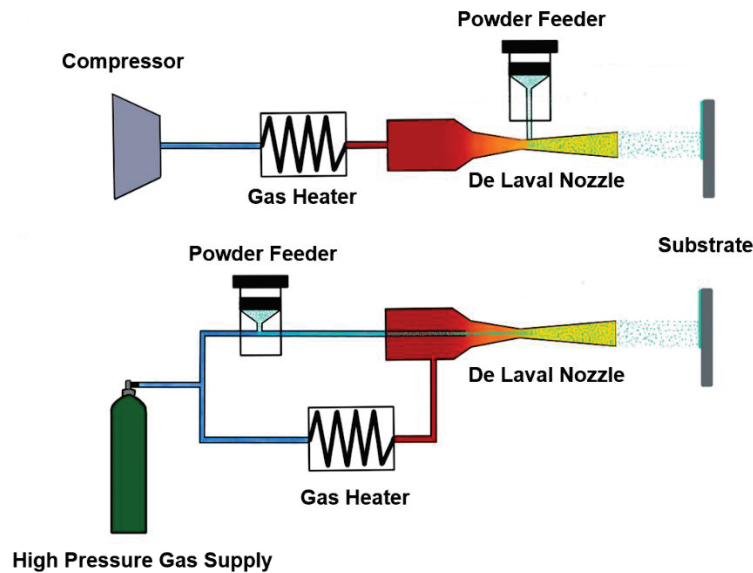


Figure 1.3. Schematic of cold spray processes: (top) low-pressure cold spray (LPCS), (bottom) high-pressure cold spray (HPCS).

In LPCS the operating pressure varies in a range between 5-10 bar, while the gas temperature can be set from room temperature to 650°C. Usually, compressed air is used as the accelerating gas, however nitrogen can also be used. The particles are injected downstream by a pressure difference (siphon effect) into the divergent part of the nozzle and then accelerated by the expanded gas to velocities of 300-600 m/s. LPCS is generally used as a portable CS system for on-site repair applications or short run productions of materials with low melting point and yield strength, such as aluminum bronze, babbitt alloys, magnesium alloys, zinc, etc. [11,12].

Table 1.2. Comparison between LPCS and HPCS process parameters.

Process parameters	LPCS	HPCS
Pressure (bar)	5-10	30 - 60
Temperature (°C)	< 650	200 - 1100
Feedstock injection	Downstream (siphon effect)	Upstream (carrier gas)
Working gas	Compressed air, nitrogen	Nitrogen, helium
Materials	Low melting point and low yield strength	High melting point and high yield strength
Applications	On-site repair, biomedical coatings	Wear and corrosion resistant coatings, repair, additive manufacturing

Moreover, the HPCS can be operated at a pressure range of 30-60 bar, with preheating gas temperatures of 200-1100°C (up to date). Regularly, nitrogen, helium or a mixture of both are used as the working gas. In this process, the feedstock is injected into the equipment with a carrier gas and mixed in the main chamber with the preheated gases before flowing through the nozzle; with this upstream type of injection, the pressure of the powder feeder has to be slightly higher than the one of the working gas to prevent the powder from flowing back. Moreover, the acceleration of the particles is limited by the maximum gas velocity, which depends on the operating process parameters, the nozzle design, and the feedstock characteristics [11]. This is why it is crucial to understand the process parameters and their relationship to the particles' impact velocity, as this will ultimately determine the formation of a dense coating.

In this sense, the HPCS process can achieve higher particle velocities can compared to LPCS, thereby increasing the range of materials that can be sprayed, including metals, alloys, composites, polymers, etc.

1.2.1 CS nozzle design

An essential component in CS systems is the convergent-divergent De Laval nozzle, as it is responsible for accelerating both the carrier gas and the particles to supersonic velocities. The nozzle itself is composed of three main sections: the convergent section, the divergent or barrel section, and the throat,

which represents the narrowest cross-sectional area where the geometry transitions from convergent to divergent. Figure 1.4 shows the schematic of typical nozzle geometries used in CS.

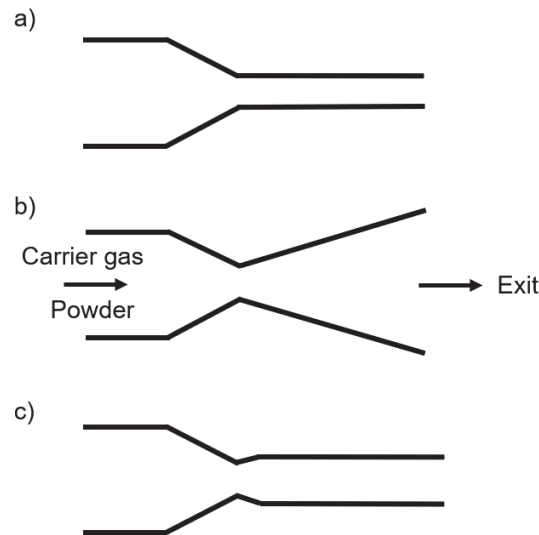


Figure 1.4. Typical nozzle geometries in CS equipment: a) convergent-barrel, b) convergent-divergent, and c) convergent-divergent-barrel.

To fully understand the theory behind the CS deposition mechanisms, it is important to first understand the fundamentals of the particles' acceleration, which are explained with the dynamic principles of the working gas [13]. A preheated gas at high pressure is fed through the convergent section of the nozzle, in which, according to the fluid dynamic principles, changes in cross-sectional area can accelerate or decelerate the gas flow. Hence, the gas is accelerated as it progresses towards the throat, which is specifically designed to induce choking and achieve a flow rate corresponding to a Mach number of 1 (sonic condition) [14]. As the gas keeps flowing through the divergent section, the cross-sectional area is gradually increased, causing the gas to expand. Consequently, the gas pressure and temperature are rapidly decreased, ensuring particle acceleration without melting. These particles, propelled by the gas, gain sufficient kinetic energy to impact the substrate at high velocities in the solid state.

In this sense, the nozzle geometric design is critical to apply the principles of gas dynamics to accelerate the gas-particles mixture; being one key parameter the expansion ratio, defined as the ratio between the exit and throat area of the nozzle. Smaller expansion ratios cause the gas to behave with an under-expansive behavior (pressure of the gas at the exit is greater than ambient

pressure), while high expansive ratios can cause an over-expansive behavior (exit pressure of the gas is lower than the ambient pressure) [15]. Under-expansion causes the gas to expand outside the nozzle, which hinders thrust; while over-expansion causes the gas-particles mixture to flow back inward and separate from the walls of the nozzle. Thus, the optimal operation is either an in-between of these two regimes, referred as perfect expansion, or a slight over-expansion [16]. In addition to the expansion ratio, the nozzle length also impacts the flow of the mixture, as the wall friction decelerates the flowrate [17].

Since many factors during the cold spray process influence the particle velocity (e.g. operation conditions, nozzle design, feedstock characteristics, etc.), previous studies focused on the effect of nozzle design in particle acceleration can be found in the literature [16–20]. These works implement computational fluid dynamics and numerical simulations as a reliable method to investigate the relationship between these factors. For instance, Li et al. [18] investigated the impact of nozzle design on particle acceleration and its influence on the microstructure of stainless steel (SS) 316L coatings. The authors conducted numerical simulations to optimize the expansion ratio of the nozzle for particle acceleration. The findings revealed that the optimal expansion ratio increases with increased gas pressure and nozzle divergent length, while it decreases with the increase in gas temperature, particle size, and nozzle throat diameter. Moreover, Tabbara et al. [20] studied the effects of the cross-sectional shape of the nozzle on the gas flow characteristics and particle velocity with CFD simulations. They found that circular or squared nozzle cross-sections promoted the highest particle velocities.

Considering all of these factors, the selection of the nozzle is imperative in the CS process and should be optimized based on the characteristics of the feedstock material.

1.2.2 Cold spray deposition & adhesion mechanisms

In CS, the residence time of the particles inside the hot chamber of the gun is very short, followed by a rapid expansion and cooling of the gas. As a consequence, the particle temperature consistently remains lower than the initial preheating gas temperature, making it possible to process the powder particles

in the solid state during the whole deposition process. This characteristic allows to spray heat sensitive materials, minimizing thermally induced defects such as oxidation or undesired phases in the final coating. The ability to process different materials in the solid-state, rather than melting and subsequent solidification, represents a fundamental feature of CS. Therefore, it has attracted great interest due to its potential applications within the industries of advanced coatings, repair, additive manufacturing, and so on [21].

This solid-state processing of CS is based on the deformation mechanisms of powder particles. Primarily, the deformation of the particles in CS is attributed to their kinetic energy upon impact; up to 90% of the kinetic energy can be converted into heat, according to Vlcek et al. [22] FEM dynamic simulation experiments for a 316L powder. Secondly, the deformation of particles is determined by the intrinsic characteristics of the different metals and alloys. Depending on the material, different degrees of deformation can be reached in function of their dislocations' mobility and interactions within their structure. Therefore, characteristics such as crystal structure, grain size, and composition determine the deformation kinetics of the particles. Considering these factors, the ability to deposit by cold spray different metals can be categorized, for instance, based on their crystal structures [22–24].

- **Face centered cubic (FCC):** Metals with an FCC crystal structure tend to have a high deformability due to its largest number of sliding planes, making them well-suited for the CS process. Examples of FCC metals include Al, Cu, Ag, Au, Ni, etc.
- **Close-packed hexagonal (CPH):** In metals with a CPH structure, such as Ti, Cd, Zn, Co, Mg, etc., fewer sliding planes are present due to the arrangement of atoms. While still suitable for CS, processing these metals requires highly optimized conditions due to the reduced deformability compared to FCC metals.
- **Body centered cubic (BCC):** The BCC crystal structure presents the lowest deformability; metals with this structure are not suited for CS. Examples of BCC metals include W, Ta, Mo, Nb, Cr, etc.

Thus, the deposition of the feedstock powder and the subsequent formation of the coating are highly dependable on the deformation mechanisms of the particles. At the point of impact, two distinct stages can be observed in the deformation process of the particles. In the first phase, pressure rapidly accumulates within the particles upon impact, inducing elastic deformation. This contact pressure increases so rapidly that the dynamic flow limit of the particles is surpassed, triggering a transition from the elastic to the plastic behavior. When there are sufficiently high impact velocities, the elastic mechanisms of the deformation may become negligible, and the second phase is initiated, predominated by plastic deformation in the particles' structure. This severe plastic deformation results in localized warming due to the high strain rates, subsequently promoting bonding [23]. Consequently, the localized melting promotes the fracture of the particles' oxide layer, thereby enhancing diffusion processes crucial for a successful adhesion between particles and substrate, and among particles [24].

In this sense, the impact particle velocity (or kinetic energy of the particle) represents the driving force that triggers plastic deformation, being a crucial factor in CS deposition. Particles that impact at low velocities bounce off and do not promote deposition, in some cases generating abrasion on the substrate. On the contrary, impact at excessive velocities can erode the surface of the substrate as a result of an excess of energy available for the deflection of the particles. Moreover, particles that impact the substrate at or above a so-called critical velocity (v_{cr}) undergo plastic deformation and adhere to the substrate, thereby promoting the formation of a dense coating. Strong and hard to deform materials (e.g. Ti and its alloys, stainless steel, Ni and its alloys, etc.) usually require a higher v_{cr} than soft and ductile materials (e.g. copper and aluminum), due to a lack of plastic deformation. Hence, a successful deposition of particles occurs when the spraying parameters have been optimized within a deposition window, in which the v_{cr} has to be reached for the particles to undergo deformation, as shown in Figure 1.5 [25,26].

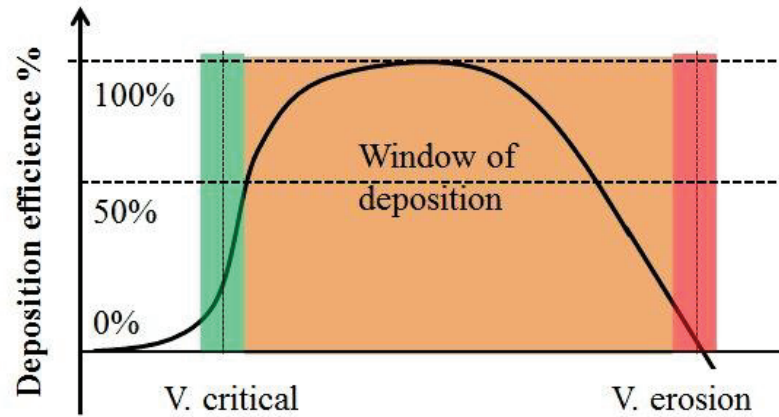


Figure 1.5. CS window deposition. Figure obtained from [26].

The v_{cr} is specific to each feedstock powder, being highly dependent on factors such as material composition, particle size, morphology, as well as substrate characteristics. For instance, v_{cr} values for different materials have been reported in the literature: 339 m/s for Zn, 451 m/s for Cu, 482 m/s for Al, 655 m/s for stainless steel 316L, 712 m/s for Ti, and 1013 m/s for Ti6Al4V, among many others [27].

Since the velocity of the particles upon impact has such great influence in CS deposition, the factors that determine the impact velocity of the particles need to be understood and adjusted in order to surpass the v_{cr} correspondent to each material. These process variables include the particle size distribution, substrate characteristics, and process temperature and pressure, among others [12]. The influence of these parameters on particles' acceleration and their interconnection will be discussed in detail in subsequent sections.

Moreover, another factor to take into consideration during the CS process is the deposition efficiency (DE), which is defined as the relation of deposited mass over the overall mass sprayed. In other words, the DE is a parameter that shows the proportion of sprayed particles that effectively adhere to the substrate surface and contribute to coating formation [28]. This parameter is really useful to determine the coating manufacturing efficiency and it is highly correlated to the particles' velocity, as shown in Figure 1.6. In this regard, Meng et al. [29] investigated this behavior, where the evolution of the DE was shown to be linearly correlated with the plastic deformation of the particles for particles/substrate systems with similar deformability. Metals with face-centered cubic (FCC) crystal

structure, usually exhibit low v_{cr} due to its high deformability and low mechanical strength, usually reaching high DE values. On the other hand, body-centered cubic (BCC) and close-packed hexagonal (CPH) metals are considerably harder to deform, consequently exhibiting high v_{cr} values [30].

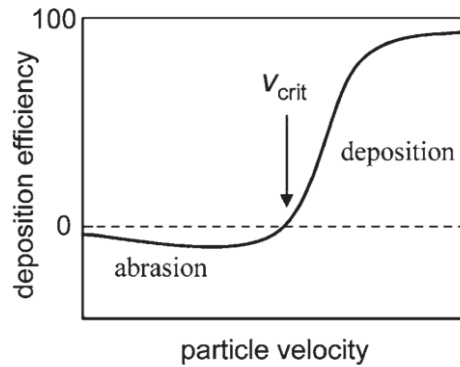


Figure 1.6. Correlation between particle velocity and deposition efficiency. Figure obtained from [28].

With an understanding of the crystal structure of the spraying materials, the deformation mechanisms of the particles, and the importance of impact velocity and v_{cr} , further phenomena of this solid-state process can be comprehended, such as the adhesion mechanisms, and, most importantly, the selection of CS process variables to obtain high quality deposits.

In CS, the coating formation can be divided into two stages: in the first layer, particles impact with the substrate and bond at the particle-substrate interface. As the deposition progresses, subsequent particles impact into the previously deformed particles, establishing further bonding at the particle-particle interface. As already explained in the previous sections, CS is a solid-state technology where no melting and solidification processes are involved during the coating formation process. Therefore, the bonding strength is principally attributed to the high plastic deformation of the particles upon impact.

Until today, the bonding mechanisms are under constant discussion among scholars, nonetheless, several studies have been conducted in an effort to elucidate this phenomenon [31–35]. The most well-established theory was presented in the work of Assadi et al. [31], in which adiabatic shear instability (ASI) was proposed as the main mechanism responsible for the bonding of the particles. This phenomenon occurs as a result of the high strain rate deformation

processes during impact, which disrupt the superficial oxide film of the particles and create a metal jet that establishes an intimate contact between the particles and the substrate, consequently forming a metallurgical bonding, as shown in Figure 1.7. In this sense, the v_{cr} represents the minimum required energy to reach ASI.

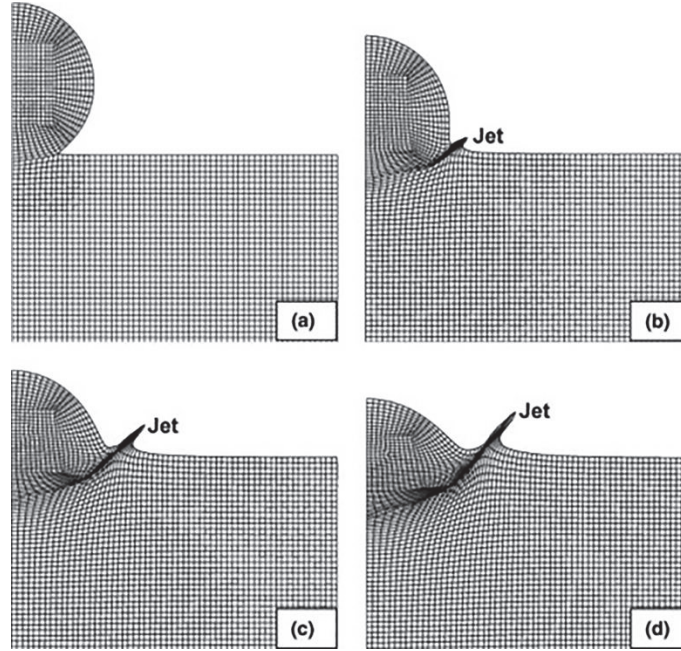


Figure 1.7. Simulation of particle deformation evolution during impact at a contact time of a) 4.4 ns, b) 13.2 ns, c) 22.0 ns, and d) 30.8 ns. Figure obtained from [35].

Moreover, the investigation conducted by Li et al. [34] further complemented this bonding mechanism theory by examining the interaction between aluminum particles and an aluminum substrate. It was found that by increasing the superficial oxide layer thickness, the plastic deformation was hindered and the metallurgical bonding became difficult. Although the ASI phenomenon is the most accepted bonding mechanism, these studies are only based on numerical simulations.

Another bonding mechanism in CS was proposed by Hussain et al. [33] after observing the behavior of cold sprayed copper particles in an aluminum substrate, in which the copper particles became embedded within the substrate, creating a mechanical interlock between the substrate and the initial layer of particles. This interlocked layer acted as a well-adhered base for the particles in the subsequent layers.

Figure 1.8 shows examples of single-particle impact bonding mechanisms, where particles that have formed metallurgical bonds due to ASI (left) show signs of plastic deformation and metal jetting, and the particles that are mechanically interlocked (right) are observed to be embedded within the substrate.

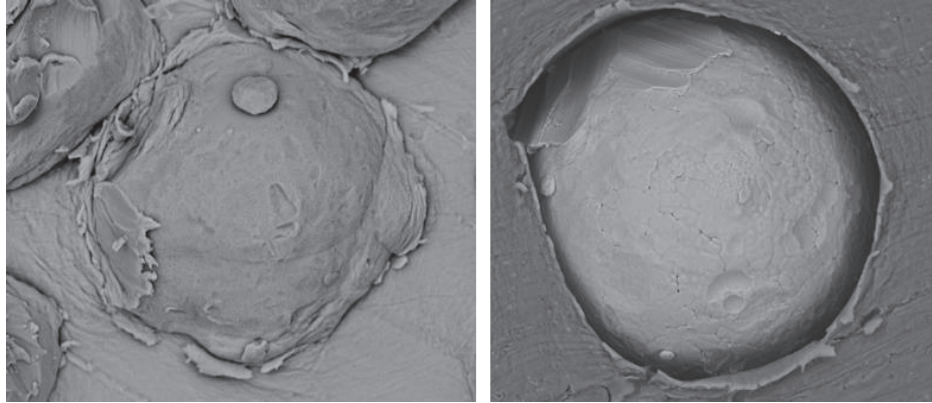


Figure 1.8. Bonding mechanisms in CS (left) metallurgical bonding (right) mechanical interlocking.

Overall, CS coating formation depends on numerous factors, that range from the characteristics of the feedstock material to the dynamics of particle acceleration and its subsequent interaction with the substrate. A comprehensive study of the bonding mechanisms between particles, along with an insight of the controllable spraying variables and their impact on particle acceleration, serves as a basis for further development of this technology. Moreover, understanding the role of the spraying parameters contributes to keep refining the CS deposition process and expand its applicability.

1.3 Cold spray process variables

Many factors influence the impact velocity and the resulting plastic deformation of the particles; hence the understanding of the process variables that accelerate the particles is essential in the CS process. The parameters that define a successful deposition can be divided into four categories: (1) Feedstock powder characteristics, including size distribution, morphology, and oxide layer; (2) Operating process parameters, such as gas type, temperature, pressure, and substrate characteristics; (3) Robotic parameters, including spraying standoff distance and incidence angle; and (4) Substrate characteristics, such as surface characteristics and material nature [18].

1.3.1 Feedstock powder

The effect of the particle/gas flow interaction is of great interest for researchers in the field of CS, as the composition, morphology, and particles size distribution of the feedstock powder have a central role on the overall process efficiency. Therefore, the selection of the feedstock powder needs to be carefully considered.

For CS feedstock powders, gas or water atomization powder metallurgy manufacturing methods are the most common. These processes are very popular for fabricating metal and alloy powders by involving the dispersion molten metal into droplets that are rapidly solidified in a fluid. In the gas atomization process, the source metal is melted and fed through a nozzle, which is then dispersed into droplets by a high-pressure jet of gas (argon or helium) and then finally collected at the base of the chamber. This method generally produces predominantly spherical particles with minimal levels of oxygen content. Monitoring the process parameters is essential for precise control over droplet size, i.e. particle size. However, one important drawback of this method is the generation of satellite particles that broaden the range of the size distribution of the final powder. On the other hand, the water atomization process is very similar to gas atomization, with the exception that it employs a water jet instead of gas, making it a more cost-effective process. However, this method generates irregular shaped particles with higher levels of oxygen content [36].

Furthermore, parameters such as morphology and size distribution of the powder have a great influence on the impact velocity distribution of the particles and consequently on the quality of the final coating. It is consistently found in the literature that under the same process conditions, irregular particles reach higher particle velocities than their spherical counterparts [37–40]. This phenomenon is attributed to higher drag coefficients among irregular particles, facilitating their acceleration to higher velocities. However, due to fluid dynamics, irregular particles usually impinge the substrate using their smaller sides, inducing an asymmetrical impact that promotes particle rotation instead of deformation; this additional torque can hinder the DE despite having higher impact velocities [41]. Nonetheless, in terms of coating quality (dense, homogeneous, well-bonded, etc.), studies have shown that irregular powders can have properties very similar

or even better than spherical ones in some cases [39,40]. For instance, Vaz et al. [40] evaluated the properties of SS 316L CS coatings sprayed with different powders under the same conditions. It was concluded that there is no particular advantage on using a spherical powder over an irregular one.

Moreover, the powder size distribution significantly determines impact velocity; smaller particles experience greater acceleration to higher velocities compared to larger particles, because of a higher susceptibility to the propelling gas due to a lower momentum [36]. However, for the same reason, smaller particles decrease abruptly their velocity at the exit of the nozzle. In contrast, larger particles do not undergo such rapid changes; their increased mass allows them to maintain a steadier velocity during the in-flight trajectory. In addition, smaller particles are more easily affected by temperature than larger particles because of their lower thermal momentum. Thus, smaller particles reach higher temperatures inside the gun, nevertheless, as the gas expands at the exit of the nozzle they cool rapidly and impact into the substrate at lower temperatures [42]. Therefore, an optimum size range of the particles must be selected to successfully optimize the CS process parameters. Figure 1.9 shows an optimum window of deposition with a schematic of the relation between impact and critical velocities in function of particle size.

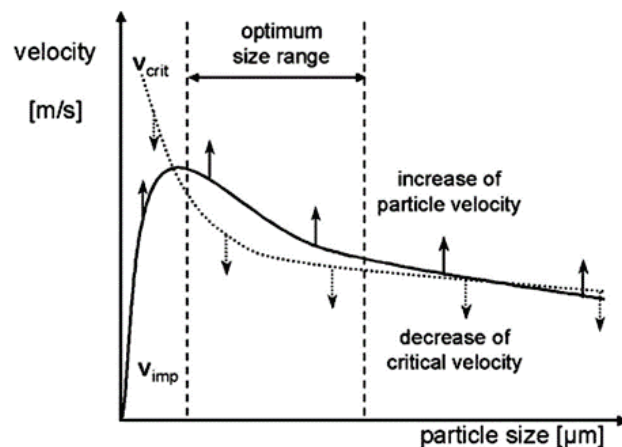


Figure 1.9. CS window deposition in terms of particle size. Solid line represents the particle velocity upon impact, and dashed line its corresponding critical velocity. Figure obtained from [43].

To obtain a successful deposition the selected powder size should be one that fits in the range when the impact velocity is greater than the v_{cr} . Schmidt et

al. [43] proposed an approach, applicable to a variety of materials, that reduced the critical velocities of the particles by selecting powder sizes and particle impact temperatures. It was found that the v_{cr} of the powder was decreased by optimizing its size distribution and by thermal softening when increasing the process gas temperature.

1.3.2 Cold spray operating process parameters

Even though CS deposits are free of thermally induced defects, including oxidation, undesired phases generation or thermally induced residual stresses, this processing technology has also some limitations. As an example, depending on the feedstock material, some imperfections may be present within the deposit's microstructure, such as voids or inter-particle boundaries, that result from the packing of the particles.

Despite the fact that all of these characteristics are attributed to the inherent imperfections of the deposit, they can also result from a lack of adjustment of the CS process parameters [8]. Therefore, the optimization of the controllable operating process variables (type of carrier gas, temperature, and pressure) is essential for the obtention of a dense, well-bonded deposit.

The type of carrier gas greatly influences the particles velocity. Usually, nitrogen gas is preferred because of its low-cost and accessibility, however helium also can be used when higher particle velocities need to be achieved. The differences in particle acceleration depending on the type of gas can be understood with the equation for local gas velocity (Equation 1.1):

Equation 1.1

$$v = \left(\frac{\gamma RT}{M_w} \right)^{\frac{1}{2}}$$

Where γ is the ratio of heat capacities of the gas (specifically, the ratio of constant pressure C_p to constant volume C_v). This ratio is typically accepted as 1.66 for He and 1.4 for N_2 . R is the gas constant, T stands for gas temperature, and M_w for the molecular weight of the gas. Given that He has a higher ratio of heat capacities, and a lower molecular weight, the final velocity results greater when compared to N_2 [21]. Nevertheless, He is much more expensive than N_2 ,

therefore it is only used with materials that are difficult to spray, such as Ti and its alloys, Ni alloys, and metal-matrix ceramics. The effect of the type of gas on the quality coating has been well investigated [42,44,45]. For instance, Wong et al. [44] studied the influence of helium or nitrogen as propellant gases on CS titanium coatings. It was found that, with optimized parameters, helium allowed to produce thick and fully dense titanium coatings, whereas the coatings sprayed with nitrogen showed a slightly porous microstructure. However, the authors concluded that the coating quality was primarily influenced by the impacting particle temperature rather than gas type.

As described by Equation 1.1, Increasing the process gas temperature leads to an increase in gas velocity inside the nozzle. Additionally, particles that impact the substrate with higher temperatures have a decreased critical velocity due to thermal softening. This behavior was investigated by Lee et al. [46] through numerical simulations, and their findings suggest that an elevated gas temperature not only diminished the particles critical velocity, but also increased the deposition efficiency of the coating. This was also experimentally explored by Meng et al. [47], who demonstrated that an increase in gas temperature results in denser 304 stainless steel coatings, with a porosity decrease from 6% to 2%. Furthermore, Binder et al. [48] compared the adhesion and cohesion of CS Ti coatings deposited with different gas temperatures; it was found that the coatings produced with higher gas temperatures exhibited a superior bonding strength.

Another significant parameter associated with the process conditions is the gas pressure; according to the gas dynamic principle, an increase in the pressure of the process gas results in an increased acceleration rate of the feedstock powder within the gun, leading to higher particle velocities, and promoting an improved bonding at the particles-substrate and particles-particles interfaces [49].

1.3.3 Robotic parameters

In addition to the operating process parameters, the robotic parameters are defined as the gun (nozzle) position and spraying velocity. These robotic parameters include the spraying standoff distance (SoD), the traversal velocity of the robot, and the angle of deposition.

The SoD is defined as the distance between the nozzle and the substrate. Pattinson et al. [50] identified three standoff regions that significantly influence the deposition of particles: (1) Short SoD, in this region, a bow shock is formed at the impingement zone due to the flow perturbation caused by the interaction of the supersonic jet with the substrate [49,50]. The presence of the bow shock affects both the velocity and trajectory of the particles, leading to a decrease in deposition performance; (2) Optimized SoD region, where the bow shock disappears, and, the optimal particle impact velocity can be reached; and (3) Large SoD, where gas velocity starts to decrease, resulting in a negative drag force that decelerates the particles, decreasing the final properties of the deposit.

Furthermore, the traversal velocity of the robot refers to the speed at which the robot moves along its spraying path trajectory. This velocity plays a critical role in determining the number of particles that impact the substrate during the spraying process, consequently influencing the build-up of the coating per layer. Lower traversal velocities allow for a greater number of particles to reach the substrate, resulting in a thicker coating layer per pass. Moreover, the traversal velocity also influences the shape of the deposit. When the scanning speed is low (or the number of passes is high), the deposits tend to grow with a pyramid-shape profile. This is attributed to the velocity profile of the particles when they exit the nozzle; particles in the center of the jet spot acquire greater velocities than on the periphery, leading to a better deposition of particles in the center. Some studies in the literature show that the traverse scanning speed can significantly determine the microstructure and overall quality of the coating [51,52]. Particularly, Tan et al [51] investigated the influence of the traverse scan speed on the characteristics of Ti6Al4V coatings. Their findings revealed that spraying at a lower traversal velocity (100 mm/s) promoted a higher coating thickness per pass, and produced a denser coating (0.5% porosity) compared with higher traversal velocities (300 and 500 mm/s) that showed a lower coating thickness and higher porosity values (2.7 and 3.2%, respectively). However, the adhesion strength of the coatings sprayed with higher traversal velocities was considerably higher, which was attributed to the severe deformation of particles at the interface that promoted a metallurgical bonding.

Finally, the angle of deposition is crucial for the particle impact velocity. When spraying at a non-normal angle, the impact velocity is decomposed into a tangential component, based on the spray angle θ , and a normal component. This behavior is schematically shown in Figure 1.10, whereas the normal and tangential velocities are described by Equations 1.2 and 1.3, respectively.

Equation 1.2

$$V_N = V_P \sin \theta$$

Equation 1.3

$$V_t = V_P \cos \theta$$

Where V_P is the particle impact velocity, V_N and V_t are the normal and tangent components, respectively, and θ is the spraying angle. When particles impact at 90° with respect to the substrate surface, the tangential component is equal to zero and the normal component equals the impact velocity. However, when the value of θ is decreased below 90° , the tangential component increases its value, thereby decreasing the overall impact velocity.

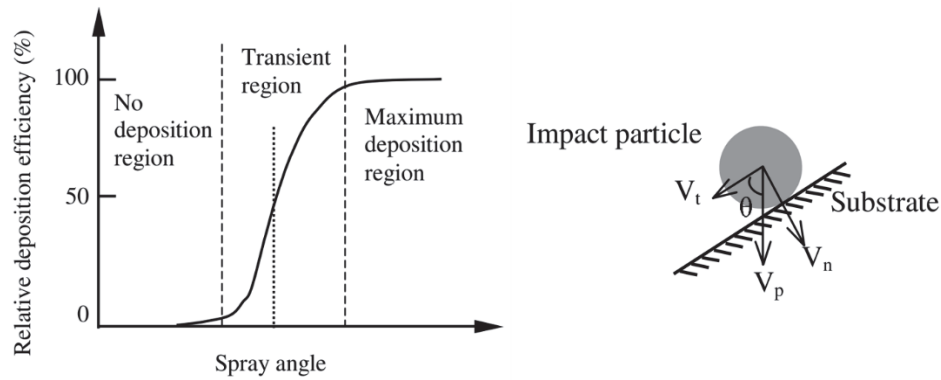


Figure 1.10. Dependency of relative deposition efficiency on spray angle, and particle impact velocity components when spraying at an angle θ . Figure obtained from [53].

Based on this behavior, Li et al. [53] categorized the relationship between the spraying angle and the relative DE into three ranges (Figure 1.10). Firstly, the “maximum deposition angle range” (between 80° and 90°), representing the angles at which the impact velocity reaches its maximum value, resulting in a high relative DE. Secondly, the “transient angle range” (between 50° and 80°), where the normal component of the impact velocity decreases, and deposition only occurs when the V_N at the angle θ exceeds the critical velocity of the particles.

Finally, the “no deposition angle range” (angles $< 40^\circ$), where particle deposition is nearly impossible.

It is worth indicating that although these three geometrical parameters have been discussed separately, they are highly correlated. In addition, their selection depends on several factors, including the nature of the material (whether it exhibits ductility or not), the characteristics of the feedstock (such as morphology and particle size distribution), and, most importantly, the intended application and desired final characteristics of the deposit.

1.3.4 Substrate characteristics

Substrate conditions, such as surface roughness and material nature, strongly influence the bonding behavior of the particles with the substrate, which is established within the first layers of deposition. Hence, the superficial characteristics of the substrate determine in great part the impact and adhesion behavior of the particles.

In general, the surface of the substrate is often subjected to grit blasting, which involves propelling abrasive particles, such as Al_2O_3 particles, onto the substrate to roughen its surface, with the purposes of providing a greater area of interaction at the particles-substrate interface, and of removing the superficial oxide layer of the substrate to promote intimate contact between the particles and the substrate [54].

The effect of the substrate roughness on bonding strength has been widely studied [49,55–59]. A grit blasted substrate has been shown to increase the adhesion strength of softer materials, such as aluminum [55] or copper [57]. This behavior is attributed to the larger contact area at the interface, which promotes mechanical interlocking and enhances adhesion strength. However, for harder materials, such as Ti6Al4V [56] or IN718 [59], a rough surface hinders the jet formation of the particles, resulting in poor bonding. Therefore, for these harder materials, a polished surface is preferred to allow for the particles to deform and experience adiabatic shear instability processes without restriction. Particularly, Sun et al. [59] investigated the deposition characteristics of IN718 powder on IN718 substrates. In this study it was found that spraying onto a polished substrate greatly increases the bonding between particles and substrate; the

authors reported an adhesion strength value of 23.7 MPa with adhesive failure (failure at the coating-substrate interface) for grit blasted samples, while a value of > 65 MPa with glue failure (meaning that the bonding strength of these specimens were at least 65 MPa) for polished samples.

Furthermore, the characteristics of the materials involved in the CS process also play an important role in the particles' deformation behavior, consequently influencing the bonding mechanism. Depending on the hardness difference between particles and substrate, four distinct cases can be identified: soft particle/soft substrate, soft/hard, hard/soft and hard/hard. In general, soft substrates absorb the kinetic energy from the impacting particles, leading to substrate deformation and the formation of craters, the depth of which depend on the hardness of the particles. On the other hand, when particles impact on hard substrates minimal deformation of the substrate occurs, resulting in significant deformation of the particles themselves.

This phenomenon has been widely investigated experimentally and numerically [21,60,61]. Yin et al. [60] proposed a particle impact model to evaluate the particle deformation degree in relation to substrate hardness. Their findings revealed that the substrate hardness had some effects on the deformation of the particles. For instance, when using a SS substrate, the particles suffered intense deformation, whereas when using a softer Al substrate, the particles only experienced a minimal deformation. Additionally, their study indicated that the substrate's influence was predominantly observed with the initial layers of the spraying process; as the layers increase, the deformation behavior of the particles becomes independent to the substrate hardness.

The CS process encompasses several factors that determine coating formation. The progression of this technology lies in the understanding of the interplay among these process variables and their collective influence on the resultant performance of the deposited material. Years of extensive research have made it possible to elucidate the complex interrelation between all these factors. This deep understanding has expanded the applicability of CS across several engineering areas, such as additive manufacturing (AM).

1.3 Cold Spray Additive Manufacturing

As the field of metal AM continues to expand, new technologies emerge; in 2021 the ASTM ISO/ASTM52900 [5] included the Solid-State AM category into the AM technologies classification, featuring the CSAM technology.

Historically, CS emerged as a coating technology intended for the repair and protection of damaged components typically with a thickness not greater than 1 mm [30]. However, it has been proven, as the technology develops, that CS exhibits no theoretical constraint on the thickness deposition of metallic parts, which allows to extend its applicability as an AM technology, giving rise to what is termed as CSAM.

The main difference between CSAM and CS lies only in the dimensions of the final deposits, allowing the 3D printed parts to benefit from the advantages of the CS technology. In particular, this development broadens the boundaries of the metal AM technology, as it enables the manufacturing of individual parts or reconstruction of damaged components in the solid-state at high deposition rates [36]. In a more detailed way, the CSAM process can offer numerous advantages compared to other AM technologies, such as SLM, DMD, and EBM [8,62]:

- **Solid-state technology:** CSAM distinguishes itself as a solid-state technology, in which the material feedstock is processed below its melting point. This characteristic eliminates the risk of oxide-formation and phase changes.
- **Induction of compressive residual stresses:** CSAM induces compressive residual stresses within the fabricated parts, which contribute to improving the overall mechanical performance of the components.
- **High deposition rates:** CSAM allows for rapid layer-by-layer buildup of material, with high deposition rates of 300–400 cm³/h or, in some cases, up to 1500 cm³/h, resulting in shorter production lead times [62].
- **Material versatility:** CSAM offers the possibility to deposit metals sensitive to temperature, as well as the possibility to manufacture multi-material parts. In addition, the dimensions of the final part are not restricted by any process chamber, in contrast to other AM methods.

However, the main advantage of the heat-focused AM techniques over CSAM is the geometrical accuracy, which allows to manufacture complex-shaped metallic parts. To date, there are only a few studies that directly compare the properties of deposits manufactured by CSAM to other AM technologies. One example is the work of Bagherifard et al. [62], in which the mechanical properties of freestanding Inconel 718 (IN718) fabricated by CSAM and SLM were compared. The authors concluded that a notable advantage of CSAM was the preservation of the original microstructure. In addition, the specimens manufactured by both technologies showed comparable mechanical properties, highlighting the potential of CS as a consolidated AM technology. In this sense, each metal AM technology offers distinct advantages. Table 1.3 provides a summary and comparison of these principal advantages and applications of the most relevant metal AM technologies [1,4,9].

Table 1.3. Characteristics and main applications of the metal AM technologies.

Feature	CSAM	SLM	EBM	LMD
Deposition characteristics	Direct deposition (Solid-State)	Powder bed (Melting)	Powder bed (Melting)	Direct deposition (Melting)
Feedstock limitations	Limitation depositing high strength materials with low ductility	Limitation depositing metals with high reflectivity and poor conductivity	Limitation depositing metals with low melting temperature	Limitation depositing metals with high reflectivity
Geometrical precision	Low	High	High	Medium
Mechanical properties	Low	High	High	High
Production time	Short	Long	Long	Long
Main applications	Repair, coatings, aerospace components	Aerospace, medical, and automotive components	Aerospace and medical components, customized parts	Repair, prototyping, medical components

The previously mentioned advantages of CS as AM technology have centered the attention of the scholars in further developing this technique, as studies can be found in the literature that address the fundamentals of this technology, its potential as an AM method, and state-of-the-art applications, among others [8,9,36,63,64]. Vaz et al. [64] conducted a comprehensive review on the advancements of CSAM over the past decade included in articles, books, standards, and patents, which include relevant findings that contribute to the development of CSAM, such as the deposition of new materials, exploration of new applications, and use of post-treatments steps. Their work not only highlights the current trends and state of the art in CSAM but also addresses the challenges that still need to be overcome. The authors concluded that the innovation potential of CSAM is outstanding, and the current trend of this AM technology points to a future consolidation as an industrial process.

1.3.1 Properties of CSAM deposits

One of the most basic concepts in the field of Materials Science is the relationship between properties, process, and crystal structure and microstructure within a material. Each of these steps are fundamental to understand the behavior and performance of any manufactured part. In the CS process, these three factors are interrelated with one another and its comprehension allows to design and optimize materials for a wide range of applications:

- **Process:** the process involves the method used to manufacture or modify the feedstock materials. These include a broad range of technologies, from traditional fabrication methods, such as casting, forging, and machining, to cutting-edge technologies, such as additive manufacturing, surface engineering technologies (including physical and chemical vapor deposition), friction stir welding, among others, to post-process methods including machining and heat treatments. The choice of process depends on the material of interest and the intended application, as it highly influences the final properties and microstructure of the fabricated material.

- **Microstructure:** the microstructure refers to the arrangement of grains, atoms, phases, crystals, etc. within the material at the microscopic level. In particular, the arrangement of atoms that conform the crystal structure of metals is fundamental to their properties. These set of characteristics determine the macroscopic properties of the material, such as strength, ductility, conductivity, etc. and can be tailored with the processing techniques.
- **Properties:** the properties of the material determine its behavior and performance under real application conditions. These characteristics can be measured and include mechanical, thermal, and electrical properties, among many others. These properties are defined by the microstructure, which can be controlled with the processing conditions.

Understanding each element of this intricate relationship is fundamental in the development of CS as an AM technology. Since the feature characteristic of CS lies in the solid-state processing of feedstock powders through plastic deformation induced by kinetic energy, the comprehension of the relationship process-microstructure-properties is critical to manufacture quality parts that meet the performance criteria of the intended applications. Figure 1.11 shows schematically this relationship along with some examples applicable to the CSAM technology.

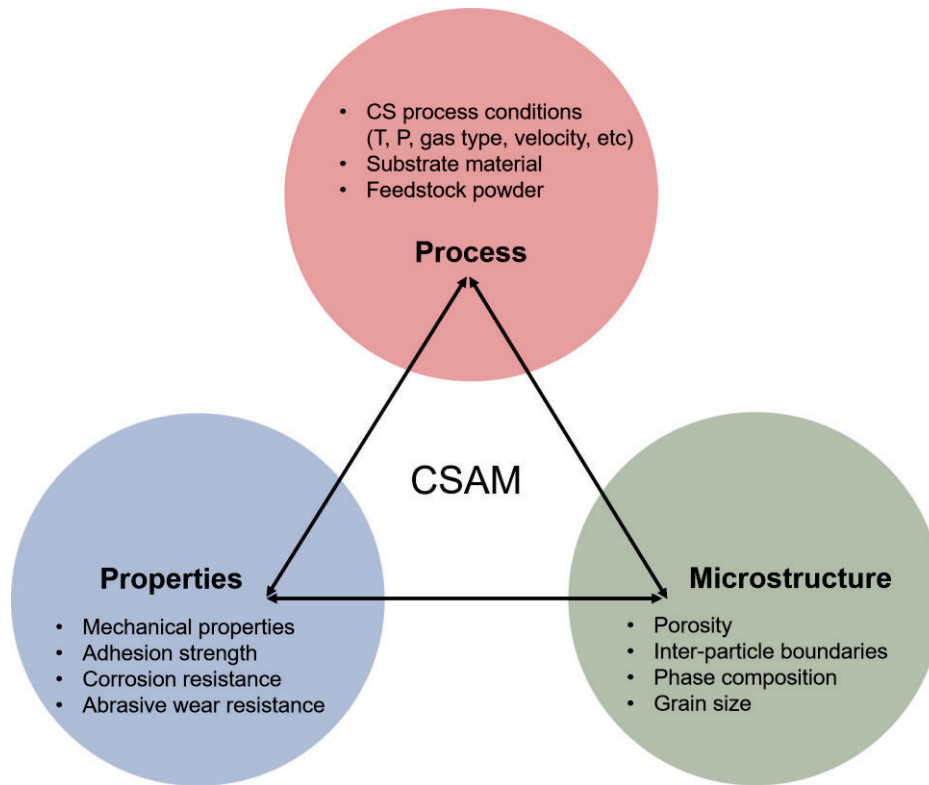


Figure 1.11. Relationship between properties, processing, and microstructure in CSAM.

In the as-sprayed state, the microstructure of the CS deposits is made up of deformed and packed particles that, in most cases, show an identical microstructure to that of the feedstock powder; no oxidation or phase changes typically occur during the spraying process [12]. However, if there is insufficient plastic deformation or the packing of the particles is not perfectly arranged, defects, such as voids and inter-particle boundaries may be present within the microstructure. For this reason, CSAM deposits are considered to have inferior mechanical properties in their as-sprayed state compared to bulk materials. As discussed earlier, the ease or difficulty of plastic deformation (and the consequent generation of pores) depends on the intrinsic characteristics of the feedstock material.

Cavaliere and Silvello [65] characterized the microstructural and mechanical properties of different coatings (Al-, Ti-, and Ni-based powders) deposited into different substrates (Al-, Ti-, Fe-, Ni-, and Mg-based substrates) and developed a database in which properties such as microhardness, porosity, and adhesion size were modelled based on the selected processing parameters. The model developed by the authors allowed to predict the CS coatings' quality

in function of the different experimental conditions. The most straightforward strategy to promote plastic deformation is by increasing the critical velocity, (v_{cr}) by optimizing the spraying parameters for each material to align with the ideal microstructure for the intended final application [27]. In this sense, the properties of the final CS deposits can be tailored by adjusting the process variables. While dense microstructures are crucial for optimal performance in certain fields, such as repair or manufacturing of freestanding parts [8], some other applications require porous microstructures; for instance, titanium coatings in biomedical applications [66].

Many studies that investigate the properties of CSAM deposits are found in the literature for many materials from pure metals such as Cu [67], Al [68], and Ti [69], to alloys such as Al7075 [70], aluminum bronze [71], Ti6Al4V [69], stainless steel 316L [40], and HEAs [72]. In general, CS deposits tend to be brittle with poor ductility due to the intensive plastic deformation of the particles and low interparticle cohesion. Moreover, poor mechanical properties such as yield strength, ultimate tensile strength and elongation in the as-sprayed state have been reported [67,73,74]. In particular, soft materials such as Al and Cu exhibit a tensile strength levels similar to their bulk counterparts. Conversely, high-strength materials such as Ti and SS 316L demonstrate significantly reduced values compared to bulk parts. Moreover, due to the work-hardening effect of the impinging particles, commonly known as peening effect, the microhardness in the as-sprayed deposits is typically higher as the bulk parts fabricated by other conventional methods [74].

Despite the advantages induced by the peening effect of the particles impacting at high kinetic energies (increased microhardness and particle deformation), it can also generate an excess of residual stresses in the final deposit. Typically, the higher the plastic strain on the sprayed particles, the higher the residual stresses that are generated [75]. The presence of residual stresses within metallic components are an important factor to consider when evaluating its properties and lifetime performance. In particular, CS coatings can exhibit both tensile or compressive residual stresses, the last ones being considered to enhance the fatigue and strength properties of the final part [76].

Moreover, several phenomena in relation to the residual stress evolution during CS can be observed: On one hand, compressive residual stresses are generated from the already mentioned peening effect of the particles. On the other hand, the high gas temperature can induce an annealing effect during the spraying process, resulting in a simultaneous relieve of the residual stress generated by the cold-working effects of the particles. Finally, thermal residual stresses can be generated between the deposit and the substrate during cooling [77].

The simultaneous presence of these effects during the deposit build/growth can complicate the control of the residual stresses in the final CS coatings, as they are generated and relieved simultaneously [76]. Thus, investigating its evolution during the spraying process is critical to obtain deposits with enhanced properties. In this sense, Suhonen et al. [77] studied the residual stress development in Al, Cu, and Ti CS coatings. The authors concluded that the generation of compressive or tensile stresses in the coatings depend in great part on two factors: i) material factors: the characteristics of the feedstock material (hardness, plasticity, composition, etc.) in terms of their deformation behavior upon impact, along with the tamping effect, and ii) thermal factors: the difference of the coefficient of thermal expansion (CTE) between the deposit and the substrate; the greater the difference in CTE between them, the greater the generation of residual stresses generated after the deposition.

Moreover, a more complex residual stresses profile within the deposits is generated when spraying thick deposits or 3D parts, for instance, the adhesion strength is highly influenced by the accumulation of residual stresses, which in excess can cause debonding, delamination, and can act as critical factors in crack initiation and propagation that negatively affect the final properties of the CS parts. This effect is more pronounced in the deposition of thick deposits of high strength materials, since the plastic strain is much higher compared to ductile materials such as Al or Cu [73,78]. Therefore, understanding and controlling the residual stresses in CSAM is essential to ensure the integrity of the manufactured parts [79], especially for repair applications where the adhesion strength is a critical factor.

