

Development of a Sustainable Solution for the Elimination of Helium in the Copper Cold Spray Process for Used Nuclear Fuel Containers

By

Rocio Dominguez Medrano

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Abstract

Successful deposition of thick copper coatings on low carbon steel is a challenge for the Cold Gas Dynamic Spray (CGDS) process if one is to avoid the use of helium as the process gas for the initial pre-coat layer. The issue stems from the presence of accumulated residual stresses, which causes delamination of the weakly bonded coating. Even after exploring different deposition parameters, several copper powders and various steel substrate preparations, copper coating delamination still occurs.

The purpose of the current study is to produce copper coatings using only nitrogen as the process gas, while avoiding delamination of the deposited material. To this end, the current work focuses on the study of the effect of steel substrate temperature on particle deposition and adhesion processes. Steel substrates were heated to temperatures between 25°C and 600°C using induction heating and laser. Once the substrate reached the desired temperature, three different copper particle sizes were deposited using the CGDS process.

Individual particle impact tests (wipe-tests) were performed to characterize bonded particles and craters from rebounded particles. Further analysis was performed by extracting particles from the surface to understand the effect of substrate temperature and particle size on the particle/substrate deformation and bonding processes. Mechanical adhesion prediction modeling at substrate preheated was also performed to obtain a greater understanding of the bonding mechanism. This prediction is in order to compare with the coating developed with a bond layer coating with helium as process gas and then build the rest of the coating with nitrogen. The experimental results show a significant trend as the substrate temperature increases, indicating proper conditions for enhanced adhesion.

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Nomenclature

R_c	Compression ratio
C_t	Crater depth
C_d	Crater diameter
C_v	Crater volume
d	Diameter
A	Elastic limit
σ_{eq}	Equivalent stress
n	Exponent of strain hardening
m	Exponent of thermal weakening
H	Hardness
h	Height
T_m	Melting temperature
B	Modulus of strain hardening
P_d	Particle diameter
ω	Particle diameter after impact
P_{d_0}	Particle diameter before impact
P_h	Particle height
Pe_t	Penetration depth
Pe_d	Penetration diameter
ε_p	Plastic strain
r	Radius
ε_{ref}	Reference strain
T_{ref}	Reference temperature
c	Strain rate sensitivity index
V	Volume
σ_y	Yield strength

1. Introduction

1.1 Background

One of the most complicated concepts when working with the management of used nuclear fuel is the time frame for which the used fuel must be stored, which is up to a million years [1]. The Canada Deuterium Uranium (CANDU) nuclear fuel bundle is ceramic pellets made from uranium dioxide. These pellets are enclosed in zircaloy fuel elements. 28 to 37 of these are welded together in a circular pattern forming the used fuel bundles. The fuel bundles are consumed by the nuclear reactor to produce electricity and approximately 120,000 fuel bundles are used every year [1][2].

Presently, the used fuel is stored by removing the bundles from the reactor and moving them into a water pool for seven to ten years, where the heat generation and radioactivity decreases. After that, the bundles are deposited in a dry box for radiation protection, which is made of high-density concrete with a thickness of 50.8 cm and a layer of steel plate of ~1.27 cm inside and outside of the concrete. By the end of 2019, the number of used fuel bundles (UFB) produced in Canada was 2.9 million with a prediction of 120,000 bundles being consumed per year going forward [1][2]. This rate of fuel consumption is the reason that a plan is required for long term used fuel storage. The Nuclear Waste Management Organization (NWMO) is responsible for designing and developing a long-term storage plan for the used nuclear fuel. The facility named in this plan is the deep geological repository (DGR).

The DGR is a multiple-barrier system that uses engineered and natural barriers to provide a physical and chemical environment that will limit the motion and exposure of radioactive elements. Once the fuel bundle's useful life is carried out and all energy has been consumed, it is planned to be deposited in a used fuel container (UFC). This container has essential design requirements including mechanical strength, capacity, compatibility with its surrounding sealing materials, and most importantly corrosion resistance. The UFC is planned to be deposited in a bentonite clay buffer box. This box is intended to prevent the growth of microbiological life and to prevent water flow around the UFCs. Finally, once the UFCs are stored in the buffer box, it is to be deposited into the DGR.

The most important elements in the DGR are the UFCs, which will be in direct contact with the used fuel. In Europe, there is an existing design for the UFC where a tube of copper is machined to contain the used fuel. The drawback of this approach is the amount of copper waste that is introduced during the manufacturing of the UFCs. In contrast, the Canadian design is made of low carbon steel (A516 steel Grade 70) with a copper coating, which aims to achieve corrosion protection. The thickness of the copper coating is 3 mm because the corrosion caused by groundwater over 100 000 years is predicted to be less than 0.4 mm and the copper loss due to corrosion over 1 000 000 years is predicted to be less than 1.27 mm [3].