Another phenomenon present in CSAM parts that has raised a significant concern is the microstructural and mechanical anisotropy caused by the stacking of the powder particles along the 3D planes, which is defined as the difference in properties when measuring in different directions. Hence, some researchers have focused their attention on investigating the anisotropic behavior of CSAM bulk parts, with specific emphasis on Cu [80,81] and Al [82]. Although these materials are known to produce dense microstructures when being processed by CS, the subtle inter-particle boundaries present in the microstructure can cause differences in the mechanical properties along the different directions within the bulk part.

In this sense, Yin et al. [80] evaluated the effect of two nozzle scanning strategies on the mechanical anisotropy of CSAM Cu deposits: bidirectional and cross-hatch, as shown in Figure 1.12.

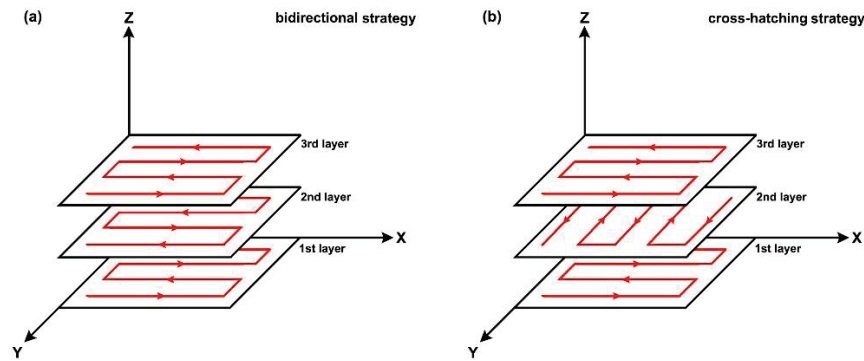


Figure 1.12. Nozzle scanning strategies. Figure obtained from [80].

Their findings revealed that the deposited Cu particles varied its deformation shape across the spraying planes: an equiaxed particle shape was observed across the plane XY, perpendicular to the spraying direction, while lens-like shape particles were observed in the XZ and YZ planes parallel to the nozzle trajectory. Moreover, Yang et al. [81] investigated the tensile strength of thick Cu as-sprayed deposits in different directions ranging between 0° and 90° , the first one corresponding to the YZ plane (parallel to the nozzle traverse direction), while the last to the XY plane (growing plane with each layer), as shown in Figure 1.13.

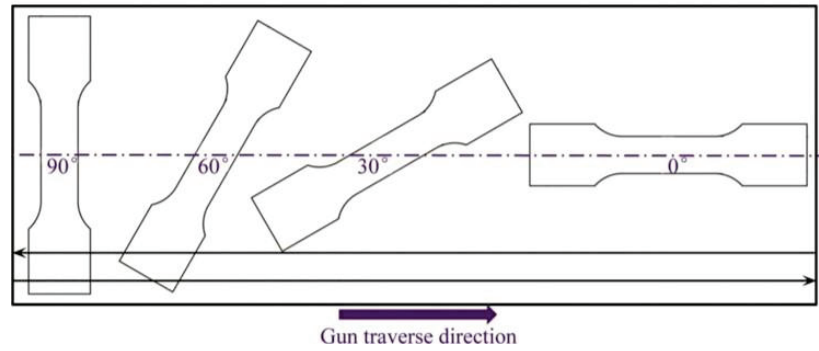


Figure 1.13. Tensile strength test directions. Figure obtained from [81].

It was found that the tensile strength showed important differences depending on the tested angle, with the highest value of 175 MPa resulting in a 30° direction, while the lowest value, 69 MPa, in the 90° direction (XY plane). Two factors were attributed to this behavior: the weak interface bonding between the particles across the different layers in the spraying direction (90° or XY plane), decreasing the tensile strength, and the frictional force that resulted from the interparticle stacking across layers, which enhanced the tensile strength at any angle different than 90° due to the inter-packing of the particles. Moreover, this mechanical anisotropy was observed to become more evident with the increase of thickness. This described trend in the tensile strength has been reported in other studies with Al alloys [82,83]. For example, Rokni et al. [83] investigated the mechanical anisotropy of CS 5056 aluminum alloy. In this study, the lowest tensile strength was also obtained in the growing plane XY. Furthermore, Ren et al. [82] obtained the same trend of results for CSAM 7075 Al parts; the authors observed that the tensile strength decreased as the angle increased relative to the substrate surface (with the lowest value in the 90° direction) and, in alignment with the other authors, attributed this behavior to the stacking of the particles that is composed of deformed particles.

Moreover, considering the overall microstructural characteristics of as-sprayed CSAM deposits, it is essential to not only assess their mechanical properties, but also other properties relevant to various applications; the already mentioned internal defects and the subsequent anisotropic behavior also impact other properties of the CSAM materials. For instance, the pores and inter-particle boundaries have been shown to hinder current and heat transfer along the deposit, which lead to lower electrical and thermal conductivities [8,9]. Another

example is the effect of the porosity on the corrosion resistance of the CS deposits. Hussain et al. [84] evaluated the corrosion performance of CS Ti coatings sprayed onto carbon steel substrates. The results revealed that porosity significantly affects corrosion resistance. This influence is attributed to two primary factors: an increase in the true surface area of the tested specimen and a deficient isolation of the substrate. The latter becomes particularly relevant when the substrate consists of a less noble material, thereby decreasing the corrosion performance of the CS coating.

Thus far, it is evident that the CSAM process allows to produce as-sprayed deposits with a very particular microstructure. Typically, this microstructure exhibits some generalized characteristics including porosity, brittle behavior, limited ductility, work-hardening effects, generation of residual stresses and anisotropic behavior. Consequently, these inherent characteristics condition other properties that ultimately determine their potential performance for specific applications. Referring again to the process-microstructure-properties relationship presented in Figure 1.11, a way to tailor the microstructure and enhance the final properties is through the processing conditions of the feedstock material. However, this is not limited to the initial processing. Once the part is manufactured it can be subjected to several post-process steps that adjust the microstructural characteristics and serve as processing strategies to overcome the limitations of the intrinsic characteristics of the CSAM technology.

A more in-depth discussion about heat treatments post-processes and other strategies for the microstructure densification of CSAM will be described in the subsequent sections.

1.3.2 Applications of CSAM

The capability of the CSAM technology to produce dense deposits with unlimited theoretical thickness has unlocked its potential in the metal manufacturing field. Nowadays it is possible to obtain CSAM bulk components with simple geometries such as cubic blocks, walls or cylindrical shaped-parts [10]. In this sense, the aerospace and defense industries have adopted this AM technology; some companies or research centers that have implemented CSAM for repair purposes of high-value parts include Boeing, GE, Pratt & Whitney,

Honeywell, Airbus, Safran, Rolls-Royce, TWI, etc. [11]. As a result, this technology has been predominantly implemented in two key areas: the fabrication of freestanding parts and the repair of damaged metallic components [36].

1.3.2.1 Freestanding components by CSAM

The fabrication of freestanding parts with CSAM has been widely studied in the literature because the low spatial resolution of CS still limits the capability to manufacture complex geometries. Hence, different deposition strategies can be considered to obtain near-net-shape components. For instance, machining can be implemented either at the end of the process to tailor the required dimensions of the final CSAM parts, or during the spraying process. In this last case, a machining tool is utilized as an integral part of the spraying equipment, providing an in-situ finishing of the object layer by layer [9].

Moreover, the use of masks allows to manufacture CSAM parts with patterned surfaces that may be used for several applications in specific use cases where the near-net-shape metallic fins can be implemented [85,86]. One example is the production of near-net-shape pyramidal fin arrays as components for heat transfer applications. These fin components enhance heat transfer performance compared to flat surfaces due to the increased surface area [87–90]. Cormier et al. [87] evaluated the heat transfer properties of pyramidal and rectangular fin arrays made from pure Al and stainless steel for their implementation in a new type of heat exchanger, known as Wire Mesh Heat Exchanger (WMHE). Additionally, Cormier et al. [88] extended this research by investigating the effects of varied fin height and fin density for heat sink applications with the objective of obtaining a component that maximizes heat dissipation, while maintaining compactness. In addition, Dupuis et al. [90] studied the thermal and hydraulic performance of round, square, and diamond pin fins in various density configurations for heat transfer applications. They found that the fin array configuration played an important role on the thermal performance.

All of these studies suggest that the pin fin array CSAM components can be effectively applied in heat transfer applications or in specific cases where flow fields with higher surface areas are required, such as microreactors. Overall, the

fabrication of freestanding parts by CS offers a versatile and efficient manufacturing solution for producing components for a wide range of applications. The possibility to use CSAM in specific use cases represents one of the main areas of opportunity for this technology, a topic that has been constantly explored and discussed in the literature.

1.3.2.2 Repair by CSAM

Up to date, the mostly addressed application of CSAM is the repair of damaged components, as it provides the capability to remanufacture damaged metallic parts, thereby reducing the need for costly replacements and extending their service life [64]. Due to its unique solid-state characteristic, which preserves the substrate and maintains the microstructural characteristics of the feedstock powder, the CSAM technology can overcome the limitations of traditional repairing technologies, such as welding, electroplating, and other AM technologies [9]. Particularly, the advantages of CSAM for the repair of metallic components include [9,91]:

a) High efficiencies & total cost savings: The CSAM process allows to successfully repair the damaged parts instead of replacing the entire component. It is characterized by high deposition rates, leading to high repair efficiencies and short leading times. In addition, a portable CS system can be used for the in-situ repair of large components, further reducing logistic costs.

b) Substrate preservation & material compatibility: The solid-state deposition prevents the thermal damage of the substrate that may arise with other repairing technologies. Additionally, CS allows to repair the damaged unit with powders of the same material, which allows to restore the damaged part to its initial state.

c) Enhanced fatigue properties: CSAM deposition results in the generation of compressive residual stresses, which prevents cracks initiation and propagation, resulting in enhanced fatigue properties.

In this sense, the advantages of CSAM over other repair methods position this technology as a potential AM repair solution. Faccoli et al. [92] compared the microstructural characteristics of martensitic SS parts repaired by CS and

welding. Their findings revealed that the CS repair offers some advantages compared to welding, including beneficial compressive residual stresses, a preserved interface repair-substrate, and a higher microhardness, suggesting the possibility to implement CSAM as a reliable method for the restoration of martensitic SS components.

As mentioned before, many institutions have focused their attention on the repair of diverse components with CSAM, for example, turbine blades, propellers, engine parts, gearboxes, etc. [9]. Typically, these components operate under aggressive conditions, which eventually lead to damage caused by several factors. The sources of damage can be classified into two main categories: corrosive or erosive damage, and mechanical damage.

Damaged parts by corrosive or erosive environments are ideal candidates for repair using CS. In particular, the most promising application is the repair of aerospace components subjected to high temperature and humid conditions that operate at high-speed rotations. In this sense, magnesium and its alloys are excellent materials due to their enhanced properties (low density, high thermal conductivity, machinability, etc.) widely used in this field. However, these materials tend to corrode when paired with other metals, a behavior that significantly reduces their lifetime service [8]. A solution for this problem has been the CSAM repair of these components by spraying the corroded area with aluminum and aluminum alloys, which present excellent adhesion and corrosion resistance in these conditions [93]. Another important material used in the aerospace industry is Ni-based superalloy Inconel superalloy with excellent corrosion resistance and high mechanical strength at high temperatures. As an example, Shell et al. [94] presented a corroded actuator barrel repaired with the CSAM deposition of this Ni-alloy. The repair of corroded and eroded components represents a significant opportunity for CSAM to be established as a reliable repair method in industries that require high-performance components.

Moreover, parts with mechanical damage caused by wear, fatigue, or impact can also be repaired with CSAM. Typically, the conventional procedure to repair a damaged part by CSAM involves pre-machining the damaged area, i.e. grounding or grit-blasting the surface, spraying the powder, and post-machining the deposit according to the final geometrical requirements [63]. Examples of this

repair process are documented in the literature [95,96]. Villafuerte and Wright [95] reported the CSAM repair of an Al part of the utility engine of a private jet damaged by corrosion, Figure 1.14. shows the steps of the repair process: a) the damaged component, b) the as-sprayed Al part, c) the as-machined part, and d) the final part. Moreover, Petráčková et al. [96] developed a procedure for characterizing the fatigue strength of an A357 aluminum alloy CS repair, intended for structural components. The authors machined a cavity simulating a damaged zone and repaired it with CS. Subsequently, the axial fatigue of the specimens was evaluated. The results revealed that the fatigue strength of the CS deposit resulted similar to that of the base material. In addition, the crack initiation points were always located in the substrate and no delamination of the deposit was observed.

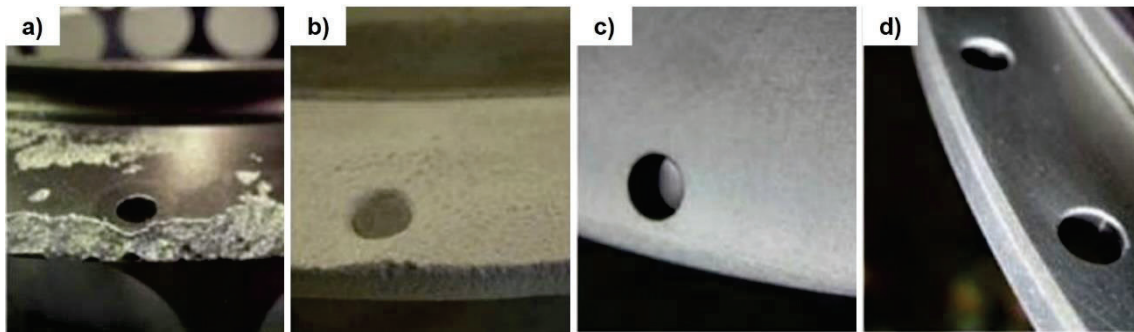


Figure 1.14. CSAM steps repair of an Al engine component: a) part with corrosion damage, b) CSAM as-sprayed Al part, c) as-machined, and d) finished part [95].

In Figure 1.15, various examples parts manufactured or repaired using different CSAM strategies are presented. Figure 1.15-a shows a steel bracket fabricated at the United Technologies Research Center [8]. This metallic part was sprayed onto a substrate that acted as a mandrel. The steel part was removed and machined to its required geometric tolerances [9]. Additionally, Cormier et al. [87] manufactured patterned parts with pyramidal pin fins using masks of steel wire, which served as a barrier between the spraying gun and the substrate, as exhibited in Figure 1.15-b. Furthermore, a CSAM copper flange manufactured by Plasma Giken Co. is shown in Figure 1.15-c [97]. This component was manufactured using an external spindle to rotate a mandrel substrate and spraying directly onto it. Other components have been documented in the literature as well; Pattison et al. [98] sprayed a Ti hemisphere component with the aid of a mould tool (Figure 1.15-d). Stamey [99] reported the CS repair of a marine

pump made of a tin-bronze alloy, which is not weld-repairable, for marine applications in which a high wear resistance is required (Figure 1.15-e). Stoltenhoff et al. [100] restored Al-alloy blades (Figure 1.15-f) that had undergone erosion due to the impact of dust, debris, and water droplets. The damaged parts were successfully ground and repaired using CSAM before being returned to service. Moreover, Lee et al. [101] repaired a damaged Al6061 mould using CS, which allowed to extend its service life.

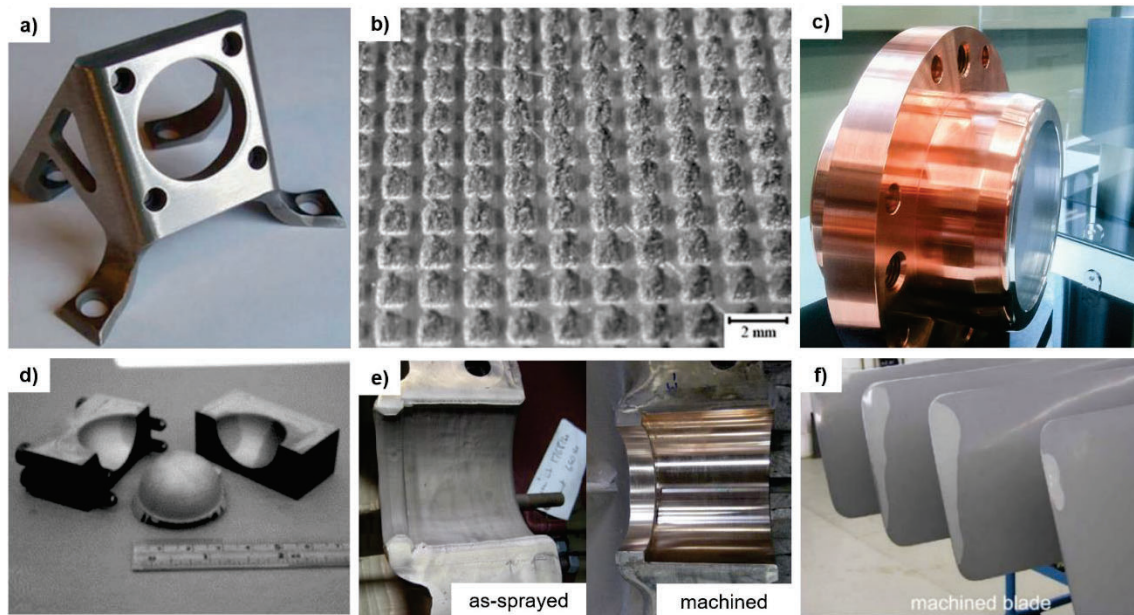


Figure 1.15. a) CSAM bracket [8] b) Pin fin arrays [87], c) Cu flange [97], d) Ti hemisphere [98], e) Marine pump [99], f) Restored Al-alloy blades [100]

Certainly, the potential of CSAM as a repair technology has been explored in the last decade, demonstrating significant advantages compared to other repairing methods. However, studies on further applications and materials are encouraged to be able to implement CSAM as a large-scale industrial repair technology.

1.3.3 Challenges in CSAM

As mentioned before, each AM technology offers distinct advantages and disadvantages depending on several factors, such as feedstock characteristics, intended application, production time, etc. On top of that, all these methods are in constant development and have to face different restrictions to upgrade the technology. This is also the case for CSAM; as it is still an emerging technology, several challenges need to be investigated to reach the full potential that this

solid-state technology can offer in the realm of AM. Challenges such as precise control over the geometrical shape of the deposits, inferior mechanical properties in comparison to bulk materials, debonding between deposit-substrate due to excessive residual stresses in repair applications, and poor deposition of hard materials, are factors that determine these limitations and highlight the research gaps that need to be addressed in the coming years. Figure 1.16 shows schematically these challenges, along with various deposition strategies that are currently being investigated to overcome them, which are explained in detail in the following sections.

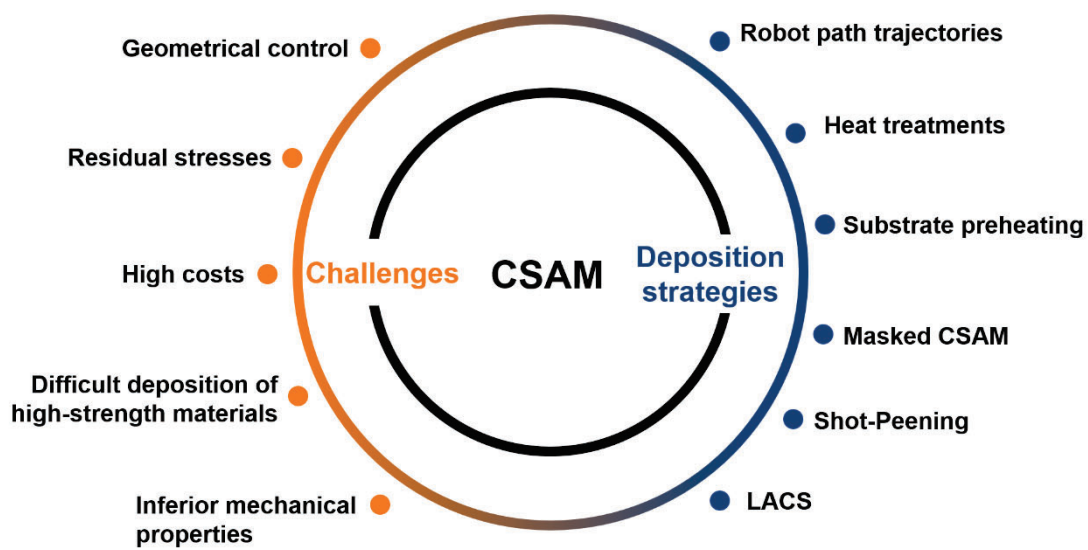


Figure 1.16. CSAM challenges & deposition strategies

- **Geometrical control:** In general, one of the most featured attributes of AM is their bottom-up approach, wherein an object is decomposed into numerous cross-sectional sections and constructed layer by layer, allowing to manufacture high-complex shapes that would not be possible to produce with other traditional methods. However, in the case of CSAM the geometrical control over the shape of the as-sprayed parts is restricted within two factors: first, the layer thickness for each layer, which depending on the feedstock material can range between 50 μm and 200 μm , and second to the spraying spot size and the inherent velocity distribution of the particles at the exit of the nozzle that causes the deposits to grow with a pyramidal shape; the particles in the center of the spot achieve greater velocities than the ones at the periphery, consequently a higher deposition

of particles is obtained in the center than on the edges [52,102]. In this sense, Cai et al. [102] investigated the relationship between the robotic parameters (spray distance and scanning step) and the obtained coating profile. The authors developed a method for simulating the coatings' profile and found out that the profile of the deposited particles fitted into a typical Gaussian curve. Moreover, Kotoban et al. [52] explored the correlation between the cross-sectional shape of a single-track coating and the DE. Their findings indicated that during the initial layer deposition, particles at the periphery of the jet exhibited a marginal decrease in DE compared to those in the jet core. This resulted in the formation of a triangular-shaped deposit, that gradually increased with each subsequent layer.

- **High costs:** The implementation of CSAM in industry is still limited by its significant costs associated with the equipment investment. These costs not only include the spraying gun, but also the infrastructure establishment of the CSAM spraying environment [103]. In addition, the operational costs also contribute to this limitation, primarily comprised by the process gas and the feedstock powder. Typically, N₂ and He are used, with the former preferred for its availability and cost-effectiveness [104]. Furthermore, the specific requirements of the feedstock powders amplify the process costs; however, these expenses can be reduced by using water atomized particles instead of gas atomized ones [40].
- **Deposition of high strength materials:** The CS technology has been used for a wide range of materials. In the case of metals, both ductility and hardness are factors that can be used to determine the feasibility of obtaining quality deposits. The former is related with the deformation ability of the metal; only particles with enough ductility at the impingement conditions can be easily deposited [21]. According to Sun et al. [11] metals with hardness lower than 300 HV are suitable to produce high quality CS specimens; metals with hardness in the range of 300 HV and 400 HV can be sprayed, however the optimization of spraying conditions is imperative, and a post-process strategy may be required (i.e. heat treatment); metals with hardness values over 400 HV can be difficult to deposit due to a lack of deformation of the particles that may lead to high porosity values,

depending on the intended application cold spraying of these materials can be a suitable method for obtaining porous materials. Examples of metallic materials that can be challenging to deposit with CSAM are Ti and its alloys, stainless steel, IN718, and high entropy alloys (HEA's) [8,11].

- **Properties of CSAM deposits:** In relation with the high costs, the primary applications of CSAM are found in industries where its cost-effectiveness can be leveraged, such the aerospace, automotive, marine, and defense [9,63]. In these industries, the quality and performance requirements of the final objects are highly demanding [63]. For these applications, the properties and quality of the CSAM deposits need to be carefully assessed following strict quality control processes. It has been observed that CS as-sprayed deposits can exhibit mechanical properties that are less favorable compared to bulk materials, including reduced strength, ductility, electrical and thermal conductivity, as well as wear resistance [8]. This behavior is attributed to inherent defects that may arise from the spraying technology. During the coating build-up, the particles are plastically deformed and compacted in the solid state; when processing materials with limited ductility or sprayed under low impact velocities, microstructural flaws such as micropores and interparticle boundaries may appear. In addition to the intrinsic defects within the microstructure, anisotropic behavior has also been observed in CSAM deposits due to the layered arrangement of the particles [80].
- **Residual stresses:** As CS coatings are sprayed layer by layer with particles impacting the growing surface of the substrate, residual stresses typically emerge within the deposit. In general, these deposits are characterized by exhibiting compressive residual stresses, attributed to the peening effect of the particles during spraying, which often enhance their mechanical properties [64]. However, an excessive accumulation of these residual stresses in thick deposits may affect their integrity, leading to issues such as debonding or delamination. This detachment and lack of cohesion is mostly observed when depositing high strength materials or when there is a significant thermal mismatch between the feedstock

material and the substrate, particularly disadvantageous for repair applications [75,105].

For these reasons, as shown in Figure 1.16, various deposition strategies have been proposed and studied to advance the development of CSAM technology by addressing its challenges. These innovative approaches aim to bridge the existing gaps and maximize the CSAM technology within its full potential in the AM field. The state-of-the-art deposition strategies that have been developed by the CSAM researchers are described in detail in the next section.

1.3.4 CSAM deposition strategies

Nowadays, the efforts of the research community in the CSAM field are focused on developing this technology beyond its inherent challenges. To do so, scholars have proposed and investigated different deposition strategies that allow the CSAM technology to be implemented in its full potential in the field of AM with the objective of providing new solutions that expand the metal 3D printing technology.

These new deposition strategies can include improvements in the current deposition process, implementing post-process methods to tailor the characteristics of the final objects, or investing in supplementary equipment to upgrade the CSAM process. Some examples of deposition strategies include optimizing the robotic path trajectories or employing masks to overcome constraints to manufacture objects with a more complex shape; introducing advanced strategies during spraying or process modifications, such as substrate preheating or in-situ shot peening to tailor the deposits characteristics; incorporating the laser-assisted cold spray (LACS) equipment to broaden the CSAM processing capability; and implementing post-process methods such as heat treatments or machining that help to enhance microstructure densification and surface finish, respectively. These current state-of-the-art deposition strategies, under development, will be described and discussed in detail in the following subsections.

1.3.4.1 Robot path trajectories

In CSAM, the robot path trajectory is defined as the movement that the nozzle follows during the spraying process. The primary objective of this trajectory is to produce a homogeneous deposit on the substrate surface with a desired geometry [8].

Typically, CS coatings are sprayed perpendicularly to the substrate, with the nozzle maintained at a constant angle of 90° . This involves following a straightforward path from one side to the other with a constant scanning step that ensures that the deposit covers the entire surface of the substrate, as shown in Figure 1.17. In this sense, some studies are found in the literature that investigate different trajectories with the 90° angle kept constant [106,107]. Wu et al. [106] studied four different spraying trajectories to obtain Cu deposits, including trajectories such as zigzag, cross path, parallel path, and spiral path. The results only revealed differences on the residual stress distribution, thus no differences in the microstructure nor mechanical properties of the produced coatings were found. Furthermore, Chaoyue et al. [107] investigated a novel trajectory for the repair of damaged parts that followed a path determined by the Archimedean spiral, which is characterized by having a constant distance between its successive turns. The authors adjusted the traversal velocity of the robot based on the crater's depth caused by the damage, resulting in a successful repair of an aluminum alloy damaged substrate with a high-quality coating. Since these strategies explore different toolpaths in the growing XY plane, they are only effective for fabricating deposits with simple geometries.

As mentioned before, at high thicknesses, the deposits tend to grow with a pyramidal shape due to the velocity profile of the particles when exiting the nozzle, which conform the spraying spot. Consequently, fabricating parts with complex geometries remains challenging with this technology. Therefore, novel robot path trajectories that involve optimizing the CS robotical parameters in the three-dimensional space need to be developed. These trajectories should account for the nozzle deflection to compensate for material loss at the edges of the pyramidal deposit, facilitating the fabrication of near-net-shape components.

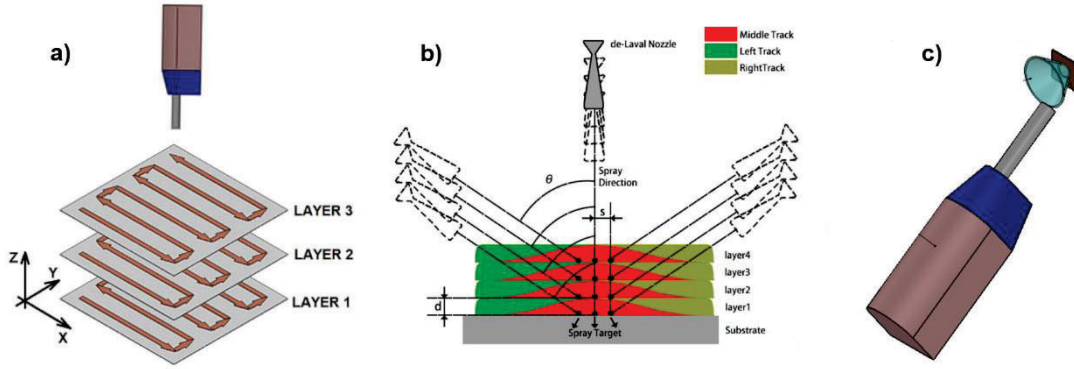


Figure 1.17. Robot path trajectories: a) Traditional strategy, b) Stable-layer building strategy, c) Metal Knitting strategy. Figures obtained from [108] (Figure a and c), and [109] (b).

As opposed to other AM technologies, where a 3D object is modeled and then automatically manufactured additively, CSAM currently does not have a standardized methodology for obtaining complex parts [110]. Therefore, it is crucial to investigate and develop new robot path trajectories and to standardize a methodology that enables the fabrication of complex geometries using CSAM from an initial digital model. To achieve this, a comprehensive understanding of the behavior of sprayed deposits of various materials is essential for setting a basis for the fabrication of CSAM deposits with a controlled geometry.

In this sense, some works in the literature have investigated different robot path trajectories for the fabrication of complex-shaped parts. The first approach for the fabrication of CSAM free-standing components with controlled shape was proposed by Pattison et al. [98] The authors investigated a triangular-tessellation strategy that consisted on tilting the nozzle and spraying into the inclined face of the deposit formed in the initial layer. This strategy was developed with the intention to obtain deposits with a vertical wall without the need of edge milling post-processes. However, for this approach to be effective, a pyramid-shape deposit first needs to be deposited before the subsequent layers with the inclined nozzle, causing an overall reduction in the deposition efficiency. Subsequently, Wu et al. [109] introduced another building strategy to form complex 3D shapes layer-by-layer (Figure 1.17). The authors focused on optimizing three key robotic parameters based on the approximation that the sprayed single tracks can be represented as a normal Gaussian curve: the deflection angle, the scanning step, and the retreat distance of the nozzle. In particular, this strategy is able to

compensate the thickness difference at the edges of the deposit by spraying a layer at a deflection angle, resulting in the obtention of thick deposits with straight walls. Another alternative for the fabrication of straight wall CSAM deposits was developed by Vaz et al. [108]. This deposition strategy, known as Metal Knitting, involves spraying at a constant deflected angle while making circular movements (Figure 1.17). This approach maximizes deposition efficiency at the edges of the deposit rather than at the center. Although this method allows for the successful creation of thick deposits with straight walls, the consistent deposition at an angle other than 90° results in higher porosity in the CSAM parts compared to other deposition methods.

Taking this into account, the development of new path trajectories must consider their influence not only on the geometry of the final deposit but also on its microstructural characteristics, specifically to minimize porosity and avoid subsequent detrimental effects on the mechanical properties of the final part. Vargas-Uscategui et al. [111] focused their research on understanding the impact of robot path trajectories and the robotic parameters of the CS process on both the shape and porosity of a CSAM object. To achieve this, the authors sprayed squared Ti frames while varying the contour spray angle, traverse velocity, and corner radius. The results revealed that the toolpath trajectories generated a porosity distribution within the microstructure of the deposits, with pore values of 20-30 % at the edges of the deposit, 10-15 % in the interlayers, and 5-10 % within each track layer.

Moreover, another approach currently being investigated is the standardization of robotic paths from a more automatized perspective, instead of the individual adjustment of the toolpath for each spraying case. The implementation of robot programming models and artificial intelligence has contributed to great advancements in this context. Wu et al. [112] explored novel strategies for robot programming and post-spray analyses, establishing a foundation for the industrialization of the CSAM process and its subsequent quality control of the final printed parts. Specifically, the authors developed an application capable of processing geometries in CAD form that can translate these models as robotic toolpaths that allow a precise control over the geometry of CSAM objects. Li et al. [110] proposed another standardized methodology for

the fabrication of complex components by CSAM with the aim of reducing the overall cost of spraying large parts. This methodology relies on a digitalized 3D model of the desired component, which is sliced by a novel algorithm that generates intersecting points, i.e. the contour, for the nozzle trajectory. The authors concluded that their proposed methodology enables CSAM to manufacture workpieces with complex geometries. Moreover, Liu et al. [113] predicted the shape of multiple single tracks profile using an artificial neural network when spraying onto heterogeneous substrate surfaces.

Even though these studies have propelled the development of CSAM with new toolpath methodologies, the fabrication of CSAM parts with complex geometries remains challenging, especially when compared to other metal AM technologies with higher geometrical precision. Therefore, understanding the behavior of the various cold-sprayable materials for manufacturing near-net-shape components or reconstructing damaged parts, along with the subsequent development of a standardized programming of the robot path trajectory is crucial for reaching the full potential of CSAM.

1.3.4.2 Heat treatments

One of the most studied deposition strategies to enhance the properties of the CSAM parts are the heat treatments (HT). As mentioned before, both the microstructure and the final properties of materials are influenced by their processing, including post-processing techniques such as HT. In this context, HT is among the most effective methods for tailoring the microstructure of CSAM deposits, consequently improving their mechanical properties based on their intended application [8].

In this sense, HT have become a successful strategy for overcoming some challenges associated with the CSAM technology, primarily addressing the inferior mechanical properties and the excessive accumulation of residual stresses. During the HT, the microstructure of the CSAM deposits evolves based on the temperature, time, and environment during the process. After the particles are deposited, they remain plastically deformed and packed into layers.

Depending on the material, a dense or porous coating is obtained. In the second case, defects such as particle boundaries and pores are present within

the microstructure. When applying the HT to the CSAM parts, the particles undergo transformation through three distinct phases: diffusion, recrystallization, and grain growth [74]. The diffusion process involves the movement of atoms within the particles due to the available thermal energy. This phase relieves some of the internal stresses and is critical for healing the defects within the microstructure, thus the particle interfaces tend to disappear. Furthermore, the recrystallization phase enhances the ductility of the CSAM parts by removing the work hardening effects caused by the intensive plastic deformation of the particles. Finally, grain growth takes place, and the new grains formed increase in size. Usually, fine grains contribute to enhanced mechanical properties, so the temperature and time of the HT must be controlled to avoid excessive grain growth [74]. Figure 1.18 schematically illustrates these evolution steps during HT.

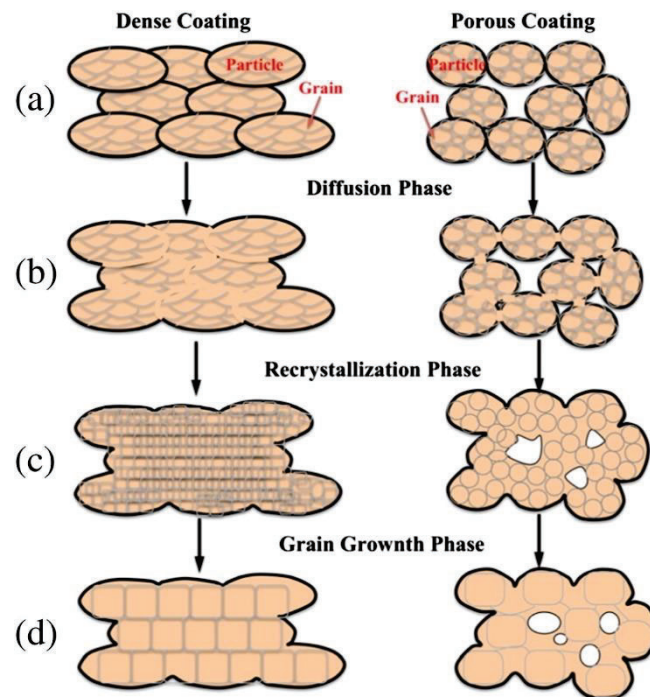


Figure 1.18. CSAM microstructure evolution steps during HT. Figure obtained from [74].

In addition to the relief of residual stresses, densification of the microstructure, and improvement of mechanical properties, HT also has been shown to increase the adhesion strength by promoting metallurgical bonding between the deposit and the substrate [33,114,115], and eliminate the anisotropy typically present in CSAM parts due to the recrystallization processes [10,80,81,116].

In particular, annealing has been implemented as a simple and straightforward post-processing method for various metallic materials fabricated by CSAM, including Cu [67,117], Al and its alloys [70,118–120], Ti and its alloys [121–124], stainless steel [125] and Ni alloys [115,126,127]. Huang et al. [74] studied the effects of annealing on the porosity and mechanical properties of four typical materials used in CSAM: Al, Cu, Ti, and stainless steel 316L. Their findings indicated that, as mentioned before, the microstructure of all materials, along with their subsequent HT process, determined their mechanical properties. The authors concluded the extent of the effect of the annealing depending on the material: For Cu, being a highly ductile material with completely dense microstructure, the mechanical properties resulted equivalent to Cu bulk materials after the annealing. This indicates that CSAM can be an excellent technology for the production or repair of Cu components. In the case of Al and stainless steel 316L, where some pores and defects were present within the microstructure, the annealing improved the strength of the deposits by fixing these defects. However, the tensile strength resulted slightly lower than their bulk counterparts. Finally, the Ti coating showed a porous microstructure that was difficult to improve through annealing. Specifically, the large pores remained unchanged due to the lack of intimate contact between the particles.

Another HT that has been widely studied for the densification of CSAM parts is the hot isostatic pressing (HIP) technology. HIP is a well-known method in the aerospace industry to reduce porosity, as it compresses the material in all directions with an inert gas at the same time it applies temperature. This HT method has been particularly studied for high strength metallic materials that lead to porous microstructures in the as sprayed state, such as Ti [128] and IN718 [127]. Petrovskiy et al. [128] investigated the influence of HIP on the microstructure and tensile strength of CS Ti coatings. In this study the porosity was reduced from 4.3 to 2.2%, while the tensile strength increased from 110 to 480 MPa, in the as sprayed and HIP-treated conditions, respectively. This demonstrated HIP as a successful deposition strategy for the microstructure densification of these high strength materials, however only the small pores were eliminated and the large pores remained intact after the HIP treatment, suggesting that a simpler method such as annealing is a better method in terms

of cost-efficiency. This is supported by the work of Pérez-Andrade et al. [127], who evaluated the microstructural characteristics of IN718 subjected to HIP-treatment. The authors concluded that annealing was enough to obtain samples with porosities below 1%, and HIP-treatment is not essential in CSAM.

Annealing HT is an effective way to enhance both the microstructure and the mechanical properties of CSAM deposits. However, this deposition strategy also has its limitations, and further methods still need to be investigated as a complement to obtain CSAM parts of high-strength materials comparable to bulk parts.

1.3.4.3 Substrate preheating

A crucial variable during the CSAM deposition is the substrate. In addition to the substrate material and surface characteristics, its temperature significantly affects the quality of the CS deposit. Thus, the substrate preheating has been extensively studied as a deposition strategy.

One of the first approaches to the investigation of the effect of the substrate temperature on the coating formation was proposed by Legoux et al. [129]. This study evaluated the deposition of Al, Zn, and Sn onto preheated substrates at temperatures that varied from room temperature to a high fraction of the melting point of the feedstock material. The authors established the importance of temperature in the CS process: the substrate temperature is as important as the particles temperature for coating formation. In the same way, Fukumoto et al. [130] evaluated the impact of substrate preheating on the deposition behavior of individual Cu particles. The authors concluded that the higher the substrate temperature, the higher the deposition rate of the Cu particles.

These two works set a basis for further studies on substrate preheating, since it was clear that the temperature was a key factor on particle bonding and the subsequent coating formation. Yin et al. [131] studied numerically and experimentally the heat exchange between the process gas and the substrate temperature when spraying Cu, Al, SS, and Ti coatings. Moreover, Suo et al. [132] improved the bonding strength of Mg coatings by preheating Al substrates to 100, 200 °C. The adhesion strength improved from 3.3 ± 0.8 to 11.6 ± 0.5 MPa, respectively. In the same way, Xie et al. [133] evaluated the bonding strength of

SS 316L when preheating the substrate at room temperature, 400, 600, and 700 °C. It was found that adhesive strength increased with the increased substrate temperature with resulting values of 13.4, 31.0, 63.2, and 74.1 MPa, respectively. Ortiz-Fernandez and Jodoin [134] developed a hybrid additive manufacturing process that involved coupling the CS process with induction preheating of the substrate. In their work, pure Al was sprayed onto hard Ti6Al4V preheated substrates. The results exhibited that the DE and the coating thickness doubled with this deposition strategy in comparison with the traditional CS process.

To understand the effects of substrate temperature on the deposition mechanisms of the particles, it is essential to study the influence of temperature on particle-substrate interaction. Upon impact, the kinetic energy of the particles is converted into heat, facilitating the dislocation motion within the materials and increasing both substrate and particle deformation [23]. This thermal softening of the substrate promotes the formation of the metal jet necessary to fracture the oxide layer of the particles, promoting metallurgical bonding at the interface [131].

As it has been established, the substrate preheating strategy has a great influence on the adhesion mechanisms and strength of various materials. However, no studies are found in the literature regarding the use of substrate preheating on specific applications, such as the repair or reconstruction of damaged high-strength materials.

1.3.4.4 Masked CSAM

The CSAM process is well known for its unique capability of fabricating components using a solid-state, bottom-up approach, ideally without the need for post-process machining. As a result, various deposition strategies have been developed to produce metallic parts with simple geometries. In addition to developing diverse robot path trajectories, another approach is the implementation of a mask, which enables the straightforward and efficient manufacturing of 3D patterned parts.

The use of this approach in CS was first proposed in 2013 by Cormier et al. [87], who explored the viability of producing near-net-shaped pyramidal fin arrays using a steel wire mesh. This masked CSAM methodology involves

placing a mask between the nozzle and the substrate to selectively shield the deposition of the particles, as shown in Figure 1.19. The deposition pattern mirrors the inverse of the mask geometry, enabling the fabrication of 3D patterns. In this sense, the authors provided an initial insight into the fabrication of metallic parts with patterned geometries.

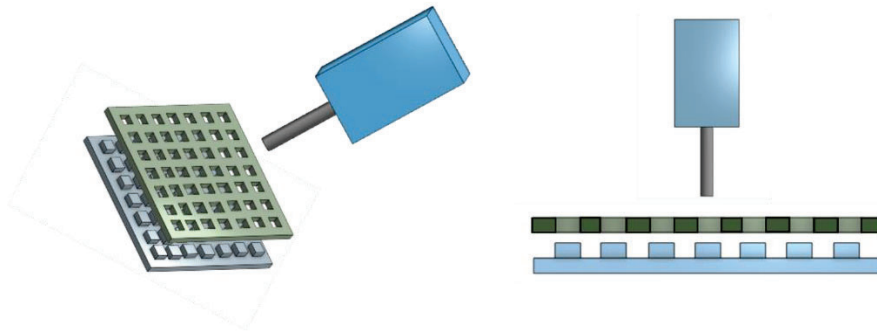


Figure 1.19. CSAM masking process.

This study established a foundation for further research on masked CSAM technology [89,135–137]. Dupuis et al. [89] modified the geometry of the pyramidal fin arrays with varying base angle by grinding, obtaining trapezoid fins with constant height. The results indicated that the overall performance of the fins was very similar, which indicated that grinding is an effective way to control the end quality of the parts. Furthermore, Klinkov et al. [135] examined the effects of the mask's transverse size (0.3 – 1 mm) and its distance from the substrate. The results showed that for Al and Cu powders, the placement of the mask should be set as close as possible from the substrate, considering the intended coating thickness. Cormier et al. [136] explored the fabrication of pin fins of several materials such as pure Al, pure Ni, and stainless steel 304. Finally, to assess the properties of parts produced with this methodology for possible applications, Cormier et al. [137] evaluated the adhesion and thermal performance of Al alloy pin fins deposited on various bond coats. The authors concluded that the fin density, height, and substrate roughness did not affect the adhesion strength. Thus, the bonding strength between the deposit and the substrate remains unchanged regardless of the pin fins' size and geometry.

The CSAM masking methodology shows promising potential for producing patterned deposits with various geometries. Therefore, research exploring the

performance and potential applications of these CSAM components is highly encouraged.

1.3.4.5 Shot-peening

In the CS process, a feedstock powder is sprayed at supersonic velocities. It has already been mentioned that during the first layer, the sprayed particles are plastically deformed upon the impact with the substrate. With each additional layer, the particles impinge on the previously deposited particles, which induces a so-called tamping effect. This phenomenon, first described by Li et al. [138], refers to the compaction that occurs when new particles impact and compress the already deposited layers, generating a shot peening (SP) effect that densifies the microstructure of the sprayed deposit. Based on this behavior, a new CS deposition strategy emerged with the intention of reducing the overall porosity of the sprayed part.

In-situ SP, also called in-situ micro-forging (MF) consist in mixing the feedstock powder with a large-sized powder (150 – 300 μm) that enables the tamping of the deposited particles and produces a dense deposit using moderate-energy spraying process conditions of temperature and pressure, without the need of using expensive He gas [139,140]. However, the challenge that arises with the SP strategy is that the inclusion of the SP powder may be observed within the microstructure. In general, since these particles have a much larger size than the feedstock powder, their critical velocity is also greater, meaning that, under the optimized spraying conditions, these particles impact the surface and are rebounded. Luo et al. [141] introduced for the first time the mixing of large-sized stainless steel particles with Ti and Ti6Al4V feedstock powders to obtain dense deposits by SP. As mentioned before, these materials usually present some porosity within their microstructure when produced by CS due to a lack of particle deformation. The authors varied the volumetric SP proportion ranging from 0 to 70 vol.% for the Ti and Ti6Al4V deposits, as shown in Figure 1.20, which decreased the porosity from 13.7% to 0.3% for Ti, and from 15.3% to 0.7% for Ti6Al4V. In the first case no SP particles were embedded in the deposit, while the last case only a ≤ 2.3 vol.% of SP particles were observed within the microstructure.

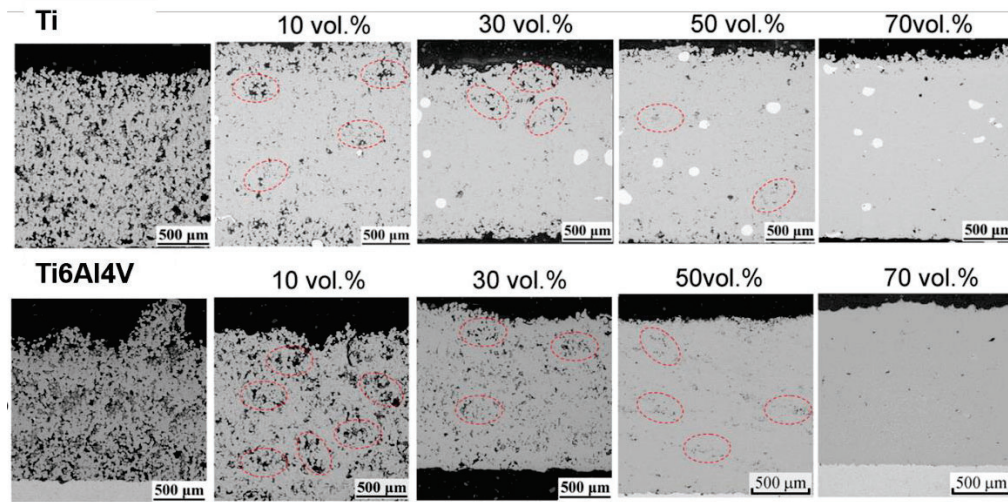


Figure 1.20. Cross-sectional microstructures of Ti and Ti6Al4V CS coatings with different proportions of the SP particles. Figure obtained from [141].