The UFC is divided into two parts: the head and the body. The copper coating is to be applied before the used fuel is deposited into the UFC, by electrodeposition. Once the used fuel is deposited into

the UFC it is no longer safe to weld the two parts together using the electrodeposition technique. Consequently, the technique of cold gas dynamic spray (CGDS) was selected to apply the copper coating to the closure zone sealing the UFC. Successful deposition of a thick copper coating on low carbon steel is however a challenging process. The issue stems from the presence of accumulated residual stresses at the coating/substrate interface, which causes delamination. Even after exploring different deposition parameters, several copper powders, and various steel substrate preparation methods, copper coating delamination still occurs as the coating is built up to 3 mm thick.

CGDS was successful in achieving the required thickness without delamination when a bond coat of approximately 100µm is applied using helium as the carrier gas and then the rest of the coating thickness is applied using nitrogen. Although successful, this method of using helium to produce the bond coat increases the cost and complexity of the UFC manufacturing process with the added concern that helium is a non-renewable resource. Consequently, there is a need to develop a viable solution for the elimination of the helium bond coat in the process.

One method used to improve coating adhesion strength has been demonstrated by preheating the substrate. As the substrate is preheated, its yield strength is reduced and thermal softening is increased, which enhances the substrate deformation allowing the mechanical anchoring and metallic bonds to be improved [4]. This might be a safe, highly efficient, and cost-effective solution to employ, allowing the use of only nitrogen as the carrier gas during the CGDS copper coating process.

One technique to preheat the substrate during the CGDS process that has been developed is by using a laser which is installed next to the CGDS nozzle and a pyrometer in order to monitor the substrate temperature. This set-up allows the substrate to be preheated just before the copper particle deposition and reduces the possibility for oxidization of the substrate surface.

The objective of this thesis is to understand the deformation level of the substrate and particles upon impact and the bonding mechanism when the substrate is preheated. In this research, two different methods of preheating the substrate were used. The first method used an induction heater and the second used a laser. The induction heater technique was carried out using the CGDS system located at the University of Ottawa (uOttawa). The CGDS system of National Research Council Canada (NRC-IMI) (Boucherville, QC) is set-up with a pyrometer and a laser to preheat the substrate just before particle impact.

1.2 Research Objectives

The motivation of this research was to develop a sustainable solution for the elimination of helium in the CGDS copper coating process for the sealing of the UFC by exploring the effects of substrate temperature on copper particle and substrate deformation and bonding. The approach of this research was to deposit single copper particles on low carbon steel substrates that are at various temperatures in order to characterize and understand the deformation level of the substrate and particles upon impact and the bonding mechanisms that exist between them. This research was

carried out in collaboration with NWMO and NRC-IMI. The findings of this research are expected to be helpful to use for the development of the final UFC manufacturing process. To accomplish the objectives, the following sequence of steps was performed:

1. Deposition of single copper particles of three different diameters using the CGDS system at the uOttawa facilities. The particles were deposited with the substrate at room temperature and varying temperatures from 100°C to 600°C with increments of 100°C. The substrate preheating was carried out using an induction heater.
2. A second set of tests were carried out using the CGDS system at the NRC-IMI facility with the substrate at room temperature and the substrate preheated to 600°C. In this test, the substrate was preheated using a heating laser attached to the system that preheated the substrate just before particle impact.
3. Characterization of the craters (resulting from the bounced off particles), bonded particles, and detached particles were performed for all sprayed tests.
4. Comparison of substrate temperature effects between the two techniques mentioned above and different parameters for velocity and temperature of the sprayed particles.
5. Measurement of the metallic bonding area identified by dimple features for the case where the substrate was preheated by laser.
6. Simulations to predict the adhesion as a result of mechanical anchoring for a coating developed with a helium bond coat and a coating developed into a substrate preheated by laser using the same CGDS parameters and only nitrogen.

1.3 Thesis Outline

This thesis is divided into six chapters.

Chapter 1 presents an introduction that includes the motivation and objectives of this research and the outline of this document.

Chapter 2 provides a review of the up-to-date literature on topics relevant to the work. The first section presents the research that has previously been carried out and the advances in the area of the development of long-term storage of used nuclear fuel by NWMO and other organizations. The second section deals with the CGDS process and bonding mechanisms. Additionally, the effects of preheating the substrate at the time of the CGDS process are shown.

Chapter 3 enumerates the research objectives which guide the work plan of this research. Each objective is detailed to successfully achieve the fundamental objective of this research; to support a potential solution for helium removal in the CGDS process.

The experimental procedures and methods for the characterization of deposited particles are described in **Chapter 4**. This includes information about the experimental material and equipment, characterization equipment, and methods that were employed throughout this research.

Chapter 5 presents the results and discussion on the characterizations completed during the research to achieve the goal of understanding, at a fundamental level, the effects of substrate temperature on the bonding process. Lastly, the results relating to mechanical anchoring are explained.

Finally, **Chapter 6** outlines a summary of the outcomes during this research. A list of future work is presented that is being suggested in order to further advance knowledge relating to the research objectives of this thesis. A list of references and appendices can be found following this chapter.

2. Literature review

2.1 CANDU Fuel

A CANDU nuclear fuel bundle is a set of 28 to 37 fuel made of zirconium-tin alloy that contains uranium dioxide (UO_2) powder compressed into solid pellets baked into a ceramic form, as illustrated in **Figure 2.1**. The fuel bundle is 50 cm in length, 10 cm in diameter and a total of 24 kg [5][1][2].