In a subsequent study, Luo et al. [139] investigated the effect of large-sized SS SP particles on the adhesion of Al sprayed onto a AZ31BMg substrate. It was observed that the SP particles greatly improved the plastic deformation of the feedstock powder in the interface substrate-deposit by generating a vortex-like material intermixing that promoted both mechanical interlocking and metallurgical bonding that resulted in an increased adhesion from 47.9 MPa to 107.2 MPa, when sprayed traditionally and with the SP strategy, respectively. These two studies showed that both the microstructure and the adhesion can be greatly improved by inducing this MF effect during the spraying process. Moreover, Wei et al. [142] were able to deposit three types of Al-based coatings; pure Al, AA2219, and AA6061, onto AZ21B magnesium alloy substrates with porosities as low as $0.34 \pm 0.11\%$, $0.23 \pm 0.09\%$, and $0.24 \pm 0.08\%$, respectively. Based on these studies and the possibility of SP to enhance the microstructure and, consequently, the mechanical properties of various materials sprayed by CSAM, Liu et al. [140] developed a universal processing map for the SP spraying strategy applicable to commonly used metals in CSAM: pure Al and its alloys, pure Ti and its alloys, and pure Ni. These feedstock powders were mixed with the SP powder and sprayed under the conventional parameters for each material. The authors concluded that the SP effect is more pronounced when depositing soft metals, with the inclusion of the SP particles being more evident in these materials. Moreover, it was determined that the densification level of the SP particles depends on the energy input to the unit volume of the depositing materials.

Specifically, the microstructure of the sprayed material can only be densified when the energy input of the SP particles exceeds a certain threshold level.

The SP deposition strategy offers a successful methodology to overcome the porosity limitations of conventional CSAM spraying methods. The peening effect enhances the microstructure of the final part and, subsequently, improves its final mechanical properties. Further studies related to the type of depositing materials, SP particle size, and spraying parameters are encouraged to obtain dense CSAM components without the need for post-processing steps.

1.3.4.6 Laser Assisted Cold Spray

Another deposition strategy that involves the incorporation of complementary equipment is the laser assisted cold spray (LACS). This method involves the combination of the CS process with an external laser that selectively heats the desired deposition area during spraying. The temperature of the particles increases further during impact due to the laser beam, still remaining below their melting point. Consequently, the particles undergo significant deformation upon impact with the substrate, due to both the kinetic and the thermal energies, resulting in an enhanced bond formation between them [10].

Only a few studies are found in the literature that investigate the LACS deposition strategy [143–146]. In addition to the CSAM process variables, the quality of the 3D parts depends as well on the laser parameters (e.g. laser rate application) [143]. One particular advantage of LACS is that hard materials, which are usually difficult to spray with CSAM, can be successfully deposited; some examples include the work of Bray et al. [143], who obtained dense Ti coatings free of oxides with LACS; Nikbakht et al. [145], who were able to fabricate a 250 μm thick CrMnCoFeNi high entropy alloy using N_2 as the process gas; and Barton et al. [147], who sprayed AISI 4340 steel coatings and concluded that the high surface temperatures of the substrate induced by the laser improved the deposition efficiency of this material.

The implementation of the laser during the spraying process broadens the range of materials that can be fabricated with CSAM and clearly densifies the microstructure due to the thermal energies supplied by the laser. Therefore, its investigation is encouraged to further develop the CSAM technology.

Overall, all these described deposition strategies represent the state-of-the-art research in CSAM, enabling the further development of this technology and its implementation across a wide range of applications. Consequently, this thesis will be focused on investigating of some of the already mentioned deposition strategies with the objective of advancing CSAM as solid AM technology. The general and specific objectives of this work are described in detail in the following chapter.

1.4 References

- [1] D. Godec, J. Gonzalez-Gutierrez, A. Nordin, E. Pei, J. Ureña, A Guide to Additive Manufacturing, Springer International Publishing, Cham, 2022. <https://doi.org/10.1007/978-3-031-05863-9>.
- [2] W.E. Frazier, Metal additive manufacturing: A review, *J Mater Eng Perform* 23 (2014) 1917–1928. <https://doi.org/10.1007/s11665-014-0958-z>.
- [3] T.J. Horn, O.L.A. Harrysson, Overview of current additive manufacturing technologies and selected applications, *Sci Prog* 95 (2012) 255–282. <https://doi.org/10.3184/003685012X13420984463047>.
- [4] E. Toyserkani, D. Sarker, F. Liravi, P. Russo, K. Taherkhani, Metal Additive Manufacturing, Wiley, Ontario, Canada, 2022.
- [5] International Organization for Standardization, UNE-EN ISO/ASTM 52900:2022 - Additive manufacturing - General principles - Terminology, 2022.
- [6] D. Herzog, V. Seyda, E. Wycisk, C. Emmelmann, Additive manufacturing of metals, *Acta Mater* 117 (2016) 371–392. <https://doi.org/10.1016/j.actamat.2016.07.019>.
- [7] R.N. Raelison, C. Verdy, H. Liao, Cold gas dynamic spray additive manufacturing today: Deposit possibilities, technological solutions and viable applications, *Mater Des* 133 (2017) 266–287. <https://doi.org/10.1016/j.matdes.2017.07.067>.
- [8] S. Yin, P. Cavaliere, B. Aldwell, R. Jenkins, H. Liao, W. Li, R. Lupoi, Cold spray additive manufacturing and repair: Fundamentals and applications, *Addit Manuf* 21 (2018) 628–650. <https://doi.org/10.1016/j.addma.2018.04.017>.
- [9] W. Li, K. Yang, S. Yin, X. Yang, Y. Xu, R. Lupoi, Solid-state additive manufacturing and repairing by cold spraying: A review, *J Mater Sci Technol* 34 (2018) 440–457. <https://doi.org/10.1016/j.jmst.2017.09.015>.
- [10] W. Li, C. Cao, G. Wang, F. Wang, Y. Xu, X. Yang, ‘Cold spray +’ as a new hybrid additive manufacturing technology: a literature review, *Science and Technology of Welding and Joining* 24 (2019) 420–445. <https://doi.org/10.1080/13621718.2019.1603851>.
- [11] W. Sun, X. Chu, H. Lan, R. Huang, J. Huang, Y. Xie, J. Huang, G. Huang, Current Implementation Status of Cold Spray Technology: A Short Review, *Journal of Thermal Spray Technology* 31 (2022) 848–865. <https://doi.org/10.1007/s11666-022-01382-4>.
- [12] P.L. Fauchais, J.V.R. Heberlein Maher, I. Boulos, Thermal Spray Fundamentals From Powder to Part, 1st ed., Springer, 2014.
- [13] R.C. Dykhuizen, M.F. Smith, Gas Dynamic Principles of Cold Spray, *Journal of Thermal Spray Technology* 7 (1998) 205–212. <https://doi.org/10.1361/105996398770350945>.
- [14] K. Sakaki, The influence of nozzle design in the cold spray process, in: *The Cold Spray Materials Deposition Process: Fundamentals and Applications*, Elsevier Ltd., 2007: pp. 117–126. <https://doi.org/10.1533/9781845693787.2.117>.

- [15] L. Alonso, M.A. Garrido, P. Poza, An optimisation method for the cold-spray process: On the nozzle geometry, *Mater Des* 214 (2022). <https://doi.org/10.1016/j.matdes.2022.110387>.
- [16] M. Grujicic, C. Tong, W.S. DeRosset, D. Helfrich, Flow analysis and nozzle-shape optimization for the cold-gas dynamic-spray process, in: *Proc Inst Mech Eng B J Eng Manuf*, 2003: pp. 1603–1613. <https://doi.org/10.1243/095440503771909980>.
- [17] V. Varadaraajan, P. Mohanty, Design and optimization of rectangular cold spray nozzle: Radial injection angle, expansion ratio and traverse speed, *Surf Coat Technol* 316 (2017) 246–254. <https://doi.org/10.1016/j.surfcoat.2017.03.005>.
- [18] W.Y. Li, H. Liao, G. Douchy, C. Coddet, Optimal design of a cold spray nozzle by numerical analysis of particle velocity and experimental validation with 316L stainless steel powder, *Mater Des* 28 (2007) 2129–2137. <https://doi.org/10.1016/j.matdes.2006.05.016>.
- [19] A.P. Alkhimov, V.F. Kosarev, S.V. Klinkov, The Features of Cold Spray Nozzle Design, *Journal of Thermal Spray Technology* 10 (2001) 375–381. <https://doi.org/https://doi.org/10.1361/105996301770349466>.
- [20] H. Tabbara, S. Gu, D.G. McCartney, T.S. Price, P.H. Shipway, Study on process optimization of cold gas spraying, *Journal of Thermal Spray Technology* 20 (2011) 608–620. <https://doi.org/10.1007/s11666-010-9564-2>.
- [21] M.R. Rokni, S.R. Nutt, C.A. Widener, V.K. Champagne, R.H. Hrabec, Review of Relationship Between Particle Deformation, Coating Microstructure, and Properties in High-Pressure Cold Spray, *Journal of Thermal Spray Technology* 26 (2017) 1308–1355. <https://doi.org/10.1007/s11666-017-0575-0>.
- [22] A. Nastic, B. Jodoin, D. Poirier, J.G. Legoux, Particle temperature effect in cold spray: A study of soft particle deposition on hard substrate, *Surf Coat Technol* 406 (2021). <https://doi.org/10.1016/j.surfcoat.2020.126735>.
- [23] J. Vlcek, L. Gimeno, H. Huber, E. Lugscheider, A systematic approach to material eligibility for the cold-spray process, *Journal of Thermal Spray Technology* 14 (2005) 125–133. <https://doi.org/10.1361/10599630522738>.
- [24] R. Ortiz-Fernandez, B. Jodoin, Toward Efficient Cold Spraying of Inconel 718: Understanding the Influence of Coating and Particle Impact Temperatures, *Journal of Thermal Spray Technology* 32 (2023) 188–207. <https://doi.org/10.1007/s11666-022-01490-1>.
- [25] T. Schmidt, F. Gärtner, H. Assadi, H. Kreye, Development of a generalized parameter window for cold spray deposition, *Acta Mater* 54 (2006) 729–742. <https://doi.org/10.1016/j.actamat.2005.10.005>.
- [26] F.S. Da Silva, N. Cinca, S. Dosta, I.G. Cano, J.M. Guilemany, A.V. Benedetti, Cold gas spray coatings: Basic principles, corrosion protection and applications, *Ecletica Quimica* 42 (2017) 9–32. <https://doi.org/10.26850/1678-4618eqj.v42.1.2017.p09-32>.

- [27] H. Assadi, H. Kreye, F. Gärtner, T. Klassen, Cold spraying – A materials perspective, *Acta Mater* 116 (2016) 382–407. <https://doi.org/10.1016/j.actamat.2016.06.034>.
- [28] F. Gärtner, T. Stoltenhoff, T. Schmidt, H. Kreye, The cold spray process and its potential for industrial applications, *Journal of Thermal Spray Technology* 15 (2006) 223–232. <https://doi.org/10.1361/105996306X108110>.
- [29] F. Meng, S. Yue, J. Song, Quantitative prediction of critical velocity and deposition efficiency in cold-spray: A finite-element study, *Scr Mater* 107 (2015) 83–87. <https://doi.org/10.1016/j.scriptamat.2015.05.026>.
- [30] P. Cavaliere, *Cold-Spray Coatings: Recent Trends and Future perspectives*, Springer International Publishing, 2017. <https://doi.org/10.1007/978-3-319-67183-3>.
- [31] H. Assadi, F. Gärtner, T. Stoltenhoff, H. Kreye, Bonding mechanism in cold gas spraying, *Acta Mater* 51 (2003) 4379–4394. [https://doi.org/10.1016/S1359-6454\(03\)00274-X](https://doi.org/10.1016/S1359-6454(03)00274-X).
- [32] M. Grujicic, Particle/substrate interaction in the cold-spray bonding process, in: *The Cold Spray Materials Deposition Process: Fundamentals and Applications*, Elsevier Ltd., 2007: pp. 148–177. <https://doi.org/10.1533/9781845693787.2.148>.
- [33] T. Hussain, D.G. McCartney, P.H. Shipway, D. Zhang, Bonding mechanisms in cold spraying: The contributions of metallurgical and mechanical components, *Journal of Thermal Spray Technology* 18 (2009) 364–379. <https://doi.org/10.1007/s11666-009-9298-1>.
- [34] W.Y. Li, H. Liao, C.J. Li, H.S. Bang, C. Coddet, Numerical simulation of deformation behavior of Al particles impacting on Al substrate and effect of surface oxide films on interfacial bonding in cold spraying, *Appl Surf Sci* 253 (2007) 5084–5091. <https://doi.org/10.1016/j.apsusc.2006.11.020>.
- [35] M. Grujicic, C.L. Zhao, W.S. DeRosset, D. Helfrich, Adiabatic shear instability based mechanism for particles/substrate bonding in the cold-gas dynamic-spray process, *Mater Des* 25 (2004) 681–688. <https://doi.org/10.1016/j.matdes.2004.03.008>.
- [36] S. Pathak, G.C. Saha, *Cold Spray in the Realm of Additive Manufacturing*, Springer, 2020. <https://doi.org/10.1007/978-3-030-42756-6>.
- [37] A. Silvello, P.D. Cavaliere, V. Albaladejo, A. Martos, S. Dosta, I.G. Cano, Powder properties and processing conditions affecting cold spray deposition, *Coatings* 10 (2020). <https://doi.org/10.3390/coatings10020091>.
- [38] D.L. Gilmore, R.C. Dykhuizen, R.A. Neiser, T.J. Roemer, M.F. Smith, Particle Velocity and Deposition Efficiency in the Cold Spray Process, *Journal of Thermal Spray Technology* 8 (1999) 576–582. <https://doi.org/10.1361/105996399770350278>.
- [39] W. Wong, P. Vo, E. Irissou, A.N. Ryabinin, J.G. Legoux, S. Yue, Effect of particle morphology and size distribution on cold-sprayed pure titanium coatings, *Journal of Thermal Spray Technology* 22 (2013) 1140–1153. <https://doi.org/10.1007/s11666-013-9951-6>.

- [40] R.F. Vaz, A. Silvello, J. Sanchez, V. Albaladejo, I. García-Cano, The influence of the powder characteristics on 316L stainless steel coatings sprayed by cold gas spray, *Coatings* 11 (2021) 1–18. <https://doi.org/10.3390/coatings11020168>.
- [41] S. Yin, P. He, H. Liao, X. Wang, Deposition features of Ti coating using irregular powders in cold spray, *Journal of Thermal Spray Technology* 23 (2014) 984–990. <https://doi.org/10.1007/s11666-014-0116-z>.
- [42] S. Yin, M. Meyer, W. Li, H. Liao, R. Lupoi, Gas Flow, Particle Acceleration, and Heat Transfer in Cold Spray: A review, *Journal of Thermal Spray Technology* 25 (2016) 874–896. <https://doi.org/10.1007/s11666-016-0406-8>.
- [43] T. Schmidt, F. Gaertner, H. Kreye, New developments in cold spray based on higher gas and particle temperatures, in: *Proceedings of the International Thermal Spray Conference*, 2006: pp. 488–494. <https://doi.org/10.1361/105996306X147144>.
- [44] W. Wong, E. Irissou, A.N. Ryabinin, J.G. Legoux, S. Yue, Influence of helium and nitrogen gases on the properties of cold gas dynamic sprayed pure titanium coatings, in: *Journal of Thermal Spray Technology*, 2011: pp. 213–226. <https://doi.org/10.1007/s11666-010-9568-y>.
- [45] O.C. Ozdemir, C.A. Widener, D. Helfrich, F. Delfanian, Estimating the Effect of Helium and Nitrogen Mixing on Deposition Efficiency in Cold Spray, *Journal of Thermal Spray Technology* 25 (2016) 660–671. <https://doi.org/10.1007/s11666-016-0394-8>.
- [46] M.W. Lee, J.J. Park, D.Y. Kim, S.S. Yoon, H.Y. Kim, S.C. James, S. Chandra, T. Coyle, Numerical studies on the effects of stagnation pressure and temperature on supersonic flow characteristics in cold spray applications, *Journal of Thermal Spray Technology* 20 (2011) 1085–1097. <https://doi.org/10.1007/s11666-011-9641-1>.
- [47] X. Meng, J. Zhang, J. Zhao, Y. Liang, Y. Zhang, Influence of Gas Temperature on Microstructure and Properties of Cold Spray 304SS Coating, *J. Mater. Sci. Technol* 27 (2011) 809–815. [https://doi.org/10.1016/S1005-0302\(11\)60147-3](https://doi.org/10.1016/S1005-0302(11)60147-3).
- [48] K. Binder, J. Gottschalk, M. Kollenda, F. Gärtner, T. Klassen, Influence of impact angle and gas temperature on mechanical properties of titanium cold spray deposits, in: *Journal of Thermal Spray Technology*, 2011: pp. 234–242. <https://doi.org/10.1007/s11666-010-9557-1>.
- [49] S. Singh, R.K.S. Raman, C.C. Berndt, H. Singh, Influence of cold spray parameters on bonding mechanisms: A review, *Metals (Basel)* 11 (2021). <https://doi.org/10.3390/met11122016>.
- [50] J. Pattison, S. Celotto, A. Khan, W. O'Neill, Standoff distance and bow shock phenomena in the Cold Spray process, *Surf Coat Technol* 202 (2008) 1443–1454. <https://doi.org/10.1016/j.surfcoat.2007.06.065>.
- [51] A.W.Y. Tan, W. Sun, Y.P. Phang, M. Dai, I. Marinescu, Z. Dong, E. Liu, Effects of Traverse Scanning Speed of Spray Nozzle on the Microstructure and Mechanical Properties of Cold-Sprayed Ti6Al4V Coatings, *Journal of Thermal Spray Technology* 26 (2017) 1484–1497. <https://doi.org/10.1007/s11666-017-0619-5>.

- [52] D. Kotoban, S. Grigoriev, A. Okunkova, A. Sova, Influence of a shape of single track on deposition efficiency of 316L stainless steel powder in cold spray, *Surf Coat Technol* 309 (2017) 951–958. <https://doi.org/10.1016/j.surfcoat.2016.10.052>.
- [53] C.-J. Li, W.-Y. Li, Y.-Y. Wang, Effect of Spray Angle on Deposition Characteristics in Cold Spraying, in: *Thermal Spray 2003: Advancing the Science & Applying the Technology*, ASM International, Ohio, USA, 2003: pp. 91–96. <https://doi.org/https://doi.org/10.31399/asm.cp.itsc2003p0091>.
- [54] R. Singh, K.H. Rauwald, E. Wessel, G. Mauer, S. Schrufer, A. Barth, S. Wilson, R. Vassen, Effects of substrate roughness and spray-angle on deposition behavior of cold-sprayed Inconel 718, *Surf Coat Technol* 319 (2017) 249–259. <https://doi.org/10.1016/j.surfcoat.2017.03.072>.
- [55] C.W. Ziemian, M.M. Sharma, B.D. Bouffard, T. Nissley, T.J. Eden, Effect of substrate surface roughening and cold spray coating on the fatigue life of AA2024 specimens, *Mater Des* 54 (2014) 212–221. <https://doi.org/10.1016/j.matdes.2013.08.061>.
- [56] W. Sun, A.W.Y. Tan, N.W. Khun, I. Marinescu, E. Liu, Effect of substrate surface condition on fatigue behavior of cold sprayed Ti6Al4V coatings, *Surf Coat Technol* 320 (2017) 452–457. <https://doi.org/10.1016/j.surfcoat.2016.11.093>.
- [57] T. Stoltenhoff, C. Borchers, F. Gärtner, H. Kreye, Microstructures and key properties of cold-sprayed and thermally sprayed copper coatings, *Surf Coat Technol* 200 (2006) 4947–4960. <https://doi.org/10.1016/j.surfcoat.2005.05.011>.
- [58] S. Kumar, G. Bae, C. Lee, Influence of substrate roughness on bonding mechanism in cold spray, *Surf Coat Technol* 304 (2016) 592–605. <https://doi.org/10.1016/j.surfcoat.2016.07.082>.
- [59] W. Sun, A.W.Y. Tan, A. Bhowmik, I. Marinescu, X. Song, W. Zhai, F. Li, E. Liu, Deposition characteristics of cold sprayed Inconel 718 particles on Inconel 718 substrates with different surface conditions, *Materials Science and Engineering: A* 720 (2018) 75–84. <https://doi.org/10.1016/j.msea.2018.02.059>.
- [60] S. Yin, X.F. Wang, W.Y. Li, H.E. Jie, Effect of substrate hardness on the deformation behavior of subsequently incident particles in cold spraying, *Appl Surf Sci* 257 (2011) 7560–7565. <https://doi.org/10.1016/j.apsusc.2011.03.126>.
- [61] G. Bae, Y. Xiong, S. Kumar, K. Kang, C. Lee, General aspects of interface bonding in kinetic sprayed coatings, *Acta Mater* 56 (2008) 4858–4868. <https://doi.org/10.1016/j.actamat.2008.06.003>.
- [62] S. Bagherifard, S. Monti, M.V. Zuccoli, M. Riccio, J. Kondás, M. Guagliano, Cold spray deposition for additive manufacturing of freeform structural components compared to selective laser melting, *Materials Science and Engineering A* 721 (2018) 339–350. <https://doi.org/10.1016/j.msea.2018.02.094>.
- [63] A. Saboori, S. Biamino, P. Di Torino, D. Gitardi, M. Lombardi, The Capacity of Cold Spray Additive Manufacturing Technology for Metallic Part Repairing, in: *Euro PM2018, Bilbao*, 2018. <https://www.researchgate.net/publication/328407397>.

- [64] R.F. Vaz, A. Garfias, V. Albaladejo, J. Sanchez, I.G. Cano, A Review of Advances in Cold Spray Additive Manufacturing, *Coatings* 13 (2023). <https://doi.org/10.3390/coatings13020267>.
- [65] P. Cavaliere, A. Silvello, Processing parameters affecting cold spray coatings performances, *International Journal of Advanced Manufacturing Technology* 71 (2014) 263–277. <https://doi.org/10.1007/s00170-013-5465-0>.
- [66] K. Wathanyu, K. Tuchinda, S. Daopiset, S. Sirivisoot, J. Kondas, C. Bauer, Study of the Properties of Titanium Porous Coating with Different Porosity Gradients on 316L Stainless Steel by a Cold Spray Process, *Journal of Thermal Spray Technology* 31 (2022) 545–558. <https://doi.org/10.1007/s11666-021-01316-6>.
- [67] F. Gärtner, T. Stoltenhoff, J. Voyer, H. Kreye, S. Riekehr, M. Koçak, Mechanical properties of cold-sprayed and thermally sprayed copper coatings, *Surf Coat Technol* 200 (2006) 6770–6782. <https://doi.org/10.1016/j.surfcoat.2005.10.007>.
- [68] D. Zhang, P.H. Shipway, D.G. McCartney, Cold gas dynamic spraying of aluminum: The role of substrate characteristics in deposit formation, *Journal of Thermal Spray Technology* 14 (2005) 109–116. <https://doi.org/10.1361/10599630522666>.
- [69] W. Li, C. Cao, S. Yin, Solid-state cold spraying of Ti and its alloys: A literature review, *Prog Mater Sci* 110 (2020). <https://doi.org/10.1016/j.pmatsci.2019.100633>.
- [70] M.R. Rokni, C.A. Widener, V.K. Champagne, G.A. Crawford, Microstructure and mechanical properties of cold sprayed 7075 deposition during non-isothermal annealing, *Surf Coat Technol* 276 (2015) 305–315. <https://doi.org/10.1016/j.surfcoat.2015.07.016>.
- [71] Y. Liu, T. Xiong, J. Wu, Microstructure of aluminum bronze coating sprayed by Cold Gas Dynamic Spraying (CGDS), in: *Materials Science Forum*, Trans Tech Publications Ltd, 2012: pp. 1112–1116. <https://doi.org/10.4028/www.scientific.net/MSF.704-705.1112>.
- [72] A. Silvello, P. Cavaliere, S. Yin, R. Lupoi, I. Garcia Cano, S. Dosta, Microstructural, Mechanical and Wear Behavior of HVOF and Cold-Sprayed High-Entropy Alloys (HEAs) Coatings, *Journal of Thermal Spray Technology* 31 (2022) 1184–1206. <https://doi.org/10.1007/s11666-021-01293-w>.
- [73] V. Luzin, O. Kirstein, S.H. Zahiri, D. Fraser, Residual Stress Buildup in Ti Components Produced by Cold Spray Additive Manufacturing (CSAM), *Journal of Thermal Spray Technology* 29 (2020) 1498–1507. <https://doi.org/10.1007/s11666-020-01048-z>.
- [74] R. Huang, M. Sone, W. Ma, H. Fukanuma, The effects of heat treatment on the mechanical properties of cold-sprayed coatings, *Surf Coat Technol* 261 (2015) 278–288. <https://doi.org/10.1016/j.surfcoat.2014.11.017>.
- [75] V. Luzin, K. Spencer, M.X. Zhang, Residual stress and thermo-mechanical properties of cold spray metal coatings, *Acta Mater* 59 (2011) 1259–1270. <https://doi.org/10.1016/j.actamat.2010.10.058>.

- [76] R. Ghelichi, S. Bagherifard, D. Macdonald, I. Fernandez-Pariente, B. Jodoin, M. Guagliano, Experimental and numerical study of residual stress evolution in cold spray coating, *Appl Surf Sci* 288 (2014) 26–33. <https://doi.org/10.1016/j.apsusc.2013.09.074>.
- [77] T. Suhonen, T. Varis, S. Dosta, M. Torrell, J.M. Guilemany, Residual stress development in cold sprayed Al, Cu and Ti coatings, *Acta Mater* 61 (2013) 6329–6337. <https://doi.org/10.1016/j.actamat.2013.06.033>.
- [78] R. Singh, S. Schrufer, S. Wilson, J. Gibmeier, R. Vassen, Influence of coating thickness on residual stress and adhesion-strength of cold-sprayed Inconel 718 coatings, *Surf Coat Technol* 350 (2018) 64–73. <https://doi.org/10.1016/j.surfcoat.2018.06.080>.
- [79] V. Luzin, O. Kirstein, S.H. Zahiri, D. Fraser, Residual Stress Buildup in Ti Components Produced by Cold Spray Additive Manufacturing (CSAM), *Journal of Thermal Spray Technology* 29 (2020) 1498–1507. <https://doi.org/10.1007/s11666-020-01048-z>.
- [80] S. Yin, R. Jenkins, X. Yan, R. Lupoi, Microstructure and mechanical anisotropy of additively manufactured cold spray copper deposits, *Materials Science and Engineering A* 734 (2018) 67–76. <https://doi.org/10.1016/j.msea.2018.07.096>.
- [81] K. Yang, W. Li, X. Guo, X. Yang, Y. Xu, Characterizations and anisotropy of cold-spraying additive-manufactured copper bulk, *J Mater Sci Technol* 34 (2018) 1570–1579. <https://doi.org/10.1016/j.jmst.2018.01.002>.
- [82] Y. Ren, N. ul H. Tariq, H. Liu, L. Zhao, X. Cui, Y. Shen, J. Wang, T. Xiong, Study of microstructural and mechanical anisotropy of 7075 Al deposits fabricated by cold spray additive manufacturing, *Mater Des* 212 (2021). <https://doi.org/10.1016/j.matdes.2021.110271>.
- [83] M.R. Rokni, A.T. Nardi, V.K. Champagne, S.R. Nutt, Effects of Preprocessing on Multi-Direction Properties of Aluminum Alloy Cold-Spray Deposits, *Journal of Thermal Spray Technology* 27 (2018) 818–826. <https://doi.org/10.1007/s11666-018-0723-1>.
- [84] T. Hussain, D.G. McCartney, P.H. Shipway, T. Marrocco, Corrosion behavior of cold sprayed titanium coatings and free standing deposits, *Journal of Thermal Spray Technology* 20 (2011) 260–274. <https://doi.org/10.1007/s11666-010-9540-x>.
- [85] H. Singh, M. Kumar, R. Singh, An overview of various applications of cold spray coating process, *Mater Today Proc* 56 (2022) 2826–2830. <https://doi.org/10.1016/j.matpr.2021.10.160>.
- [86] A. Farjam, Y. Cormier, P. Dupuis, B. Jodoin, A. Corbeil, Influence of Alumina Addition to Aluminum Fins for Compact Heat Exchangers Produced by Cold Spray Additive Manufacturing, *Journal of Thermal Spray Technology* 24 (2015) 1256–1268. <https://doi.org/10.1007/s11666-015-0305-4>.
- [87] Y. Cormier, P. Dupuis, B. Jodoin, A. Corbeil, Net shape fins for compact heat exchanger produced by cold spray, *Journal of Thermal Spray Technology* 22 (2013) 1210–1221. <https://doi.org/10.1007/s11666-013-9968-x>.

- [88] Y. Cormier, P. Dupuis, A. Farjam, A. Corbeil, B. Jodoin, Additive manufacturing of pyramidal pin fins: Height and fin density effects under forced convection, *Int J Heat Mass Transf* 75 (2014) 235–244. <https://doi.org/10.1016/j.ijheatmasstransfer.2014.03.053>.
- [89] P. Dupuis, Y. Cormier, A. Farjam, B. Jodoin, A. Corbeil, Performance evaluation of near-net pyramidal shaped fin arrays manufactured by cold spray, *Int J Heat Mass Transf* 69 (2014) 34–43. <https://doi.org/10.1016/j.ijheatmasstransfer.2013.09.072>.
- [90] P. Dupuis, Y. Cormier, M. Fenech, B. Jodoin, Heat transfer and flow structure characterization for pin fins produced by cold spray additive manufacturing, *Int J Heat Mass Transf* 98 (2016) 650–661. <https://doi.org/10.1016/j.ijheatmasstransfer.2016.03.069>.
- [91] S. Pathak, G.C. Saha, Development of sustainable cold spray coatings and 3D additive manufacturing components for repair/manufacturing applications: A critical review, *Coatings* 7 (2017). <https://doi.org/10.3390/coatings7080122>.
- [92] M. Faccoli, G. Cornacchia, D. Maestrini, G.P. Marconi, R. Roberti, Cold Spray Repair of Martensitic Stainless Steel Components, *Journal of Thermal Spray Technology* 23 (2014) 1270–1280. <https://doi.org/10.1007/s11666-014-0129-7>.
- [93] V.K. Champagne, The repair of magnesium rotorcraft components by cold spray, *Journal of Failure Analysis and Prevention* 8 (2008) 164–175. <https://doi.org/10.1007/s11668-008-9116-y>.
- [94] J. Schell, Cold Spray Aerospace Applications, in: Cold Spray Action Team, 2016.
- [95] J. Villafuerte, D. Wright, Practical cold spray success: repair of Al and Mg alloy aircraft components., *Advanced Materials & Processes* 165 (2010).
- [96] K. Petráčková, J. Kondás, M. Guagliano, Fixing a hole (with cold spray), *Int J Fatigue* 110 (2018) 144–152. <https://doi.org/10.1016/j.ijfatigue.2018.01.014>.
- [97] Fukuda, Powders for Cold Spray Deposition, (2024). <https://www.fukuda-kyoto.co.jp/en/technology/research/cold-spray.html> (accessed May 14, 2024).
- [98] J. Pattison, S. Celotto, R. Morgan, M. Bray, W. O'Neill., Cold gas dynamic manufacturing: A non-thermal approach to freeform fabrication, *Int J Mach Tools Manuf* 47 (2007) 627–634. <https://doi.org/10.1016/j.ijmachtools.2006.05.001>.
- [99] T. Stamey, Main circulating water pump: case study, in: Cold Spray Action Team Conference, 2016.
- [100] T. Stoltenhoff, F. Zimmermann, P. Surface, T. Gmbh, Coatings for Aluminum Aerospace Components Exposed to High Dynamic Stresses, in: Ratingen, 2012.
- [101] J.C. Lee, H.J. Kang, W.S. Chu, S.H. Ahn, Repair of Damaged Mold Surface by Cold-Spray Method, *CIRP Ann Manuf Technol* 56 (2007) 577–580. <https://doi.org/10.1016/j.cirp.2007.05.138>.
- [102] Z. Cai, S. Deng, H. Liao, C. Zeng, G. Montavon, The effect of spray distance and scanning step on the coating thickness uniformity in cold spray process, *Journal of*

Thermal Spray Technology 23 (2014) 354–362. <https://doi.org/10.1007/s11666-013-0002-0>.

[103] G. Prashar, H. Vasudev, A comprehensive review on sustainable cold spray additive manufacturing: State of the art, challenges and future challenges, *J Clean Prod* 310 (2021). <https://doi.org/10.1016/j.jclepro.2021.127606>.

[104] N. Fan, J. Cizek, C. Huang, X. Xie, Z. Chlup, R. Jenkins, R. Lupoi, S. Yin, A new strategy for strengthening additively manufactured cold spray deposits through in-process densification, *Addit Manuf* 36 (2020). <https://doi.org/10.1016/j.addma.2020.101626>.

[105] G. Benenati, R. Lupoi, Development of a Deposition Strategy in Cold Spray for Additive Manufacturing to Minimize Residual Stresses, in: *Procedia CIRP*, Elsevier B.V., 2016: pp. 101–108. <https://doi.org/10.1016/j.procir.2016.08.042>.

[106] H. Wu, C. Huang, X. Xie, S. Liu, T. Wu, T. Niendorf, Y. Xie, C. Deng, M. Liu, H. Liao, S. Deng, Influence of spray trajectories on characteristics of cold-sprayed copper deposits, *Surf Coat Technol* 405 (2021). <https://doi.org/10.1016/j.surfcoat.2020.126703>.

[107] C. Chen, S. Gojon, Y. Xie, S. Yin, C. Verdy, Z. Ren, H. Liao, S. Deng, A novel spiral trajectory for damage component recovery with cold spray, *Surf Coat Technol* 309 (2017) 719–728. <https://doi.org/10.1016/j.surfcoat.2016.10.096>.

[108] R.F. Vaz, V. Albaladejo-Fuentes, J. Sanchez, U. Ocaña, Z.G. Corral, H. Canales, I.G. Cano, Metal Knitting: A New Strategy for Cold Gas Spray Additive Manufacturing, *Materials* 15 (2022) 6785. <https://doi.org/10.3390/ma15196785>.

[109] H. Wu, X. Xie, M. Liu, C. Verdy, Y. Zhang, H. Liao, S. Deng, Stable layer-building strategy to enhance cold-spray-based additive manufacturing, *Addit Manuf* 35 (2020). <https://doi.org/10.1016/j.addma.2020.101356>.

[110] W. Li, Y. Yao, H. Wu, H. Liao, S. Costil, S. Deng, Spray Trajectory Planning for Complex Structural Components in Robotized Cold Spray Additive Manufacturing, *Journal of Thermal Spray Technology* 33 (2024) 71–87. <https://doi.org/10.1007/s11666-023-01696-x>.

[111] A. Vargas-Uscategui, P.C. King, S. Yang, C. Chu, J. Li, Toolpath planning for cold spray additively manufactured titanium walls and corners: Effect on geometry and porosity, *J Mater Process Technol* 298 (2021). <https://doi.org/10.1016/j.jmatprotec.2021.117272>.

[112] H. Wu, S. Liu, W. Li, M. Lewke, R.N. Raelison, A. List, F. Gärtner, H. Liao, T. Klassen, S. Deng, Generic implementation of path design for spray deposition: Programming schemes, processing and characterization for cold spraying, *Surf Coat Technol* 458 (2023). <https://doi.org/10.1016/j.surfcoat.2023.129368>.

[113] M. Liu, H. Wu, Z. Yu, H. Liao, S. Deng, Description and Prediction of Multi-layer Profile in Cold Spray Using Artificial Neural Networks, *Journal of Thermal Spray Technology* 30 (2021) 1453–1463. <https://doi.org/10.1007/s11666-021-01212-z>.

[114] A. Bruera, P. Puddu, S. Theimer, M. Villa-Vidaller, A. List, G. Bolelli, F. Gärtner, T. Klassen, L. Lusvarghi, Adhesion of cold sprayed soft coatings: Effect of substrate

- roughness and hardness, *Surf Coat Technol* 466 (2023). <https://doi.org/10.1016/j.surfcoat.2023.129651>.
- [115] W. Ma, Y. Xie, C. Chen, H. Fukanuma, J. Wang, Z. Ren, R. Huang, Microstructural and mechanical properties of high-performance Inconel 718 alloy by cold spraying, *J Alloys Compd* 792 (2019) 456–467. <https://doi.org/10.1016/j.jallcom.2019.04.045>.
- [116] Y. Ren, D. Zhou, G. Xie, H. Liu, X. Cui, J. Wang, T. Xiong, Effects of different heat treatments on anisotropy of cold sprayed 7075 Al deposits, *Mater Charact* 199 (2023). <https://doi.org/10.1016/j.matchar.2023.112828>.
- [117] W.Y. Li, C.J. Li, H. Liao, Effect of annealing treatment on the microstructure and properties of cold-sprayed Cu coating, *Journal of Thermal Spray Technology* 15 (2006) 206–211. <https://doi.org/10.1361/105996306X108066>.
- [118] A.C. Hall, D.J. Cook, R.A. Neiser, T.J. Roemer, D.A. Hirschfeld, The effect of a simple annealing heat treatment on the mechanical properties of cold-sprayed aluminum, *Journal of Thermal Spray Technology* 15 (2006) 233–238. <https://doi.org/10.1361/105996306X108138>.
- [119] K.S. Al-Hamdani, J.W. Murray, T. Hussain, A.T. Clare, Heat-treatment and mechanical properties of cold-sprayed high strength Al alloys from satellited feedstocks, *Surf Coat Technol* 374 (2019) 21–31. <https://doi.org/10.1016/j.surfcoat.2019.05.043>.
- [120] M.R. Rokni, C.A. Widener, S.P. Ahrenkiel, B.K. Jasthi, V.R. Champagne, Annealing behaviour of 6061 Aluminium deposited by high pressure cold spray, *Surface Engineering* 30 (2014) 361–368. <https://doi.org/10.1179/1743294413Y.0000000209>.
- [121] J.S. Yu, H.J. Kim, I.H. Oh, K.A. Lee, Densification and purification of cold sprayed Ti coating layer by using annealing in different heat treatment environments, in: *Adv Mat Res*, 2013: pp. 1604–1608. <https://doi.org/10.4028/www.scientific.net/AMR.602-604.1604>.
- [122] P. Vo, E. Irissou, J.G. Legoux, S. Yue, Mechanical and microstructural characterization of cold-sprayed Ti-6Al-4V after heat treatment, *Journal of Thermal Spray Technology* 22 (2013) 954–964. <https://doi.org/10.1007/s11666-013-9945-4>.
- [123] W.Y. Li, C. Zhang, X. Guo, J. Xu, C.J. Li, H. Liao, C. Coddet, K.A. Khor, Ti and Ti-6Al-4V coatings by cold spraying and microstructure modification by heat treatment, *Adv Eng Mater* 9 (2007) 418–423. <https://doi.org/10.1002/adem.200700022>.
- [124] C. Chen, Y. Xie, X. Yan, S. Yin, H. Fukanuma, R. Huang, R. Zhao, J. Wang, Z. Ren, M. Liu, H. Liao, Effect of hot isostatic pressing (HIP) on microstructure and mechanical properties of Ti6Al4V alloy fabricated by cold spray additive manufacturing, *Addit Manuf* 27 (2019) 595–605. <https://doi.org/10.1016/j.addma.2019.03.028>.
- [125] L.H. Brassart, J. Besson, F. Delloro, D. Haboussa, F. Delabrouille, G. Rolland, Y. Shen, A.F. Gourgues-Lorenzon, Effect of Various Heat Treatments on the Microstructure of 316L Austenitic Stainless Steel Coatings Obtained by Cold Spray, *Journal of Thermal Spray Technology* 31 (2022) 1725–1746. <https://doi.org/10.1007/s11666-022-01402-3>.

- [126] X. Li, J.J. Shi, C.H. Wang, G.H. Cao, A.M. Russell, Z.J. Zhou, C.P. Li, G.F. Chen, Effect of heat treatment on microstructure evolution of Inconel 718 alloy fabricated by selective laser melting, *J Alloys Compd* 764 (2018) 639–649. <https://doi.org/10.1016/j.jallcom.2018.06.112>.
- [127] L.I. Pérez-Andrade, F. Gärtner, M. Villa-Vidaller, T. Klassen, J. Muñoz-Saldaña, J.M. Alvarado-Orozco, Optimization of Inconel 718 thick deposits by cold spray processing and annealing, *Surf Coat Technol* 378 (2019). <https://doi.org/10.1016/j.surfcoat.2019.124997>.
- [128] P. Petrovskiy, A. Sova, M. Doubenskaia, I. Smurov, Influence of hot isostatic pressing on structure and properties of titanium cold-spray deposits, *International Journal of Advanced Manufacturing Technology* 102 (2019) 819–827. <https://doi.org/10.1007/s00170-018-03233-5>.
- [129] J.G. Legoux, E. Irissou, C. Moreau, Effect of substrate temperature on the formation mechanism of cold-sprayed aluminum, zinc and tin coatings, *Journal of Thermal Spray Technology* 16 (2007) 619–626. <https://doi.org/10.1007/s11666-007-9091-y>.
- [130] M. Fukumoto, H. Wada, K. Tanabe, M. Yamada, E. Yamaguchi, A. Niwa, M. Sugimoto, M. Izawa, Effect of substrate temperature on deposition behavior of copper particles on substrate surfaces in the cold spray process, *Journal of Thermal Spray Technology* 16 (2007) 643–650. <https://doi.org/10.1007/s11666-007-9121-9>.
- [131] S. Yin, X. Suo, Z. Guo, H. Liao, X. Wang, Deposition features of cold sprayed copper particles on preheated substrate, *Surf Coat Technol* 268 (2015) 252–256. <https://doi.org/10.1016/j.surfcoat.2014.11.009>.
- [132] X.K. Suo, M. Yu, W.Y. Li, M.P. Planche, H.L. Liao, Effect of substrate preheating on bonding strength of cold-sprayed Mg coatings, *Journal of Thermal Spray Technology* 21 (2012) 1091–1098. <https://doi.org/10.1007/s11666-012-9803-9>.
- [133] Y. Xie, M.P. Planche, R. Raelison, H. Liao, X. Suo, P. Hervé, Effect of Substrate Preheating on Adhesive Strength of SS 316L Cold Spray Coatings, *Journal of Thermal Spray Technology* 25 (2016) 123–130. <https://doi.org/10.1007/s11666-015-0312-5>.
- [134] R. Ortiz-Fernandez, B. Jodoin, Hybrid Additive Manufacturing Technology: Induction Heating Cold Spray—Part I: Fundamentals of Deposition Process, *Journal of Thermal Spray Technology* 29 (2020) 684–699. <https://doi.org/10.1007/s11666-020-01005-w>.
- [135] S. V. Klinkov, V.F. Kosarev, N.S. Ryashin, V.S. Shikalov, Experimental study of cold gas spraying through a mask. Part 1, *Thermophysics and Aeromechanics* 23 (2016) 735–740. <https://doi.org/10.1134/S0869864316050115>.
- [136] Y. Cormier, P. Dupuis, B. Jodoin, A. Corbeil, Pyramidal Fin Arrays Performance Using Streamwise Anisotropic Materials by Cold Spray Additive Manufacturing, *Journal of Thermal Spray Technology* 25 (2016) 170–182. <https://doi.org/10.1007/s11666-015-0267-6>.

- [137] Y. Cormier, P. Dupuis, B. Jodoin, A. Corbeil, Mechanical Properties of Cold Gas Dynamic-Sprayed Near-Net-Shaped Fin Arrays, *Journal of Thermal Spray Technology* 24 (2015) 476–488. <https://doi.org/10.1007/s11666-014-0203-1>.
- [138] C.J. Li, W.Y. Li, Deposition characteristics of titanium coating in cold spraying, *Surf Coat Technol* 167 (2003) 278–283. [https://doi.org/10.1016/S0257-8972\(02\)00919-2](https://doi.org/10.1016/S0257-8972(02)00919-2).
- [139] X.-T. Luo, X. Liu, Y. Wei, X. Han, C.-J. Li, Improving the adhesion of cold sprayed Al deposits through in-situ micro-forging, *J Mater Process Technol* (2024) 118302. <https://doi.org/10.1016/j.jmatprotec.2024.118302>.
- [140] Q. Liu, Y.K. Wei, X.T. Luo, C.Y. Chen, J. Wang, C.J. Li, Processing map of the in-situ micro-forging (MF) assisted cold spray for additive manufacturing of fully dense metals without MF particle inclusion, *Addit Manuf* 73 (2023). <https://doi.org/10.1016/j.addma.2023.103644>.
- [141] X.T. Luo, Y.K. Wei, Y. Wang, C.J. Li, Microstructure and mechanical property of Ti and Ti6Al4V prepared by an in-situ shot peening assisted cold spraying, *Mater Des* 85 (2015) 527–533. <https://doi.org/10.1016/j.matdes.2015.07.015>.
- [142] Y.K. Wei, X.T. Luo, Y. Ge, X. Chu, G.S. Huang, C.J. Li, Deposition of fully dense Al-based coatings via in-situ micro-forging assisted cold spray for excellent corrosion protection of AZ31B magnesium alloy, *J Alloys Compd* 806 (2019) 1116–1126. <https://doi.org/10.1016/j.jallcom.2019.07.279>.
- [143] M. Bray, A. Cockburn, W. O'Neill, The Laser-assisted Cold Spray process and deposit characterisation, *Surf Coat Technol* 203 (2009) 2851–2857. <https://doi.org/10.1016/j.surfcoat.2009.02.135>.
- [144] D. K., M. Jeandin, E. Irissou, J.-G. Legoux, W. Knapp, Laser-Assisted Cold Spray (LACS), in: *Nd YAG Laser, InTech*, 2012. <https://doi.org/10.5772/36104>.
- [145] R. Nikbakht, C. V. Cojocar, M. Aghasibeig, É. Irissou, T.S. Kim, H.S. Kim, B. Jodoin, Cold Spray and Laser-Assisted Cold Spray of CrMnCoFeNi High Entropy Alloy Using Nitrogen as the Propelling Gas, *Journal of Thermal Spray Technology* 31 (2022) 1129–1142. <https://doi.org/10.1007/s11666-022-01361-9>.
- [146] A. Cockburn, W. O'Neill, M. Sparkes, M. Cole, C. Jones, J. Randolph, F. Laguines, D. Crawford, Influence of laser heating on adhesion and coating properties in Laser Assisted Cold Spray, *Laser Fusion Technologies Ltd* (2023).
- [147] D.J. Barton, V.S. Bhattiprolu, G.B. Thompson, L.N. Brewer, Laser assisted cold spray of AISI 4340 steel, *Surf Coat Technol* 400 (2020). <https://doi.org/10.1016/j.surfcoat.2020.126218>.

Chapter 2: Scope of work

This chapter outlines the scope of work and objectives for this thesis, which are established based on the knowledge gaps identified in the literature review in Chapter 1.

Chapter 2: Scope of work

CSAM has demonstrated significant potential as an AM technology due to its ability to fabricate metallic parts in the solid-state with high deposition rates. However, as an emerging technology, CSAM still faces some challenges that must be addressed to reach its full potential.

In this thesis, these challenges are categorized as follows:

Challenge 1: Achieving precise control over the geometrical shape of damaged CSAM parts for their reconstruction to their original state.

Challenge 2: Enhancing the mechanical properties of the CSAM parts to achieve comparability with bulk materials.

Challenge 3: Addressing debonding between the deposit and substrate caused by excessive residual stresses in repair applications.

Challenge 4: Enabling the deposition of high-strength materials that are difficult to process with CSAM.

Challenge 5: Fabricating patterned CSAM parts with controlled topography for novel applications.

To address these challenges, the following objectives are proposed:

General objective: To investigate the CSAM process variables and deposition strategies for its further development and application as an additive manufacturing technology.

Specific objectives:

- **O1:** To optimize robot path trajectories for precise geometry control of CSAM reconstructed parts for repair applications.
- **O2:** To evaluate the impact of heat treatments on the microstructure, adhesion, and final properties of CSAM parts.
- **O3:** To study the influence of substrate preheating on the microstructure and bonding quality of high-strength materials sprayed by CSAM.

- **O4:** To design and evaluate the application of masks for the manufacture of patterned geometries in CSAM parts, focusing on their potential use in the energy sector.

Objectives 1 and 2 are addressed in Chapter 4, objective 3 in Chapter 5, and objective 5 in Chapter 6.

Chapter 3: Materials & Methods

This chapter describes the materials and methods used in this thesis. It lists the feedstock materials and the CSAM process parameters utilized in this research. Additionally, it details the implemented CSAM deposition strategies, including robot path trajectories, heat treatments, substrate preheating and masking process. Finally, it describes in detail the methodology used throughout this thesis and explains the fundamentals of the experimental procedures for the CSAM parts characterization.

Chapter 3: Materials and Methods

3.1 Raw materials

The CSAM process is fed by raw materials in powder form. In this thesis, all powders used were bought from commercial companies dedicated to the fabrication of these feedstock powders; all the powder materials used in this work are included in Table 3.1, along with the data provided by their commercial manufacturer. These powders were selected based on their chemical composition, morphology, size distribution, and price; all of them characteristics that define their suitability for CSAM.

Table 3.1. Feedstock powders.

Material	Commercial Name	Manufacturer	Morphology	Particle size distribution
Al	Al	Aluminum Industries (Hyderabad, India)	Irregular	-45 +15
Cu	Cu	Safina (Vestec, Czech Republic)	Spherical	-53 +15
Ti	Cp-Ti grade 2	AP&C (Boisbriand, QC, Canada)	Spherical	-44 +17
Ti	CNPC-Ti300	CNPC (Shanghai China)	Irregular	-53 +15
Ti6Al4V	Spherical APA Ti-6Al4V	AP&C (Boisbriand, QC, Canada)	Spherical	-45 +15
IN718	Diamalloy 1006	Oerlikon (Westbury, NY, USA)	Spherical	-45 +11

All the mentioned powders were sprayed onto various substrates of different materials and dimensions. These substrates, described in Table 3.2, were selected based on the objective of each research study.

Table 3.2. CSAM substrates.

Material	Substrate dimensions	Surface finish
Al	20 mm × 50 mm × 5 mm	Grit-blasted
Cu	20 mm × 50 mm × 5 mm	Grit-blasted
Ti	20 mm × 50 mm × 5 mm	Grit-blasted
Ti6Al4V	20 mm × 50 mm × 5 mm	Grit-blasted
Carbon Steel	Various dimensions with constant 1.5 mm thickness	Grit-blasted
Carbon Steel	Diameter 25 mm discs	Grit-blasted
Inconel 718	Diameter 25 mm discs	Polished

3.2 CSAM equipment and process parameters

A high-pressure CS Plasma Giken PCS-100 (Saitama, Japan) equipment, shown in Figure 3.1, was used for the fabrication of all samples throughout this thesis, using N₂ as the working gas.

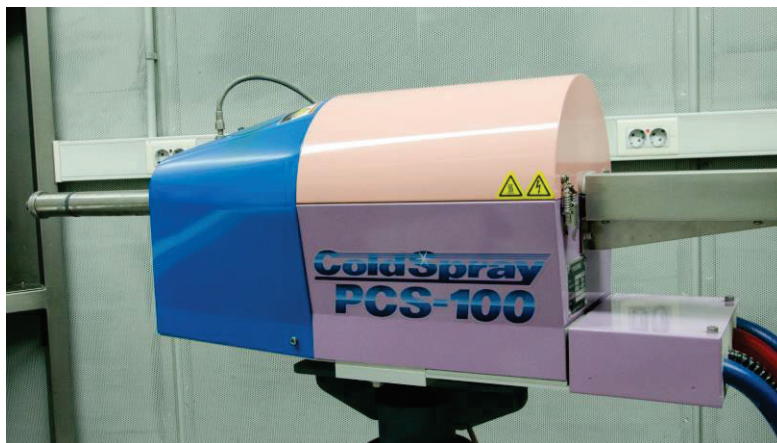


Figure 3.1. High-pressure CS equipment Plasma Giken PCS-100.

The specific CS operating process parameters and nozzle equipment used are detailed in Table 3.3. These parameters were chosen based on optimized values for the feedstock powder material found in the literature and the expertise of the CPT research group.

Table 3.3. CS operating process parameters and nozzle equipment.

Material	Pressure [MPa]	Temperature [°C]	Standoff Distance [mm]	Nozzle material
Al	3.0	450	25	Polymer
Cu	3.0	700	25	WC
Ti	6.5	900	25	WC
Ti6Al4V	6.5	1000	25	WC
Inconel 718	6.5	1100	30	SiC

3.3 CSAM deposition strategies

3.3.1 Robot path trajectories

Two robot path trajectories were used in this work. The Traditional (T) one, and the Metal Knitting (MK) deposition strategy developed by Vaz et al. [4]. The T toolpath involves spraying perpendicularly to the substrate, following a straightforward path from one side to the other with a constant scanning step that ensures that the deposit covers its entire surface. The MK toolpath involves spraying at a constant deflected angle while making circular movements. This approach maximizes DE at the edges of the deposit rather than at the center due to the circular movement.

For each robot path trajectory, different CS robotic parameters were selected, including the spraying standoff distance, the traversal velocity of the robot, and the angle of deposition. For the T strategy, a traversal velocity of 500 mm/s and an angle of 90° were selected, while for the MK strategy, 200 mm/s and a 20° nozzle deflection were used.

3.3.2 Heat treatments

To study the effects of the HT on the CSAM samples, the as-sprayed samples were subjected to an annealing post-process. The annealing was performed in a Carbolite GHA 12/450 (Hope, England) tubular furnace in an inert atmosphere. The parameters selected for the annealing of each material were

based on studies from the literature on the densification of each CS material. All samples were annealed for 4 h under an argon atmosphere and cooled down in the furnace until room temperature. Annealing temperatures were as follows: 600 °C for Cu, 400 °C for Al, and 1000 °C for Ti and Ti6Al4V. All annealed samples were labelled as -HT throughout this thesis.

3.3.3 Substrate preheating

The IN718 substrates were preheated using a hotplate Schott CERAN 500 (Jena, Germany); the hotplate's setpoint temperature was maintained during the spraying. The temperature of the substrates before spraying was measured using an infrared thermometer FLIR TG56 (OR, USA), and the CSAM spraying process was initiated when the substrates reached preheating temperatures of room temperature (without preheating), 250 °C, and 400 °C.

3.3.4 CSAM masking process

The masked CSAM process was firstly proposed by Cormier et al. [5]. It involves selectively shielding the substrate from deposition using a laser-cut steel mesh mask with a pattern that mirrors the inverse of the geometry to be deposited. During spraying, the particles flow through the designated geometry and are deposited, forming a 3D pattern.

In this thesis, masks with various patterns were used for the fabrication of Ti patterned parts: big squares (mesh with squared holes 3 x 3 mm), small squares (mesh with squared holes 1.5 x 1.5 mm), rows, and cylinders. In addition, the mask-substrate distance was systematically optimized to achieve homogeneity and precise control of the geometry. This masking process is schematically shown in Figure 3.2.

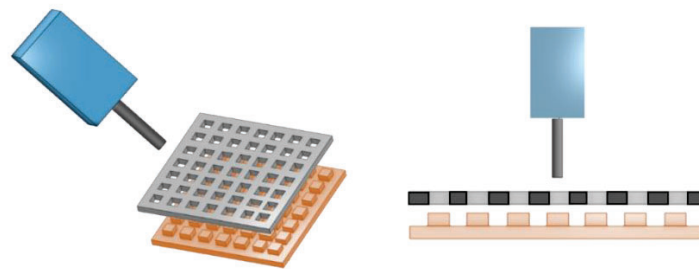


Figure 3.2. CSAM masking process.

3.4 Characterization techniques

3.4.1 Feedstock powders characterization

All feedstock powders were characterized in terms of particle size distribution, microstructural characteristics, morphology, and chemical composition to verify these characteristics against those provided by the supplier. All these characteristics determine in great part the CSAM parameters for obtaining a quality part.

3.4.1.1 Particle size distribution

The particle size distribution was analyzed in triplicate with a dry mode Laser Scattering (LS) technique using a particle sizing analyzer LS 13 320 Model Dry Powder System (CA, USA) according to standard ASTM B822-02 [1]. The laser scattering (LS) test involves passing light through a dry powder module and measuring the resulting scattered light intensity to produce a pattern. In this pattern, larger particles scatter light at smaller angles, while smaller particles scatter light at larger angles. The particle size distribution, expressed as volume, is then calculated from the resulting light distribution pattern.

3.4.1.2 Microstructural characteristics

To observe the microstructural characteristics, the feedstock powders were hot mounted in conductor Bakelite, and grinded and polished following the metallographic preparation ASTM E1920-03 [2] and ASTM E3-11 [3] standards. The cross-section of the powders was observed in a Thermo Fisher Phenom ProX Desktop (Eindhoven, the Netherlands) or JEOL 5310 (Tokyo, Japan) scanning electron microscope (SEM). The scanning electron microscope (SEM) generates a beam of electrons from a filament, which is focused onto the surface of the sample. As the electron beam scans the surface, it interacts with the sample's atoms, producing various signals that are detected by multiple detectors. The most commonly used detectors are the secondary electron detector (SED), which provides topographic information, and the backscattered electron detector (BSD), which is used for surface composition imaging. Additionally, elemental microanalysis of the surface composition can be performed using energy dispersive X-ray spectroscopy (EDS) detectors.

The elemental microanalysis of the powders to analyze the chemical composition of the powders was carried out with a Quantax energy dispersive spectroscopy (EDS) Bruker Nano (MA, USA) integrated into a SEM JEOL 5310 (Tokyo, Japan).

3.4.1.3 Morphology

The morphology of all powders was observed using a Thermo Fisher Phenom ProX Desktop (Eindhoven, the Netherlands) or JEOL 5310 (Tokyo, Japan) scanning electron microscope (SEM).

3.4.2 CSAM parts characterization

The CSAM parts were characterized by various techniques to evaluate their chemical composition, microstructural characteristics, mechanical properties, adhesion strength and mechanisms, erosive and abrasive wear resistance, electrochemical behavior, and interfacial contact resistance.

3.4.2.1 Metallographic preparation

The metallographic preparation of the cross-section of the samples was completed following the ASTM E1920-03 standard [2] to reveal their microstructure. All samples were cut, mounted, grinded, and polished using Struers Minatom (Copenhagen, Denmark), Struers CitoPress-1 (Copenhagen, Denmark), and Struers TegraPol-11 (Copenhagen, Denmark) equipment, respectively.

To reveal the microstructure, the polished samples were etched in specific solutions based on their material composition. The Cu samples were etched in a reagent composed of 30 ml HCl, 10 g FeCl₃, and 120 ml distilled water. The Al samples were etched with Keller's reagent. The Ti and Ti6Al4V samples using Kroll's reagent. The IN718 samples were etched in a reagent composed of 5 ml HF, 5 ml HNO₃, 5 ml H₂O₂, 10 ml HCl, and 5 ml distilled water.

3.4.2.2 Microstructural evaluation

The microstructural characteristics of the polished and etched samples was observed with the optical microscope (OM) Leica DMI5000M (Wetzlar, Germany) or with the Keyence VK-X series (Osaka, Japan) laser microscope.

The etched microstructure of the samples was observed in a Thermo Fisher Phenom ProX Desktop (Eindhoven, the Netherlands) or JEOL 5310 (Tokyo, Japan).

The mean porosity was calculated using image analysis software ImageJ (v. 153e) according to the standard ASTM E2109-01 from 3 cross-sectional OM images at 20x magnification [6].

The flattening ratio (FR), which is defined as a measurement of particle deformability, was calculated according to Equation (3.1), where w = width and h = height of the sprayed particles observed in the etched cross-sectional surface of the deposit [7]. The width was considered the widest part of the particle, indistinctive of the impact direction.

Equation 3.1

$$FR = \frac{w}{h}$$

To evaluate the chemical composition of the samples, an elemental mapping was obtained with EDS detector GATAN MONO-CL4 (CA, USA) attached to a FESEM JEOL J-7100 (Tokyo, Japan).

3.4.2.3 Crystal structure characterization

To evaluate the phase changes during the CSAM process, XRD patterns were measured using equipment PANalytical X'Pert PRO MPD (Malvern, UK). The XRD technique gives detailed information about the crystallographic structure and chemical composition of a material by irradiating the sample with X-rays and measuring the diffracted rays by the crystals in the material, resulting in patterns with various intensities.

The evaluation of IN718 was done with a Ni filtered $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) from 5 to $100^\circ 2\theta$ with a step size of 0.026° and measuring time of 100 s.

3.4.2.4 Superficial roughness

A Mitutoyo SJ-210 (Kawasaki, Japan) profilometer was used to measure the superficial roughness of the samples. The average R_a and R_z values were recorded from ten measurements.

3.4.2.5 Topography

To evaluate the dimensions and superficial characteristics of the CSAM patterned parts, the profilometry of the samples, along with their 3D topography was measured with confocal microscope Sensofar Plu2300 (Catalonia, Spain). Confocal microscopy works by focusing laser light on a specific point within the sample, causing fluorescence to occur precisely at the focal point. The sample is scanned in a raster pattern, producing images of individual optical planes. These planes are then stacked using deconvolution software to generate a 3D image of the sample's surface.

3.4.2.6 Microhardness

The Vickers microhardness was obtained from a mean value of ten indents for each sample in accordance with ASTM E384-22 standard [8], with a 0.3 kgf ($HV_{0.3}$) using a Shimadzu HV-2/HMV-2T (Tokyo, Japan) equipment.

3.4.2.7 Tensile strength tests

Tensile strength tests were performed with tensile test equipment SERVOSIS MCH-102ME (Madrid, Spain) to evaluate the adhesive strength deposit-substrate of the reconstructed thin wall parts (Cu, Al, Ti, and Ti6Al4V) fabricated with the MK deposition strategy. To do so, three samples of each component (Figure 3.3) were tested at a rate of 0.01 mm/s until failure, which was observed with a JEOL 5310 (Tokyo, Japan) SEM.

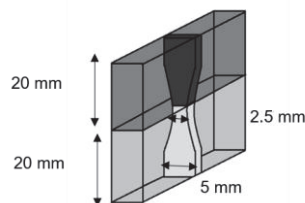


Figure 3.3. Tensile test specimens for adhesion strength testing.

3.4.2.8 Adhesion tests

The adhesion strength of the Ti and IN718 CSAM samples was measured using the tensile test equipment SERVOSIS MCH-102ME (Madrid, Spain) according to the ASTM C633-13 [9] standard, which is based on a tensile test essay. The coated samples were adhered to a grit-blasted counterpart using an

HTK Ultrabond 100 (Hamburg, Germany) epoxy resin adhesive cured at 180 °C. Three samples of each material were tested at a rate of 0.01 mm/s until cohesive, adhesive or glue failure occurred, as shown in Figure 3.4.

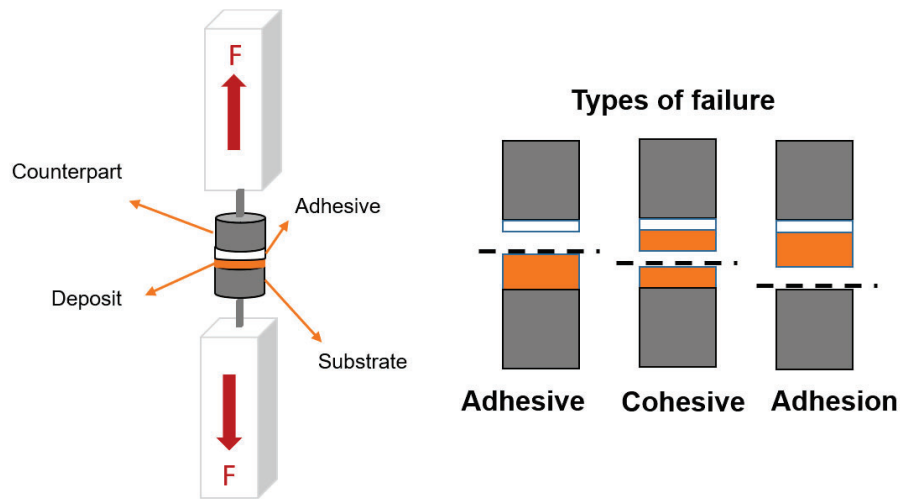


Figure 3.4. Adhesion test (left) test components scheme (right) types of failure.

To observe the adhesion mechanisms at the different preheating temperatures, single impact particle splats were sprayed with the optimized CS process parameters included in Table 3.3, sprayed with a traversal velocity of 1000 mm/s. A Thermo Fisher Phenom ProX Desktop (Eindhoven, the Netherlands) SEM was used to observe the sprayed single particles and their impact on the substrate.

3.4.2.9 Erosive wear resistance

The resistance to erosion of the MK HT samples was evaluated in accordance with standard ASTM G76-04 [10]. Erosion is defined as the progressive loss of material caused by the impingement of a fluid or solid particles onto its surface. In this test, alumina particles with a diameter of 50 μm , were propelled at a constant feed rate towards the surface of the samples at a perpendicular angle to calculate the average erosion value (mm^3/g) by dividing the erosion rate (slope of the mass loss of the sample over time) by the abrasive flow rate and the density of the material. To compare the behavior of the CSAM parts with the bulk material, this erosion test was also conducted on the substrates. In addition, the failure mechanism of the tested samples was observed with a JEOL 5310 (Tokyo, Japan) SEM.

3.4.2.10 Abrasive wear resistance

The resistance to abrasive wear was calculated using the Rubber Wheel method following the standard ASTM G65-16e1 [11] with homemade equipment CM4 OL-2000 (Barcelona, Spain) shown in Figure 3.5.

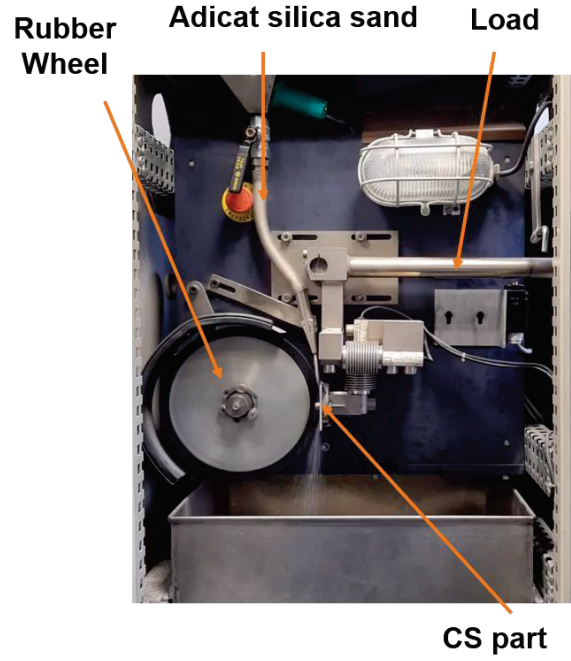


Figure 3.5. Rubber Wheel equipment components.

Abrasive wear is defined as the damage a solid surface suffers due to the process of rubbing against protuberances or hard particles. In this method, the CS part is placed in a sample holder that is pressed with a specified force against a rotating rubber wheel, while an abrasive agent flows between the wheel and the sample. The test was performed at a velocity of 139 rpm with a force of 20 N, a wheel diameter of 22.9 cm, and Adicat silica sand (Barcelona, Spain) as an abrasive agent. The abrasive wear [mm^3/Nm] was calculated by dividing the change in the specimen's volume (ΔV) by the product of the applied force (F) and the total distance covered by the wheel (d) at a specific time, as described by Equation 3.2.

Equation 3.2

$$\text{abrasive wear rate} = \frac{\Delta V}{F \cdot d}$$

3.4.2.11 Electrochemical behavior

The corrosion resistance of sprayed materials was tested by subjecting a 1 cm² sample to electrochemical measurements under similar conditions to those experimented in the anodic side of an operating PEM electrolyzer.

To assess the corrosion behavior, polarization curves were recorded using a BioLogic VSP potentiometer (Grenoble, France). The experiments were performed in a 0.5 M H₂SO₄ solution with oxygen saturation. A Metrohm (Madrid, Spain) double bridge Ag/AgCl reference electrode was positioned in close proximity to the CSAM sample, which served as the working electrode; a platinum rod was used as the counter electrode, as illustrated in Figure 3.6.

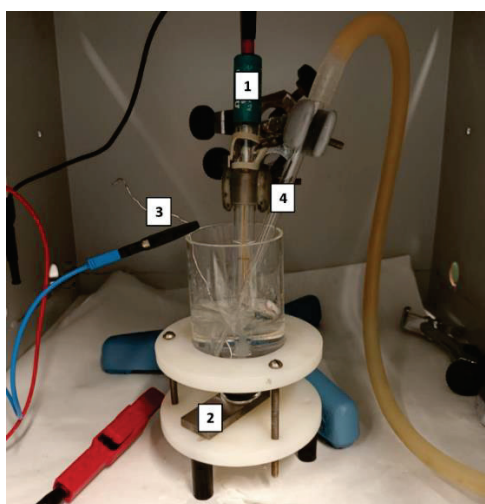


Figure 3.6. Resistance to corrosion test setup: (1) reference electrode, (2) working electrode, (3) counter electrode, (4) oxygen supply.

The polarization curves were generated by varying the potential from -100 to 2400 mV compared to the open circuit potential (E_{OCP}). Subsequently, Tafel fit extrapolation method was evaluated with EC-Lab software (V10.44) to determine E_{corr} (corrosion potential) and I_{corr} (corrosion current). These potentials were chosen to show the corrosion properties of both powders within the potential range of an operating PEM electrolyzer. The corrosion rate (CR), expressed in mm/yr, was calculated based on Equation 3.3.

Equation 3.3

$$CR [mm/yr] = \frac{(0.00327)(I_{corr})(EW)}{d}$$

Where I_{corr} is the corrosion current in $\mu A/cm^2$, EW the equivalent weight of the material, and d the density of the material.

To assess the stability of the materials, they were immersed in a 0.5 M H_2SO_4 solution and subjected to a constant potential of 2 V for 100 h. The E_{corr} and I_{corr} were measured both before and after the stabilization test. Subsequently, all samples evaluated after the stability test are referred to as "post-mortem" samples.

3.4.2.12 Interfacial contact resistance

To evaluate the interfacial contact resistance (ICR) the Ti powders were cold-sprayed onto both sides of a 9 cm² steel substrate with 1 mm of thickness. The sprayed samples were subsequently grinded on both sides with a 120 SiC paper until 1 mm of Ti coating remained on each side. To determine the interfacial contact resistance (ICR), the approach proposed by Wang et al. [12], based on the Davies' method [13], was employed. In this method, the total resistance is measured in two setups: first, the evaluated sample is sandwiched between two pieces of Toray conductive carbon paper and two copper plates, and second, only one piece of Toray paper is inserted between the copper plates, as shown in Figure 3.7. A current of 1 A is fed between both copper plates, and the total voltage drop is measured while the compaction force is increased. The total resistance R of each setup at each compaction force is calculated using Ohm's law (Equation 3.4).

Equation 3.4

$$R = \frac{VA_s}{I}$$

Where V is the voltage drop across the Cu plates, A_s the sample's surface area, and I the applied current. The final ICR, which consists on the resistance at the interface of the sample and the Toray carbon papers, is calculated by subtracting the total resistance of the first setup by the second setup at each compaction force (Figure 3.7).

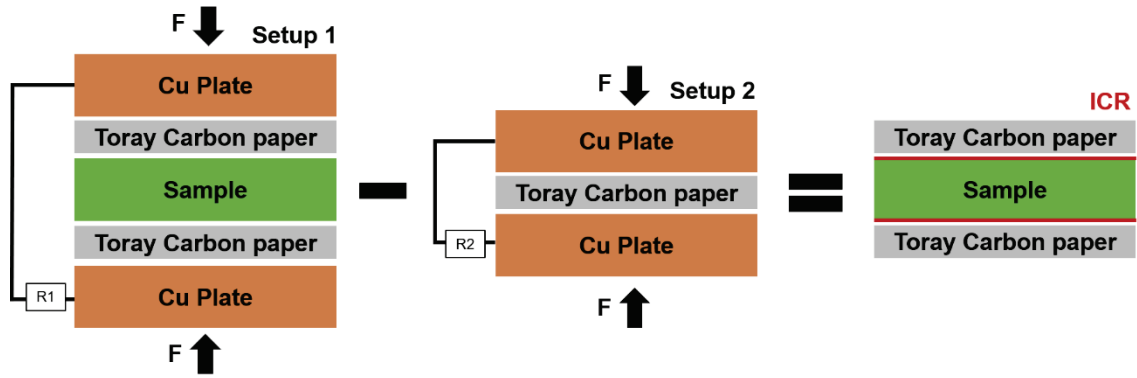


Figure 3.7. ICR test setups.

A compaction force ranging from 0.25 to 2 kN/cm² was applied using the SERVOSIS ME 402-10 equipment (Madrid, Spain). The ICR setup consisted of two polished Cu bulk plates, two Themo Fisher Toray carbon paper sheets (Eindhoven, the Netherlands), and the CSAM Ti sample, as shown in Figure 3.8.

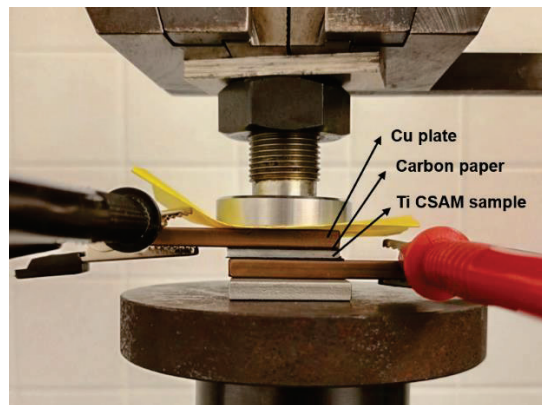


Figure 3.8. Interfacial contact resistance setup.

For each compaction force, a current of 1 A was passed (between the copper plates) using the Velleman DC power supply LABPS1503 (Gavere, Belgium). The voltage drop across the system was measured using a Keysight HP 3458A (CA, USA) multimeter and calculated employing Ohm's law.

The ICR was measured before and after the post-mortem experiment.

3.5 References

- [1] R.F. Vaz, V. Albaladejo-Fuentes, J. Sanchez, U. Ocaña, Z.G. Corral, H. Canales, I.G. Cano, Metal Knitting: A New Strategy for Cold Gas Spray Additive Manufacturing, *Materials* 15 (2022) 6785. <https://doi.org/10.3390/ma15196785>.
- [2] Y. Cormier, P. Dupuis, B. Jodoin, A. Corbeil, Net shape fins for compact heat exchanger produced by cold spray, *Journal of Thermal Spray Technology* 22 (2013) 1210–1221. <https://doi.org/10.1007/s11666-013-9968-x>.
- [3] ASTM International, ASTM B822-02 - Standard test method for particle size distribution of metal powders and related compounds by laser scattering, USA, 2002.
- [4] ASTM International, ASTM E1920-03 - Standard guide for metallographic preparation of thermal sprayed coatings., USA, 2021.
- [5] ASTM International, ASTM E3-11 - Standard guide for preparation of metallographic specimens, USA, 2017.
- [6] ASTM International, ASTM E2109-01 - Standard test methods for determining area percentage porosity in thermal sprayed coatings, PA, USA, 2021.
- [7] A.A. Tiarniyu, C.A. Schuh, Particle flattening during cold spray: Mechanistic regimes revealed by single particle impact tests, *Surf Coat Technol* 403 (2020). <https://doi.org/10.1016/j.surfcoat.2020.126386>.
- [8] ASTM International, ASTM E384-22 - Standard test for microindentation hardness of materials., USA, 2022.
- [9] ASTM International, ASTM C633-13 - Standard test method for adhesion or cohesion strength of thermal spray coatings., USA, 2021.
- [10] ASTM International, ASTM G76-04 - Standard test method for conducting erosion tests by solid particle impingement using gas jets, n.d. <https://doi.org/10.1520/G0076-18>.
- [11] ASTM International, ASTM G65-16e1 - Standard test method for measuring abrasion using the dry sand/rubber wheel apparatus, n.d.
- [12] H. Wang, M.A. Sweikart, J.A. Turner, Stainless steel as bipolar plate material for polymer electrolyte membrane fuel cells, *J Power Sources* 115 (2003) 243–251. [https://doi.org/10.1016/S0378-7753\(03\)00023-5](https://doi.org/10.1016/S0378-7753(03)00023-5).
- [13] D.P. Davies, P.L. Adcock, M. Turpin, S.J. Rowen, Bipolar plate materials for solid polymer fuel cells, *J Appl Electrochem* 30 (2000) 101–105. <https://doi.org/10.1023/A:1003831406406>.

Chapter 4: Results & Discussion

Geometry and Microstructure Control of Remanufactured Metallic Parts by Cold Spray Additive Manufacturing

In this chapter, Cu, Al, Ti, and Ti6Al4V substrates were reconstructed by two CSAM robot path trajectories: a traditional (T) toolpath, and a novel strategy called Metal Knitting (MK). The final geometry, microstructure, and mechanical properties of the reconstructed parts were assessed and compared. In addition, the effects of annealing on the components' microstructure and its influence on adhesion, resistance to erosion, and abrasive wear were evaluated. The results indicated that MK is a successful toolpath for the fabrication of thin-straight walls with controlled geometry. In addition, the annealing HT effectively reduced the microstructure defects of the remanufactured parts and improved the adhesive strength from 26 ± 2 MPa to 43 ± 4 MPa for Cu, 25 ± 7 MPa to 114 ± 7 MPa for Ti, and 9 ± 3 MPa to 160 ± 20 MPa for Ti6Al4V. The abrasive and erosive resistance of the MK-Cu HT and MK-Al HT parts resulted equivalent to their bulk counterparts, suggesting that the MK toolpath followed by annealing HT is an efficient method for the reconstruction of Cu and Al damaged parts.

Chapter 4: Geometry and Microstructure Control of Remanufactured Metallic Parts by Cold Spray Additive Manufacturing

4.1 Introduction

Included among the novel AM technologies by the ASTM F42—Additive Manufacturing Committee [1], Cold Spray (CS) is a process that can overcome some limitations of the most established metal AM technologies: Selective Laser Melting (SLM), Laser Metal Deposition (LMD), and Electron Beam Melting (EBM). These methods consist of melting the feedstock material by a focused heat source (either a laser or an electron beam), which is solidified to form an object [2]. In some cases, these heat-focused methods may produce defects within the microstructure, such as undesired phase changes, oxidation, and the formation of residual stresses [3].

CS is based on accelerating a powder feedstock through a convergent-divergent de Laval nozzle with a preheated, compressed, supersonic gas (N_2 or H_2) to supersonic velocities. When the accelerated powder is sprayed into a substrate with enough kinetic energy (surpassing what is called the critical velocity), plastic deformation occurs at the point of impact, promoting the formation of a well-bonded coating [4].

In recent years, many researchers in academy and industry have made great efforts in exploring the potential of CS as an additive manufacturing (AM) process [3,5–9]. Cold Spray Additive Manufacturing (CSAM) is an emerging technology that offers some advantages compared to other AM methods, including high deposition rates, deposition of temperature-sensitive materials, and minimization of tensile residual stresses [10]. However, CSAM is still restricted to those applications in which an accurate control of strict tolerances is not mandatory due to its inherent limitation in geometrical control. In addition, some studies have shown that the as-sprayed CSAM components may present intrinsic defects, including rough surfaces and micropores that cause poor cohesion between particles as a result of a lack of particle deformation during the spraying process.

Thus, the investigation of critical deposition strategies such as new robot path trajectories and the optimization of the process parameters to improve the geometrical accuracy of the CS parts, along with the implementation of post-processes (e.g. heat treatments (HT), or machining) to minimize the defects within the microstructure is considered a key point for the further development of CS as an AM technology [11–13].

Traditionally, CS coatings are sprayed perpendicularly towards the substrate, following a straightforward path from one side to the other with a specific step, as shown in Figure 4.1. Spraying at a constant angle of 90° enhances the velocity component of the impacting particles. When this impact velocity exceeds the critical velocity, the bonding between the particles and the substrate occurs, leading to the particles' deposition [12]. However, with this deposition strategy, the geometrical control over the shape of the as-sprayed parts is limited by the inherent velocity distribution of the particles when they exit the nozzle. In this sense, the velocity profile of the particles in the impinging jet spot is not homogeneous; the particles in the center of the spot achieve greater velocities than the ones at the periphery, causing a higher deposition of particles in the core [14,15], which causes the deposits to grow with an uncontrolled pyramidal shape.

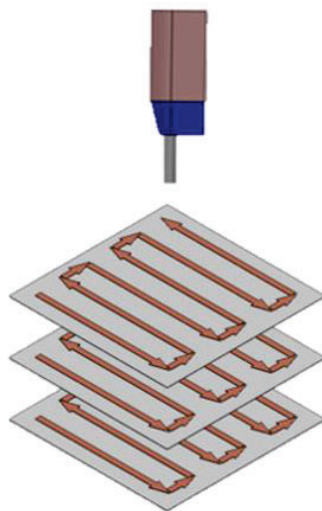


Figure 4.1. Traditional CS robot path trajectory. Figure obtained from [16].

To assess this geometrical limitation and obtain CSAM deposits with a controlled shape, robotic parameters such as spraying angle, scanning step, standoff distance and traversal velocity need to be optimized. Recently, several

studies have focused on the development of new robot path trajectories by investigating the impact of these parameters on the characteristics of CSAM deposits. The first approach for the fabrication of CSAM free-standing components with controlled shape was proposed by Pattison et al. [17]. In this work, the authors investigated a triangular-tessellation strategy that consisted on tilting the nozzle and spraying into the inclined face of the deposit formed in the initial layer. This strategy was developed with the intention to obtain deposits with a vertical wall without the need of edge milling post-processes. However, for this approach to be effective, a pyramid-shape deposit needs to be deposited before the subsequent layers with the inclined nozzle, causing an overall reduction in the deposition efficiency of the process. Subsequently, Wu et al. [18] introduced another building strategy to form complex 3D shapes layer-by-layer. The authors focused on optimizing three key robotic parameters to avoid the generation of the pyramid-shape deposits: the deflection angle, the scanning step, and the retreat distance of the nozzle. In particular, this strategy compensates the thickness difference at the edges of the deposit by spraying a layer at a deflection angle, resulting in the obtention of thick deposits with straight walls.

Recently, another alternative for the fabrication of straight wall CSAM deposits was developed by Vaz et al. [16] This deposition strategy, called Metal Knitting (MK), consists in spraying at a constant deflected angle making circular movements that maximize the deposition efficiency on the edges of the deposit, allowing the manufacturing of deposits with straight walls, as shown in Figure 4.2.

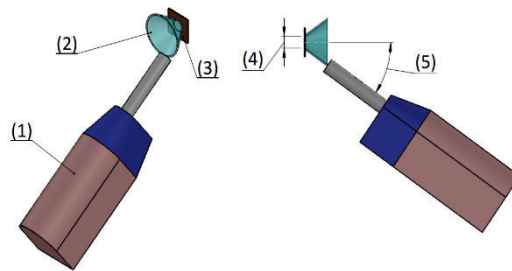


Figure 4.2. Knitting strategy scheme. (1) Cold Spray gun, (2) virtual cone path, (3) substrate, (4) radius, (5) deflection angle. Figure obtained from [16].

Nevertheless, spraying at a deflected angle increases the generation of intrinsic defects within the microstructure of the deposits, such as micropores and interparticle boundaries. Therefore, the implementation of heat treatments (HT)

for the densification of the CSAM parts' microstructure is imperative. In this context, annealing has been proven to be an efficient HT method to tailor the microstructure, enhance adhesion strength, and improve the final mechanical properties of various metallic materials fabricated by CSAM, including Cu [19], Al and its alloys [20,21], Ti and its alloys [22,23], stainless steel [24] and Ni alloys [25,26]. Huang et al. [11] studied the effects of annealing on the porosity and mechanical properties of four typical materials used in CSAM: Al, Cu, Ti, and stainless steel 316L. Their findings indicated that annealing improved the microstructure and greatly enhanced their mechanical properties of the studied materials.

These works are focused on the development of free-form building strategies and microstructure enhancement for CSAM technology. However, not many studies have considered a deposition strategy for the repair or remanufacture of a component in which the final geometry is restricted to the original state of the specimen; for instance, thin-walled components. In this sense, the MK strategy enables the reconstruction of thin-wall deposits at high deposition rates with a geometrical control of the deposits with a resolution falling within the range of millimeters. Thus, the aim of this study is to assess the microstructure and final shape of reconstructed Cu, Al, Ti, and Ti6Al4V substrates fabricated with the new MK CSAM deposition strategy and compare their final geometry, microstructure, and mechanical properties with the traditional (T) toolpath. Furthermore, the effect of annealing on the microstructure and performance of the deposits was evaluated in terms of adhesion strength and resistance to erosion and abrasive wear.

4.2 Materials and Methods

4.2.1 Feedstock Powder Characterization

Commercial irregular and spherical powders, Al (Aluminum Industries Pvt Ltd., Hyderabad, India), Ti (CNPC Powder, Shanghai, China), Cu (SAFINA A.S., Vestec, Czech Republic), and Ti6Al4V (AP&C Powders Metallurgy, Montreal, Canada), respectively, were sprayed with Plasma Giken PCS100 (Saitana, Japan) equipment.

The powder size distribution was analyzed with a laser diffraction particle sizing analyzer LS 13 320 Model Dry Powder System (CA, USA) while particle morphology was observed in a Phenom ProX Desktop SEM (Eindhoven, The Netherlands).

4.2.2 CSAM Spraying Parameters

All powders were sprayed with the Metal Knitting (MK) and traditional (T) methods using the optimized spraying parameters of each material included in Table 4.1.

Table 4.1. CSAM process parameters.

Feedstock Powder	Pressure (MPa)	Temperature (°C)	Standoff Distance (mm)	Deposition Strategy Label
Cu	3.0	700	30	Metal Knitting: MK
Al	3.0	450	30	
Ti	6.0	900	25	Traditional: T
Ti6Al4V	6.5	1000	25	

All samples were deposited on the grit-blasted thin face (50 mm × 5 mm) of 20 mm × 50 mm × 5 mm substrates of the same material as the sprayed powder (Cu, Al, Ti, or Ti6Al4V).

4.2.3 Heat Treatment of CSAM Deposits

All samples were annealed for 4 h in a tubular Carbolite Gero (Hope, England) furnace under an argon atmosphere and cooled down in the furnace until room temperature. Annealing temperatures were as follows: 600 °C for Cu, 400 °C for Al, and 1000 °C for Ti and Ti6Al4V.

4.2.4 Characterization and Mechanical Properties

The metallographic preparation of all components was completed according to the standard ASTM E1920-03(2014) [27]. The cross-sectional surface of the polished samples was analyzed with the optical microscope (OM) Leica DMI5000M (Wetzlar, Germany). The software ImageJ (version 1.53e) was used to calculate the mean porosity value according to the standard ASTM E2109-01(2014) [28]. The Vickers microhardness was tested following the

standard ASTM E384-22 [29] with a force of 0.2 and 1 kgf with Shimadzu HV-2/HMV-2T (Tokyo, Japan) equipment. The flattening ratio (FR) was calculated according to Equation 4.1.

Equation 4.1

$$FR = \frac{w}{h}$$

Tensile strength tests were performed with tensile test equipment SERVOSIS MCH-102ME (Madrid, Spain) to evaluate the adhesive strength deposit-substrate of the reconstructed thin wall parts (Cu, Al, Ti, and Ti6Al4V) fabricated with the MK deposition strategy. To do so, three samples of each component (Figure 4.3) were tested at a rate of 0.01 mm/s until failure, which was observed with a JEOL 5310 (Tokyo, Japan) SEM.

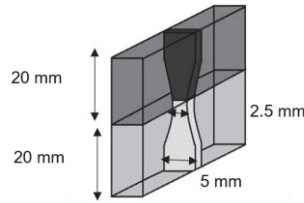


Figure 4.3. Tensile test specimens for adhesion strength testing

4.2.5 Resistance to Erosion and Abrasive Wear

The resistance to erosion of the thermally treated MK samples was tested following the standard ASTM G76-04 [30]. Alumina particles with a diameter of 50 μm , were propelled at a constant feed rate towards the surface of the samples at a perpendicular angle. To compare the behavior of the CSAM parts with the bulk material, this erosion test was also conducted on the substrates. In addition, the failure mechanism of the tested samples was observed with a JEOL 5310 (Tokyo, Japan) SEM.

The resistance to abrasive wear was calculated using the Rubber Wheel method following the standard ASTM G65-16e1 [31] with homemade equipment CM4 OL-2000 (Barcelona, Spain). The test was performed at a velocity of 139 rpm with a force of 20 N, a wheel diameter of 22.9 cm, and Adicat silica sand (Barcelona, Spain) as an abrasive agent.

4.3 Results and Discussion

4.3.1 Feedstock Powder Characterization

In CS, the feedstock characteristics such as material, shape, and size distribution determine in great part the spraying parameters needed to obtain an optimal microstructure of the produced part. Table 4.2 and Figure 4.4 show the mean particle size, as well as SEM micrographs and size distribution curves of the powders.

Table 4.2. Feedstock powder characteristics

Powder	Shape	Mean Particle Size (μm)	d10 (μm)	d90 (μm)
Cu	Spherical	29.7 ± 2.9	18.7 ± 2.6	43.2 ± 5.2
Al	Irregular	54.8 ± 4.5	19.4 ± 1.2	97.3 ± 4.9
Ti	Irregular	40.1 ± 2.8	9.7 ± 0.8	89.5 ± 6.4
Ti6Al4V	Spherical	30.7 ± 3.1	13.2 ± 8.6	45.2 ± 0.4

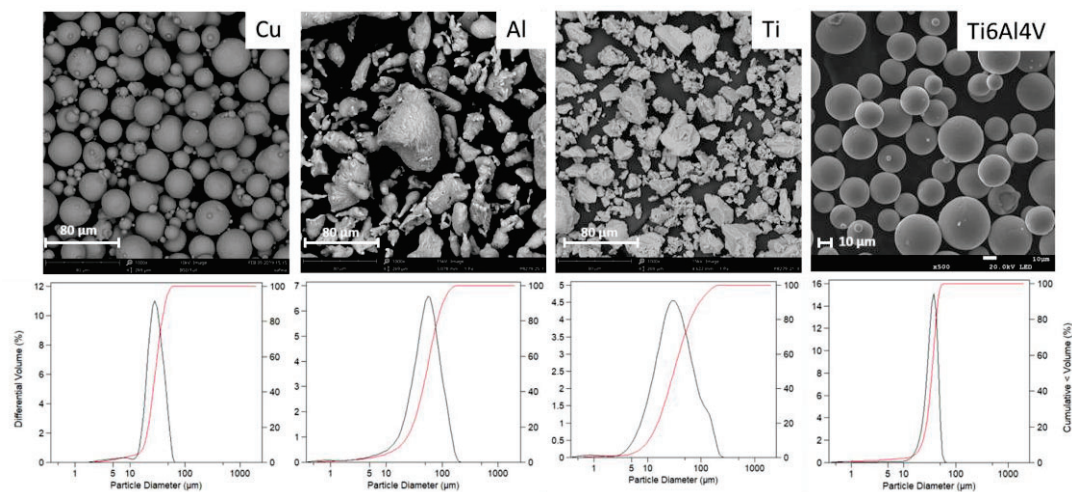


Figure 4.4. SEM micrographs of the sprayed powders and particle size distribution graphs

These results show that all powders exhibited a size distribution with a mean particle size between 30 μm and 55 μm . Both irregular and spherical powders were selected; being Cu and Ti6Al4V spherical, while Al and Ti irregular. As pointed out by Vaz et al. [32] the characteristics of the deposits are influenced more by the nature of the material than by powder morphology. The selection of irregular and spherical powders allows to evaluate the influence of the powders'

morphology in the properties of the deposits when the robot path trajectory is adapted to a non-normal angle.

4.3.2 Geometry Analysis of the Reconstructed Metallic Parts

To investigate the possibility of reconstructing straight walls or remanufacturing components in which the final geometry is restricted to the original state of the specimen, Cu, Al, Ti, and Ti6Al4V powders were sprayed by T and MK toolpaths onto the thin face of substrates made from the same materials. The resulting parts fabricated using both methods are shown in Figure 4.5. The T samples were only able to achieve a short height without starting to generate an inclination in the sidewalls, producing a pyramid-shape deposit with an angle that varied depending on the material. This pyramid-shape behavior is intrinsic of the CSAM technology and is attributed to the velocity profiles of the particles as they exit the nozzle during spraying. Particles in the core of the jet spot tend to reach higher velocities, promoting a higher deposition in the center compared to the periphery [17]. This height limitation and wall inclination represents a restriction for the T deposition strategy of the CSAM technology in applications such as the remanufacture of damaged structures.

Moreover, the T-Cu sample was surprisingly poorly adhered and detached from the substrate. After spraying, a clear crack appeared at the deposit–substrate interface that ended up with the built wall easily separated. Copper is known for being a good material for CS technology due to its high plastic deformability; nonetheless, this issue might have been associated with excess residual stresses accumulated in the deposit–substrate interface when a high copper thickness with a specific/required geometry is intended to be deposited by CS [8]. This result clearly indicates that, for some materials, the possibility of reconstructing straight wall geometries with conventional strategies is completely restricted and justifies the need to study new CSAM deposition strategies. Therefore, new deposition robot path trajectories that involve the deflection of the nozzle are under development; since each material has its own inclination angle, a profile study for every material is necessary when using this strategy.

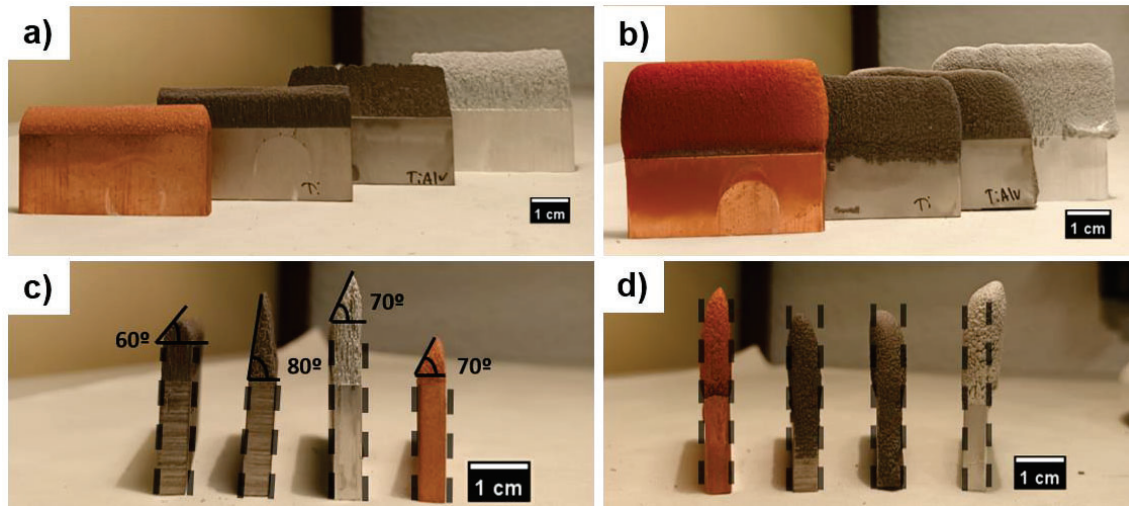


Figure 4.5. Images of the as-sprayed samples produced by (a,c) T and (b,d) MK strategies.

Furthermore, the MK toolpath allowed the samples to grow vertically without an apparent height limitation, producing straight walls without cracks or delamination neither in the deposited section nor in the interface between the part and the substrate. In this sense, with MK, the deflection of the particle impact angle with the surface lead to a reduction of accumulated residual stresses in the interface, which allowed to obtain well-bonded thick deposits. The typical inclination of the T strategy was not observed in the MK samples because the nozzle was moved in a circular way, which hindered the effects of the velocity differences in the jet spot and promoted a more homogeneous deposition of the particles. Furthermore, the MK method overcame the limitations of the T strategy enabling a more accurate control of the shape of the deposits. Despite of these advances for CSAM, the samples exhibited a rough finish, and their shape still deviated from the precision required for most final applications and the components had to be subjected to post-machining processes, as shown in Figure 4.6. In this Figure, it can be observed that the samples were well-bonded at the interface and that an almost identical part was reconstructed on top of the thin wall of the substrate, suggesting that MK is a successful approach for controlling the geometry for reconstructing damaged parts with CSAM.