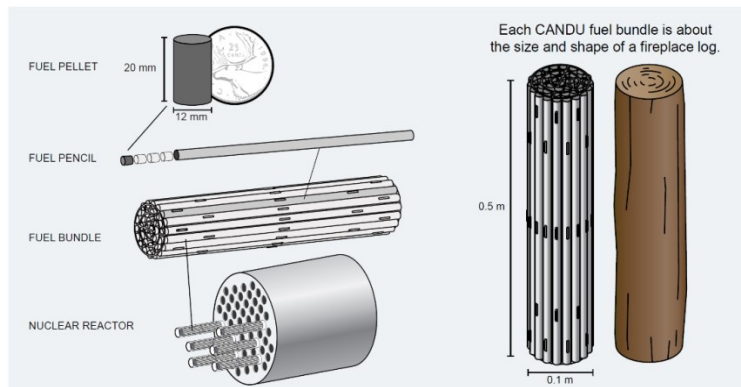


Figure 2.1 Schematic of CANDU fuel [1].

The bundles are used in a nuclear reactor to produce electricity. Once their useful life ends, they become a radioactive waste product. **Figure 2.2** shows the radiation decrease over time. It is observed that the radioactivity reduces rapidly in the first years. However, the residual radioactivity and chemical toxicity still have a potential health risk for one million years and must be handled carefully [1].

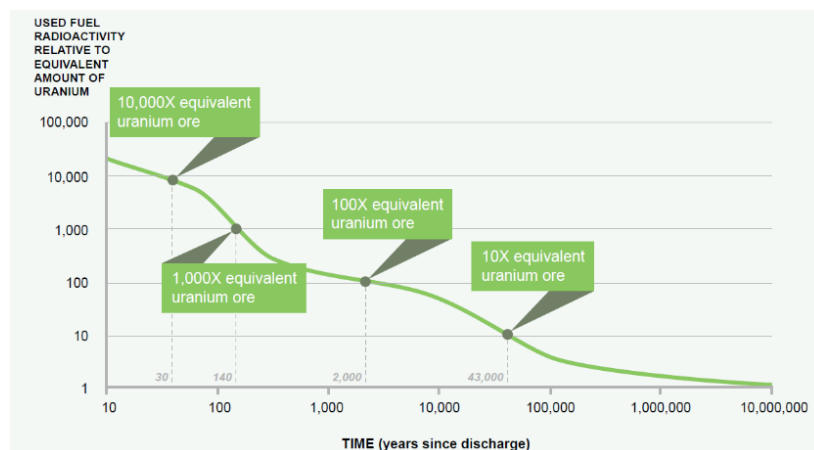


Figure 2.2 Radiation decay over time in a used CANDU fuel [1].

By the end of 2019, the number of UFBs produced in Canada was 2.9 million with a prediction of 120,000 per year for future years [1][2]. The increasing number of UFB is a sign that it is essential to design and implement a long term storage strategy. NWMO is responsible for the design and implementation of a nuclear waste long term storage plan which has been named adaptive phased management (APM)[3].

2.2 Long Term Storage for Used Fuel

Currently, the storage process for all the UFB is to remove them from the nuclear reactor and relocate them to a water pool for seven to ten years. Once this time passes the fuel bundles are moved to a dry box made of high dense concrete and then safely stored in nuclear facilities [5][1].

The Canadian plan for long term management for UFB is similar to the ones approved by other countries including Finland, Japan, Belgium, Sweden, Switzerland, the United Kingdom, and France [6]. It consists of a DGR with multiple natural and engineered barriers. This Canadian APM plan was introduced in 2007 [2] and is divided into six phases: site selection, site preparation and construction, operations, extended monitoring, decommissioning and closure, and post-closure monitoring [1].

NWMO started the site selection process to find a suitable location for the DGR in 2010. The approximate timeline for the site selection phase is planned at 15 years, which will then be followed by the site preparation and construction phase that will take approximately ten years. After the used fuel has been transported to the new facility, the management and arrangement operation phase will commence lasting approximately 40 years. For some time after that phase, the DGR will be monitored before deciding on the closure of the facility. Finally, after the closure, the facility will transition into the post-closure monitoring phase in case of an accident [1].

The idea for fuel transportation is to use a used fuel transport package (UFTP) and transfer this package via ground shipment methods. The UFTP is designed to contain two used fuel storage modules, one stacked on top of the other. This storage module holds 96 bundles aligned in a rectangular frame, as shown in **Figure 2.3** [3].

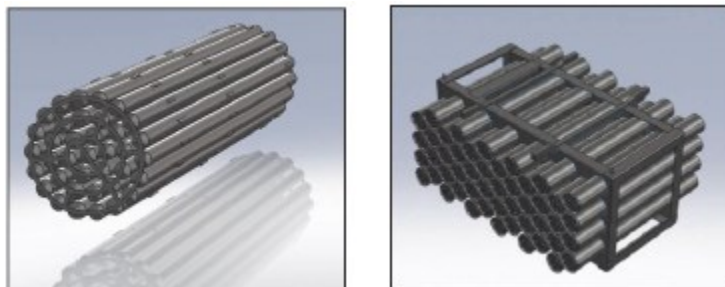


Figure 2.3 UFB (left) and UFTP with the 96 bundles (right) [3].