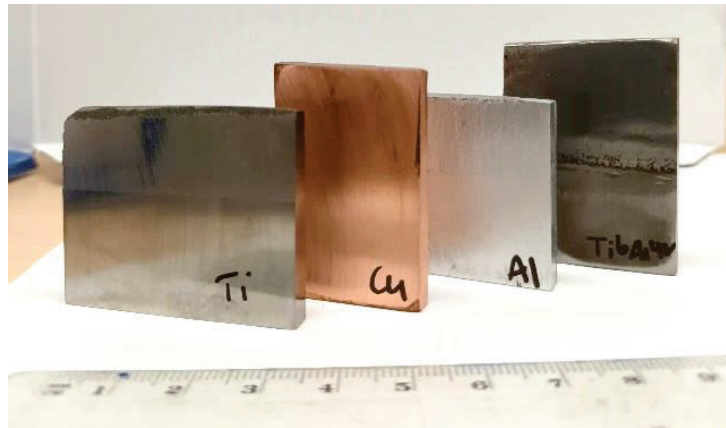


Figure 4.6. Post-machined Metal Knitting samples.

4.3.3 Microstructure Characterization and Physical Properties of the CS Deposits

Along with the component's geometry, the study of the microstructure characteristics is very important to understand further the effects that the spraying strategies may have on the final properties of the deposits. To investigate this, the polished and etched cross-section of the T and MK samples were observed by optical microscopy. The surface characteristics and particle boundaries of the as-sprayed samples produced by both strategies are shown in Figure 4.7, while the flattening ratio of the particles along with the porosity and microhardness results are shown in Table 4.3. For a good comparison of results, the evaluation of the T-Cu sample was done in the detached copper deposit.

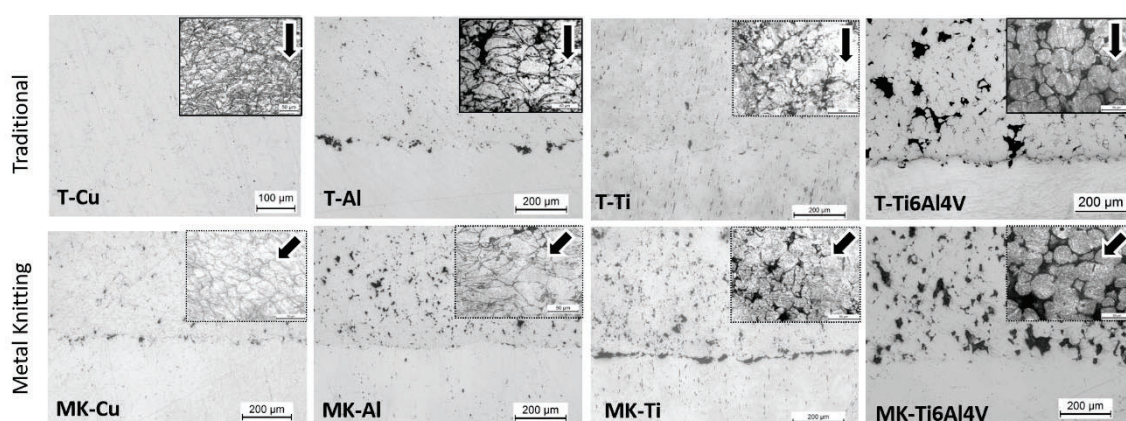


Figure 4.7. Polished and etched cross-section OM images of T (top) and MK (bottom) samples. Arrows indicate the spraying direction.

Table 4.3. Microstructural characterization of the T and MK as-sprayed samples

Material	Traditional			Metal Knitting		
	Flattening Ratio	Porosity (%)	Microhardness (HV _{0.2})	Flattening Ratio	Porosity (%)	Microhardness (HV _{0.2})
Cu	2.2 ± 0.8	3 ± 2	91 ± 7	2.3 ± 0.6	6 ± 2	88 ± 10
Al	2.4 ± 1.0	3 ± 1	49 ± 8	2.7 ± 0.7	10 ± 4	50 ± 3
Ti	1.8 ± 0.5	7 ± 3	262 ± 43	1.7 ± 0.3	12 ± 3	199 ± 22
Ti6Al4V	1.3 ± 0.4	14 ± 4	236 ± 32	1.2 ± 0.3	21 ± 5	229 ± 31

In general, all fabricated deposits with the T toolpath exhibited a dense microstructure, with the exception of T-Ti6Al4V, which showed a porous microstructure with a value of $14 \pm 4\%$. T-Cu, T-Al and T-Ti showed the common lamellae microstructure of CS deposits composed of plastically deformed particles with resulting porosity values of $3 \pm 2\%$, $3 \pm 1\%$, and $7 \pm 3\%$, respectively. No effect from the powder morphology in the microstructure or the degree of plastic deformation was observed, as the irregular particles, Al and Ti, were well-packed.

In the case of T-Ti6Al4V, the particles were barely deformed, with a flattening ratio of 1.3 ± 0.4 , mostly maintaining their original shape, which resulted in high porosity despite the previously optimized spraying parameters. However, this alloy is difficult to deposit by CS because of its low plastic deformability and high critical velocity needed for deposition (above 1000 m/s), sometimes not achievable with commercial CS equipment [33,34]. Therefore, many studies have reported Ti alloys with high porosity [35–37]. Li et al. [35] have collected porosity values of CS Ti and Ti alloy of several works, resulting in porosity values that range from $<1\%$ up to 20%, depending on spraying parameters such as gas temperature, pressure, or propulsive process gas.

In contrast to the T strategy, the MK method enabled the fabrication of well-bonded deposits of all the tested materials, including Cu. The etched images exhibited in Figure 4.7 clearly demonstrate the modification of the impact angle of the particles, as these appeared deformed consistent with the spraying direction. Due to the deflection of the spraying angle to values lower than 90° throughout the entire MK process, the MK deposits exhibited higher porosity and

interparticle voids compared to the deposits generated by the T strategy. However, this porosity appeared to be homogeneous, and no clear cracks or lines of continuous porosity were observed in the microstructure of the deposits. When comparing the T- and MK-Ti6Al4V deposits, a similar flattening ratio was found, but a much higher porosity resulted with the MK method ($14 \pm 4\%$ vs. $21 \pm 5\%$, respectively), indicating that the modification of the spraying angle caused insufficient deformation at impact but the tampering effect of the subsequent impacting particles was greater in the case of the T strategy.

As expected, the deposits sprayed with the MK toolpath exhibited more porous microstructures compared to those produced with the T strategy. However, the MK trajectory allowed for the reconstruction of parts without a thickness limit, while maintaining geometrical control to produce straight walls.

4.3.4 Effect of Heat Treatment on the Microstructure of CSAM Deposits

It has been observed that CSAM as-sprayed deposits can exhibit mechanical properties that are less favorable compared to bulk materials, including reduced strength, ductility, electrical and thermal conductivity, as well as wear resistance [3]. This is particularly true when spraying at an angle different than normal, as it is the case of the MK samples.

Several studies related to the enhancement of the microstructure of the CS deposits with different types of HT, e.g. annealing or hot isostatic pressing (HIP), are found in the literature [11,23,26]. In this sense, the MK samples were subjected to an annealing process to densify their microstructure and improve their final properties. Only the sprayed parts by MK were subjected to annealing, as these samples could be deposited without height limitations, and allowed the successful deposition of all of metals under study in this work. Although HIP is a well-known method in the aerospace industry to reduce porosity, annealing was the selected HT because it is simpler and a more cost-effective method. This is supported by the work of Pérez-Andrade et al. [26], who evaluated the microstructural characteristics of IN718 subjected to HIP-treatment. The authors concluded that annealing was enough to obtain samples with porosities below 1%, and HIP-treatment is not essential in CSAM.

The temperature and dwell time used for the annealing process of each material are detailed in the Materials and Methods section. Figure 4.8 shows OM and SEM micrographs of the polished HT MK samples, while their microstructural properties are presented in Table 4.4.

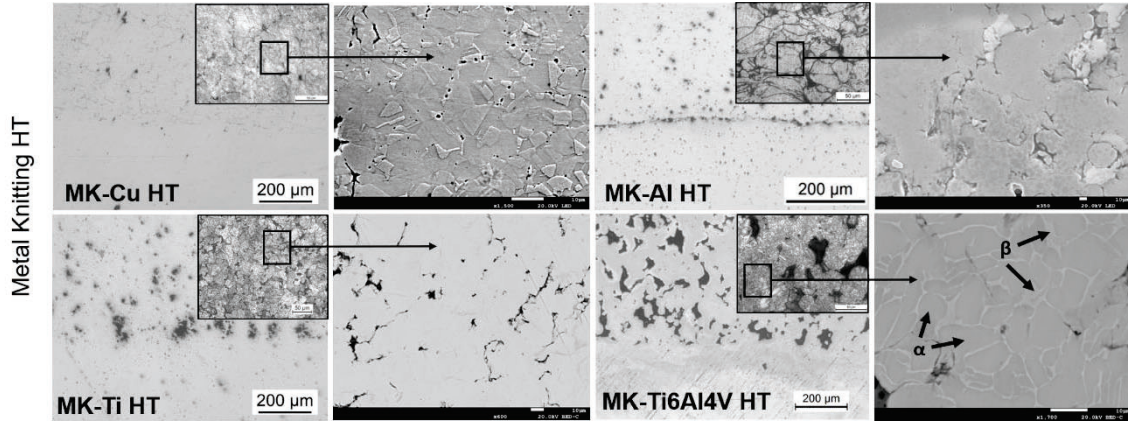


Figure 4.8. Polished and etched cross-section images (OM and SEM) of MK HT samples.

The OM images in Figure 4.8 show a clear densification of the microstructure of the MK deposits when compared with the microstructures of their as-sprayed counterparts exhibited in Figure 4.7. In this sense, some differences between as-sprayed and HT samples are noteworthy. Firstly, it is clearly seen that the lamellae microstructure was densified due to diffusion and recrystallization processes occurring during annealing [11]. The boundaries of the particles mostly disappeared, indicating that the temperature was adequate for promoting metal diffusion across the particle boundaries for all materials. Finally, the voids present in the interparticle boundaries and small pores disappeared, resulting in a reduction in porosity from $6 \pm 2\%$ to $4 \pm 1\%$ for Cu, $10 \pm 4\%$ to $7 \pm 2\%$ for Al, $12 \pm 3\%$ to $8 \pm 2\%$ for Ti, and $21 \pm 5\%$ to $16 \pm 3\%$ for Ti6Al4V between the MK as-sprayed and the HT deposits.

Table 4.4. Microstructural characterization of the MK as-sprayed and HT samples.

Feedstock	Metal Knitting				
	As-Sprayed			Heat Treated	
	Flattening Ratio	Porosity (%)	Microhardness (HV _{0.2})	Porosity (%)	Microhardness (HV _{0.2})
Cu	2.3 ± 0.6	6 ± 2	88 ± 10	4 ± 1	60 ± 8
Al	2.7 ± 0.7	10 ± 4	50 ± 3	7 ± 2	31 ± 7
Ti	1.7 ± 0.3	12 ± 3	199 ± 22	8 ± 2	203 ± 27
Ti6Al4V	1.2 ± 0.3	21 ± 5	229 ± 31	16 ± 3	275 ± 25

Despite the general reduction in porosity values achieved for all materials after HT, the large pores and voids generated between particles during deposition remained present. These defects resulted from the insufficient plastic deformation of particles upon impact. This issue was even more significant for the MK-Ti6Al4V deposits, as their microstructure revealed a notable absence of deformed particles.

The microhardness of the T and MK as-sprayed and MK HT deposits was measured to analyze the modification of this property after annealing. Similar microhardness values were measured for as-sprayed deposits regardless of the deposition strategy used. The small variations in microhardness between T and MK deposits can be attributed to the different particle impact angles used in each strategy. A reduction in the impact angle of the particles is known to result in less plastic deformation, which has two main consequences: (i) lower work hardening of the particles and therefore, lower hardness of the deposit, and (ii) reduced particle–particle cohesion, leading to weaker mechanical performance [38].

After the annealing, two tendencies were observed in the microhardness depending on the material; on the one hand, in the case of MK-Cu HT, MK-Al HT, and MK-Ti HT, the microhardness values were maintained or slightly decreased, which is typical behavior of CS deposits, since the annealing recrystallization phase enhances the ductility of the CSAM parts by removing the work hardening effects caused by the intensive plastic deformation of the particles [11]. On the other hand, the microhardness of MK-Ti6Al4V HT presented an increase in this value, suggesting that the HT generated a decrease in porosity and enhanced

the cohesion of particles, increasing the microhardness values [39] and promoting the appearance of harder β phases [40], as can be observed in Figure 4.8.

4.3.5 Adhesion Strength of the Reconstructed Part to the Substrate

Spraying at an angle different than normal directly onto a previously sprayed deposit has been reported to have a negative influence on deposition efficiency, adhesion strength, and porosity of the deposits [12,41,42]. Yin et al. [42] studied the effects of spray angles (90° , 75° , and 60°) on the deposition behavior of Ti particles. The results revealed that deflecting the spray angle significantly hindered particle deformation, increased porosity within the coating microstructure, and subsequently negatively affected the quality of the coating.

Since the use of these CSAM components is intended for the reconstruction of metallic parts, high adhesion values between particles and substrate are required. To achieve this, a smooth interface with intimate contact of the particles with the substrate is critical [19]. Figure 4.9 displays the cross-sectional images of the interface of the MK as-sprayed and HT samples. The as-sprayed MK samples showed porous microstructures, mostly with a rough deposit–substrate interface, which may indicate poor bonding between the particles and the substrate caused by a lack of intimate contact due to the spraying angle. In general, it is considered that two bonding mechanisms are responsible for the particle–surface adhesion and particle–particle cohesion in CS: mechanical interlocking, and metallurgic bonding. The extent of each bonding mechanism depends on the particle size, velocity, and impact angle [43]. The images of the interfaces of the as-sprayed MK deposits (Figure 4.9) clearly show that as a consequence of the modification of the impact angle, mechanical interlocking is the predominant bonding mechanism of these deposits to the substrate. An improvement in the adhesion of the deposits can be observed by looking at the interface of the HT MK samples which are smoother, without porosity, and more homogeneous than the MK- as-sprayed deposits. These images indicate that metallurgical bonding occurred during HT of the MK deposits, suggesting an increased adhesion of the deposit compared to the as-sprayed samples [44,45].

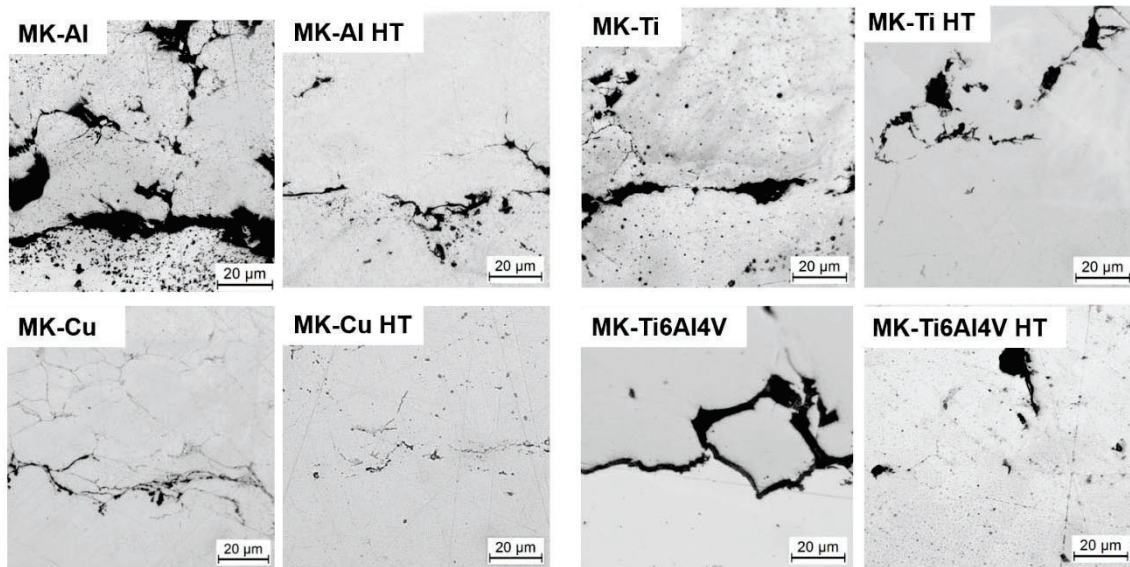


Figure 4.9. Optical microscope images of the CSAM interfaces.

Furthermore, a tensile test was performed to investigate the adhesion strength of the MK deposits, as shown in Figure 4.10. As expected, from observing the interfacial characteristics in Figure 4.9, all MK as-sprayed samples showed adhesive failures at the deposit–substrate interface with values below 30 MPa, suggesting a poor bonding between the remanufactured part and the substrate. Conversely, the MK-Cu, -Ti, and -Ti6Al4V HT samples presented a cohesive failure with greater tensile strength values, 43 MPa, 114 MPa, and 160 MPa, respectively, than their as-sprayed counterparts. This further confirms that annealing is an adequate strategy to increase the bonding between particles and substrate. It is worth indicating that the Al samples showed no change in the tensile strength value after the HT, probably because annealing did not promote enough diffusion across the splat boundaries to improve the deposit–substrate adhesion strength, as can be observed in Figure 4.10 [12].

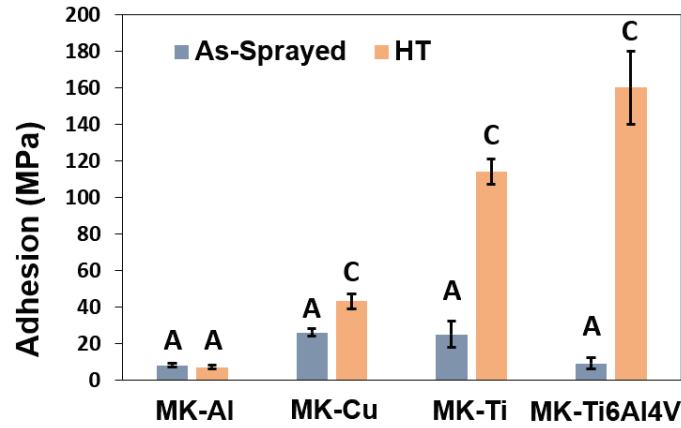


Figure 4.10. Tensile test results of as-sprayed and HT specimens; (A) and (C) labels indicate adhesive or cohesive failure, respectively.

The failure mechanism of the HT MK samples that presented cohesive failure was observed with the SEM, and the resulting images are presented in Figure 4.11.

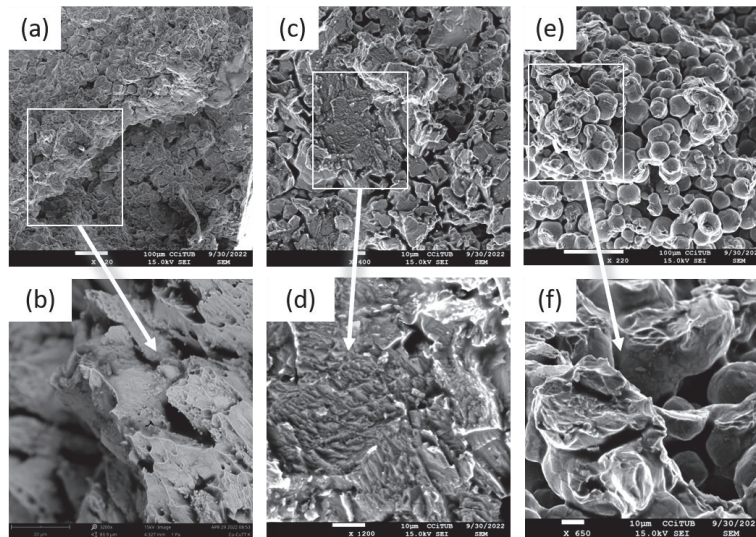


Figure 4.11. SEM micrographs of the specimens' failure after tensile test of (a,b) MK-Cu HT, (c,d) MK-Ti HT, and (e,f) MK-Ti6Al4V HT.

Overall, the samples showed signs of plastic deformation, indicative that the annealing strengthened the bonding between particles. The MK-Cu HT sample was highly deformed before failure, revealing a high deformation in the form of peaks in the specimen, while the MK-Ti HT and MK-Ti6Al4V HT samples showed a mixture of interparticle and intraparticle fracture propagation with the characteristic dimples that appear during plastic deformation in the intraparticle failure regions. All these results demonstrate that annealing is a good strategy to

overcome the poor adhesion and cohesion obtained when spraying at an angle other than 90°.

4.3.6 Erosive and Abrasive Wear Resistance

One of the main challenges when reconstructing a damaged part for remanufacturing purposes is to achieve the required performance of the deposits for operating conditions; ideally, similar to that of the original component [46]. In order to guarantee that the new reconstructed part shows a similar behavior compared to the original bulk material, the enhancement of particle cohesion is mandatory. In this sense, HT are expected to improve not only the deposit microstructure and deposit adhesion strength with the substrate, but also the internal cohesion of the remanufactured section by CSAM. Therefore, an evaluation of the resistance to erosive and abrasive wear for the MK HT samples was carried out, along with a comparative analysis of the HT samples with a bulk plate of the same material.

The average erosion values results are presented in Figure 4.12 and included in Table 4.5.

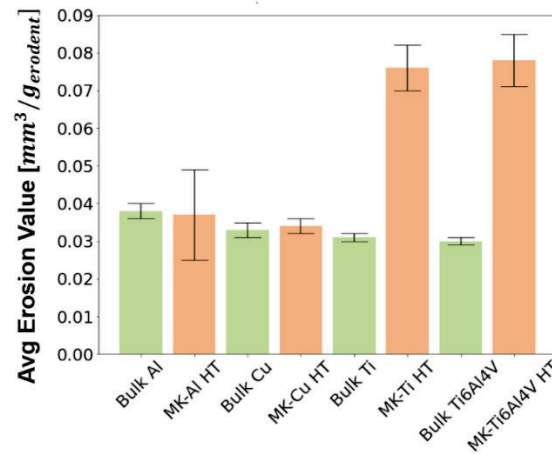


Figure 4.12. Average erosion value of the bulk and MK heat treated samples.

These results indicate that the bulk and MK-Cu and -Al HT samples exhibited a similar behavior, with no significant differences in their average erosion value. In contrast, the MK-Ti HT and MK-Ti6Al4V HT samples showed lower resistance to erosion compared to their bulk counterparts, which is attributed to a lack of cohesive strength between particles even after the HT process.

Table 4.5. Resistance to erosion and abrasive wear results.

Sample	Erosion	Abrasive Wear Resistance	
	Resistance	Wear Rate	Volume Loss
	Avg Erosion Value (mm ³ /g)		
Bulk Al	0.038 ± 0.002	1.6 × 10 ⁻³	240
MK-Al HT	0.037 ± 0.012	1.8 × 10 ⁻³	259
Bulk Cu	0.033 ± 0.002	8.0 × 10 ⁻⁴	41
MK-Cu HT	0.034 ± 0.002	8.0 × 10 ⁻⁴	41
Bulk Ti	0.031 ± 0.001	1.5 × 10 ⁻³	76
MK-Ti HT	0.076 ± 0.006	4.4 × 10 ⁻³	222
Bulk Ti6Al4V	0.030 ± 0.001	1.0 × 10 ⁻³	53
MK-Ti6Al4V HT	0.078 ± 0.007	5.0 × 10 ⁻³	248

For a better understanding of the different results obtained for Cu and Al and Ti and Ti6Al4V pairs, SEM micrographs of the eroded surfaces were recorded for the MK samples after erosion testing, as shown in Figure 4.13. Two main wear mechanisms are generally involved in erosion damage—plastic deformation, and brittle fracture [47,48]. As could be expected for the case of ductile materials, the images of the eroded surface for MK-Cu HT and MK-Al HT showed clear signs of predominant erosion by plastic deformation of the surface, associated with the detachment of small portions of metals by plastic rupture due to the impact of hard particles. Two types of deformation were identified in Figure 4.13a-b, which confirm this conclusion: ploughing and cutting. This behavior can be perfectly explained considering that for these two materials, a dense microstructure was obtained after the HT. As a result, high particle–particle cohesion was achieved, which resulted in a similar erosion resistance than the bulk material.

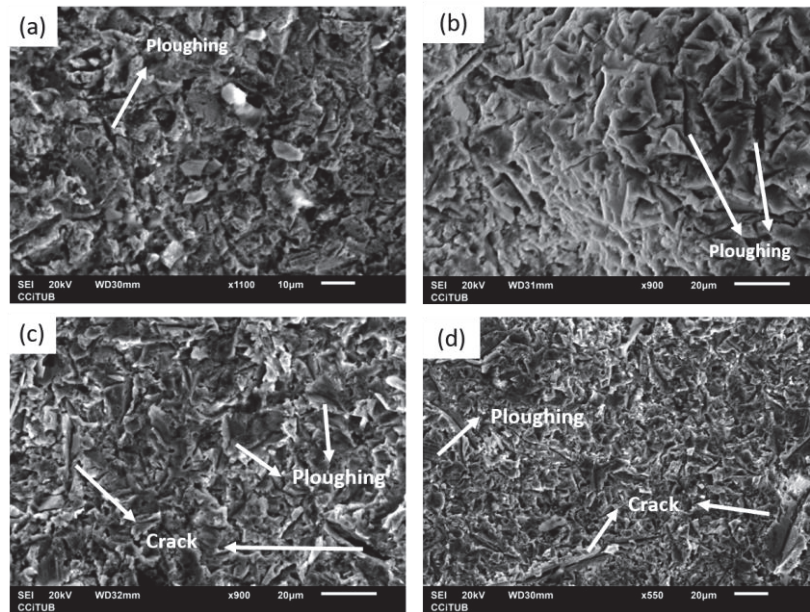


Figure 4.13. SEM micrographs of the erosion mechanism of (a) MK-Cu HT, (b) MK-Al HT, (c) MK-Ti HT, and (d) MK-Ti6Al4V HT.

In contrast, MK-Ti HT and MK-Ti6Al4V HT clearly showed a different behavior than the Cu and Al samples. Certainly, the SEM images of the eroded Ti and Ti6Al4V surfaces also showed signs of plastic deformation (mainly the ploughing type) as one of the mechanisms contributing to the wear of the samples; however, for these two materials clear and big cracks were additionally identified in the surface. These cracks revealed the presence of voids or big pores in the microstructure of the deposits even after annealing, as previously observed in the MO microstructure analysis (Figure 4.8). These crack patterns suggest the easy propagation of interparticle cracks due to the low cohesive strength of these deposits. Consequently, extended collisions with erosive materials dislodged the deposited particles, which explains the high erosion values measured for these two samples [49].

In agreement with the erosion tests, the abrasive wear resistance of the samples was evaluated by the Rubber Wheel test. The wear rate behavior of the MK HT samples is shown in Figure 4.14, while numerical results for the volume loss and wear rate are shown in Table 4.5. During the first 5 min, most samples showed a steep increase or decrease in the wear rate, followed by a stabilization of this value after this time. This behavior is attributed to a rapid decrease of the superficial roughness and to the pull-out of the last layer of the deposited particles

which are those showing the lowest particle–particle cohesion since they were not affected by the tamping effect of a new layer of particles.

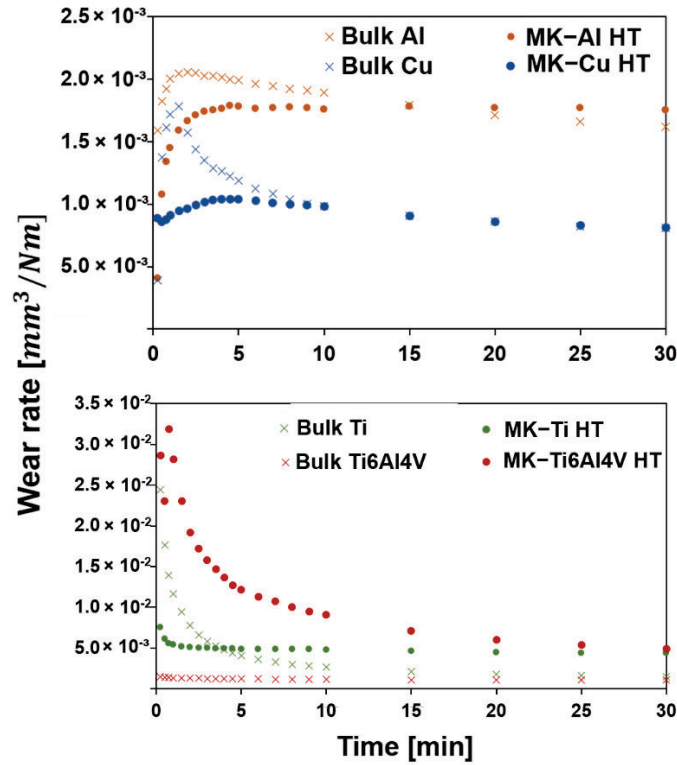


Figure 4.14. Wear rate of the bulk and MK HT samples.

According to the work presented by Fu et al. [50], the abrasive wear resistance of materials is directly associated with properties such as Young's modulus, toughness, hardness, and compactness. A similar trend to that observed in the erosion resistance test can be seen.

On one hand, MK-Cu HT and MK-Al HT samples exhibited very similar resistance to abrasive wear and volume loss values compared to pure Cu and Al bulk plates, confirming that MK is a suitable technique for repairing components fabricated with these two materials. On the other hand, the MK-Ti HT and MK-Ti6Al4V HT samples showed a considerable difference in the wear rate and volume loss compared to their Ti and Ti6Al4V counterparts, indicating that their behavior is not comparable to that of the bulk materials and further deposition strategies need to be investigated for a successful reconstruction of these materials by CSAM.

4.4 Conclusions

CSAM is an AM method with great benefits compared to other heat-focused techniques. It is still an emerging technology in which some challenges are yet to be studied. This work focused on improving the geometry control accuracy using a spraying strategy for remanufacturing metallic parts and tailoring the final microstructure of CSAM deposits with annealing heat treatments. Several findings can be concluded:

- The T CSAM are not suitable for the production of thick coatings with strict geometric tolerance, because as the deposits are sprayed, a pyramid-shaped part starts to grow. This normal deposition strategy does not allow the successful deposition of all kinds of materials.
- MK is an effective CSAM deposition strategy for the reconstruction of metallic parts compared to the T method. With MK, straight walls of different materials with unlimited height and without detachment of the deposits can be obtained. However, the deposition angle reduces the plastic deformation of the particles, increasing porosity within the microstructure and hindering adhesion with the substrate.
- Regardless the feedstock material, annealing was found to be an effective HT process to tailor the microstructure of the samples by improving the cohesion between particles and adhesion with the substrate, as well as densifying the deposited counterparts.
- The MK-Cu HT and MK-Al HT samples showed similar characteristics as the bulk materials in terms of mechanical properties and resistance to abrasive and erosive wear, suggesting that the manufacturing of these materials by CSAM MK followed by annealing could be comparable to other bulk production methods.
- The porosity and low particle-particle cohesion observed in the microstructure of the MK-Ti and MK-Ti6Al4V samples were not significantly enhanced, even after the annealing treatment, which explains their low resistance to erosive and abrasive wear in comparison to the bulk. For these alloys showing high critical impact velocities, the results of this study suggest that the combination of MK and a heat-thermal

treatment might be insufficient to achieve the deposit properties needed in certain applications and other densification strategies should be explored.

4.5 Acknowledgements

Authors R. Vaz and A. Garfias would like to thank AGAUR for grant 2020 FISDU 00305; and grant 2021 FISDU 00300, respectively. V. Albaladejo Fuentes is a Serra Hunter Fellow. The authors of this study would like to thanks the support of Generalitat of Catalunya (SGR, 2021SGR00712). Finally, this work is part of the project PID2020-115508RB-C21 funded by MCIN/AEI/10.13039/501100011033 and by the European Union "NextGenerationEU"/PRTR.

4.6 References

- [1] International Organization for Standardization, UNE-EN ISO/ASTM 52900:2022 - Additive manufacturing - General principles - Terminology, 2022.
- [2] D. Herzog, V. Seyda, E. Wycisk, C. Emmelmann, Additive manufacturing of metals, *Acta Mater* 117 (2016) 371–392. <https://doi.org/10.1016/j.actamat.2016.07.019>.
- [3] S. Yin, P. Cavaliere, B. Aldwell, R. Jenkins, H. Liao, W. Li, R. Lupoi, Cold spray additive manufacturing and repair: Fundamentals and applications, *Addit Manuf* 21 (2018) 628–650. <https://doi.org/10.1016/j.addma.2018.04.017>.
- [4] H. Assadi, F. Gärtner, T. Stoltenhoff, H. Kreye, Bonding mechanism in cold gas spraying, *Acta Mater* 51 (2003) 4379–4394. [https://doi.org/10.1016/S1359-6454\(03\)00274-X](https://doi.org/10.1016/S1359-6454(03)00274-X).
- [5] A. Saboori, S. Biamino, P. Di Torino, D. Gitardi, M. Lombardi, The Capacity of Cold Spray Additive Manufacturing Technology for Metallic Part Repairing, in: *Euro PM2018*, Bilbao, 2018. <https://www.researchgate.net/publication/328407397>.
- [6] R.F. Vaz, A. Garfias, V. Albaladejo, J. Sanchez, I.G. Cano, A Review of Advances in Cold Spray Additive Manufacturing, *Coatings* 13 (2023). <https://doi.org/10.3390/coatings13020267>.
- [7] W. Li, K. Yang, S. Yin, X. Yang, Y. Xu, R. Lupoi, Solid-state additive manufacturing and repairing by cold spraying: A review, *J Mater Sci Technol* 34 (2018) 440–457. <https://doi.org/10.1016/j.jmst.2017.09.015>.
- [8] G. Benenati, R. Lupoi, Development of a Deposition Strategy in Cold Spray for Additive Manufacturing to Minimize Residual Stresses, in: *Procedia CIRP*, Elsevier B.V., 2016: pp. 101–108. <https://doi.org/10.1016/j.procir.2016.08.042>.
- [9] R.N. Raelison, C. Verdy, H. Liao, Cold gas dynamic spray additive manufacturing today: Deposit possibilities, technological solutions and viable applications, *Mater Des* 133 (2017) 266–287. <https://doi.org/10.1016/j.matdes.2017.07.067>.
- [10] S. Bagherifard, S. Monti, M.V. Zuccoli, M. Riccio, J. Kondás, M. Guagliano, Cold spray deposition for additive manufacturing of freeform structural components compared to selective laser melting, *Materials Science and Engineering A* 721 (2018) 339–350. <https://doi.org/10.1016/j.msea.2018.02.094>.

- [11] R. Huang, M. Sone, W. Ma, H. Fukanuma, The effects of heat treatment on the mechanical properties of cold-sprayed coatings, *Surf Coat Technol* 261 (2015) 278–288. <https://doi.org/10.1016/j.surfcoat.2014.11.017>.
- [12] C.-J. Li, W.-Y. Li, Y.-Y. Wang, Effect of Spray Angle on Deposition Characteristics in Cold Spraying, in: *Thermal Spray 2003: Advancing the Science & Applying the Technology*, ASM International, Ohio, USA, 2003: pp. 91–96. <https://doi.org/https://doi.org/10.31399/asm.cp.itsc2003p0091>.
- [13] A. Vargas-Uscategui, P.C. King, S. Yang, C. Chu, J. Li, Toolpath planning for cold spray additively manufactured titanium walls and corners: Effect on geometry and porosity, *J Mater Process Technol* 298 (2021). <https://doi.org/10.1016/j.jmatprotec.2021.117272>.
- [14] Z. Cai, S. Deng, H. Liao, C. Zeng, G. Montavon, The effect of spray distance and scanning step on the coating thickness uniformity in cold spray process, *Journal of Thermal Spray Technology* 23 (2014) 354–362. <https://doi.org/10.1007/s11666-013-0002-0>.
- [15] D. Kotoban, S. Grigoriev, A. Okunkova, A. Sova, Influence of a shape of single track on deposition efficiency of 316L stainless steel powder in cold spray, *Surf Coat Technol* 309 (2017) 951–958. <https://doi.org/10.1016/j.surfcoat.2016.10.052>.
- [16] R.F. Vaz, V. Albaladejo-Fuentes, J. Sanchez, U. Ocaña, Z.G. Corral, H. Canales, I.G. Cano, Metal Knitting: A New Strategy for Cold Gas Spray Additive Manufacturing, *Materials* 15 (2022) 6785. <https://doi.org/10.3390/ma15196785>.
- [17] J. Pattison, S. Celotto, R. Morgan, M. Bray, W. O'Neill., Cold gas dynamic manufacturing: A non-thermal approach to freeform fabrication, *Int J Mach Tools Manuf* 47 (2007) 627–634. <https://doi.org/10.1016/j.ijmachtools.2006.05.001>.
- [18] H. Wu, X. Xie, M. Liu, C. Verdy, Y. Zhang, H. Liao, S. Deng, Stable layer-building strategy to enhance cold-spray-based additive manufacturing, *Addit Manuf* 35 (2020). <https://doi.org/10.1016/j.addma.2020.101356>.
- [19] W.Y. Li, C.J. Li, H. Liao, Effect of annealing treatment on the microstructure and properties of cold-sprayed Cu coating, *Journal of Thermal Spray Technology* 15 (2006) 206–211. <https://doi.org/10.1361/105996306X108066>.
- [20] A.C. Hall, D.J. Cook, R.A. Neiser, T.J. Roemer, D.A. Hirschfeld, The effect of a simple annealing heat treatment on the mechanical properties of cold-sprayed

aluminum, *Journal of Thermal Spray Technology* 15 (2006) 233–238. <https://doi.org/10.1361/105996306X108138>.

[21] K.S. Al-Hamdani, J.W. Murray, T. Hussain, A.T. Clare, Heat-treatment and mechanical properties of cold-sprayed high strength Al alloys from satellited feedstocks, *Surf Coat Technol* 374 (2019) 21–31. <https://doi.org/10.1016/j.surfcoat.2019.05.043>.

[22] J.S. Yu, H.J. Kim, I.H. Oh, K.A. Lee, Densification and purification of cold sprayed Ti coating layer by using annealing in different heat treatment environments, in: *Adv Mat Res*, 2013: pp. 1604–1608. <https://doi.org/10.4028/www.scientific.net/AMR.602-604.1604>.

[23] C. Chen, Y. Xie, X. Yan, S. Yin, H. Fukanuma, R. Huang, R. Zhao, J. Wang, Z. Ren, M. Liu, H. Liao, Effect of hot isostatic pressing (HIP) on microstructure and mechanical properties of Ti6Al4V alloy fabricated by cold spray additive manufacturing, *Addit Manuf* 27 (2019) 595–605. <https://doi.org/10.1016/j.addma.2019.03.028>.

[24] L.H. Brassart, J. Besson, F. Delloro, D. Haboussa, F. Delabrouille, G. Rolland, Y. Shen, A.F. Gourgues-Lorenzon, Effect of Various Heat Treatments on the Microstructure of 316L Austenitic Stainless Steel Coatings Obtained by Cold Spray, *Journal of Thermal Spray Technology* 31 (2022) 1725–1746. <https://doi.org/10.1007/s11666-022-01402-3>.

[25] W. Ma, Y. Xie, C. Chen, H. Fukanuma, J. Wang, Z. Ren, R. Huang, Microstructural and mechanical properties of high-performance Inconel 718 alloy by cold spraying, *J Alloys Compd* 792 (2019) 456–467. <https://doi.org/10.1016/j.jallcom.2019.04.045>.

[26] L.I. Pérez-Andrade, F. Gärtner, M. Villa-Vidaller, T. Klassen, J. Muñoz-Saldaña, J.M. Alvarado-Orozco, Optimization of Inconel 718 thick deposits by cold spray processing and annealing, *Surf Coat Technol* 378 (2019). <https://doi.org/10.1016/j.surfcoat.2019.124997>.

[27] ASTM International, ASTM E1920-03 - Standard guide for metallographic preparation of thermal sprayed coatings., USA, 2021.

[28] ASTM International, ASTM E2109-01 - Standard test methods for determining area percentage porosity in thermal sprayed coatings, PA, USA, 2021.

[29] ASTM International, ASTM E384-22 - Standard test for microindentation hardness of materials., USA, 2022.

- [30] ASTM International, ASTM G76-04 - Standard test method for conducting erosion tests by solid particle impingement using gas jets, n.d. <https://doi.org/10.1520/G0076-18>.
- [31] ASTM International, ASTM G65-16e1 - Standard test method for measuring abrasion using the dry sand/rubber wheel apparatus, n.d.
- [32] R.F. Vaz, A. Silvello, J. Sanchez, V. Albaladejo, I. García-Cano, The influence of the powder characteristics on 316l stainless steel coatings sprayed by cold gas spray, *Coatings* 11 (2021) 1–18. <https://doi.org/10.3390/coatings11020168>.
- [33] H. Assadi, H. Kreye, F. Gärtner, T. Klassen, Cold spraying – A materials perspective, *Acta Mater* 116 (2016) 382–407. <https://doi.org/10.1016/j.actamat.2016.06.034>.
- [34] T. Schmidt, F. Gärtner, H. Assadi, H. Kreye, Development of a generalized parameter window for cold spray deposition, *Acta Mater* 54 (2006) 729–742. <https://doi.org/10.1016/j.actamat.2005.10.005>.
- [35] W. Li, C. Cao, S. Yin, Solid-state cold spraying of Ti and its alloys: A literature review, *Prog Mater Sci* 110 (2020). <https://doi.org/10.1016/j.pmatsci.2019.100633>.
- [36] G. Bae, S. Kumar, S. Yoon, K. Kang, H. Na, H.J. Kim, C. Lee, Bonding features and associated mechanisms in kinetic sprayed titanium coatings, *Acta Mater* 57 (2009) 5654–5666. <https://doi.org/10.1016/j.actamat.2009.07.061>.
- [37] P. Vo, E. Irissou, J.G. Legoux, S. Yue, Mechanical and microstructural characterization of cold-sprayed Ti-6Al-4V after heat treatment, *Journal of Thermal Spray Technology* 22 (2013) 954–964. <https://doi.org/10.1007/s11666-013-9945-4>.
- [38] V. Luzin, K. Spencer, M.X. Zhang, Residual stress and thermo-mechanical properties of cold spray metal coatings, *Acta Mater* 59 (2011) 1259–1270. <https://doi.org/10.1016/j.actamat.2010.10.058>.
- [39] J. Ajaja, D. Goldbaum, R.R. Chromik, Characterization of Ti cold spray coatings by indentation methods, *Acta Astronaut* 69 (2011) 923–928. <https://doi.org/10.1016/j.actaastro.2011.06.012>.
- [40] W.Y. Li, C. Zhang, X. Guo, J. Xu, C.J. Li, H. Liao, C. Coddet, K.A. Khor, Ti and Ti-6Al-4V coatings by cold spraying and microstructure modification by heat treatment, *Adv Eng Mater* 9 (2007) 418–423. <https://doi.org/10.1002/adem.200700022>.

- [41] K. Binder, J. Gottschalk, M. Kollenda, F. Gärtner, T. Klassen, Influence of impact angle and gas temperature on mechanical properties of titanium cold spray deposits, in: *Journal of Thermal Spray Technology*, 2011: pp. 234–242. <https://doi.org/10.1007/s11666-010-9557-1>.
- [42] S. Yin, X. Suo, J. Su, Z. Guo, H. Liao, X. Wang, Effects of substrate hardness and spray angle on the deposition behavior of cold-sprayed ti particles, in: *Journal of Thermal Spray Technology*, 2014: pp. 76–83. <https://doi.org/10.1007/s11666-013-0039-0>.
- [43] Q. Wang, N. Birbilis, M.X. Zhang, Interfacial structure between particles in an aluminum deposit produced by cold spray, *Mater Lett* 65 (2011) 1576–1578. <https://doi.org/10.1016/j.matlet.2011.03.035>.
- [44] G. Bae, Y. Xiong, S. Kumar, K. Kang, C. Lee, General aspects of interface bonding in kinetic sprayed coatings, *Acta Mater* 56 (2008) 4858–4868. <https://doi.org/10.1016/j.actamat.2008.06.003>.
- [45] Y. Xie, C. Chen, M.P. Planche, S. Deng, R. Huang, Z. Ren, H. Liao, Strengthened Peening Effect on Metallurgical Bonding Formation in Cold Spray Additive Manufacturing, *Journal of Thermal Spray Technology* 28 (2019) 769–779. <https://doi.org/10.1007/s11666-019-00854-4>.
- [46] N.W. Khun, A.W.Y. Tan, W. Sun, E. Liu, Wear and Corrosion Resistance of Thick Ti-6Al-4V Coating Deposited on Ti-6Al-4V Substrate via High-Pressure Cold Spray, *Journal of Thermal Spray Technology* 26 (2017) 1393–1407. <https://doi.org/10.1007/s11666-017-0588-8>.
- [47] D. Cruz, M.A. Garrido, C.J. Múñez, A. Rico, P. Poza, Erosion of cold sprayed aeronautical coatings*, *Surface Engineering* 35 (2019) 792–800. <https://doi.org/10.1080/02670844.2019.1586096>.
- [48] S. Tortuero, M.A. Garrido, P. Poza, J. Rodríguez, Evaluating the erosion resistance of Ti6Al4V coatings deposited by cold spray, *Wear* 454–455 (2020). <https://doi.org/10.1016/j.wear.2020.203337>.
- [49] E. Avcu, S. Fidan, Y. Yildiran, T. Sinmazçelik, Solid particle erosion behaviour of Ti6Al4V alloy, *Tribology - Materials, Surfaces and Interfaces* 7 (2013) 201–210. <https://doi.org/10.1179/1751584X13Y.00000000043>.

[50] L. Fu, L. Li, D.Y. Li, Further look at correlation between ASTM G65 rubber wheel abrasion and pin-on-disc wear tests for data conversion, *Tribology - Materials, Surfaces and Interfaces* 7 (2013) 109–113. <https://doi.org/10.1179/1751584X13Y.0000000031>.

Chapter 5: Results & Discussion

Repair of Inconel 718 parts by Cold Spray Additive Manufacturing: the effect of substrate preheating on thick coatings properties

Cold spray additive manufacturing (CSAM) has been developed as a promising solid-state technology for repair applications. Yet, one of the main challenges of CSAM is the deposition of high-strength materials, such as Inconel 718® (IN718), due to their low particle plasticity. IN718 is a high-performance Ni-based superalloy usually used in relevant applications such as high-temperature industries or jet engines. The interest in remanufacturing IN718 damaged parts with CSAM has increased in the last years; however, different deposition strategies still need to be studied to obtain well-bonded and dense IN718 deposits. This study investigates the effect of IN718 substrate preheating on the CSAM IN718 deposit microstructure and thickness, as well as the adhesion mechanisms and strength at room and preheating temperatures: 250 and 400 °C. The results revealed that a substrate preheating temperature of 400 °C promoted a dense microstructure within a 1.2 mm thick coating with porosity values $< 0.1\%$, and an adhesion strength > 50 MPa.

Chapter 5: Repair of Inconel 718 parts by Cold Spray Additive Manufacturing: the effect of substrate preheating on thick coatings properties

5.1 Introduction

Inconel 718 (IN718) is a high-performance Ni-based superalloy, registered by the US company *International Nickel Company*, with excellent corrosion resistance and high mechanical strength at high temperatures used in relevant applications, such as jet engines that operate at temperatures as high as 700 °C. Over the years, IN718 has been processed with conventional methods, i.e., wrought and cast techniques; however, its high strength characteristics make it difficult to machine using conventional processes [1,2]. Some IN718 parts are exposed to harsh environments, and their damages by erosion, abrasion, or hot corrosion may result in volume losses, which have been repaired by welding or other processes involving high-temperature deposition, resulting in microstructural effects on the IN718 base metal. Therefore, in the last years, cold spray additive manufacturing (CSAM) has been studied as an alternative for repairing IN718 damaged parts.

Cold spray (CS) is a solid-state deposition that has been developed for coatings and has advanced as an additive manufacturing (AM) technology with the potential to be used in repairing applications [3–6]. In CS, a feedstock powder is injected inside a gun, and accelerated by a preheated gas, typically N₂ or He, through a convergent-divergent de Laval nozzle, reaching supersonic velocities. The powder particles are accelerated and propelled towards a substrate (below the materials recrystallisation temperature); when they impact with enough kinetic energy, they deform plastically and remain adhered to the substrate. The speed which must be achieved for a material application, is called the critical velocity (v_{cr}). The most established theory on bonding mechanisms in CS is the work of Assadi et al. [7], where adiabatic shear instability (ASI) is proposed as the main adhesion mechanism responsible for the bonding of the particles. This phenomenon occurs due to the high strain rate deformation processes during the impact, which disrupt the superficial oxide film of the particles, creating a metal jet that forms a metallurgical bonding by establishing an intimate contact between

the particles and the substrate. In addition to the ASI theory, Hussain et al. [8] studied the behavior of CS Cu particles on Al substrate, observing that the particles deform the substrate, creating a layer of particles mechanically interlocked, acting as a well-bonded base for further impacting particles to adhere.

Moreover, the CS deposition of high-strength materials, e.g., IN718, is still challenging; the lack of particle deformability at the impact hinders the bonding processes and may lead to a porous or low-adhesion deposit. Hence, the use of high-energy parameters is required to obtain dense deposits of IN718, which can result in an accumulation of residual stresses that may cause the detachment of the deposits from the substrate [9,10]. To overcome this, scholars have focused on different deposition strategies to obtain well bonded-dense CS IN718 deposits [9,11–16]. Singh et al. [14] measured the residual stress distribution in CS IN718 coatings with varying thicknesses, indicating that residual stresses significantly influences adhesion strength, which decreases by improving the coating thickness. Additionally, Sun et al. [13] studied the impact of surface roughness and substrate preheating on the coating-substrate bonding mechanism, revealing that a smoother substrate surface enhanced the plastic deformation of the particles without constraint. Moreover, the substrate preheating promoted metal jetting of the particles, resulting in higher bonding strength under shear loading. Pérez-Andrade et al. [9] optimized the CS process gas temperature conditions to produce thick IN718 coatings with low porosities, high hardnesses, and low tensile residual stresses in the substrate-coating interface. The authors also evaluated the effect of annealing and hot isostatic pressing (HIP) on the microstructure of the coatings. Annealing improves the deposit density, > 99%. Ma et al. [12] compared the characteristics of CS IN718 produced with different propelling gases, He and N₂. Higher ductility and ultimate tensile strength were reported for IN718 coatings by using He instead of N₂. However, He increases CS repairing costs.

The interest in repairing IN718 parts with CSAM has grown in recent years [4–6]. However, studies on the CS process for IN718 are still limited. Consequently, various deposition strategies require further investigation to achieve well-bonded and dense IN718 thick deposits suitable for repairing

applications. Substrate preheating has been shown to improve the adhesion strength when spraying hard materials due to the softening of the substrate, which allows to remove the native oxide layer by ASI, resulting in an improved metallic bonding [17]. Ortiz-Fernandez et al. [17] showed an improvement of 30% in the CS Al adhesion on Ti6Al4V substrate by its preheating by an induction system. Moreover, Ortiz-Fernandez and Jodoin [18] used an induction system for the Ti6Al4V substrate and the IN718 deposit, and an IN718 feedstock powder heater to control the temperatures of the materials during the deposition, promoting higher deposition efficiency (DE) and inter-particle bonding strength. Xie et al. [19] evaluated the bonding strength of CS 316L stainless steel on a preheated 316L substrate, resulting in adhesion of 13.4 MPa and 74.1 MPa at preheating temperatures of 25 and 700 °C, respectively.

Up to date, the impact of substrate preheating on IN718 coatings sprayed onto IN718 substrates have not been reported. This deposition strategy is an alternative for repairing damaged IN718 parts without detrimental effects on their material microstructures. This work investigates the influence of substrate preheating on CS IN718 thick deposits for repair applications. The variations in microstructural characteristics, including porosity, microhardness, and phase composition, of the deposits sprayed at different preheating temperatures (room temperature (RT), 250, and 400 °C) were evaluated. The interaction between the coating and the substrate at the different preheating temperatures was investigated, focused on the adhesion mechanisms of single impact splats. Furthermore, the bonding strength of the samples at varying thicknesses and preheating temperatures was tested to determine the effectiveness of the CS process for repairing IN718 parts.

5.2 Materials and Methods

5.2.1 Feedstock powder

A commercial IN718 powder with dendritic microstructure (Diamalloy 1006, Oerlikon) was used in this study. Its particle shape and cross-section images were obtained by scanning electron microscopy (SEM) in a Phenom ProX Desktop microscope (Eindhoven, the Netherlands), as seen in Figure 5.1(a-b). An elemental microanalysis was carried out with Quantax EDS Bruker Nano (MA,

USA) integrated into a SEM Jeol 5310 (Tokyo, Japan) to measure the IN718 chemical composition, shown in Table 5.1. The IN718 particle size distribution was analyzed with a laser diffraction particle sizing analyzer Beckman Coulter LS 13 320 via dry mode (CA, USA), presented in Figure 5.1(c).

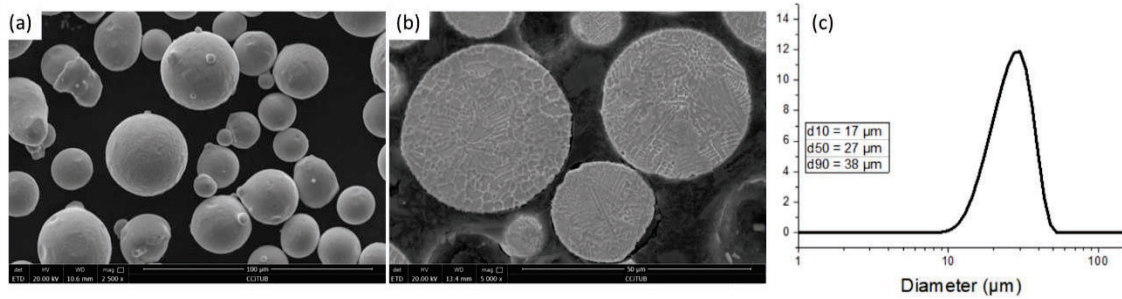


Figure 5.1. Feedstock powder IN718 (a) particle shape, (b) cross-section microstructure, and (c) particle size distribution.

Table 5.1. Feedstock powder IN718 chemical composition (wt.%).

Ni	Cr	Fe	C	Nb	Mo	Al	Ti
49.17	19.06	17.33	4.69	4.69	3.02	1.05	0.99

5.2.2 CSAM parameters and substrate preheating conditions

All samples were sprayed with a high-pressure CS Plasma Giken PCS 100 (Saitama, Japan) equipment on polished dia. 25 mm IN718 discs. To examine the impact of substrate preheating and thickness on the samples' microstructure and adhesion, the experiments detailed in Table 5.2 were conducted using the optimized CS parameters for IN718, included in Table 5.3. The IN718 substrates were preheated using a hotplate CERAN 500 (Jena, Germany); the hotplate's setpoint temperature was maintained during the spraying. The temperature of the substrates before spraying was measured using an infrared thermometer FLIR TG56 (OR, USA).

To evaluate the adhesion mechanisms at the different preheating temperatures, single impact particle splats were sprayed with the preheating temperatures detailed in Table II with a traversal velocity of 1000 mm/s.

Table 5.2. CS samples nomenclature and characteristics.

Label	Preheating Temperature (°C)	Number of layers
RT-10	Room Temperature	10
RT-15		15
RT-20		20
RT-40		40
250-10	250	10
250-15		15
250-20		20
250-40		40
400-10	400	10
400-15		15
400-20		20
400-40		40

Table 5.3. CS parameters.

Pressure (MPa)	Temperature (°C)	Standoff Distance (mm)	Traversal velocity (mm/s)
7.0	1080	30	500

5.2.3 Microstructural characterization

The metallographic preparation of the samples was completed following the ASTM E1920-03 standard; the polished samples were etched in a reagent composed of 5 ml HF, 5 ml HNO₃, 5 ml H₂O₂, 10 ml HCl, and 5 ml distilled water to reveal their microstructure. Each samples' cross-sectional surface and thickness were evaluated with a Keyence VK-X (Osaka, Japan) series laser microscope according to the ASTM E3-11 standard. The mean porosity values were obtained using *ImageJ* software of images obtained by optical microscopy (OM) in a Leica DM5000 microscope (Wetzlar, Germany), following the ASTM E2109-01 standard. The Vickers microhardness was obtained from a mean value of ten indents for each sample in accordance with ASTM E384-17 standard, with a 0.3 kgf (HV_{0.3}) using a Shimadzu HV-2/HMV-2T (Tokyo, Japan) equipment.

To evaluate the composition of the deposits, an elemental mapping was obtained with EDS detector GATAN MONO-CL4 (CA, USA) attached to a FESEM JEOL J-7100 (Tokyo, Japan). To evaluate the phase changes, XRD patterns

were performed for the feedstock powder and CS samples, using an equipment PANalytical X'Pert PRO MPD (Malvern, UK) with Ni filtered $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) from 5 to $100^\circ 2\theta$ with a step size of 0.026° and measuring time of 100 s .

5.2.4 Adhesion mechanisms & evaluation

To investigate the adhesion mechanisms, the single impact splats were observed with a Phenom ProX Desktop SEM (Eindhoven, the Netherlands). The adhesion strength of the CS IN718 deposits with an IN718 substrate was evaluated with equipment Servosis ME 402-10 (Madrid, Spain), according to the ASTM C633-13 standard. For each variable, three samples were glued to a grit-blasted counterpart with the adhesive HTK Ultrabond 100 (Hamburg, Germany) with a strength of 50 MPa ; a tensile test at a rate of 0.01 mm/s was performed until failure. The fracture surfaces were observed in the SEM to interpret the type of failure: adhesive (on the interface substrate-coating), cohesive (between the coating particles), or glue failure (in the interface coating-counterpart).

5.3 Results and Discussion

5.3.1 Microstructural characterization

Figure 5.2 shows the samples' cross-sectional microstructures, while the porosity and microhardness are also presented in Figure 5.3. Overall, dense and homogeneous CS IN718 deposits were obtained with no visible cracks nor delamination areas, which is consistent with other studies of CS IN718 in the literature [9,14,16]. Furthermore, all micrographs revealed a smooth substrate-deposit interface, indicating a strong bonding between particles and substrate, and an adequate selection of the CS parameters and substrate activation. In addition, the microstructural characteristics of the 40 layered deposits were similar to the ones sprayed with fewer layers; despite the higher thickness, a dense microstructure with a smooth interface without defects was observed.

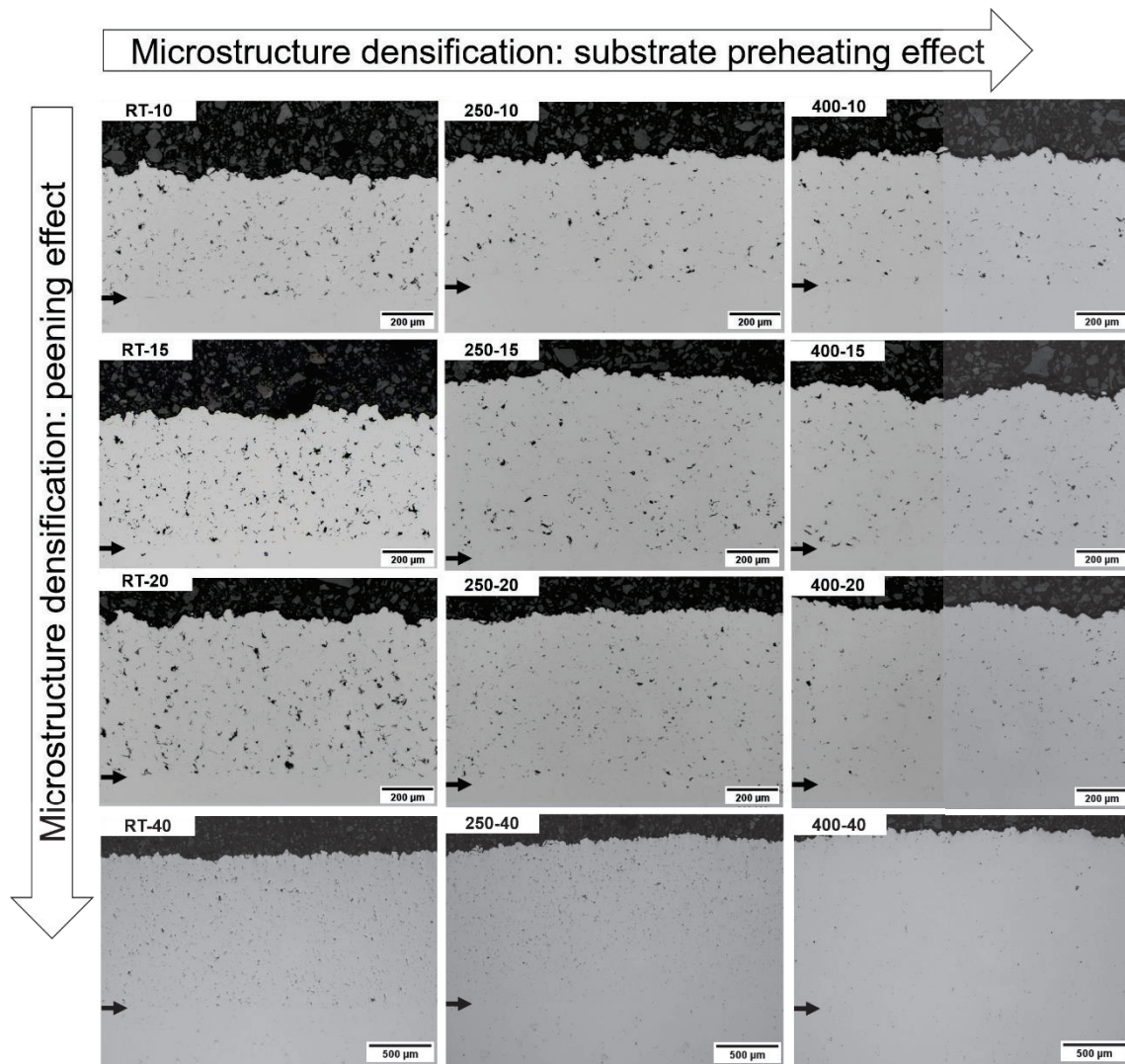


Figure 5.2. OM images of the CS IN718 deposits. The arrows indicate the interface deposit-substrate.

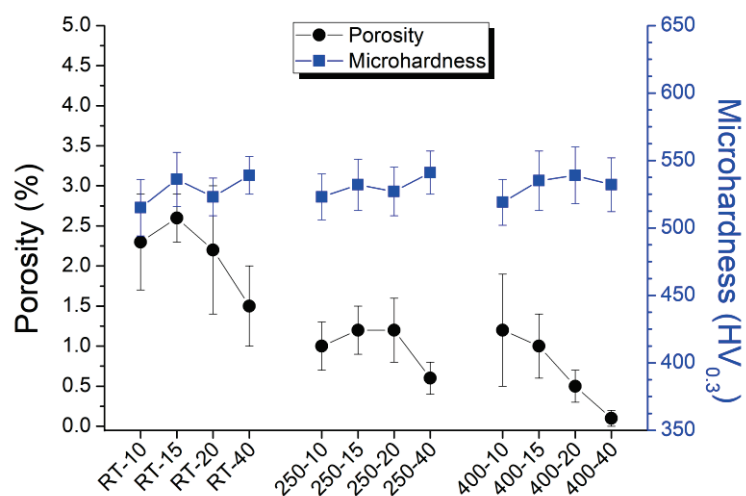


Figure 5.3. Porosity and microhardness of CS IN718 deposits.

As observed in Figure 5.2, two effects that led to microstructure densification can be clearly distinguishable: the temperature effect from the substrate preheating and the peening effect of the particles related to the increase in coating thickness. The effect of the substrate preheating on the microstructure densification of the samples was notable, especially on the first deposited layer, where the temperature transfer from the substrate was more influential. In this case, regardless of the number of layers sprayed, the samples exhibited higher porosity values when sprayed at RT compared to those sprayed with preheating temperatures of 250 and 400 °C. This effect was the most evident in the 20 layered samples; the porosity decreased with the preheating substrate temperature increase, resulting in porosity values of $2.2 \pm 0.8\%$, $1.2 \pm 0.4\%$, and $0.5 \pm 0.2\%$ for RT-20, 250-20, and 400-20, respectively. This is attributed to an enhanced plastic deformation of the particles when impacting a surface at a higher temperature, promoting metallurgical bonding and micro welding between particles-substrate and particles-particles [19]. Moreover, the peening effect from the subsequent impingent particles was also observed in the porosity. In all cases, the porosity decreased when increasing the deposits' thickness: resulting in values of $2.3 \pm 0.6\%$ and $1.5 \pm 0.5\%$ for samples RT-10 and RT-40, $1.0 \pm 0.3\%$ and $0.6 \pm 0.2\%$ for samples 250-10 and 250-40, and $1.2 \pm 0.7\%$ and $0.1 \pm 0.1\%$ for samples 400-10 and 400-40, respectively. In particular, as reported by Singh et al. [14] at higher thicknesses the peening effect is intensified, leading to a higher deformation of the already deposited particles by the impact of the subsequent particles, acting to reduce the previous deposited layers' thickness and densifying them.

In particular, sample 400-40 presented a fully dense microstructure (99.9%) comparable to an IN718 bulk part. It is worth noting that there are no reported CS IN718 deposits within the literature exhibiting such a high dense microstructure. For instance, Singh et al. [14] studied the influence of deposit thickness (ranging from 216 to 1173 μm) on the residual stress development of CS IN718 deposits sprayed with N_2 onto IN718 substrates, obtaining deposits with low porosity values of $0.7 \pm 0.3\%$. However, discontinuous gaps between the particles-substrate for all thicknesses can be observed in the interface, suggesting a weak adhesion strength. Another example is the study of Ma et al.

[12], in which the microstructures of CS IN718 deposits fabricated using N₂ and He were compared. The deposits sprayed with N₂ exhibited a dense microstructure, yet even after a heat treatment post-processing, the porosity resulted in a value of $1.24 \pm 0.14\%$. On the other hand, the deposits obtained with He, showed a fully dense microstructure with porosity values of $0.21 \pm 0.05\%$ in the as-sprayed state and $0.18 \pm 0.04\%$ after the heat treatment. Nonetheless, using He severely increases the costs associated with the CS processing, making its utilization difficult to justify [20]. Finally, Pérez-Andrade et al. [9] produced CS IN718 deposits with 1.3 mm thickness and investigated the effects of a three-step heat treatment post-processing, obtaining a thick as-sprayed deposits sprayed with optimized conditions with a porosity value of $1.3 \pm 0.1\%$ and no debonding signs, as well as heat treated specimens with dense microstructures containing $0.3 \pm 0.1\%$ porosity.

In terms of microhardness, all values were comparable among all the CS IN718 deposits. In contrast to the work of Singh et al. [14], no difference in the microhardness was observed by increasing the deposits' thickness since all the samples in this work presented a dense microstructure with a strong cohesion between particles. Moreover, all the obtained microhardness values resulted in higher than the ones reported in the literature for bulk IN718 ($450 \text{ HV}_{0.3}$) [14,21] due to the inherent cold-working effect of the particles in the CS process [22].

Moreover, Figure 5.4 presents graphically the thickness evolution of the IN718 deposits with the substrate preheating and number of layers. As expected, the deposits' thickness varied with the number of CS layers. For all 10 layered samples, the deposits' thickness remained constant, independently of the preheating temperature, resulting in similar values of $495 \pm 23 \text{ }\mu\text{m}$, $498 \pm 14 \text{ }\mu\text{m}$, and $467 \pm 25 \text{ }\mu\text{m}$, for RT-10, 250-10, and 400-10, respectively. Each of the ten layers had a thickness close to $50 \text{ }\mu\text{m}$. In the case of the RT samples, as the total number of layers was increased, thinner individual layers were obtained with mean values of $35 \text{ }\mu\text{m/layer}$, $34 \text{ }\mu\text{m/layer}$, and $29 \text{ }\mu\text{m/layer}$ for RT-15, RT-20, and RT-40 samples, respectively. This tendency was less accentuated by controlling the substrate temperature, in which more than $40 \text{ }\mu\text{m/layer}$ were obtained until 20 layers for 250 and 400 °C preheating temperatures, which may be attributed to the temperature transfer resultant from both a higher substrate surface

temperature and a higher temperature of the sample when spraying at longer times [10]. However, as the number of layers was increased to 40, the effect of the temperature was less influential in the deposit and a progressive decrease in the individual layers in all cases was observed regardless of the substrate temperature. This behavior is attributed to the fact that the CS process gas was sprayed at a higher temperature than the preheating temperatures, hence, after a prolonged spraying time the surface temperature of all samples eventually stabilized and no further differences in layers' thickness was observed. This steady-state temperature behavior is consistent with the work of Legoux et al. [23] and Ortiz-Fernandez et al. [10], in which they recorded the temperature evolution of samples with and without preheating. In this sense, the measured thickness was similar for all preheating temperatures at 40 layers, with values of $1172 \pm 26 \mu\text{m}$, $1166 \pm 53 \mu\text{m}$, and $1117 \pm 29 \mu\text{m}$, for samples RT-40, 250-40, and 400-40, respectively.

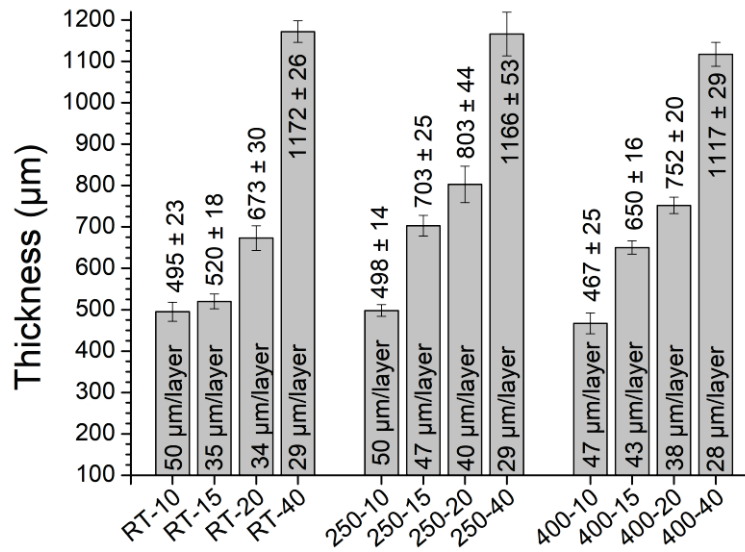


Figure 5.4. Thickness of CS IN718 deposits.

Furthermore, the initial dendritic microstructure of the feedstock powder was maintained after the CS processing, as confirmed by the SEM micrograph and the EDS analysis shown in Figure 5.5. The SEM image clearly shows the splats with the deformed dendritic microstructure localized in the periphery of the particles. In addition, the compactness of the particles was notably apparent since the particle boundaries were barely distinguished. The EDS element map

distribution revealed a segregation of Nb, Mo, and C in the inter-dendritic regions [24,25].

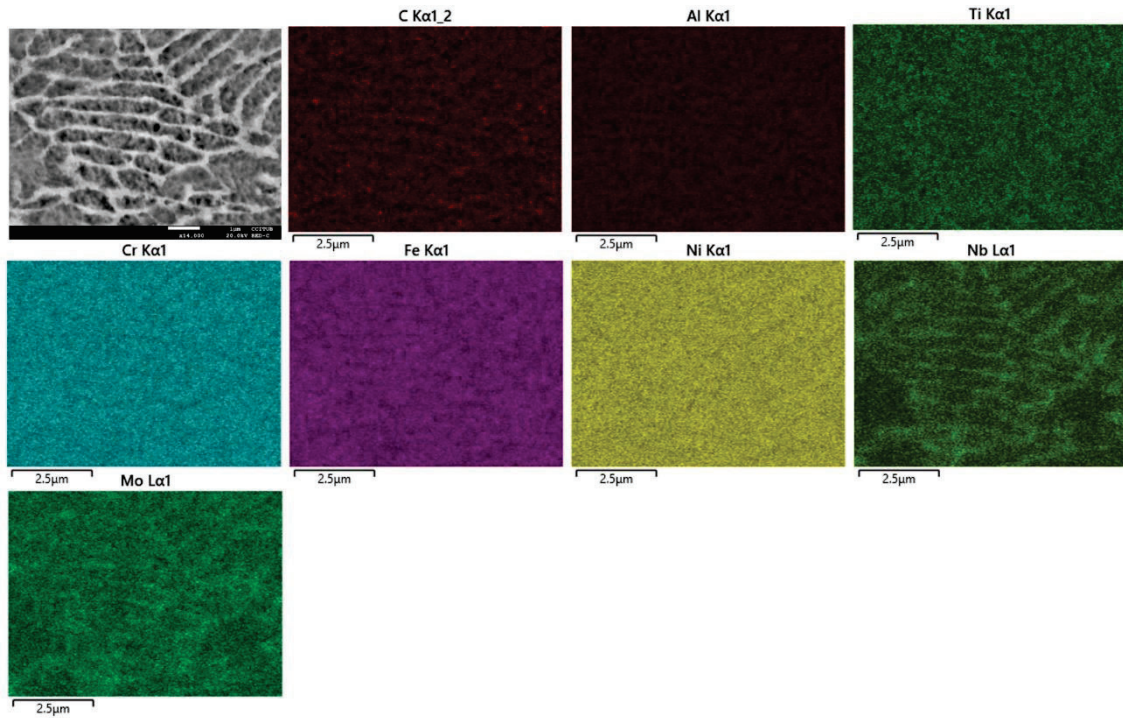


Figure 5.5. EDS elemental map of the 400-40 deposit microstructure.

One drawback of substrate preheating is that depending on the temperature and material involved, it may cause oxidation and hinder the bonding strength between the particles and the substrate [10,26]. Therefore, an XRD analysis was done to confirm the absence of oxides in the specimens at RT and 400 °C, the highest preheating temperature. The diffractograms are shown in Figure 5.6. There were no oxides present, and all the samples exhibited the same peaks, which correspond to the single-phase FCC solid solution (γ phase) of IN718 [24,27]. Typically, IN718 is a material known to form several phases and precipitates. In particular, the phases γ' and γ'' determine its mechanical characteristics. Even though these phases were not observed in the CS IN718 deposits, post-processing heat treatments can be applied to tailor the microstructure of the deposits, promoting the nucleation of the γ' and γ'' precipitates, while controlling other undesired phases [21].

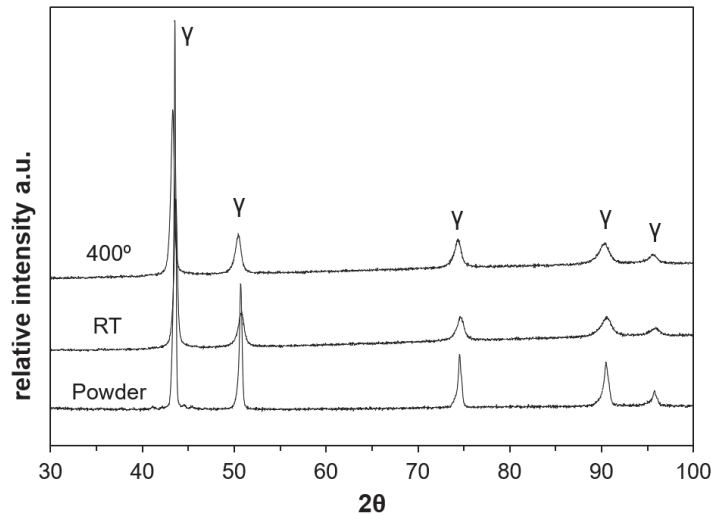


Figure 5.6. XRD diffractograms of the IN718 feedstock powder, RT-40, and 400-40 deposits.

5.3.2 Adhesion mechanisms and strength

Dense IN718 coatings were obtained by selecting the optimized parameters for this material, in which the sprayed particles impacted the substrate at a velocity within the window of deposition, i.e., above the v_{cr} (between 787 and 830 m/s) and below the erosion velocity [11,12]. The fact that the substrate and the deposit were made from the same material influenced positively on both the particles' and the substrate plasticity at impact, which enhanced bonding due to their similar mechanical and microstructural properties; in general, the deposition of different materials still has been a challenge for CS processing because of the dissimilar material response at the impact, which can produce the erosion of the softer side and none deformation of the harder counterpart [17,28].

The two densification effects mentioned in the previous section, a higher substrate temperature and the peening effect of the particles at a high number of layers, facilitated the deformation and subsequent packing of the IN718 particles. Figure 5.7 shows the OM images of the cross-sectional as-sprayed and etched microstructures of 40 layered IN718 deposits. As delineated by the dashed lines, the particles sprayed without preheating temperature exhibited a slight deformation, while generally retaining a semi-spherical shape. In contrast, the deposits subjected to both preheating temperatures exhibited highly deformed particles, which facilitated a tighter packing that minimized inter-particle voids. This increased particle deformation with temperature is consistent with the

findings of Ortiz-Fernandez et al. [10], which demonstrated that applying temperature to the specimen while spraying softens the deposit due to heat transfer processes. In this sense, the temperature transfer from the substrate to the deposit softened, up to a certain thickness, the already deposited particles, enhancing its deformation. When increasing the thickness beyond this point, the tampering effect of the particles becomes more influential, thereby densifying the microstructure [29].

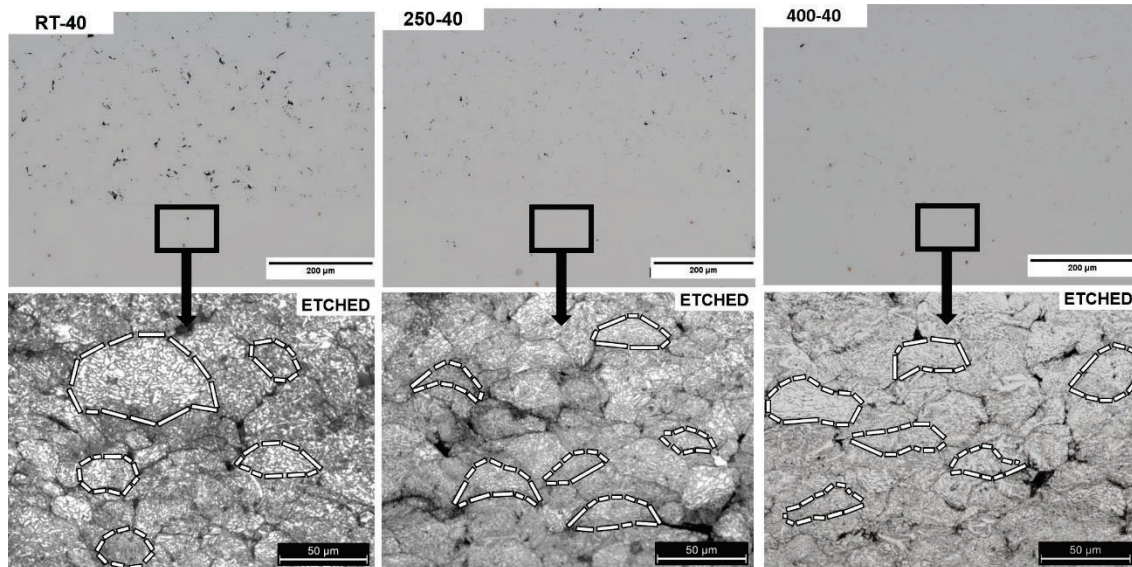


Figure 5.7. OM images of the cross-sectional as-sprayed and etched 40 layered CS IN718 microstructures.

To further investigate the interaction of the substrate at different temperatures and the particles, single splats were deposited by CS. Figure 5.8 shows the SEM images of the sprayed particles and their cross-sectional microstructures. In neither case, the substrate exhibited any craters formed by the impact of bounced particles, which is attributed to the high-strength characteristics of the IN718 substrate. In addition, the particles in all cases were well attached and were plastically deformed with evidence of the metal jetting phenomenon [7,17,30]. In particular, the particles' cross-section showed this interaction with more detail; the particles sprayed onto the RT substrate only formed a slight jet, and their impact caused a slight deformation of the substrate. In this case, a gap at the center-bottom of the particles was present, which can be attributed this discontinuity in the interface to the higher temperature of the particles at the periphery than at the center, indicating that a lower temperature

is reached in this center-bottom part of the particle, consequently hindering the bonding [13]. The same gap was observed in some of the particles sprayed onto the substrates preheated at 250 °C; however, for the substrates preheated at 400 °C, this void was almost nonexistent, indicating that the temperature of the substrate promoted adhesion [13,18,31,32]. To understand this phenomenon, the influence of temperature on the plastic deformation mechanisms of the particles must be considered. Upon impact, most kinetic energy from the particles is converted into heat. This increase in the local temperature facilitates the dislocation motion within the materials, increasing both substrate and particle deformation [33]. Consequently, localized melting occurs, which promotes the fracture of oxide layer, thereby enhancing diffusion processes crucial for a successful adhesion between particles and substrate, and improved cohesion among particles [30,34]. Thus, an increased substrate or coating temperature induces a softening effect [18]. In the initial layers, this effect manifests as an enhanced metallurgical bonding at the interface, characterized by a strong intimate contact between the particles-substrate (Figure 8). Subsequently, in the succeeding layers, this softening effect influences the already deposited particles, which subsequently undergo further deformation due to the peening effect. As a result, a densification in the microstructure and an increased adhesion strength are achieved.

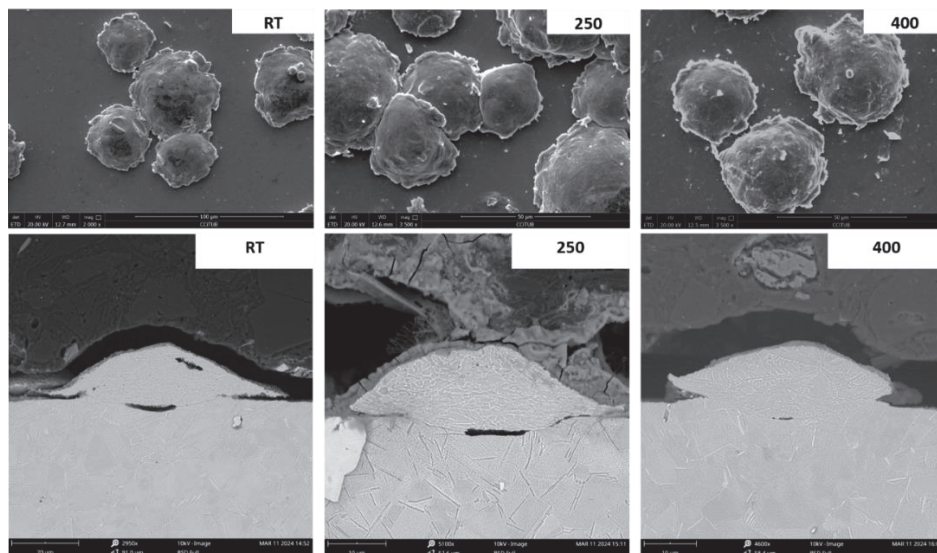


Figure 5.8. SEM images of single splats of RT, 250, and 400 substrate preheating temperatures.

The adhesion strength of the CS IN718 deposits on IN718 substrates is a critical requirement for ensuring adequate performance in repairing applications [5,35]. In general, the deposition of these high-strength materials remains challenging in the CSAM technology due to both a lack of particle deformability that hinders the bonding processes and the accumulation of residual stresses that promote the deposit detachment [14,36]. Therefore, investigating of different deposition strategies, such as the robot path trajectory, substrate preheating, and optimization of the CS parameters are essential to ensure a strong bonding with the substrate [37]. Consequently, the effect of the substrate preheating on the adhesion of the CS IN718 deposits was investigated in this work; Figure 5.9 shows the values obtained for CS IN718 deposits with different preheating conditions and layers.

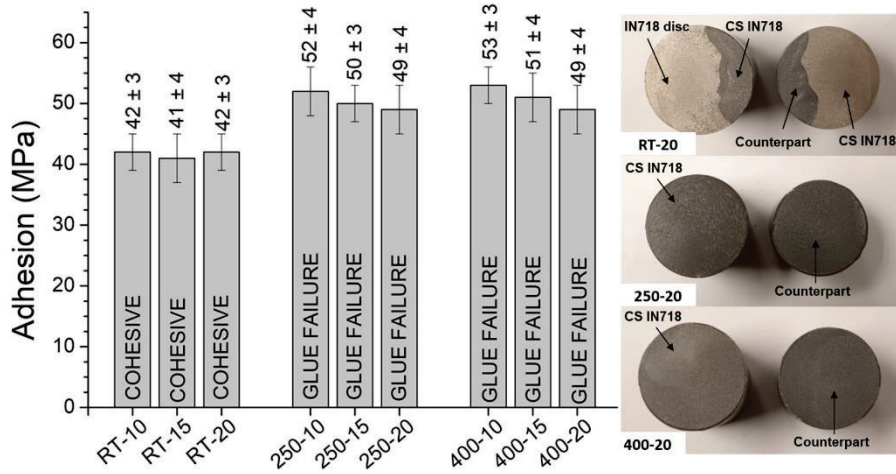


Figure 5.9. Adhesion testing results of CS IN718 deposits.

In particular, the samples deposited without substrate preheating exhibited an adhesion strength with cohesive failure around 42 MPa. In contrast with the work of Singh et al. [14], in which the reported adhesion strength of 17 ± 3 MPa for CS IN718. The very close adhesion values for different RT coating thickness suggests that the accumulation of compressive residual stresses did not influence the cohesion nor adhesion of the CS IN718 deposits, which may be attributed to the quality of the deposits sprayed under optimized conditions.

Moreover, all samples subjected to substrate preheating exhibited glue failures, meaning that all these samples presented bonding strengths > 50 MPa, which indicated that the cohesion between particles and the adhesion to the

IN718 substrate were greater than the RT specimens. Again, no adhesion variation with the different thicknesses was observed. The resulting adhesion strength of the deposits was notably restricted by the glue strength; to evaluate the precise adhesion strength values for future investigations, the novel adhesion strength test developed by Ma et al. [12] offers an appropriate method to overcome the glue limitation. However, a bonding strength > 50 MPa would be suitable for general repair applications [38], avoiding new tests.

Furthermore, Figure 5.9 shows representative images of the CS IN718 20 layered samples. It was evident from the images that the differences in failure were between the samples sprayed with and without substrate preheating. This trend persisted across all samples: the first presented glue failure, as the deposits remained attached to the IN718 substrate discs, while the counterparts were perfectly detached from the deposits. Whereas the second experienced cohesive failure as the deposit was delaminated, leaving some of it attached to the IN718 substrate discs and the remainder adhered to the counterpart. This suggests that the cohesion between samples was improved when applying higher temperatures to the substrate while spraying, consistent with the work of Sun et al. [39], which revealed that substrate preheating promoted metallurgical bonding and increased the deposit-substrate adhesion strength.

This enhancement of adhesion can be further investigated by observing the interface of the deposits, along with the characteristics of single impact splats and their interaction with the substrate. Figure 5.10 presents the SEM micrographs of the etched interface of the RT-40, 250-40, and 400-40 CS IN718 deposits. The micrographs clearly showed a difference between the RT specimens and the preheated ones; the first one exhibited a discontinuous gap between the particles and the substrate surface, suggesting that only localized parts of the deformed particles were able to bond metallurgically due to the occurrence of ASI. Moreover, the particle layers were also notorious, as the particle boundaries were clearly visible, indicating a lack of cohesion between them. On the contrary, by preheating the substrate, the interfaces became highly smooth. Specimen 250-40 only showed some voids in the deposit-substrate interface, while sample 400-40 exhibited a continuous and dense interface. For

these two deposits, the particles boundaries were barely distinguishable, which is consistent with the results observed in the single impact splats.

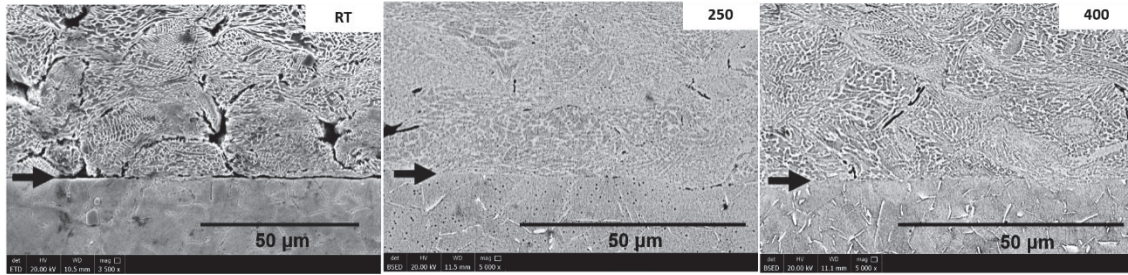


Figure 5.10. SEM images of the etched substrate-deposit interface of the RT-40, 250-40, and 400-40 deposits. The arrows indicate the interface deposit-substrate.

Overall, the substrate preheating strategy resulted in a significant reduction of porosity within the microstructure of the CS IN718 deposits. Coatings exhibiting nearly fully dense microstructures (99.9%) were manufactured without the presence of oxides or undesired phases, comparable to that of an IN718 bulk part. Moreover, thick deposits (> 1 mm) were successfully obtained with strong adhesion to the substrate and no signs of delamination. These findings demonstrate significant potential for the implementation of CS in repairing applications that involve this alloy, and overcomes the challenge of processing IN718 fabricated by other methods, such as welding.

5.4 Conclusions

In this work, CS IN718 deposits on IN718 substrate were manufactured under different substrate preheating temperatures: RT, 250, and 400 °C. After the characterization and evaluation of the deposits regarding their microstructure, adhesion, and bonding mechanisms, the following conclusions can be drawn based on the results:

- CS processing can be successfully applied for repairing IN718 damaged parts by depositing the same material without adding any bond coating or other additional pre-processing other than polishing and cleaning, preserving the feedstock material microstructure and phase composition;

- Two effects led to microstructure densification: the temperature effect induced by the substrate preheating in the first layers, and the peening effect of the particles in the subsequent layers.

- The substrate preheating improved the bonding strength, adhesion, and cohesion of CS IN718 deposits by softening the substrate, which improved the materials' plasticity;

- The substrate preheating and deposit thickness did not affect the deposit microhardness; however, increasing the preheating temperature and the deposit thickness improved the deposit density, reaching values comparable to an IN718 bulk reference, > 99.9%.

5.5 Acknowledgements

Grant PID2020-115508RB-C21 funded by MCIN/AEI/10.13039/501100011033 and, as appropriate, by “ERDF A way of making Europe”, by the “European Union” or by the “European Union NextGenerationEU/PRTR” A. Garfias would like to thank AGAUR for grant 2021 FISDU 00300 and the Universitat de Barcelona for the 2023 doctoral international stays grant. V. Albaladejo-Fuentes is a Serra Hunter Fellow.

5.6 References

- [1] B. Izquierdo, S. Plaza, J.A. Sánchez, I. Pombo, N. Ortega, Numerical prediction of heat affected layer in the EDM of aeronautical alloys, *Appl Surf Sci* 259 (2012) 780–790. <https://doi.org/10.1016/j.apsusc.2012.07.124>.
- [2] Q. Jia, D. Gu, Selective laser melting additive manufacturing of Inconel 718 superalloy parts: Densification, microstructure and properties, *J Alloys Compd* 585 (2014) 713–721. <https://doi.org/10.1016/j.jallcom.2013.09.171>.
- [3] W. Li, K. Yang, S. Yin, X. Yang, Y. Xu, R. Lupoi, Solid-state additive manufacturing and repairing by cold spraying: A review, *J Mater Sci Technol* 34 (2018) 440–457. <https://doi.org/10.1016/j.jmst.2017.09.015>.
- [4] A. Saboori, S. Biamino, P. Di Torino, D. Gitardi, M. Lombardi, The Capacity of Cold Spray Additive Manufacturing Technology for Metallic Part Repairing, in: *Euro PM2018*, Bilbao, 2018. <https://www.researchgate.net/publication/328407397>.
- [5] S. Yin, P. Cavaliere, B. Aldwell, R. Jenkins, H. Liao, W. Li, R. Lupoi, Cold spray additive manufacturing and repair: Fundamentals and applications, *Addit Manuf* 21 (2018) 628–650. <https://doi.org/10.1016/j.addma.2018.04.017>.
- [6] C.A. Widener, O.C. Ozdemir, M. Carter, Structural repair using cold spray technology for enhanced sustainability of high value assets, in: *Procedia Manuf*, Elsevier B.V., 2018: pp. 361–368. <https://doi.org/10.1016/j.promfg.2018.02.132>.
- [7] H. Assadi, F. Gärtner, T. Stoltenhoff, H. Kreye, Bonding mechanism in cold gas spraying, *Acta Mater* 51 (2003) 4379–4394. [https://doi.org/10.1016/S1359-6454\(03\)00274-X](https://doi.org/10.1016/S1359-6454(03)00274-X).
- [8] T. Hussain, D.G. McCartney, P.H. Shipway, D. Zhang, Bonding mechanisms in cold spraying: The contributions of metallurgical and mechanical components, *Journal of Thermal Spray Technology* 18 (2009) 364–379. <https://doi.org/10.1007/s11666-009-9298-1>.
- [9] L.I. Pérez-Andrade, F. Gärtner, M. Villa-Vidaller, T. Klassen, J. Muñoz-Saldaña, J.M. Alvarado-Orozco, Optimization of Inconel 718 thick deposits by cold spray processing and annealing, *Surf Coat Technol* 378 (2019). <https://doi.org/10.1016/j.surfcoat.2019.124997>.
- [10] R. Ortiz-Fernandez, B. Jodoin, Hybrid Additive Manufacturing Technology: Induction Heating Cold Spray—Part I: Fundamentals of Deposition Process, *Journal of Thermal Spray Technology* 29 (2020) 684–699. <https://doi.org/10.1007/s11666-020-01005-w>.
- [11] W. Wong, E. Irissou, P. Vo, M. Sone, F. Bernier, J.G. Legoux, H. Fukunuma, S. Yue, Cold spray forming of Inconel 718, *Journal of Thermal Spray Technology* 22 (2013) 413–421. <https://doi.org/10.1007/s11666-012-9827-1>.
- [12] W. Ma, Y. Xie, C. Chen, H. Fukunuma, J. Wang, Z. Ren, R. Huang, Microstructural and mechanical properties of high-performance Inconel 718 alloy by cold spraying, *J Alloys Compd* 792 (2019) 456–467. <https://doi.org/10.1016/j.jallcom.2019.04.045>.

- [13] W. Sun, A.W.Y. Tan, A. Bhowmik, I. Marinescu, X. Song, W. Zhai, F. Li, E. Liu, Deposition characteristics of cold sprayed Inconel 718 particles on Inconel 718 substrates with different surface conditions, *Materials Science and Engineering: A* 720 (2018) 75–84. <https://doi.org/10.1016/j.msea.2018.02.059>.
- [14] R. Singh, S. Schrufer, S. Wilson, J. Gibmeier, R. Vassen, Influence of coating thickness on residual stress and adhesion-strength of cold-sprayed Inconel 718 coatings, *Surf Coat Technol* 350 (2018) 64–73. <https://doi.org/10.1016/j.surfcoat.2018.06.080>.
- [15] R. Singh, K.H. Rauwald, E. Wessel, G. Mauer, S. Schrufer, A. Barth, S. Wilson, R. Vassen, Effects of substrate roughness and spray-angle on deposition behavior of cold-sprayed Inconel 718, *Surf Coat Technol* 319 (2017) 249–259. <https://doi.org/10.1016/j.surfcoat.2017.03.072>.
- [16] S. Bagherifard, G. Roscioli, M.V. Zuccoli, M. Hadi, G. D’Elia, A.G. Demir, B. Previtali, J. Kondás, M. Guagliano, Cold Spray Deposition of Freestanding Inconel Samples and Comparative Analysis with Selective Laser Melting, *Journal of Thermal Spray Technology* 26 (2017) 1517–1526. <https://doi.org/10.1007/s11666-017-0572-3>.
- [17] R. Ortiz-Fernandez, S. Imbriglio, R. Chromik, B. Jodoin, The Role of Substrate Preheating on the Adhesion Strength of Cold-Sprayed Soft Particles on Hard Substrates, *Journal of Thermal Spray Technology* 30 (2021) 655–667. <https://doi.org/10.1007/s11666-020-01148-w>.
- [18] R. Ortiz-Fernandez, B. Jodoin, Toward Efficient Cold Spraying of Inconel 718: Understanding the Influence of Coating and Particle Impact Temperatures, *Journal of Thermal Spray Technology* 32 (2023) 188–207. <https://doi.org/10.1007/s11666-022-01490-1>.
- [19] Y. Xie, M.P. Planche, R. Raelison, H. Liao, X. Suo, P. Hervé, Effect of Substrate Preheating on Adhesive Strength of SS 316L Cold Spray Coatings, *Journal of Thermal Spray Technology* 25 (2016) 123–130. <https://doi.org/10.1007/s11666-015-0312-5>.
- [20] R.F. Vaz, A. Garfias, V. Albaladejo, J. Sanchez, I.G. Cano, A Review of Advances in Cold Spray Additive Manufacturing, *Coatings* 13 (2023). <https://doi.org/10.3390/coatings13020267>.
- [21] J.C. Franco-Correa, E. Martínez-Franco, J.M. Alvarado-Orozco, L.A. Cáceres-Díaz, D.G. Espinosa-Arbelaez, J.A. Villada, Effect of Conventional Heat Treatments on the Microstructure and Microhardness of IN718 Obtained by Wrought and Additive Manufacturing, *J Mater Eng Perform* 30 (2021) 7035–7045. <https://doi.org/10.1007/s11665-021-06138-9>.
- [22] M.R. Rokni, S.R. Nutt, C.A. Widener, V.K. Champagne, R.H. Hrabé, Review of Relationship Between Particle Deformation, Coating Microstructure, and Properties in High-Pressure Cold Spray, *Journal of Thermal Spray Technology* 26 (2017) 1308–1355. <https://doi.org/10.1007/s11666-017-0575-0>.
- [23] J.G. Legoux, E. Irissou, C. Moreau, Effect of substrate temperature on the formation mechanism of cold-sprayed aluminum, zinc and tin coatings, *Journal of*

Thermal Spray Technology 16 (2007) 619–626. <https://doi.org/10.1007/s11666-007-9091-y>.