The destination of the used fuel is the DGR facility. This facility is divided into two sections: the surface facilities and a DGR where the used fuel will be stored long-term. The DGR is separated into

the main shaft complex, placement rooms (shown in the green square), and ventilation exhaust shafts (the ventilation exhaust shafts also have a surface facility attached), as is illustrated in **Figure 2.4** [1].

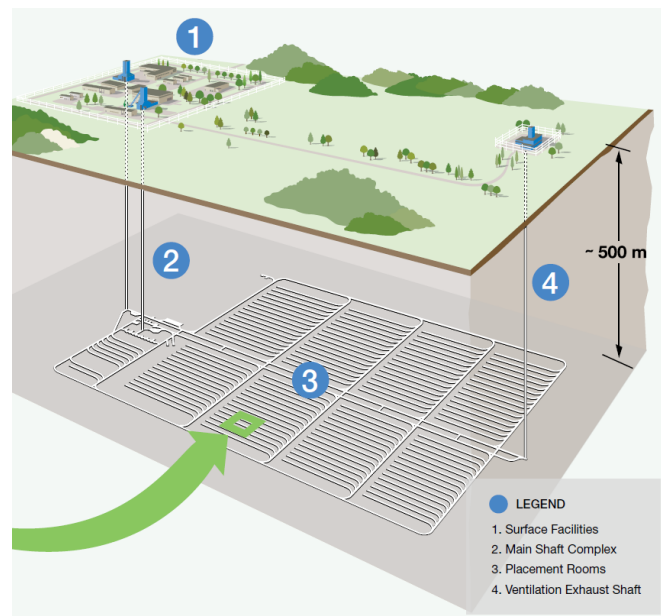


Figure 2.4 Concept of the Deep Geological Repository (DGR) with the four principal parts: surface facilities, main shaft complex, placement rooms, and ventilation exhaust shaft [1].

The land area of the facilities is planned to span around 650 by 550 meters for the above ground facilities buildings. The buildings of the surface facilities need to be designed to receive the UFBs and then transfer them into UFC. These containers have specific properties to prevent possible environmental impact, one very important property being corrosion resistance. Then the UFC needs to be put into a bentonite buffer box and to be transferred into the placement rooms of the DGR [1].

2.2.3 Deep Geological Repository

The DGR uses a multiple-barrier approach that contains man-made and natural barriers for long-term storage of the used fuel and as well to isolate them in a convenient crystalline or sedimentary rock arrangement [3]. The DGR is required to be constructed at a depth of approximately 500 meters [1]. The natural rock surrounding the selected location will prevent water flow and reduce radioactivity motion [6].

The concept for the DGR is based on the natural repository found in Saskatchewan, “The Cigar Lake”, which is a natural uranium deposit found 450 meters below ground and covered by layers of clay. This is a natural example of how long term nuclear storage can be designed due to the fact that there is no reported radiation at the surface level above the uranium deposit [7].

The DGR incorporates an array of placement rooms (as shown in **Figure 2.4**) to arrange the UFCs enclosed in buffer boxes made of bentonite clay. Additionally, there are channels to have access to and monitor the waste. DGR predetermined design size is two by three kilometers. The design incorporates the geological nature of the rocks where the DGR is going to be constructed, man-made barrier systems, safety conditions, and the inventory of the UFCs to be stored [1].

At the time of writing, the location of the DGR has yet to be determined. Original sites of interest were located in Saskatchewan and Ontario. At this time all Saskatchewan locations have been ruled out and only locations in Ontario remain (shown in **Figure 2.5**) [8]. There are two possible types of rock where the facility could be located: crystalline or sedimentary. The type of rock will have an influence on the final facility design/layout, because of the characteristics of each rock environment. One of the most significant differences is the distance between the buffer boxes in the placement rooms. Both rocks are elastic, isotropic, homogeneous, and sparsely fractured [3].



Figure 2.5 Five possible DGR locations under research in Ontario [8].

The construction of the DGR is planned to take about ten years with a layout designed to support the placement of up to 10 UFCs per day in the placement rooms [3]. The material needed for the UFC placement into a bentonite clay buffer box (as shown in **Figure 2.6**) and the enclosing of the placement rooms is a mixture of raw aggregate and bentonite clay that produces dense and light backfill blocks [1]. The properties provided by the bentonite clay will prevent any water flow and microbiological life [6].



Figure 2.6 UFC inside the bentonite clay buffer box [1].

2.3 Used Fuel Container (UFC)

2.3.1 Characteristics

The UFCs are a critical component because they will be the first and most direct point of contact with the radioactive waste material. They require specific characteristics including mechanical strength, simple manufacturing, capacity, compatibility with surrounding sealing materials, and the most important characteristic, corrosion resistance [1].

The base material selected for UFCs is low carbon steel with a copper coating to achieve the primary goal of corrosion resistance. Copper has been selected as a corrosion protective material based on the observation that only a small percentage of corrosion occurred in natural copper plates formed 200 million years ago in stones in South Devon U.K. [7]. Due to the manufacturing process and its cost, the steel vessel was selected instead of manufacturing a copper canister and attaching a copper cover as corrosion protection [3]. Another advantage of the coating process is that it requires a smaller amount of copper. The smaller amount of copper can be attributed to the possibility of a thinner layer of copper when using the new coating method as opposed to a fixed body copper shell [8]. The fully dense copper coating is planned to have a thickness of 3 mm. This is an ample thickness considering the coating thickness needed for corrosion resistance over 1 million years is predicted to be only 1.3 mm [3]. The 3 mm thickness will provide an additional 130% safe zone [3]. However, the mechanical properties of copper do not allow the manufacturing of a thin shell [9]. To solve this issue, coating techniques were investigated, where the best options were found to be electrodeposition and CGDS. The selection of this coating technique was because the comparison with other thermal techniques results in fewer residual stresses. Additionally, the

CGDS and electrodeposition techniques will be easier to automate all the manufacturing processes for healthy reason because the radioactive material is in the UFC.

The UFC has a total length of 2.5 meters and a diameter of 0.6 meters [1]. In comparison to the other designs, the selected design for the UFC will be easier to manage, specifically when the radioactivity material is deposited into the UFC [6].

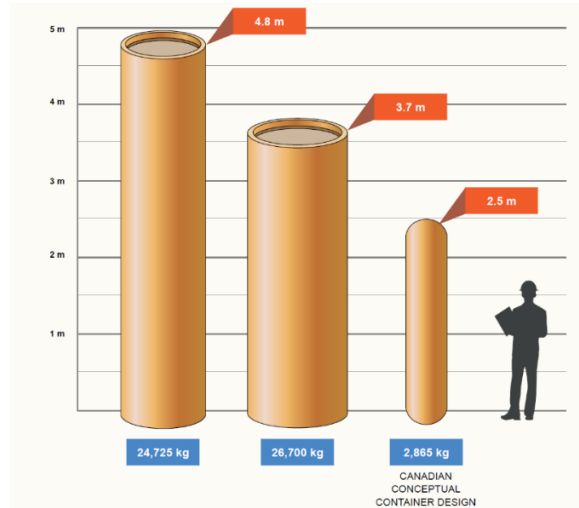


Figure 2.7 Designs for Used Nuclear Fuel Containers (UFC) [1].

To simplify the process of storing the UFB inside the UFC the final design divides the container into two partitions: the head and the body (illustrated in **Figure 2.8**). Due to the radioactivity of the bundles, it is essential that the copper coating is completed before the radioactivity material is placed inside of the UFC.

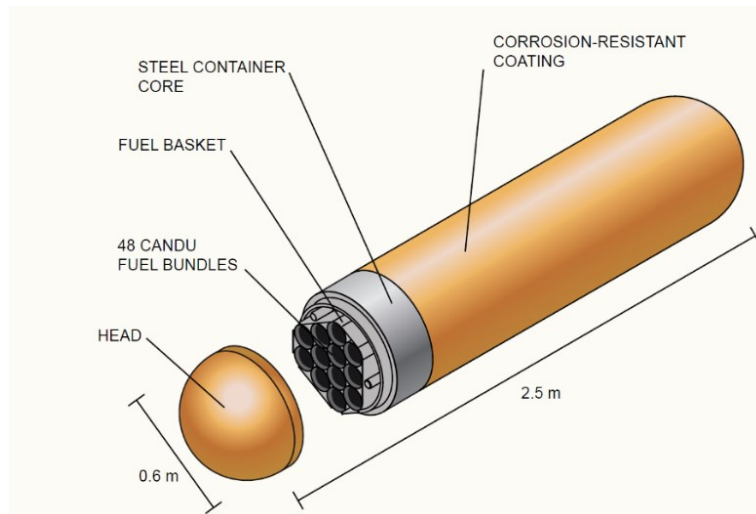


Figure 2.8 Used Fuel Container design for CANDU fuel [1].

Once the UFBs are deposited inside of the UFC, the body and the head are welded with Hybrid Laser Arc Welding (HLAW) by Novika (La Pocatière, QC). Subsequently, the CGDS technique is used to

coat the welded area (shown in **Figure 2.9**) because electrodeposition is not possible since the radioactive material inside of the UFC can react with the chemical bath solution.



Figure 2.9 Full-sized leading assembly: close-up of closure weld area after welding and machining (left), installed with collars on roller frame before the coating of the closure weld (middle), and (c) after coating and machining of the closure weld (right) [8].

After the CGDS process, the UFC is going to be enclosed in a bentonite clay buffer box, as illustrated in **Figure 2.6**. The UFC must withstand pressures exerted by the bentonite clay sealing around the container, the rock enclosing the DGR, and the next ice age. For this reason, the UFC is designed to withstand mechanical and hydraulic pressures up to 45 MPa [1]. With the estimated number of 120,000 UFB per year, there are plans to manufacture 2,500 UFCs per year.