[24] A. Balasundaram, A. Bisht, M. Anantharaman, S.R. Bakshi, M. Kamaraj, Effect of Double-Aging Heat Treatment on Microstructure and Tribological Behaviour of Cold Sprayed IN718 Coating, *Metals and Materials International* 30 (2024) 483–500. <https://doi.org/10.1007/s12540-023-01507-6>.

[25] X. Li, J.J. Shi, C.H. Wang, G.H. Cao, A.M. Russell, Z.J. Zhou, C.P. Li, G.F. Chen, Effect of heat treatment on microstructure evolution of Inconel 718 alloy fabricated by selective laser melting, *J Alloys Compd* 764 (2018) 639–649. <https://doi.org/10.1016/j.jallcom.2018.06.112>.

[26] X.K. Suo, M. Yu, W.Y. Li, M.P. Planche, H.L. Liao, Effect of substrate preheating on bonding strength of cold-sprayed Mg coatings, *Journal of Thermal Spray Technology* 21 (2012) 1091–1098. <https://doi.org/10.1007/s11666-012-9803-9>.

[27] A.M. Ralls, M. Daroonparvar, M. John, S. Sikdar, P.L. Menezes, Solid-State Cold Spray Additive Manufacturing of Ni-Based Superalloys: Processing–Microstructure–Property Relationships, *Materials* 16 (2023). <https://doi.org/10.3390/ma16072765>.

[28] A. Bruera, P. Puddu, S. Theimer, M. Villa-Vidaller, A. List, G. Bolelli, F. Gärtner, T. Klassen, L. Lusvarghi, Adhesion of cold sprayed soft coatings: Effect of substrate roughness and hardness, *Surf Coat Technol* 466 (2023). <https://doi.org/10.1016/j.surfcoat.2023.129651>.

[29] W. Li, C. Cao, S. Yin, Solid-state cold spraying of Ti and its alloys: A literature review, *Prog Mater Sci* 110 (2020). <https://doi.org/10.1016/j.pmatsci.2019.100633>.

[30] A. Nastic, B. Jodoin, D. Poirier, J.G. Legoux, Particle temperature effect in cold spray: A study of soft particle deposition on hard substrate, *Surf Coat Technol* 406 (2021). <https://doi.org/10.1016/j.surfcoat.2020.126735>.

[31] Y. Watanabe, C. Yoshida, K. Atsumi, M. Yamada, M. Fukumoto, Influence of Substrate Temperature on Adhesion Strength of Cold-Sprayed Coatings, *Journal of Thermal Spray Technology* 24 (2014) 86–91. <https://doi.org/10.1007/s11666-014-0165-3>.

[32] C.W. Ziemian, M.M. Sharma, B.D. Bouffard, T. Nissley, T.J. Eden, Effect of substrate surface roughening and cold spray coating on the fatigue life of AA2024 specimens, *Mater Des* 54 (2014) 212–221. <https://doi.org/10.1016/j.matdes.2013.08.061>.

[33] J. Vlcek, L. Gimeno, H. Huber, E. Lugscheider, A systematic approach to material eligibility for the cold-spray process, *Journal of Thermal Spray Technology* 14 (2005) 125–133. <https://doi.org/10.1361/10599630522738>.

[34] G. Bae, Y. Xiong, S. Kumar, K. Kang, C. Lee, General aspects of interface bonding in kinetic sprayed coatings, *Acta Mater* 56 (2008) 4858–4868. <https://doi.org/10.1016/j.actamat.2008.06.003>.

[35] K. Ogawa, D. Seo, Repair of Turbine Blades Using Cold Spray Technique, *InTechOpen*, 2011. <https://doi.org/10.5772/664>.

- [36] V. Luzin, K. Spencer, M.X. Zhang, Residual stress and thermo-mechanical properties of cold spray metal coatings, *Acta Mater* 59 (2011) 1259–1270. <https://doi.org/10.1016/j.actamat.2010.10.058>.
- [37] W. Li, C. Cao, G. Wang, F. Wang, Y. Xu, X. Yang, ‘Cold spray +’ as a new hybrid additive manufacturing technology: a literature review, *Science and Technology of Welding and Joining* 24 (2019) 420–445. <https://doi.org/10.1080/13621718.2019.1603851>.
- [38] X. Luo, G.M. Smith, S. Sampath, On the Interplay Between Adhesion Strength and Tensile Properties of Thermal Spray Coated Laminates—Part I: High Velocity Thermal Spray Coatings, *Journal of Thermal Spray Technology* 27 (2018) 296–307. <https://doi.org/10.1007/s11666-018-0695-1>.
- [39] W. Sun, A. Bhowmik, A.W.Y. Tan, R. Li, F. Xue, I. Marinescu, E. Liu, Improving microstructural and mechanical characteristics of cold-sprayed Inconel 718 deposits via local induction heat treatment, *J Alloys Compd* 797 (2019) 1268–1279. <https://doi.org/10.1016/j.jallcom.2019.05.099>.

Chapter 6: Results & Discussion

Manufacturing and properties characterization of Ti patterned coatings for water electrolyzers by masked CSAM

This chapter evaluates the fabrication of Ti patterned parts using a masked CSAM deposition strategy for their application as bipolar plates (BPPs) for Proton Exchange Membrane (PEM) electrolyzers. The dimensional and microstructural characteristics of pin fins were assessed. Additionally, the performance of both Ti parts for its application in PEM electrolyzers was evaluated in terms of corrosion resistance and interfacial contact resistance (ICR).

The results demonstrated that the masked CSAM technology allowed precise control and customization of the dimensions of the 3D-printed pin fins. Additionally, the performance of both Ti parts for its application in PEM electrolyzers was evaluated in terms of corrosion resistance and interfacial contact resistance (ICR). The results suggest that the masked CSAM technology shows great potential for the fabrication of Ti BPPs.

Chapter 6: Manufacturing and properties characterization of Ti patterned coatings for water electrolyzers by masked CSAM

6.1 Introduction

Hydrogen is well known to serve as a carrier gas and has emerged as a highly effective and promising energy storage method. Due to its scarcity in its elemental state, its production usually needs an energy input. As a result, it is primarily considered a secondary energy carrier, derived from either renewable sources (such as wind, solar, geothermal) or non-renewable sources (such as coal, gas, and nuclear). The ability to store hydrogen as a portable and accessible fuel represents a significant advancement in the field of energy sustainability, addressing one of the worlds' key environmental challenges: meeting the increasing demands of electricity generation [1,2]. Today, the cheapest way to produce it is by means of steam reforming of natural gas or gasification of fossil fuels, both methods leading to a considerable production of CO₂ as a by-product [3,4].

A promising alternative method for hydrogen production is through the electrochemical splitting of water with electrolyzers. This technology is powered by renewable sources, wherein electrical energy is applied to promote a reaction that separates H₂O molecules into H₂ and O₂. The resulting purity of H₂ from this process is typically close to 100% [4–6]. There are three main types of water electrolysis technologies: alkaline water electrolyzers (AWE), polymer electrolyte membrane (PEM), and solid oxide electrolysis cells (SOEC), currently being the AWE the most well established and mature technology [7]. The operation principle of these electrolyzers is different for each of them. Particularly, the PEM water electrolyzers are composed of several parts: two terminal end plates, bipolar plates (BPP), gas diffusion layers (GDL) and a PEM placed at the center, as shown in Figure 6.1.

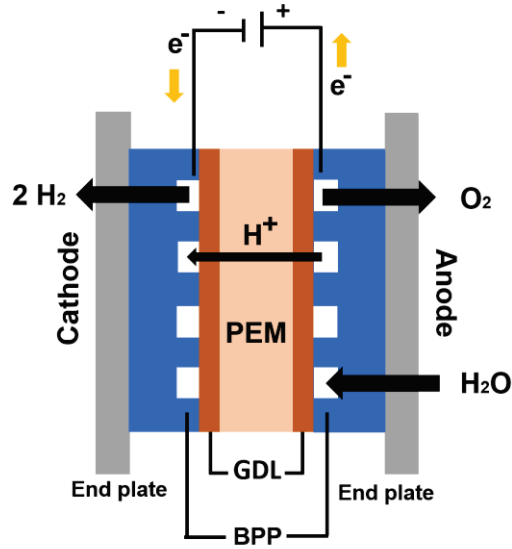
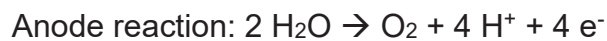


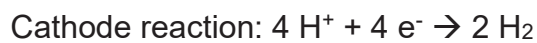
Figure 6.1. PEM electrolyzer cell components.

In PEM electrolyzer cells, water is introduced into the anodic part of the cell, where it is uniformly distributed by the anodic BPP and comes in contact with the GDL and the PEM. Upon applying an electric current to the cell, a potential difference is established, acting as the driving force for a redox reaction to occur. At the anode, the oxidation of water takes place, while at the cathode the reduction of protons occurs to form hydrogen gas. These reactions are described as follows (Equation 6.1 and 6.2):

Equation 6.1



Equation 6.2



The proton exchange membrane, usually made of a thin layer of polymer membrane of perfluorosulfonic acid (PFSA) acts as a selective barrier, allowing only for protons (H^+) to flow from the anode to the cathode. The electrons are directed through an external circuit and create an electric current. At the cathode, the protons and the electrons recombine to form H_2 gas [7].

While the potential of producing green hydrogen through PEM water electrolyzers is promising, their use in industry and large-scale production has been limited by their high costs. Specifically, BPPs contribute for 80% of the cell's weight, and account for approximately 40 – 60% of its total cost. As a result, there

is a need to develop new BPPs produced with low-cost, lightweight, and easily manufacturable materials while ensuring they possess the specific properties required for an efficient operation [8,9].

The BPPs are required to have characteristics that are highly restraining and might be contradictory, such as to be chemically and mechanically stable, while being resistant to corrosion and electrically conductive [7–9]. The previous target of the U.S. Department of Energy (DOE) initiative for 2020 determined the technical parameters required for the BPP materials, including an interfacial contact resistance (ICR) $< 10 \text{ m}\Omega \text{ cm}^2$ and a corrosion resistance $I_{\text{corr}} < 1 \text{ }\mu\text{A}$.

Currently, titanium and stainless steels (SS) are considered the most promising metals for the production of cost-effective BPPs, due to their excellent mechanical properties, resistance to corrosion, and suitability for large-scale production. However, these materials also present certain challenges that need to be addressed. Ti is notoriously difficult to machine, making manufacturing through the BPPs conventional manufacturing methods such as machining or stamping difficult [10]. Therefore, other manufacturing methods such as additive manufacturing offer a potential solution. On the other hand, SS is susceptible to corrosion in acidic media, particularly at anodic potentials. Consequently, SS BPPs are usually coated with a more noble material such as Nb or Au [11–14].

Some studies investigate the possibility to manufacture metallic BPPs with additive manufacturing, however there is still a need to explore and optimize the different technologies for a cost-effective production. For instance, Yang et al. [15] successfully demonstrated the viability of manufacturing a cathode SS 316L plate using selective laser melting (SLM), indicating that additive manufacturing (AM) could be a rapid and cost-effective approach to develop BPPs. Additionally, Yang et al. [16] conducted further research on the aforementioned BPPs, coating them with a protective layer of Au through electroplating. This additional step allowed the BPPs to withstand the aggressive acidic conditions to be implemented on both the anodic and cathodic sides of the electrolyzer cell. Furthermore, Huang et al. [17] also utilized selective laser melting (SLM) to manufacture bipolar plates using SS 316L material. The authors fabricated the BPPs with various flow-fields and evaluated their efficiencies through computational fluid dynamics (CFD) simulations, concluding that the BPPs

produced by SLM showed high forming quality. On the other hand, Sánchez-Molina et al. [18] manufactured SS 316L BPPs by powder bed fusion (PBF), and compared their properties with bipolar plates manufactured by conventional machining processes, both parts showed similar characteristics in ex-situ corrosion tests, exhibiting PBF as a potential AM technology for the production of BPPs.

Up to date, no other AM technologies have been used for the manufacturing of BPPs and the current studies in the literature focus mainly on specific materials, such as SS 316L. Therefore, in this study a methodology to manufacture Ti BPPs with cold spray additive manufacturing (CSAM) is developed. CSAM is a solid-state process that involves propelling a powder feedstock inside a gun using preheated, compressed, supersonic gas (N_2 or H_2) at high velocities (300 – 1200 m/s) through a convergent-divergent (de Laval) nozzle. When the accelerated powder impacts a substrate with sufficient kinetic energy, it undergoes plastic deformation at the point of impact, leading to particle adhesion. With this technology, bipolar plates of different materials can be built (such as Cu, Al, SS 316L, and Ti) with customized flow-fields. Since it is a bottom up approach and a solid-state technology, problems such as machinability and undesired phases and oxidation in the plates are avoided.

The objective of this work is to develop a manufacturing process for Ti patterned parts using masked CSAM and to evaluate the dimensional and microstructural characteristics of irregular (Ti-I) and spherical (Ti-S) parts. Additionally, this study evaluates the behavior and performance of the CSAM Ti deposits in aggressive environments, focusing on their corrosion resistance in acidic media and interfacial contact resistance (ICR) as required for the commercial BPPs used in PEM electrolyzers.

6.2 Materials and Methods

6.2.1 Feedstock powder characterization

Two titanium powders with notable cost differences are investigated in this work: a low-cost irregular Ti powder (CNPC powder) and a spherical Ti powder (AP&C). In this study both powders are labeled as Ti-I and Ti-S, respectively.

The particle morphology of each powder was observed in a Phenom ProX Desktop (Eindhoven, the Netherlands) scanning electron microscope (SEM). The powder size distribution was determined with a laser diffraction particle sizing analyzer LS 13 320 Model Dry Powder System (CA, USA).

6.2.2 Bipolar plates manufacturing and process parameters

Both powders were sprayed with the high pressure CGS equipment Plasma Giken PCS 100 (Saitama, Japan) on grit-blasted steel substrates with a 1 mm thickness. Both Ti-I and Ti-S were sprayed with the following the optimized CS parameters for this material: 6.5 MPa, 1000 °C, and 25 mm SoD.

The BPPs were fabricated using the masked CSAM process detailed in Chapter 3 section 3.3.4, and shown in Figure 6.2, using a laser-cut steel mesh masks with different patterns: big squares (mesh with squared holes 3 x 3 mm), small squares (mesh with squared holes 1.5 x 1.5 mm), rows, and cylinders.

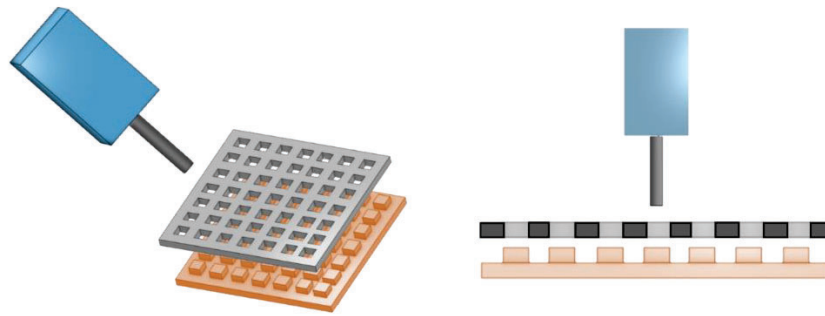


Figure 6.2. CSAM masking process.

For the manufacturing of the BPPs, a substrate was first coated by spraying a base layer that served as the bottom surface of the flow-fields. Then, a mesh was attached to the substrate plate for a second spray, which built up the pin fins forming the flow-field of the plates. Finally, the mask was removed to obtain the finished BPPs. These first two steps are illustrated in Figure 6.3.

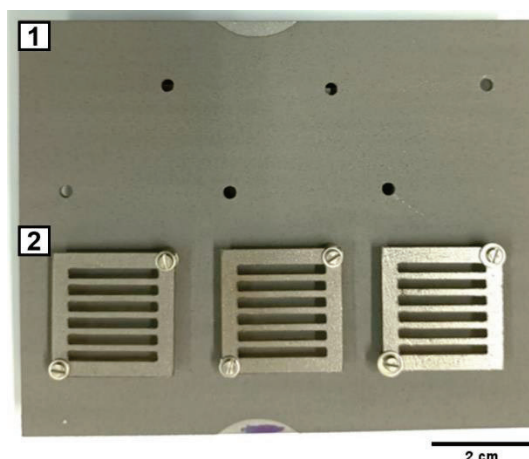


Figure 6.3. Masked CSAM process steps: (1) Ti base layer and (2) mesh setup

6.2.3 Microstructure, mechanical properties & adhesion

The microstructural characterization and the mechanical properties of the BPPs with both powders were determined. The metallographic preparation of all samples was completed according to the standard ASTM E1920-03(2014). The cross-sectional surface of the polished samples was analyzed with the optical microscope (OM) Leica DMI5000M (Wetzlar, Germany). The image analysis software ImageJ (v. 153e) was used to determine the mean porosity according to the standard ASTM E2109-01(2014). The profilometer SJ-210 Mitutoyo (Kawasaki, Japan) was used to obtain the superficial roughness of the BPPs. The Vickers microhardness was calculated from 10 indentations for each sample, following standard ASTM E384-17 with 0.2 kgF using Shimadzu HV-2/HMV-2T (Tokyo, Japan) equipment.

The adhesion of the deposits with the substrate was tested with equipment SERVOSIS ME 402-10 (Madrid, Spain) following the ASTM C633-13 standard. Three samples of each material were evaluated by adhering them to a grit-blasted counterpart with the adhesive HTK Ultrabond 100 (Hamburg, Germany); a tensile test at a rate of 0.01 mm/s was performed until failure.

6.2.4 Bipolar plates profile & 3D topography

To evaluate the dimensions and superficial characteristics of the different patterns, the profilometry of the samples, along with their 3D topography was evaluated with confocal microscope Sensofar Plu2300 (Catalonia, Spain).

6.2.5 Electrochemical experiments

The corrosion resistance of sprayed materials was tested by subjecting a 1 cm² sample to electrochemical measurements under similar conditions to those experimented in the anodic side of an operating PEM electrolyzer. The experiments were performed in a 0.5 M H₂SO₄ solution with oxygen saturation. To assess the corrosion behavior, polarization curves were recorded using a VSP potentiometer. The polarization curves were generated by varying the potential from -100 to 2400 mV compared to the open circuit potential (E_{OCP}). Subsequently, Tafel fit extrapolation method was evaluated with EC-Lab software (V10.44) to determine E_{corr} (corrosion potential) and I_{corr} (corrosion current). These potentials were chosen to show the corrosion properties of both powders within the potential range of an operating PEM electrolyzer.

To assess the stability of the materials, they were immersed in a 0.5 M H₂SO₄ solution and subjected to a constant potential of 2 V for 100 hours. The E_{corr} and I_{corr} were measured both before and after the stabilization test. Subsequently, all samples evaluated after the stability test are referred to as "post-mortem" samples.

6.2.6 Interfacial contact resistance

The powders were cold-sprayed onto both sides of a 9 cm² steel substrate with 1 mm of thickness. The sprayed samples were subsequently grinded on both sides with a 120 SiC paper until 1 mm of Ti coating remained on each side. To determine the interfacial contact resistance (ICR), the approach proposed by Wang et al. [19] based on the Davies' method [20] was employed. In this modified method, the ICR was measured in two setups: first, the Ti sample was placed between two pieces of Toray conductive carbon paper and two copper plates, and second, only one piece of Toray paper was inserted between the copper plates. The final ICR was calculated with the ICR difference of both setups.

For this, a compaction force ranging from 0.25 to 2 kN/cm² was applied using the SERVOSIS ME 402-10 (Madrid, Spain) equipment. For each setup and compaction force, a current of 1 A was passed (between the copper plates) using the DC power supply LABPS1503 (Gavere, Belgium). The voltage drop across

the system was measured using the HP 3458A multimeter and calculated employing Ohm's law equation (3).

Equation 6.3

$$R = \frac{VA_s}{I}$$

The ICR was measured before and after the post-mortem experiment. For more details see Chapter 3 section 3.4.2.12.

6.3 Results and Discussion

6.3.1 Feedstock powder

The selection of the feedstock powder in the CS process is of vital importance, as it not only affects the properties of the final deposit, but also has a great influence on the total cost of the process [21]. In addition, the morphology and particle size distribution of the powders are key factors influencing the deposition efficiency and the final quality of the coatings. Figure 6.4 and Table 6.1 show the SEM micrographs, as well as the mean particle size of both powders, respectively. The SEM micrographs exhibit the morphology for both powders. As expected, powder Ti-I exhibited irregular particles, while powder Ti-S showed spherical particles. These images also show the variation of the particle sizes. Despite both powders having a similar mean particle size, Ti-I presented a broader size distribution compared to Ti-S, which could impact the shape of the deposits due to the deflection of large particles with the mesh.

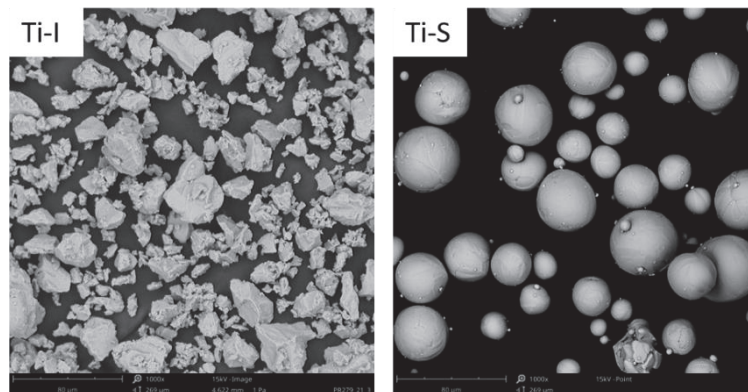


Figure 6.4. SEM micrographs of the powders.

Table 6.1. Mean particle size of the feedstock powders.

Powder	Shape	Mean Particle Size (μm)	d10 (μm)	d90 (μm)
Ti-I	Irregular	40.1 ± 2.8	9.7 ± 0.8	89.5 ± 6.4
Ti-S	Spherical	36.2 ± 2.2	20.8 ± 3.1	56.4 ± 4.4

Some studies have focused on evaluating the effects of powder morphology on coating properties such as porosity, microhardness, mechanical properties and deposition efficiency [22,23]. Vaz et al. [22] evaluated the properties of SS 316L CS coatings sprayed with different powders under the same conditions. Their findings indicated that there is no distinct advantage to using spherical powder over irregular powder in terms of coating quality, mechanical properties, resistance to corrosion, and resistance to abrasive conditions. Furthermore, Wong et al. [23] investigated the influence of different morphologies of pure Ti powder on coating properties. Although their results demonstrated that spherical powder exhibited the highest deposition efficiency, the irregular powder showed similar porosity values to those of the spherical powder. Consequently, spraying irregular powders can produce coatings with characteristics very similar to those of spherical powders under the optimal spraying conditions, with the added advantage of being more cost-effective.

6.3.2 Bipolar plates profile & 3D topography

One of the major problems of the large-scale production of PEM electrolyzers is the high costs of the BPPs. Since these plates require a material that can withstand aggressive acidic conditions, while being able to be electrically conductive, only a few materials are good candidates [4]. In general, metallic BPPs are commonly produced through methods such as stamping, hydroforming, and milling [24]. Nonetheless, these processes further limit the range of materials that can be effectively used, including titanium, due to its limited ductility at room temperature [25]. This limitation affects the accurate production of BPP with flow flined channels in the range of hundreds of microns. As mentioned before, there are only a few studies available in the literature regarding the additive manufacturing of BPPs, and none of them specifically explore titanium.

Figure 6.5 shows the resulting Ti patterned surfaces produced by CSAM that correspond to the flow field channels of a BPP. As previously indicated, four different patterns were investigated in this study starting from squared flow-fields of different dimensions (Figures 6.5 A-B), up to other patterns composed of rows or cylinders (Figures 6.5 C-D).

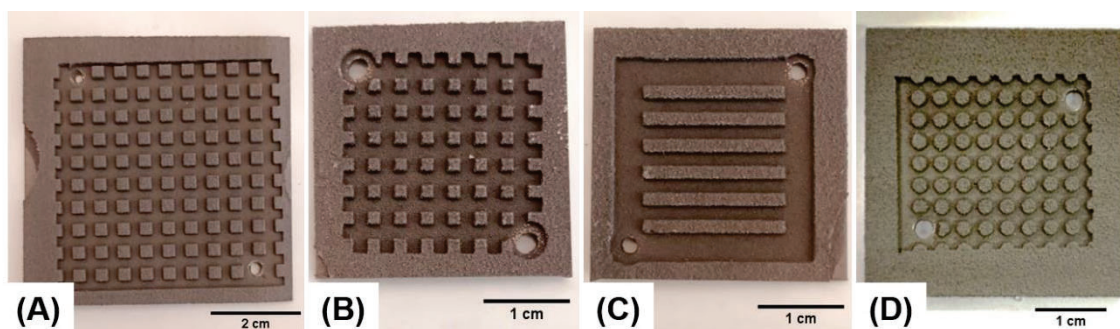


Figure 6.5. CSAM BPPs with different flow-field patterns. (A) big squares, (B) small squares, (C) rows, (D) cylinders.

The importance of the accurate manufacturing of the flow field channels lies on the crucial role that the design of the flow-field plays in optimizing the operation efficiency of the PEM electrolyzers. Particularly, the BPPs not only act as a conductive and support component of the PEM electrolyzers but they should distribute and maintain a uniform flow throughout its surface. Achieving a uniform flow helps to reduce the internal cell resistance and to prevent the risk of localized corrosion [26]. For this reason, BPPs with several patterns and sizes were sprayed in this work.

In addition to the flow-field design, achieving homogeneity in the 3D printed pins is essential to maintain an optimal contact with the gas diffusion layers, thereby minimizing the interfacial contact resistance and ensuring a uniform pressure in the cell [27]. To assess the homogeneity of the Ti deposits by CSAM, the 3D topography and the profile characteristics of the pins were evaluated using confocal microscopy. Figure 6.6 shows the flow-field dimensions exhibited by the 3D topography evaluation. Overall, the pins were uniformly distributed with similar heights, regardless of the pattern. However, it was observed that, in all cases, the pins tended to grow exhibiting a pyramid shape. This phenomenon is a characteristic of the CSAM process, attributed to the velocity profile of the

particles during the deposition; the particles in the core achieve greater velocity, promoting more deposition in the center of the jet than in its periphery [28].

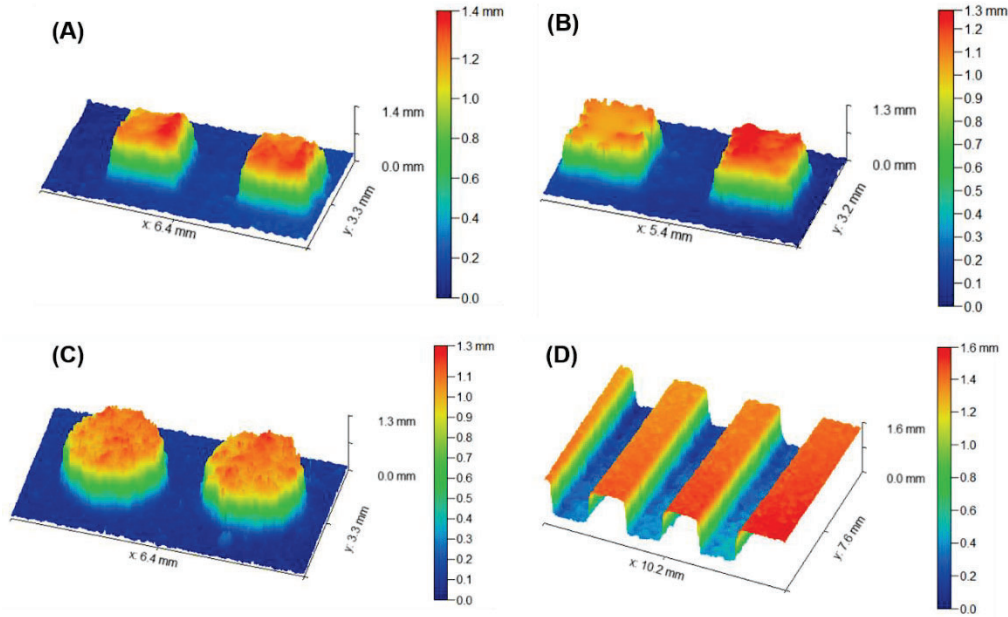


Figure 6.6. 3D topography of different CSAM BPPs patterns. (A) Ti-S small squares, (B) Ti-I small squares, (C) Ti-I cylinders, (D) Ti-S rows.

In the Figures 6.7 and 6.8 the profiles of the Ti patterned coatings produced with both powders (Ti-I and Ti-S) are shown with their corresponding microstructures, using squared patterns of two distinct dimensions (3 x 3 mm and 1.5 x 1.5 mm, respectively).

In the case of the 3 x 3 mm pattern, the pin fins of both powders were coated with an identical number of layers (Figure 6.7) in order to study the effect of the deposition efficiency of the powder in the final characteristics of the deposit. As observed in Figure 6.7, squared pin fins of big dimensions were obtained using this pattern. Despite being sprayed with the same layers, powder Ti-S was shown to almost double the height of powder Ti-I. This difference is attributed to their distinct morphologies; as mentioned before, spherical powders are known to have a higher deposition efficiency than irregular powders [23,29]. Therefore, under the same parameters, the morphology of the powder directly influences the total height of the Ti 3D coatings.

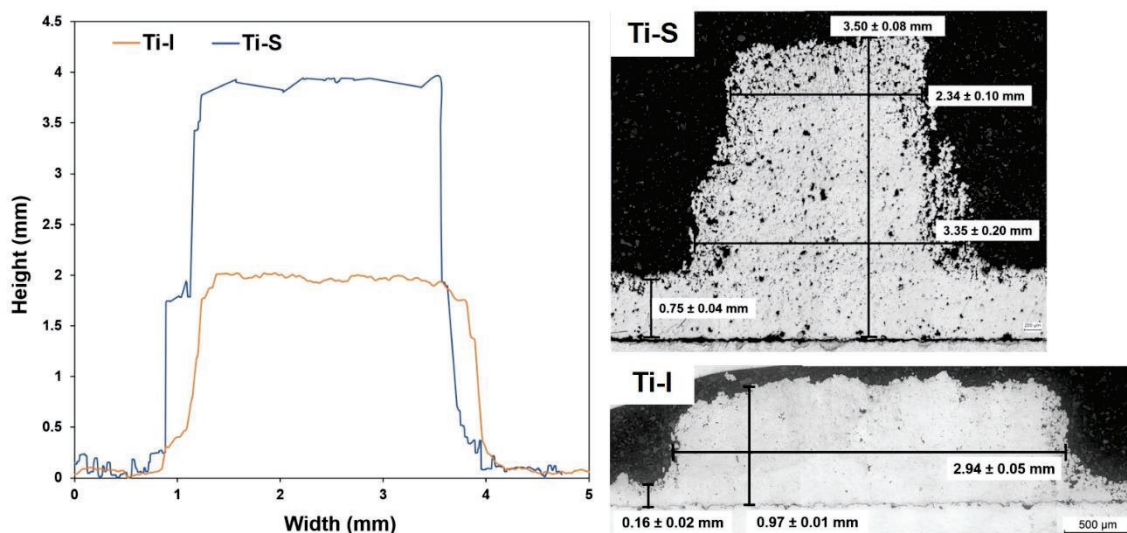


Figure 6.7. Profiles and cross-sectional optical microscope (OM) surface images of the 3D big squared patterns of the CSAM BPPs.

Figure 6.8 exhibits the 3D profiles of the Ti coatings produced with a 1.5 x 1.5 mm pattern. In this case, number of deposition layer adjustments were made to attain a height comparable to a commercial standard BPP. The profiles of the 3D coatings (Figure 6.8) revealed that the width and height of the pin fins can be tailored with accuracy based on the dimensions of the inverse pattern cut in the mask.

In the same way, the cross-sectional microstructure of the squared patterns of powders Ti-I and Ti-S are also shown in Figures 6.7-6.8. Overall, it was observed that the width of all the samples was consistent with the dimensions of the mesh. For the big squares (Figure 6.8 A-B), a mesh with voids of 3 x 3 mm was used, leading to a width of the pins of 2.94 ± 0.05 mm for Ti-I, and 2.34 ± 0.10 mm for Ti-S. Furthermore, the small squares (Figure 6.8 C-D) showed similar results; for the mesh with squared voids of 1.5 x 1.5 mm, the pins showed a width of 1.26 ± 0.05 mm (Ti-I) and 1.48 ± 0.10 mm (Ti-S). This revealed that even though there was some interference of the mesh with the particle deposition, the pins grew with similar dimensions as the voids in the masks. Consistently with the 3D topography, the tendency of all powders to form pins with a pyramid shape was also observed.

Moreover, the sprayed Ti deposits showed a higher superficial roughness than the commercial BPP. This rough surface is very common in CSAM deposits due to the impact of the particles. Hence, to ensure adequate contact of the BPPs

inside the electrolyzer cell, post-process step to reduce the superficial roughness is recommended.

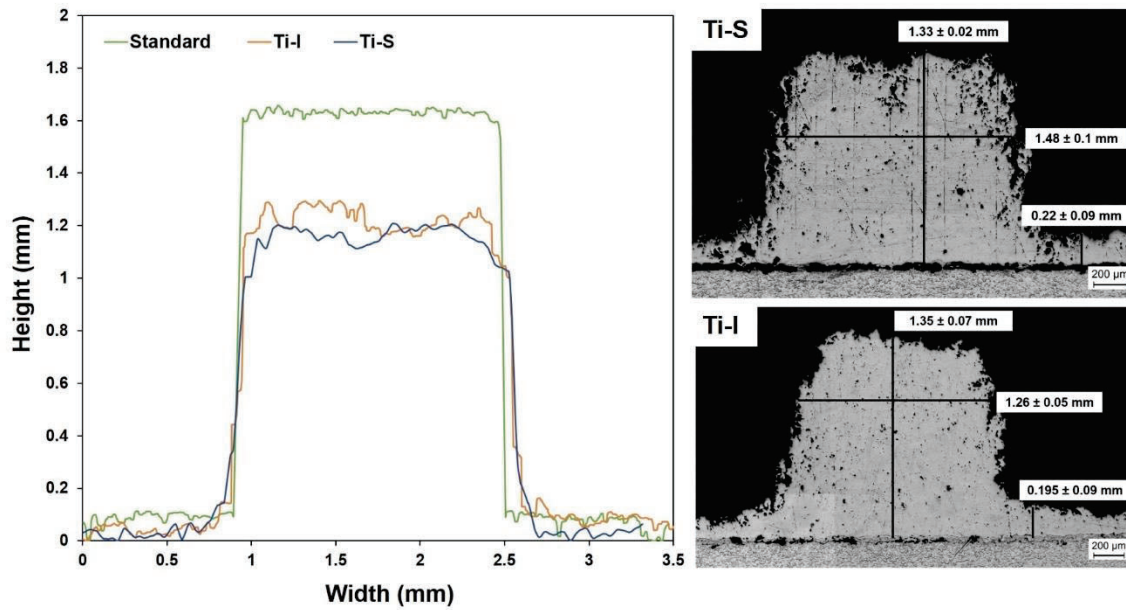


Figure 6.8. Profiles and cross-sectional optical microscope (OM) surface images of the 3D small squared patterns of the CSAM BPPs compared to a commercial standard.

6.3.3 Microstructure, mechanical properties & adhesion

In addition to the dimensional characteristics of the BPPs, the evaluation of their microstructure is very important, as intrinsic defects like cracks or pores may be present. To minimize these defects, the selected spraying parameters need to be optimized. Although CS is a suitable technology to process Ti, the literature reports challenges in obtaining dense parts, with porosities reported to be as high as 20% [30].

Table 6.2 shows the microstructural results for porosity, roughness, microhardness, and adhesion strength of the Ti-S and Ti-I small squares. In particular, the powder Ti-S presented a slightly higher porosity ($6 \pm 1\%$) compared to the irregular powder ($4 \pm 1\%$). These results are consistent with the work of Wong et al. [23] in which the porosity of several CS Ti coatings was evaluated based on powder morphology, resulting in porosity values of 3% and 5% for irregular and spherical powders, respectively. It is worth indicating that in all cases, a denser microstructure is exhibited in the center of the pins than on the edges. This may be attributed to the interference of the mesh with the in-flight particles, as well as to a lack of tampering effect of subsequent particles in these

walls. This phenomenon has also been observed in other works that studied the masked CSAM process [31,32]. For instance, Cormier et al. [32] characterized Al and SS 316L pyramidal fin arrays manufactured with masked CSAM. Their findings revealed that the Al fins presented a porosity distribution in which the core resulted denser than the exterior layers. However, the SS 316L fins exhibited a homogeneous porosity. The authors attributed this difference to the bonding characteristics of both powders; the core Al particles were more prone to compaction by the impact of the subsequent particles compared to SS 316L. In the same way, cold sprayed Ti coatings are well known to be sensitive to this tampering effect, typically Ti deposits exhibit a porosity distribution in the first layers tend to be denser compared to the external layers [30].

Table 6.2. Microstructural characteristics & adhesion of the small squares pin fins.

Sample	Porosity (%)	Roughness (Ra, Rz)	Microhardness (HV _{0.2})	Adhesion (MPa)
Ti-I	4 ± 1	(17 ± 2, 78 ± 6)	171 ± 17	59 ± 2
Ti-S	6 ± 1	(16 ± 4, 67 ± 9)	193 ± 23	45 ± 5

As mentioned before, both powders presented a high superficial roughness of Ra 17 ± 2 and Rz 78 ± 6 for Ti-I, and Ra 16 ± 4 and Rz 67 ± 9 for Ti-S. These values could affect negatively the conductivity needed in the cell due to a poor contact between the BPPs and the GDL. For this reason, a post-process step is recommended to ensure a close contact between all elements in the PEM electrolyzer stack.

Another significant aspect when manufacturing BPPs with CSAM is the adhesion of the patterned coatings to the substrate. An inadequate adhesion of the 3D pattern can impede an efficient functionality of the plates. The bonding strength between the sprayed powders and the substrate was evaluated, revealing that both of them exhibited cohesive failures at 59 ± 2 MPa for Ti-I, and 45 ± 5 MPa for Ti-S, indicating a proper bonding strength between the coating and the substrate.

In general terms, CSAM is an efficient method capable of processing titanium in its solid state, making it possible to produce BPPs with customized flow-fields within a few minutes and to overcome the challenges of other

traditional methods such as stamping or machining. The masked technology allowed to customize the size and shape of the flow fields by adjusting the quantity of layers sprayed and the patterns of the mesh.

6.3.4 Electrochemical experiments

To ensure a long-term durability and efficient functioning of the electrolyzer, a fundamental requisite for the BPPs is their inherent resistance to corrosion. In particular, the anodic side of the plate is subjected to an aggressive chemical acidic environment originating from the electrochemical reactions responsible for the splitting of the water molecules [4]. Only a limited number of materials have the characteristics to effectively operate at such conditions. Laedre et al. [4] studied the corrosion properties and ICR of non-coated materials at the conditions experienced in a PEM water electrolyzer. These materials included Mo, W, SS 316L, SS 304L, IN625, Nb, Ta, and Ti. This study revealed that, among these materials, Nb, Ta, and Ti demonstrated an excellent corrosion resistance. However, after prolonged polarizations their ICR was significantly increased. Langemann et al. [33] designed a set of experiments to determine candidate coating materials for SS 304 BPPs, based on their resistance to corrosion under the pH conditions found in an operating PEM water electrolyzer. It was found that under high potentials the pH value dropped significantly in the anode side of the electrolyzer. Under these conditions the authors proposed Au and TiN as coatings solutions for corrosion resistance enhancement, however even Au and TiN coated components revealed signs of corrosion after exposition to 0.5 M H₂SO₄ solution. Conversely, Lettenmeier et al. [34] coated SS BPPs with Ti by Vacuum Plasma Spraying (VPS) which was subsequently top-coated with Pt by magnetron sputtering Physical Vapor Deposition (PVD). The assessment of the Pt-coated BPPs in a commercial PEM electrolyzer for 1000 h revealed that the duplex Pt-Ti coatings fully protected the SS substrate, while achieving an excellent cell durability.

In this work, the CSAM Ti BPPs were tested as a basis for determining its resistance to corrosion without a top coating. A bulk Ti plate was also tested for comparative reasons. For this, corrosion measurements were performed with a three-electrode cell in the range potential of -0.1 V to 1.8 V vs Ag/AgCl, which is the potential range that can be found in an operating PEM electrolyzer cell.

Figure 6.9 shows the polarization curves recorded, while Table 6.3 shows the corrosion resistance results E_{corr} and I_{corr} .

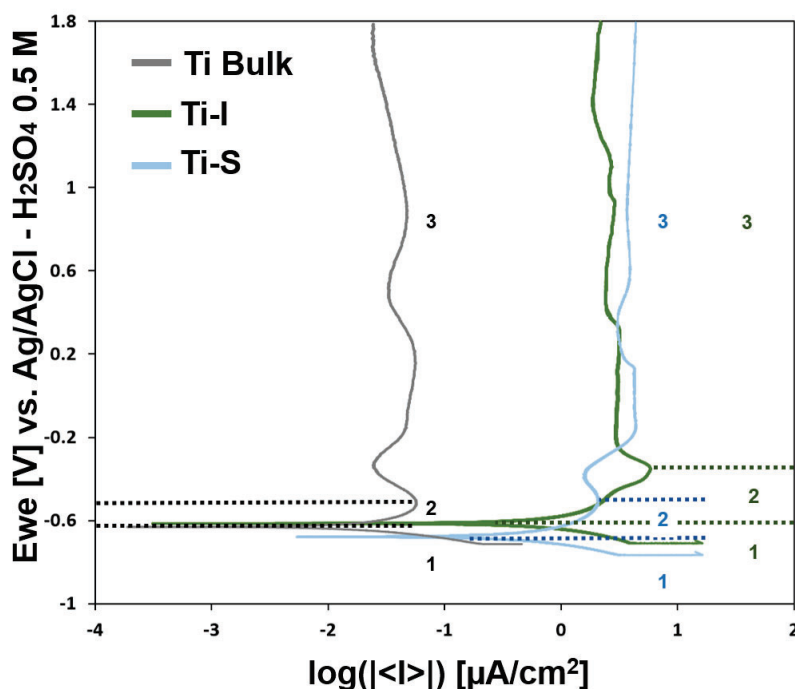


Figure 6.9. Polarization curves showing electrochemical stages (1) cathodic, (2) active zone, (3) passivation processes.

The polarization curves were recorded in the range potential of -0.1 V to 1.8 V vs Ag/AgCl to study the stability of the oxide film formed in the surface of the samples during the anodic corrosion. Of the three different zones typically observed for the corrosion processes (1. cathodic region, 2. active zone, and 3. passivation processes), the last two represent the anodic behavior of the samples [12].

All the tested samples showed an active zone (zone 2), representing the point at which the corrosion current reaches its maximum point before starting the passivation processes. Samples Ti-S and the Ti Bulk showed a subtle active peak, while the Ti-I exhibited a more prolonged active zone to higher current densities. Following the active zone, an oxide film began to form on the surface of all samples, inducing material passivation. This protective film caused a drop in the corrosion current, which remained stable until the potential reached 1.8 V. For some materials, during this passivation region (zone 3) the oxide film can break, causing a steep rise in the corrosion current, generating pitting corrosion [35]. None of the materials tested in this study exhibited this behavior, hence their

oxide films are stable enough within the operating potential range of a PEM electrolyzer.

As for the corrosion potential E_{corr} results, shown in Table 6.3, all samples exhibited similar values; -614 ± 9 mV for Ti-I, -665 ± 14 mV for Ti-S, and -640 ± 17 mV for the Ti Bulk. Similar corrosion current densities to those reported by Laedre et al. [4] for Ti plates were measured for the new Ti CSAM surfaces. Despite of this, a clear difference in the I_{corr} between the Ti CSAM powders and the Ti Bulk, with values of 250 ± 14 $\mu\text{A}/\text{cm}^2$ for Ti-I, 220 ± 10 $\mu\text{A}/\text{cm}^2$ for Ti-S, and 15 ± 4 $\mu\text{A}/\text{cm}^2$ for the Ti Bulk, is observed. As expected, the bulk exhibited a better resistance to corrosion than the manufactured BPPs by CSAM, which is attributed to the intrinsic defects within the microstructure of the CSAM BPPs. This behavior aligns with the work of Hussain et al. [35], who observed a correlation between the corrosion resistance of CS Ti and its porosity due to an increased surface area. Additionally, these values are consistent with the results obtained by Laedre et al. [4] on the potentiostatic tests; current densities of 170 $\mu\text{A}/\text{cm}^2$ for the Ti plates were reported.

Table 6.3. Corrosion resistance results.

Sample	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion rate (mm/yr)
Ti-I	-614 ± 9	250 ± 14	$2.2 \times 10^{-3} \pm 1.2 \times 10^{-4}$
Ti-S	-665 ± 14	220 ± 10	$1.9 \times 10^{-3} \pm 8.8 \times 10^{-5}$
Ti Bulk	-640 ± 17	15 ± 4	$1.3 \times 10^{-4} \pm 3.5 \times 10^{-5}$

To determine the stability of the Ti surfaces produced by CSAM, the samples were immersed in a 0.5 M H_2SO_4 solution and subjected to a constant potential of 2 V for 100 hours. Figure 6.10 shows the E_{corr} and I_{corr} results before and after the post-mortem tests for all the samples. In particular, the Ti-Bulk maintained its corrosion resistance values before and after the post-mortem tests. However, the two cold-sprayed Ti coatings showed higher higher E_{corr} and lower I_{corr} values, attributed to the formation of a stable and thick superficial oxide layer which is clearly affecting the electrochemical response of the surface and, which appearance is consistent with the behavior of both materials shown in the polarization curves in Figure 6.9. This stable protective layer allows for these Ti surfaces deposited by CSAM to perfectly withstand the aggressive conditions of

the electrolyzer cell without corroding however it might have a detrimental effect in their final electrical conductivities.

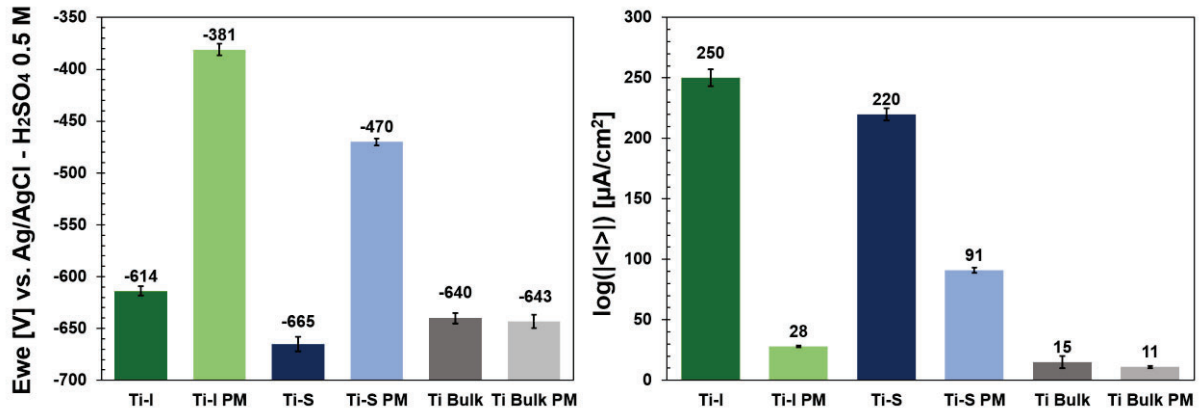


Figure 6.10. Corrosion resistance results before and after the post-mortem tests.

6.3.5 Interfacial contact resistance

Since PEM water electrolyzers require an energy input, the electrical resistance of the entire cell must be as low as possible for it to operate at its maximum efficiency. It has been shown that the most critical point for ohmic losses is at the point of contact between the BPP and the gas diffusion layer [36]. Therefore, the electrical resistance of the plates must be maintained as low as possible.

Figure 6.11 shows the results of the interfacial contact resistance tests at different compaction forces, based on the approach of Wang et al. [19]. The ICR values for all materials diminished as higher compaction pressures were applied, which is attributed to an enhancement in the superficial contact area. In general, the Ti Bulk demonstrated lower ICR values compared to both Ti patterned surfaces produced with Ti-I and Ti-S powders by CSAM. This shift is attributed to the inherent defects present in the CSAM process, such as pores and inter-particle boundaries. On the other hand, no important differences in the ICR values were found between the CS powders, which suggests that the electrical conductivity is determined by the nature of the material and not the morphology of the powder. Particularly, at a compaction pressure of 150 N/cm^2 ICR values of 42 ± 19 , 40 ± 13 , and $24 \pm 7 \text{ m}\Omega \cdot \text{cm}^2$ were obtained for Ti-I, Ti-S, and Ti Bulk, respectively; all of these values are consistent with other studies found in the literature [37,38]. Although these values are higher than what the DOE target sets

($\text{ICR} < 10 \text{ m}\Omega\cdot\text{cm}^2$ at 140 N/cm^2), CSAM is still a feasible process for the production of BPPs.

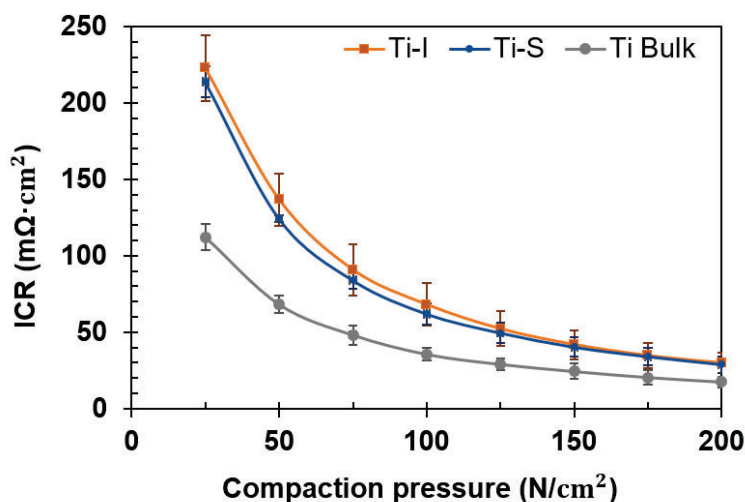


Figure 6.11. Interfacial contact resistance at different compaction pressures.

Another key property of the BPPs is their ability to maintain their electrically conductive properties at the same time as they maintain their resistance to corrosion. Figure 6.12 compares ICR values for all the samples before and after the 100 h post-mortem tests.

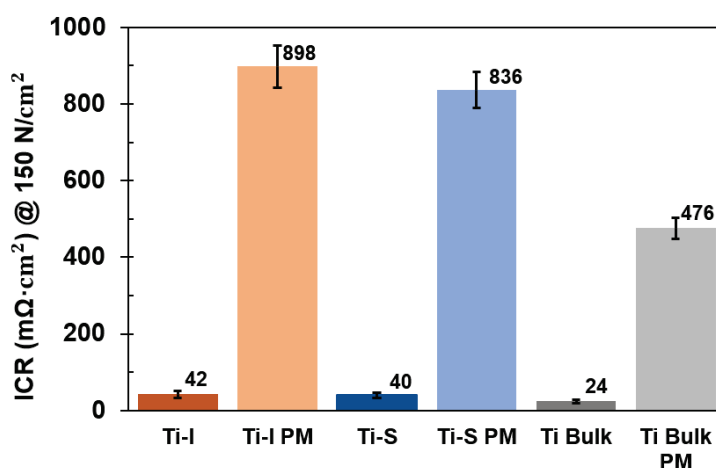


Figure 6.12. Interfacial contact resistance at 150 N/cm^2 before and after the post-mortem tests.

In all cases, after the post-mortem tests, there was a notable increase in the ICR, indicating that the oxide layer formed on the surface impeded the conductivity of the specimens after 100 h, in agreement with the results observed in the electrochemical tests. This effect was more evident in the CSAM samples,

in which the permeation of H_2SO_4 through the superficial pores may have contributed to a more pronounced corrosion, decreasing the electrical conductivity of the BPPs. In future studies, strategies to address the decrease of the ICR value for CSAM BPPs are encouraged, for example, the application of PVD coatings [14].

6.4 Conclusions

This study establishes an efficient methodology for the production of Bipolar Plates using the Cold Spray Additive Manufacturing technology with customized flow-fields within a few minutes, overcoming the challenges of other traditional methods such as stamping or machining. To summarize, the following key findings can be concluded:

- The masked CSAM process allowed to manufacture Ti BPPs with customized flow-fields within a few minutes. The produced pin fins that make of the flow-fields were homogeneous, presenting the same shape and size: the mesh with voids of 3 x 3 mm lead to a width of the pins of 2.94 ± 0.05 mm for Ti-I, and 2.34 ± 0.10 mm for Ti-S, while the mesh with squared voids of 1.5 x 1.5 mm, resulted in pins with a width of 1.26 ± 0.05 mm for Ti-I and 1.48 ± 0.10 mm for Ti-S.

- The CSAM Ti BPPs presented porosity values of $6 \pm 1\%$ and $4 \pm 1\%$ for powders Ti-S and Ti-I, respectively. Both deposits exhibited a high superficial roughness, hence a final post-processing step is suggested to ensure a good contact of the BPP in the cell.

- The evaluation of the corrosion resistance of the CSAM Ti patterned coatings showed that for both Ti-S and Ti-I powders a stable oxide film at the typical operation potential (1.8 V vs Ag/AgCl) of a PEM water electrolyzer was formed. No signs of pitting corrosion were observed in the range of potentials under assessment confirming the high stability and resistance of these Ti surfaces to acidic environments.

- At a compaction pressure of 150 N/cm² ICR values of 42 ± 19 , 40 ± 13 , and 24 ± 7 were obtained for Ti-I, Ti-S, and Ti Bulk, respectively. Furthermore, after the post-mortem tests, there was a notable increase in the ICR, indicating

that the oxide layer formed on the surface impeded the conductivity of the specimens.

-The morphology of the powder only has an influence on the deposition efficiency. The resistance to corrosion and ICR properties are dependent on the nature of the material. Therefore, using an irregular powder contributes to a cost-effective manufacturing of BPPs.

6.5 Acknowledgements

Author A. Garfias would like to thank AGAUR for grant 2021 FISDU 00300. This work is part of the project TED2021-130461B-I00, funded by MCIN/AEI/10.13039/501100011033 and by the European Union "NextGenerationEU"/PRTR. V. Albaladejo-Fuentes is a Serra Hunter Fellow

6.6 References

- [1] P.P. Edwards, V.L. Kuznetsov, W.I.F. David, Hydrogen energy, *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 365 (2007) 1043–1056. <https://doi.org/10.1098/rsta.2006.1965>.
- [2] A.Z. Arsad, M.A. Hannan, A.Q. Al-Shetwi, M. Mansur, K.M. Muttaqi, Z.Y. Dong, F. Blaabjerg, Hydrogen energy storage integrated hybrid renewable energy systems: A review analysis for future research directions, *Int J Hydrogen Energy* 47 (2022) 17285–17312. <https://doi.org/10.1016/j.ijhydene.2022.03.208>.
- [3] M. Carmo, D.L. Fritz, J. Mergel, D. Stolten, A comprehensive review on PEM water electrolysis, *Int J Hydrogen Energy* 38 (2013) 4901–4934. <https://doi.org/10.1016/j.ijhydene.2013.01.151>.
- [4] S. Lædre, O.E. Kongstein, A. Oedegaard, H. Karoliussen, F. Seland, Materials for Proton Exchange Membrane water electrolyzer bipolar plates, *Int J Hydrogen Energy* 42 (2017) 2713–2723. <https://doi.org/10.1016/j.ijhydene.2016.11.106>.
- [5] S. Dunn, Hydrogen futures: toward a sustainable energy system, *Int J Hydrogen Energy* 27 (2002) 235–264. [https://doi.org/10.1016/S0360-3199\(01\)00131-8](https://doi.org/10.1016/S0360-3199(01)00131-8).
- [6] A. Ursúa, L.M. Gandía, P. Sanchis, Hydrogen production from water electrolysis: Current status and future trends, in: *Proceedings of the IEEE, Institute of Electrical and Electronics Engineers Inc.*, 2012: pp. 410–426. <https://doi.org/10.1109/JPROC.2011.2156750>.
- [7] S.A. Grigoriev, V.N. Fateev, D.G. Bessarabov, P. Millet, Current status, research trends, and challenges in water electrolysis science and technology, *Int J Hydrogen Energy* 45 (2020) 26036–26058. <https://doi.org/10.1016/j.ijhydene.2020.03.109>.
- [8] X. Luo, C. Ren, J. Song, H. Luo, K. Xiao, D. Zhang, J. Hao, Z. Deng, C. Dong, X. Li, Design and fabrication of bipolar plates for PEM water electrolyser, *J Mater Sci Technol* 146 (2023) 19–41. <https://doi.org/10.1016/j.jmst.2022.10.039>.
- [9] A. Tang, L. Crisci, L. Bonville, J. Jankovic, An overview of bipolar plates in proton exchange membrane fuel cells, *Journal of Renewable and Sustainable Energy* 13 (2021). <https://doi.org/10.1063/5.0031447>.
- [10] S. Porstmann, T. Wannemacher, W.G. Drossel, A comprehensive comparison of state-of-the-art manufacturing methods for fuel cell bipolar plates including anticipated future industry trends, *J Manuf Process* 60 (2020) 366–383. <https://doi.org/10.1016/j.jmapro.2020.10.041>.
- [11] F. Dundar, E. Dur, S. Mahabunphachai, M. Koç, Corrosion resistance characteristics of stamped and hydroformed proton exchange membrane fuel cell metallic bipolar plates, *J Power Sources* 195 (2010) 3546–3552. <https://doi.org/10.1016/j.jpowsour.2009.12.040>.
- [12] M.J.K. Lodhi, K.M. Deen, W. Haider, Corrosion behavior of additively manufactured 316L stainless steel in acidic media, *Materialia (Oxf)* 2 (2018) 111–121. <https://doi.org/10.1016/j.mtla.2018.06.015>.

- [13] W. Yoon, X. Huang, P. Fazzino, K.L. Reifsnider, M.A. Akkaoui, Evaluation of coated metallic bipolar plates for polymer electrolyte membrane fuel cells, *J Power Sources* 179 (2008) 265–273. <https://doi.org/10.1016/j.jpowsour.2007.12.034>.
- [14] H. Sun, K. Cooke, G. Eitzinger, P. Hamilton, B. Pollet, Development of PVD coatings for PEMFC metallic bipolar plates, *Thin Solid Films* 528 (2013) 199–204. <https://doi.org/10.1016/j.tsf.2012.10.094>.
- [15] G. Yang, J. Mo, Z. Kang, F.A. List, J.B. Green, S.S. Babu, F.Y. Zhang, Additive manufactured bipolar plate for high-efficiency hydrogen production in proton exchange membrane electrolyzer cells, *Int J Hydrogen Energy* 42 (2017) 14734–14740. <https://doi.org/10.1016/j.ijhydene.2017.04.100>.
- [16] G. Yang, S. Yu, J. Mo, Z. Kang, Y. Dohrmann, F.A. List, J.B. Green, S.S. Babu, F.Y. Zhang, Bipolar plate development with additive manufacturing and protective coating for durable and high-efficiency hydrogen production, *J Power Sources* 396 (2018) 590–598. <https://doi.org/10.1016/j.jpowsour.2018.06.078>.
- [17] P. Huang, Z. Chen, J. Zhang, M. Wu, Y. Liu, F. Zhang, Y. Chen, X. Chen, Stainless steel bipolar plate fuel cell with different flow field structures prepared by laser additive manufacturing, *Int J Heat Mass Transf* 183 (2022). <https://doi.org/10.1016/j.ijheatmasstransfer.2021.122186>.
- [18] M. Sánchez-Molina, E. Amores, N. Rojas, M. Kunowsky, Additive manufacturing of bipolar plates for hydrogen production in proton exchange membrane water electrolysis cells, *Int J Hydrogen Energy* 46 (2021) 38983–38991. <https://doi.org/10.1016/j.ijhydene.2021.09.152>.
- [19] H. Wang, M.A. Sweikart, J.A. Turner, Stainless steel as bipolar plate material for polymer electrolyte membrane fuel cells, *J Power Sources* 115 (2003) 243–251. [https://doi.org/10.1016/S0378-7753\(03\)00023-5](https://doi.org/10.1016/S0378-7753(03)00023-5).
- [20] D.P. Davies, P.L. Adcock, M. Turpin, S.J. Rowen, Bipolar plate materials for solid polymer fuel cells, *J Appl Electrochem* 30 (2000) 101–105. <https://doi.org/10.1023/A:1003831406406>.
- [21] IRENA, Green Hydrogen Cost Reduction: Scaling up Electrolysers to meet the 1.5oC Climate Goal, in: *Green Hydrogen Cost Reduction: Scaling up Electrolysers to Meet the 1.5oC Climate Goal*, 2020.
- [22] R.F. Vaz, A. Silvello, J. Sanchez, V. Albaladejo, I. García-Cano, The influence of the powder characteristics on 316l stainless steel coatings sprayed by cold gas spray, *Coatings* 11 (2021) 1–18. <https://doi.org/10.3390/coatings11020168>.
- [23] W. Wong, P. Vo, E. Irissou, A.N. Ryabinin, J.G. Legoux, S. Yue, Effect of particle morphology and size distribution on cold-sprayed pure titanium coatings, *Journal of Thermal Spray Technology* 22 (2013) 1140–1153. <https://doi.org/10.1007/s11666-013-9951-6>.
- [24] S. Porstmann, T. Wannemacher, W.G. Drossel, A comprehensive comparison of state-of-the-art manufacturing methods for fuel cell bipolar plates including anticipated future industry trends, *J Manuf Process* 60 (2020) 366–383. <https://doi.org/10.1016/j.jmapro.2020.10.041>.

- [25] F.K. Chen, K.H. Chiu, Stamping formability of pure titanium sheets, *J Mater Process Technol* 170 (2005) 181–186. <https://doi.org/10.1016/j.jmatprotec.2005.05.004>.
- [26] X. Li, I. Sabir, Review of bipolar plates in PEM fuel cells: Flow-field designs, *Int J Hydrogen Energy* 30 (2005) 359–371. <https://doi.org/10.1016/j.ijhydene.2004.09.019>.
- [27] S. Karimi, N. Fraser, B. Roberts, F.R. Foulkes, A review of metallic bipolar plates for proton exchange membrane fuel cells: Materials and fabrication methods, *Advances in Materials Science and Engineering* 2012 (2012). <https://doi.org/10.1155/2012/828070>.
- [28] A. Garfias, R. Vaz, V. Albaladejo-Fuentes, J. Sánchez, I.G. Cano, Geometry and Microstructure Control of Remanufactured Metallic Parts by Cold Spray Additive Manufacturing, *Materials* 16 (2023) 4735. <https://doi.org/10.3390/ma16134735>.
- [29] M.F. Morks, S.H. Zahiri, J. Lang, X.B. Chen, S. Gulizia, I.S. Cole, The influence of powder morphology on the microstructure and mechanical properties of as-sprayed and heat-treated cold-sprayed CP Ti, *International Journal of Advanced Manufacturing Technology* 118 (2022) 3869–3881. <https://doi.org/10.1007/s00170-021-08222-9>.
- [30] W. Li, C. Cao, S. Yin, Solid-state cold spraying of Ti and its alloys: A literature review, *Prog Mater Sci* 110 (2020). <https://doi.org/10.1016/j.pmatsci.2019.100633>.
- [31] P. Dupuis, Y. Cormier, M. Fenech, B. Jodoin, Heat transfer and flow structure characterization for pin fins produced by cold spray additive manufacturing, *Int J Heat Mass Transf* 98 (2016) 650–661. <https://doi.org/10.1016/j.ijheatmasstransfer.2016.03.069>.
- [32] Y. Cormier, P. Dupuis, B. Jodoin, A. Corbeil, Net shape fins for compact heat exchanger produced by cold spray, *Journal of Thermal Spray Technology* 22 (2013) 1210–1221. <https://doi.org/10.1007/s11666-013-9968-x>.
- [33] M. Langemann, D.L. Fritz, M. Müller, D. Stolten, Validation and characterization of suitable materials for bipolar plates in PEM water electrolysis, *Int J Hydrogen Energy* 40 (2015) 11385–11391. <https://doi.org/10.1016/j.ijhydene.2015.04.155>.
- [34] P. Lettenmeier, R. Wang, R. Abouatallah, F. Burggraf, A.S. Gago, K.A. Friedrich, Coated Stainless Steel Bipolar Plates for Proton Exchange Membrane Electrolyzers, *J Electrochem Soc* 163 (2016) F3119–F3124. <https://doi.org/10.1149/2.0141611jes>.
- [35] T. Hussain, D.G. McCartney, P.H. Shipway, T. Marrocco, Corrosion behavior of cold sprayed titanium coatings and free standing deposits, *Journal of Thermal Spray Technology* 20 (2011) 260–274. <https://doi.org/10.1007/s11666-010-9540-x>.
- [36] P. Jendras, K. Lötsch, T. Von Unwerth, Requirements and testing methods for surfaces of metallic bipolar plates for low-temperature PEM fuel cells, in: *IOP Conf Ser Mater Sci Eng*, Institute of Physics Publishing, 2017. <https://doi.org/10.1088/1757-899X/181/1/012018>.
- [37] H. Zhang, M. Hou, G. Lin, Z. Han, Y. Fu, S. Sun, Z. Shao, B. Yi, Performance of Ti-Ag-deposited titanium bipolar plates in simulated unitized regenerative fuel cell (URFC) environment, *Int J Hydrogen Energy* 36 (2011) 5695–5701. <https://doi.org/10.1016/j.ijhydene.2011.01.154>.

[38] S. Lædre, O.E. Kongstein, A. Oedegaard, F. Seland, H. Karoliussen, Measuring In Situ Interfacial Contact Resistance in a Proton Exchange Membrane Fuel Cell, *J Electrochem Soc* 166 (2019) F853–F859. <https://doi.org/10.1149/2.1511912jes>.

Chapter 7: Global Discussions

This chapter summarizes the results obtained throughout this thesis and discusses the contributions of Chapters 4-6 in addressing the challenges previously identified for the CSAM technology in Chapter 2. In addition, the impact of the studied deposition strategies on the implementation of CSAM technology in relevant applications is explored.

Chapter 7: Global Discussions

In this chapter, the results from Chapters 4-6 are summarized and discussed in relation to the main objective of this thesis: *“To investigate the CSAM process variables and deposition strategies for its further development and application as an additive manufacturing technology.”*

Each chapter in the Results & Discussion section addressed the challenges described in the Scope of work (Chapter 2), by investigating various deposition strategies focused in the implementation of the CSAM technology on relevant applications and its development as an AM technology. These challenges highlight the research gaps that need to be investigated in the CSAM field, including a precise control over the geometrical shape of the deposits (Challenge 1), inferior mechanical properties in comparison to bulk materials (Challenge 2), debonding between deposit-substrate due to excessive residual stresses for repair applications (Challenge 3), poor deposition of hard materials (Challenge 4), and topography control of patterned CSAM parts (Challenge 5).

Robot path trajectories

The geometric control (Challenge 1) of the CSAM parts is limited due to two factors: the layer thickness for each layer, which depending on the feedstock material can range between 50 μm and 200 μm , and second to the spraying spot size and the inherent velocity distribution of the particles at the exit of the nozzle that causes the deposits to grow with a pyramidal shape [1,2]. In CSAM, the robot path trajectory is defined as the movement that the nozzle follows during the spraying process. The primary objective of this trajectory is to produce a homogeneous deposit on the substrate surface with a desired geometry [3]. In this sense, Chapter 4 evaluated two robot path trajectories (Traditional and Metal Knitting) for the reconstruction of damaged parts of various materials (Cu, Al, Ti, and Ti6Al4V) back to their original state. In this work it was found that the Traditional (T) trajectory (movement at a normal angle) was restricted to pyramid-shaped deposits with a limitation in height. Therefore, another toolpath known as Metal Knitting (MK) was evaluated. MK involves the deflection of the nozzle at an angle while moving it in circular ways. With this robot path trajectory, a geometric control was achieved, since straight walls of all the materials with a theoretical

unlimited height were able to be deposited without detachment, as shown in Figure 7.1.

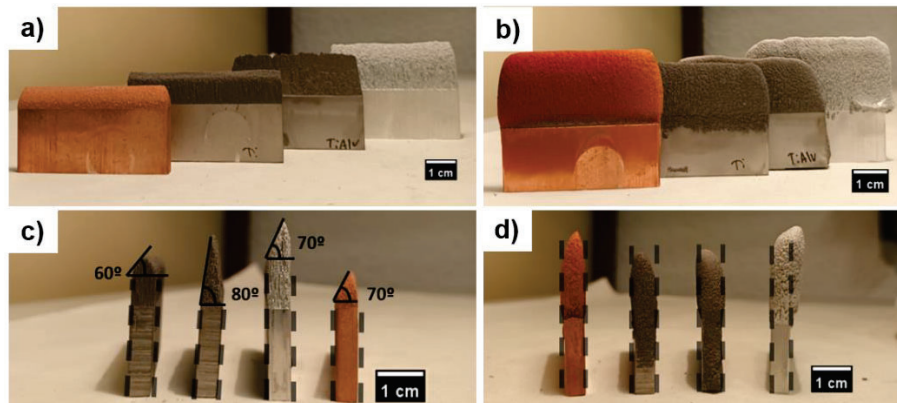


Figure 7.1. Images of the as-sprayed samples produced by (a,c) T and (b,d) MK strategies.

Heat treatments

It is well-known that CS as-sprayed deposits can exhibit mechanical properties that are less favorable compared to bulk materials, including reduced strength, ductility, electrical and thermal conductivity, as well as wear resistance [3]. This behavior is attributed to inherent defects that may arise from the spraying technology. During the coating build-up, the particles are plastically deformed and compacted in the solid state; when processing materials with limited ductility or sprayed under low impact velocities, microstructural flaws such as micropores and interparticle boundaries may appear [4]. In addition, as CSAM parts are sprayed layer by layer with particles impacting the growing surface of the substrate, residual stresses typically emerge within the deposit; an excessive accumulation of these residual stresses in thick deposits may affect their integrity, leading to issues such as debonding or delamination [5]. In repair applications, adequate performance and strong adhesion of the restored parts are essential requirements. Therefore, the effect of annealing heat treatment on improving the mechanical properties (Challenge 2) and its influence on the adhesion strength (Challenge 3) deposit-substrate was also evaluated in Chapter 4. In general annealing was found to be an effective deposition strategy to densify the microstructure of the CSAM reconstructed parts by improving cohesion between the particles and adhesion with the substrate do to the diffusion and recrystallization processes induced by the annealing, resulting in a reduction in

porosity from $6 \pm 2\%$ to $4 \pm 1\%$ for Cu, $10 \pm 4\%$ to $7 \pm 2\%$ for Al, $12 \pm 3\%$ to $8 \pm 2\%$ for Ti, and $21 \pm 5\%$ to $16 \pm 3\%$ for Ti6Al4V between the MK as-sprayed and the HT deposits. Furthermore, the results indicated that all MK as-sprayed samples showed adhesive failures at the deposit–substrate interface with values below 30 MPa, suggesting a poor bonding between the remanufactured part and the substrate. Conversely, the MK-Cu, -Ti, and -Ti6Al4V HT samples presented a cohesive failure with increased tensile strength values, 43 MPa, 114 MPa, and 160 MPa than their as-sprayed counterparts, respectively. This further confirms that annealing is an adequate strategy to increase the bonding between particles and substrate. In addition, it was found that the more ductile materials (Cu and Al) demonstrated comparable characteristics to bulk materials in terms of mechanical properties and resistance to abrasive and erosive wear, while for the harder to deform materials (Ti and Ti6Al4V) the combination of the Metal Knitting strategy and annealing was insufficient to achieve the high-performance deposit properties needed in certain repair applications, which indicated that other deposition strategies needed to be explored.

Substrate preheating

Even though that CSAM has been used for a wide range of materials, only particles with enough ductility at the impingement conditions can be deposited to produce dense parts [6,7]. Therefore, high strength materials (e.g. Ti and its alloys and Ni based alloys) can be challenging to deposit. A crucial variable during the CSAM deposition is the substrate, since it has been shown that its temperature significantly affects the quality of the CS deposit [8,9]. Hence, Chapter 5 investigated the substrate preheating deposition strategy for obtaining well-bonded deposits (Challenge 3) of high-strength materials (Challenge 4) for repair applications. In this study, the effect of substrate preheating on the microstructure, thickness, and adhesion strength of IN718 CSAM deposits was investigated. It was found that the effect of the substrate preheating on the microstructure densification of the samples was notable, especially on the first deposited layer, where the temperature transfer from the substrate was more influential. This is attributed to an enhanced plastic deformation of the particles when impacting a surface at a higher temperature, promoting metallurgical bonding and micro welding between particles-substrate and particles-particles

[10]. In this sense, the sample preheated at 400 °C sprayed with 40 layers presented a fully dense microstructure (99.9%) comparable to an IN718 bulk part, which suggests that substrate preheating during CS is a successful strategy for spraying dense deposits of high-strength materials. In addition, the adhesion mechanisms between particles and substrate were evaluated by observing the deformation of single impact splats, since the adhesion strength of the CS IN718 deposits on IN718 substrates is a critical requirement for ensuring adequate performance in repairing applications [3,11]. The particles in all cases were well attached and were plastically deformed with evidence of the metal jetting phenomenon, as shown in Figure 7.2 [12–14].

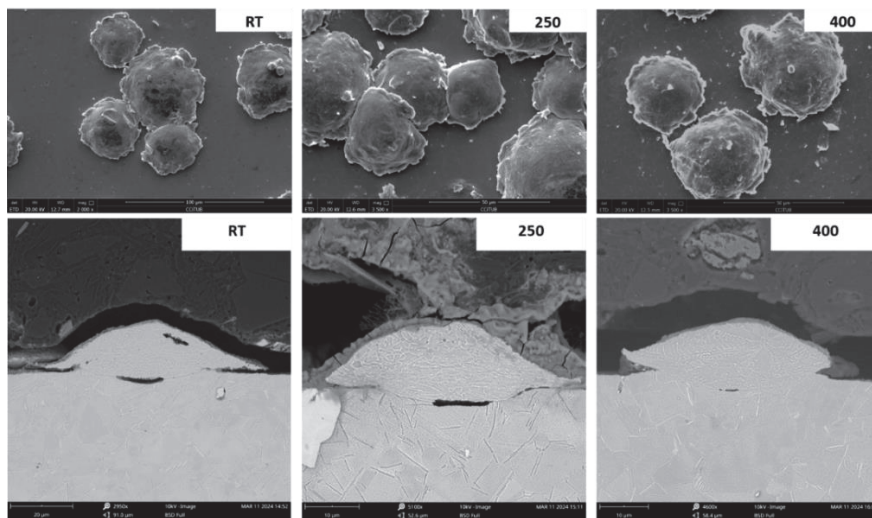


Figure 7.2. SEM images of single splats of RT, 250, and 400 substrate preheating temperatures.

The particles' cross-section showed the particle-substrate interaction with detail; the particles sprayed onto the RT substrate only formed a slight jet, and their impact caused a slight deformation of the substrate. In this case, a gap at the center-bottom of the particles was present, which can be attributed this discontinuity in the interface to the higher temperature of the particles at the periphery than at the center, indicating that a lower temperature is reached in this center-bottom part of the particle, consequently hindering the bonding [15]. The same gap was observed in some of the particles sprayed onto the substrates preheated at 250 °C; however, for the substrates preheated at 400 °C, this void was almost nonexistent, indicating that the temperature of the substrate promoted adhesion [15–18]. Overall, thick deposits (> 1 mm) were successfully obtained with strong adhesion (> 40 MPa in all cases) with the substrate and no

signs of delamination within the CS deposit. These findings demonstrate significant potential for the implementation of substrate preheating during CSAM in repairing applications that involve this alloy.

Masked CSAM

Finally, the geometric limitations (Challenge 1) of the CSAM technology in terms of fabrication of complex-shaped patterned parts with controlled topography (Challenge 5) was addressed in Chapter 6. In this study, the implementation of masks during deposition was used for the manufacture of Ti patterned parts for their application as bipolar plates (BPPs) for Proton Exchange Membrane (PEM) electrolyzers, and its performance in terms of corrosion resistance and interfacial contact resistance was evaluated. The importance of the controlled topography of the flow field channels lies on the crucial role that the design of the flow-field plays in optimizing the operation efficiency of the PEM electrolyzers. Particularly, the BPPs not only act as a conductive and support component of the PEM electrolyzers but they should distribute and maintain a uniform flow throughout its surface [19]. Achieving a uniform flow helps to reduce the internal cell resistance and to prevent the risk of localized corrosion [20]. For this reason, BPPs with several patterns and sizes were sprayed in this work; four different patterns were investigated in this study starting from squared flow-fields of different dimensions (Figures 7.3 A-B), up to other patterns composed of rows or cylinders (Figures 7.3 C-D).

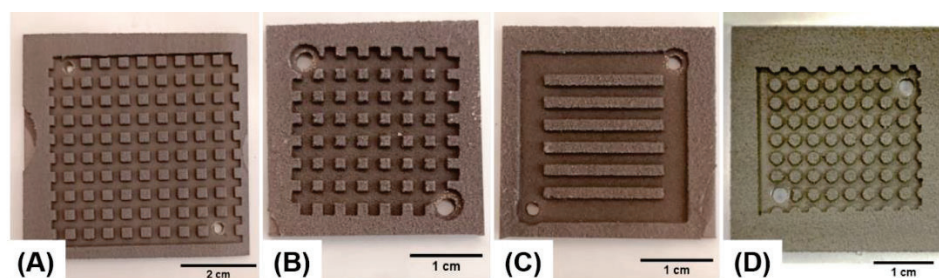


Figure 7.3. CSAM BPPs with different flow-field patterns. (A) big squares, (B) small squares, (C) rows, (D) cylinders.

Overall, it was observed that the width of all the samples was consistent with the dimensions of the utilized mask. For the big squares a mesh with voids of 3 x 3 mm was used, leading to a width of the pins of 2.94 ± 0.05 mm for Ti-I, and 2.34 ± 0.10 mm for Ti-S. Furthermore, the small squares showed similar

results; for the mesh with squared voids of 1.5 x 1.5 mm, the pins showed a width of 1.26 ± 0.05 mm (Ti-I) and 1.48 ± 0.10 mm (Ti-S). This revealed that even though there was some interference of the mesh with the particle deposition, the pins grew with similar dimensions as the voids in the masks. Therefore, the masked CSAM is an efficient deposition strategy capable of processing titanium in its solid state, making it possible to produce BPPs with customized flow-fields within a few minutes and to overcome the challenges of other traditional methods such as stamping or machining. The masked technology allowed to customize the size and shape of the flow fields by adjusting the quantity of layers sprayed and the patterns of the mesh.

In this thesis, several CSAM deposition strategies were studied to advance its development as an AM technology, with a focus on implementing it in relevant applications, particularly in the repair and reconstruction of damaged parts of a wide range of materials, as well as the fabrication of complex-shaped or patterned parts for the energy storage industry. Each of the implemented deposition strategies (robot path trajectories, heat treatments, substrate preheating, and masking technique) allowed to address the current challenges of the CSAM technology and contributed to expanding its applicability within the field of AM.

7.2 References

- [1] D. Kotoban, S. Grigoriev, A. Okunkova, A. Sova, Influence of a shape of single track on deposition efficiency of 316L stainless steel powder in cold spray, *Surf Coat Technol* 309 (2017) 951–958. <https://doi.org/10.1016/j.surfcoat.2016.10.052>.
- [2] Z. Cai, S. Deng, H. Liao, C. Zeng, G. Montavon, The effect of spray distance and scanning step on the coating thickness uniformity in cold spray process, *Journal of Thermal Spray Technology* 23 (2014) 354–362. <https://doi.org/10.1007/s11666-013-0002-0>.
- [3] S. Yin, P. Cavaliere, B. Aldwell, R. Jenkins, H. Liao, W. Li, R. Lupoi, Cold spray additive manufacturing and repair: Fundamentals and applications, *Addit Manuf* 21 (2018) 628–650. <https://doi.org/10.1016/j.addma.2018.04.017>.
- [4] S. Yin, R. Jenkins, X. Yan, R. Lupoi, Microstructure and mechanical anisotropy of additively manufactured cold spray copper deposits, *Materials Science and Engineering A* 734 (2018) 67–76. <https://doi.org/10.1016/j.msea.2018.07.096>.
- [5] T. Suhonen, T. Varis, S. Dosta, M. Torrell, J.M. Guilemany, Residual stress development in cold sprayed Al, Cu and Ti coatings, *Acta Mater* 61 (2013) 6329–6337. <https://doi.org/10.1016/j.actamat.2013.06.033>.
- [6] M.R. Rokni, S.R. Nutt, C.A. Widener, V.K. Champagne, R.H. Hrabec, Review of Relationship Between Particle Deformation, Coating Microstructure, and Properties in High-Pressure Cold Spray, *Journal of Thermal Spray Technology* 26 (2017) 1308–1355. <https://doi.org/10.1007/s11666-017-0575-0>.
- [7] W. Sun, X. Chu, H. Lan, R. Huang, J. Huang, Y. Xie, J. Huang, G. Huang, Current Implementation Status of Cold Spray Technology: A Short Review, *Journal of Thermal Spray Technology* 31 (2022) 848–865. <https://doi.org/10.1007/s11666-022-01382-4>.
- [8] M. Fukumoto, H. Wada, K. Tanabe, M. Yamada, E. Yamaguchi, A. Niwa, M. Sugimoto, M. Izawa, Effect of substrate temperature on deposition behavior of copper particles on substrate surfaces in the cold spray process, *Journal of Thermal Spray Technology* 16 (2007) 643–650. <https://doi.org/10.1007/s11666-007-9121-9>.
- [9] X.K. Suo, M. Yu, W.Y. Li, M.P. Planche, H.L. Liao, Effect of substrate preheating on bonding strength of cold-sprayed Mg coatings, *Journal of Thermal Spray Technology* 21 (2012) 1091–1098. <https://doi.org/10.1007/s11666-012-9803-9>.
- [10] Y. Xie, M.P. Planche, R. Raoelison, H. Liao, X. Suo, P. Hervé, Effect of Substrate Preheating on Adhesive Strength of SS 316L Cold Spray Coatings,

Journal of Thermal Spray Technology 25 (2016) 123–130.
<https://doi.org/10.1007/s11666-015-0312-5>.

[11] K. Ogawa, D. Seo, Repair of Turbine Blades Using Cold Spray Technique, InTechOpen, 2011. <https://doi.org/10.5772/664>.

[12] H. Assadi, F. Gärtner, T. Stoltenhoff, H. Kreye, Bonding mechanism in cold gas spraying, *Acta Mater* 51 (2003) 4379–4394. [https://doi.org/10.1016/S1359-6454\(03\)00274-X](https://doi.org/10.1016/S1359-6454(03)00274-X).

[13] R. Ortiz-Fernandez, S. Imbriglio, R. Chromik, B. Jodoin, The Role of Substrate Preheating on the Adhesion Strength of Cold-Sprayed Soft Particles on Hard Substrates, *Journal of Thermal Spray Technology* 30 (2021) 655–667. <https://doi.org/10.1007/s11666-020-01148-w>.

[14] A. Nastic, B. Jodoin, D. Poirier, J.G. Legoux, Particle temperature effect in cold spray: A study of soft particle deposition on hard substrate, *Surf Coat Technol* 406 (2021). <https://doi.org/10.1016/j.surfcoat.2020.126735>.

[15] W. Sun, A.W.Y. Tan, A. Bhowmik, I. Marinescu, X. Song, W. Zhai, F. Li, E. Liu, Deposition characteristics of cold sprayed Inconel 718 particles on Inconel 718 substrates with different surface conditions, *Materials Science and Engineering: A* 720 (2018) 75–84. <https://doi.org/10.1016/j.msea.2018.02.059>.

[16] Y. Watanabe, C. Yoshida, K. Atsumi, M. Yamada, M. Fukumoto, Influence of Substrate Temperature on Adhesion Strength of Cold-Sprayed Coatings, *Journal of Thermal Spray Technology* 24 (2014) 86–91. <https://doi.org/10.1007/s11666-014-0165-3>.

[17] C.W. Ziemian, M.M. Sharma, B.D. Bouffard, T. Nissley, T.J. Eden, Effect of substrate surface roughening and cold spray coating on the fatigue life of AA2024 specimens, *Mater Des* 54 (2014) 212–221. <https://doi.org/10.1016/j.matdes.2013.08.061>.

[18] R. Ortiz-Fernandez, B. Jodoin, Toward Efficient Cold Spraying of Inconel 718: Understanding the Influence of Coating and Particle Impact Temperatures, *Journal of Thermal Spray Technology* 32 (2023) 188–207. <https://doi.org/10.1007/s11666-022-01490-1>.

[19] X. Luo, C. Ren, J. Song, H. Luo, K. Xiao, D. Zhang, J. Hao, Z. Deng, C. Dong, X. Li, Design and fabrication of bipolar plates for PEM water electrolyser, *J Mater Sci Technol* 146 (2023) 19–41. <https://doi.org/10.1016/j.jmst.2022.10.039>.

[20] X. Li, I. Sabir, Review of bipolar plates in PEM fuel cells: Flow-field designs, *Int J Hydrogen Energy* 30 (2005) 359–371. <https://doi.org/10.1016/j.ijhydene.2004.09.019>.

Chapter 8: General Conclusions

This chapter summarizes the overall conclusions derived from the studies presented this thesis.

Chapter 8: General Conclusions

In this PhD thesis, various CSAM deposition strategies were evaluated for its further development and application as an additive manufacturing technology.

In Chapter 4 the impact of the optimization of two robot path trajectories on the geometry, microstructure and mechanical properties was evaluated. Moreover, the effects of heat treatment annealing on the adhesion, resistance to erosive and abrasive wear of the CSAM components were tested. From this Chapter, the following conclusions have been drawn:

- The CSAM Traditional (T) strategy is not suitable for the production of thick coatings with strict geometric tolerance, because as the deposits are sprayed, a pyramid-shaped part starts to grow.

- The Metal Knitting (MK) toolpath is an effective CSAM deposition strategy for the reconstruction of metallic parts compared to the T method. With MK, straight walls of different materials with unlimited height and without detachment of the deposits can be obtained. However, the deposition angle reduces the plastic deformation of the particles, increasing porosity within the microstructure and hindering adhesion with the substrate.

- Regardless the feedstock material, annealing was found to be an effective HT process to tailor the microstructure of the samples by improving the cohesion between particles and adhesion with the substrate, as well as densifying the deposited counterparts.

- The Cu and Al samples fabricated with MK followed by annealing showed similar characteristics as the bulk materials in terms of mechanical properties and resistance to abrasive and erosive wear, suggesting that the manufacturing of these materials by CSAM MK followed by annealing could be comparable to other bulk production methods.

- The porosity and low particle-particle cohesion observed in the microstructure of the MK-Ti and MK-Ti6Al4V samples were not significantly enhanced, even after the annealing treatment, which explains their low resistance to erosive and abrasive wear in comparison to the bulk. For these alloys showing high critical impact velocities, the results of this study suggest that the

combination of MK and a heat-thermal treatment might be insufficient to achieve the deposit properties needed in certain applications and other densification strategies should be explored.

Additionally, in Chapter 5, the effects of substrate preheating on the deposition of high-strength materials were investigated in terms of porosity and adhesion strength. From this work, the following points were concluded:

- The substrate preheating improved the bonding strength, adhesion, and cohesion of CS IN718 deposits by softening the substrate, which improved the materials' plasticity.

- Two effects led to microstructure densification: the temperature effect induced by the substrate preheating in the first layers, and the peening effect of the particles in the subsequent layers.

- The substrate preheating and deposit thickness did not affect the deposit microhardness; however, increasing the preheating temperature and the deposit thickness improved the deposit density, reaching values comparable to an IN718 bulk reference, > 99.9%.

- CS processing can be successfully applied for repairing IN718 damaged parts by depositing the same material without adding any bond coating or other additional pre-processing other than polishing and cleaning, preserving the feedstock material microstructure and phase composition.

Finally, in Chapter 6, the fabrication of Ti patterned parts using a masked CSAM deposition strategy was evaluated for energy storage applications. These points were concluded:

- The masked CSAM process allowed to manufacture Ti BPPs with customized flow-fields within a few minutes. The produced pin fins that make of the flow-fields were homogeneous, presenting the same shape and size.

- The CSAM Ti BPPs presented porosity values of $6 \pm 1\%$ and $4 \pm 1\%$ for powders Ti-S and Ti-I, respectively. Both deposits exhibited a high superficial roughness, hence a final post-processing step is suggested to ensure a good contact of the BPP in the cell.

-The evaluation of the corrosion resistance of the CSAM Ti patterned coatings showed that for both Ti-S and Ti-I powders a stable oxide film at the typical operation potential (1.8 V vs Ag/AgCl) of a PEM water electrolyzer was formed. No signs of pitting corrosion were observed in the range of potentials under assessment confirming the high stability and resistance of these Ti surfaces to acidic environments.

-At a compaction pressure of 150 N/cm² ICR values of 42 ± 19 , 40 ± 13 , and 24 ± 7 were obtained for Ti-I, Ti-S, and Ti Bulk, respectively. Furthermore, after the post-mortem tests, there was a notable increase in the ICR, indicating that the oxide layer formed on the surface impeded the conductivity of the specimens.

-The morphology of the powder only has an influence on the deposition efficiency. The resistance to corrosion and ICR properties are dependent on the nature of the material. Therefore, using an irregular powder contributes to a cost-effective manufacturing of BPPs.

Overall, several deposition strategies, including the robot path trajectories, heat treatments, substrate preheating, and masking were investigated throughout this thesis, allowing to broaden the CSAM technology capabilities and applications.

Appendix

In this part the scientific contributions of the PhD candidate are listed, including published articles, doctoral stays and works presented in congresses.

Appendix

Publications and scientific activities

Publications derived from this thesis:

- **A. Garfias**, P. Kindermann, M. Wunderer, R.F. Vaz, V. Albaladejo-Fuentes, J. Sánchez, I. Ünsal, G. Schlick, I.G. Cano. Repairing alloy 718 parts by cold spray additive manufacturing: the effect of substrate preheating on the deposit properties. *Journal of Manufacturing Processes*. ***Submitted on Sep 2024. Submitted on sep 2024. SJR (2023): 1.39. Impact Factor 6.2 – Q1**
- **A. Garfias**, M. Sarret, J. Sánchez, I. García-Cano, V. Albaladejo, Andreu, T. (2023). Manufacturing and properties characterization of Ti patterned coatings for water electrolyzers by CSAM. *Applied Surface Science Advances*. ***In revision on Sep 2024. SJR (2023): 1.16. Impact Factor 7.5 – Q1**
- **A. Garfias**, R. Vaz, V. Albaladejo, J. Sánchez, M. Sarret, T. Andreu, I. García-Cano. Cold Gas Spraying 3D Printing of Ti Bipolar Plates for PEM Water Electrolyzers Cost Reduction. *ITSC 2023 Proceedings*. Quebec, Canada. <https://doi.org/10.31399/asm.cp.itsc2023p0173>
- **A. Garfias**, R. Vaz, V. Albaladejo, J. Sánchez, I. García-Cano. Geometry and microstructure control of remanufactured metallic parts by Cold Spray Additive Manufacturing. *Materials*. 2023, 16(13), 4735. <https://doi.org/10.3390/ma16134735>. **SJR (2023): 0.56. Impact Factor 3.1 – Q2 (2023)**

Publications on the research area but not included in this thesis:

- R.F. Vaz, **A. Garfias**, B. Garrido, V. Albaladejo-Fuentes, J. Sánchez, I.G. Cano. Influence of Cold Spray Additive Manufacturing process parameters on Al parts properties. *Journal of Manufacturing Processes*. ***In revision on Apr 2024. SJR (2023): 1.39. Impact Factor 6.2 – Q1**
- R. F. Vaz, **A. Garfias**, V. Albaladejo, J. Sanchez, and I. G. Cano. How increasing cold spray coatings thickness affects their residual stress and properties. *Surface and Coatings Technology*, vol. 485, Jun. 2024, doi:

10.1016/j.surfcoat.2024.130867. **SJR (2023): 1.03. Impact Factor 5.3 – Q1 (2023).**

- R. Vaz, **A. Garfias**, V. Albaladejo, J. Sánchez, I. García-Cano. A review of advances in Cold Spray Additive Manufacturing. *Coatings*. 2023, 13(2). <https://doi.org/10.3390/coatings13020267>. **SJR (2023): 0.49. Impact Factor 2.9 – Q2 (2023).**

International Doctoral Stays:

- International doctoral stay at the Fraunhofer IGCV research institute in Augsburg, Germany, from July 20th, 2023, to October 20th, 2023. This enables this thesis to qualify for an International Doctorate mention Participation in congresses:

Participation in congresses:

- J. Sánchez; **A. Garfias**; Sarret, M; I. García-Cano; V. Albaladejo; Andreu, T. Cold Gas Spraying 3D printing of Ti bipolar plates for PEM water electrolyzers cost reduction. PMTi – Madrid, September 2024. **Oral.**
- J. Sánchez; **A. Garfias**; Sarret, M; I. García-Cano; V. Albaladejo; Andreu, T. Cold Gas Spraying 3D printing of Ti bipolar plates for PEM water electrolyzers cost reduction. Cold Spray Club – Barcelona, April 2024. **Oral.**
- T. Andreu; J. Boter; P. Cabot; M. Sarret; **A. Garfias**; V. Albaladejo. Highly conductive interfaces to reduce the cost of PEM electrolyzers. H2 Future nanoGe – Ibiza, April 2024. **Oral.**
- R. Vaz; **A. Garfias**; V. Albaladejo; J. Sánchez; I. García-Cano. Improving Cohesion of Particles of Cold Sprayed Materials by Heat Treatment. Cold Spray Club – Hamburg, October 2023. **Oral.**
- **A. Garfias**; M. Sarret; J. Sánchez; I. García-Cano; V. Albaladejo; T. Andreu. Cold Gas Spraying 3D printing of Ti bipolar plates for proton exchange membrane water electrolyzers. FEMS EUROMAT – Frankfurt, September 2023. **Oral.**

- J. Sánchez; **A. Garfias**; R. Vaz; V. Albaladejo; M. Sarret; T. Andreu; I. García-Cano. Cold Gas Spraying 3D Printing of Ti Bipolar Plates for PEM Water Electrolyzers Cost Reduction. ITSC 2023, Quebec – Canada, May 2023. **Oral**.
- **A. Garfias**; R. Vaz; V. Albaladejo; J. Sánchez; M. Sarret; T. Andreu; I. García-Cano. Near-net-shape repair of Ti6Al4V thin-walled structures by CSAM. ITSC 2023, Quebec – Canada, May 2023. **Poster**.
- **A. Garfias**; R. Vaz; V. Albaladejo; J. Sánchez; I. García-Cano. Reconstrucción de piezas metálicas por el método de Cold Spray Metal Knitting. CEIPM 2023, San Sebastián – Spain, May 2023. **Oral**.
- **A. Garfias**; R. Vaz; V. Albaladejo; J. Sánchez; I. García-Cano. Influence of the substrate properties on the cold gas spray deposition efficiency. ITSC 2022, Vienna – Austria, May 2022. **Poster**.