The DGR will be subject to several changes due to the radioactivity material of the UFCs. It will go from a warm and oxidizing environment to a cool and anoxic environment over an uncertain time [10]. If the temperature increases past 125°C, the electrochemical performance of the copper coating will be affected resulting in an increased rate of the corrosion process [3].

2.3.1.1 Electrodeposition

The technique of electrodeposition was selected to coat the steel vessel before the used nuclear fuel is deposited. One advantage of this technique is that it can produce coatings on a large scale via pulsed plating methods [11]. NWMO and the Ontario-based company Integran Technologies have started to develop the coating technique through a procedure involving a pyrophosphate (solution chemistry) system. The coating is carried out with a pyrophosphate solution used in conjunction with pulsed potentiometry to apply enough current to reduce the carbon and oxygen content on the coating [12]. Integran Technologies designed a manufacturing line to verify the convenience of this technique, as **Figure 2.10** shows [8]. This manufacturing line includes a pre-treatment process that involves various cycles of surface cleaning [8].



Figure 2.10 Copper electrodeposition pre-treatment and process [8].

The coating process requires a high-purity, oxygen-free copper anode. Having the copper anode, the procedure consists of the oxidative dissolution of the anode and then the reductive plating of copper ions onto the steel substrate (cathode) [6][11]. Finally, the coating is machined to the desired surface finishing [8]. **Figure 2.11** illustrates the UFC prior to and after the copper electrodeposition.

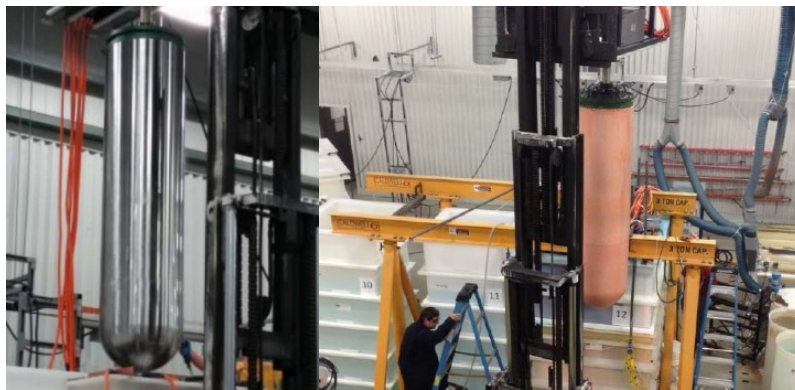


Figure 2.11 UFC prior (left) and after (right) copper electrodeposition [8].

2.3.1.2 Cold Gas Dynamic Spray

CGDS is a coating technique based on a cold high pressure carrier gas that travels through a heater and then through a converging-diverging nozzle where the gas is accelerated. Solid metallic particles are accelerated to high speeds by the carrier gas. Upon impact, solid particles have enough kinetic energy to deform plastically and bond to the substrate and form a coating.

The CGDS technique has great benefits compared to many other coating techniques that exist because it does not subject the spray material or the substrate to high temperatures, preventing melting and oxidation. This is made possible because of the particles bond to the substrate as a result of its kinetic energy at the moment of impact [13], not thermal energy.

This technique is planned to be used to coat the area that has been welded using HLAW. This area is not planned to be coated with the use of the electrodeposition technique, as the radioactive used fuel is going to already be deposited into the UFC at this point and it could react with the pyrophosphate solution. As in any coating process, the preparation of the substrate is vital. In this case, preparation involves grit-blasting the previously welded surface to remove any mill scale before continuing with the CGDS process [14]. However, at the time of writing the substrate preparation process is still being optimized and has not yet been finalized. After the CGDS coating has been completed, a thermal treatment will occur due to the brittleness of the CGDS coating, as an essential characteristic for the UFC coating is that the coating must be ductile.

The adhesion of the copper coating to the UFC steel vessel is a challenging topic when considering the overall design of the UFC. Researchers have demonstrated that coating delamination occurs because of the accumulation of residual stresses at the interface of the coating from the cold working of the powder upon deposition and due to the thermal expansion difference between the copper coating and the low carbon steel substrate (shown in **Figure 2.12**) [15]. This residual stress overcomes the coating/substrate adhesion strength and delamination occurs that usually occurs when the coating thickness reaches 1.2 to 1.5 mm [6].



Figure 2.12 Copper Coating over Steel Substrate [6].

Furthermore, chemical compatibility is hard to achieve between copper and steel to facilitate metallurgical bonding [15],[16], [17],[18]. For that reason, many copper powders (different shapes, sizes, manufacturers, and oxygen content) and different depositions parameters were studied. The studies concluded that the copper coating adhesion obtained is conceivably only achieved by the mechanical anchoring mechanisms [19], [20]. Consequently, the copper particles need to achieve a high velocity that leads to better adhesion to the substrate. High velocity particles show higher kinetic energy that is enough to the deformation upon the impact of the particle and the substrate.

Additionally, it was observed that there is no coating failure when the delamination occurs which means that the copper cohesion strength between particles is larger than the adhesion strength between coating and substrate. However, the residual stress as the thickness coating increases is more predominant than the adhesion strength by the mechanical anchoring done by the first layer of the coating. For that reason, the first layer of copper coating is might be the most important to achieve a higher adhesion strength.

The solution that has been found so far is to deposit a thin layer of copper as a bond coat (~100µm) with helium as a carrier gas and then build the rest of the coating thickness with nitrogen as the

carrier gas [6][19]. There are some advantages when using helium such as an increased gas velocity that results in an increased particle impact velocity. This increased velocity results in a more intricate/intimate bonding interface and increased adhesion strength. This is because helium has a high speed of sound, [21]. Additionally, the bond coat will result in a higher adhesion strength to the steel as result of higher plastic deformation due to the higher particle impact velocity comparing if the carrier gas is N_2 [22].

Figure 2.13 illustrates SEM images of cross section cut of copper coatings by CGDS with N_2 and helium as the carrier gas and the steel has a grit blasted preparation. It can be observed that the interface with N_2 as carrier gas has gaps between the coating and substrate while with, He there are no gaps and the mechanical anchoring is more obvious.



Figure 2.13 SEM Cross section image of the interface copper coating with low carbon steel substrate preparation of grit blasted with N_2 (left) and He (right) as carrier gas [23].

The investigation continued to search for a better way to produce the CGDS coating using nitrogen because helium is more expensive, and it is a non-renewable source. Nastic et al. [15] and Fernández et al. [24] developed coatings without delamination for the UFCs using only nitrogen as the carrier gas. With some of the parameters used in testing, the coatings exceeded expectations. The way to achieve this was to create higher initial substrate surface roughness through the use of Pulse Water Jet (PWJ) as substrate preparation treatment that results in a different roughness scale depending on the parameter employed.

Nastic et al. [15] were able to increase the adhesion strength of the copper coating on steel from delamination (polished and grit substrate) until up to 56 MPa with the PWJ as substrate preparation only with nitrogen as the carrier gas. The reason was that with the PWJ it was possible to increase the roughness to 58 μm as **Figure 2.14** illustrates. This level of roughness creates features that promote the mechanical anchoring between coating and substrates that results in higher adhesion strength.

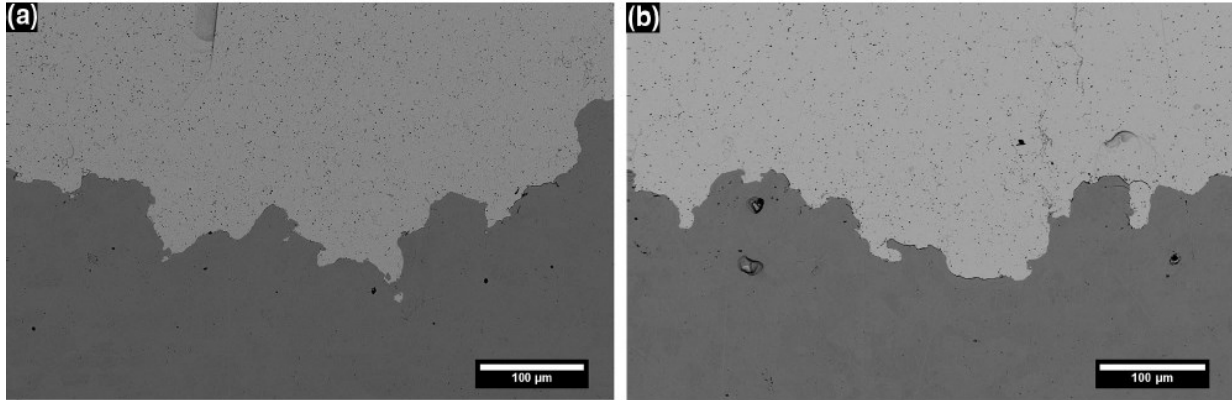


Figure 2.14 SEM images of the interfaces of coating/substrate with PWJ as substrate preparation that results in a roughness of 58 μm [15].

Even though it was successful, NWMO decided to continue with the investigation to find another method. This was because the use of water to create roughness could result in acceleration of corrosion and exposing the radioactive material inside of the UFC can react with the water during PWJ process as substrate preparation before CGDS process.

The studies are still focused on eliminating the requirement of a first bonding layer with helium. One solution that is being studied is a laser assisted CGDS. These studies are currently being carried out in conjunction with NRC-IMI[14]. This possible solution brings to the forefront of the investigation of the effect of substrate temperature. As the substrate temperature increases, the stress required for plastic deformation decreases as a result of the substrate softness. In addition, it increases the possibility of achieving metallic bonds and mechanical anchoring because of the reduction of the yield strength of the substrate and the thermal softness [4].

Figure 2.15 illustrates the robot assisted laser that is implemented next to the CGDS nozzle to preheat the substrate. In this case, the substrate is a real scale of the UFC. The laser preheated the substrate just before the copper powder impact.

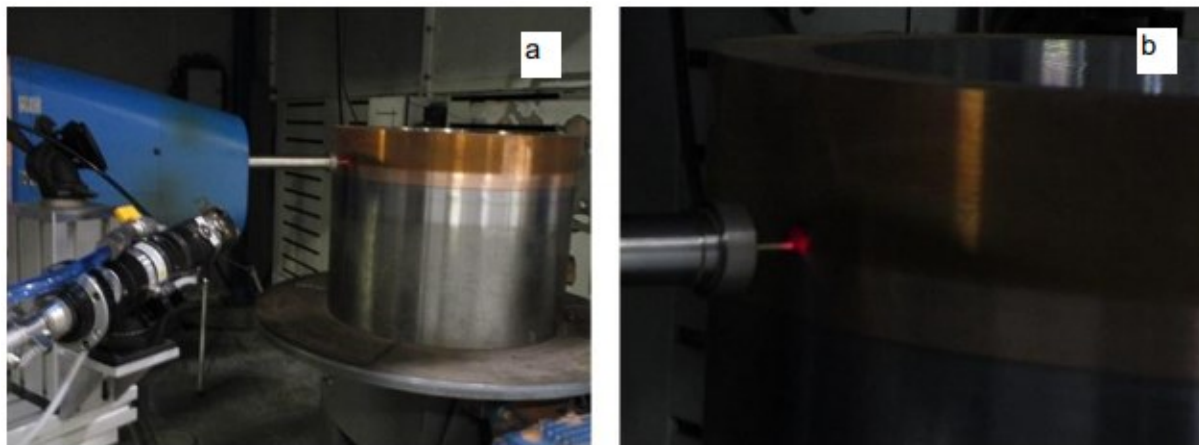


Figure 2.15 a) NRC CGDS system with the implementation of the robot-assisted laser for preheating the substrate, b) close up of the laser spot on the substrate [14].

2.3.2 Corrosion of the Internal Steel Weld Region

The closure weld area is the most prone to failure because this area consists of steel with a thickness of only 8 mm in comparison to the 47 mm steel container wall and the 30 mm thickness of the spherical head [9]. Corrosion in this welding area could produce stress on the welded section which could result in a total failure of the weld. However, the elimination of any excess H_2O will be a pre-emptive solution carried out before sealing the UFCs. As well, the welding area needs to be completed with a technique that will guarantee that corrosion of the weld area will not happen, even in the worst-case scenario.

Additionally, if crevices exist between the head and the body of the UFC, there is a risk that water droplets may condense and may encourage corrosion in this area due to the accumulation of oxide or H_2 gas. Stress corrosion can occur as a result of water condensation in the area of the weld. Experiments and simulations were carried out in this area to demonstrate that even through corrosion and irradiation, the crevice remained unharmed over time [14]. Similar galvanic corrosion will occur early on in the oxidation period when steel dissolution occurring at the base of the defect pushes O_2 onto the nearby copper surface [10]. However, the area near the coating defect will quickly absorb the oxygen. Additionally, NWMO presented results from experiments carried out with coupons of steel welded together showing that the corrosion at the weld zone occurs at a slower rate than the rest of the coupon [8].

2.4 Cold Gas Dynamic Spray Principles

The CGDS technique (shown schematically in **Figure 2.16**) is based on a gas carried at the desired pressure that travels through a heater where the temperature of the gas is increased subsequently. The gas then travels through a converging-diverging nozzle where it accelerates while its temperature decreases. Solid particles are introduced via a separate gas before or after the throat of the nozzle, depending on the type of system. Upon impact, solid particles with enough kinetic energy deform plastically and bond to the substrate to form a coating.

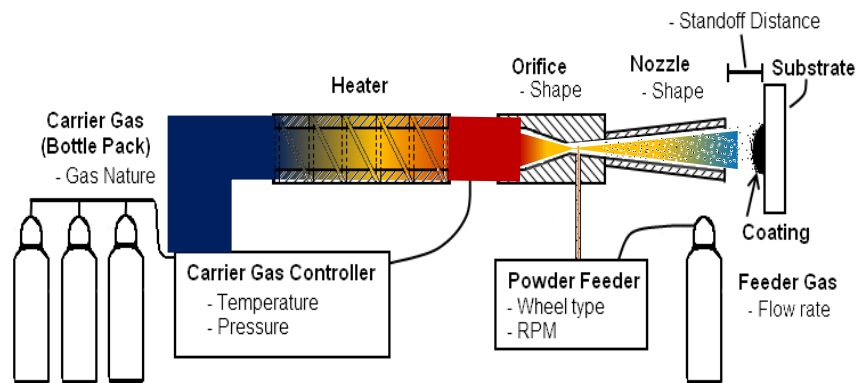


Figure 2.16 Schematic of CGDS system (image courtesy of Patrick Trahan).

The build-up of the coating is divided into four stages, sometimes occurring at the same time, as illustrated in **Figure 2.17**. The first stage is the first contact between the substrate material and the monolayer of the particles; this is the beginning of the adhesion bond between the two materials. For particles that do not adhere, craters may be created that results in some roughness that helps with subsequent particle adhesion. In addition, the roughness, hardness, particle velocity, and temperature conditions of the substrate influence the adhesion strength. The next stage is the deformation and realignment of the particles. The third stage is the particle-particle bonds. The final stage is the continuous build-up of the coating that causes an effect of shot peening resulting in work hardening.

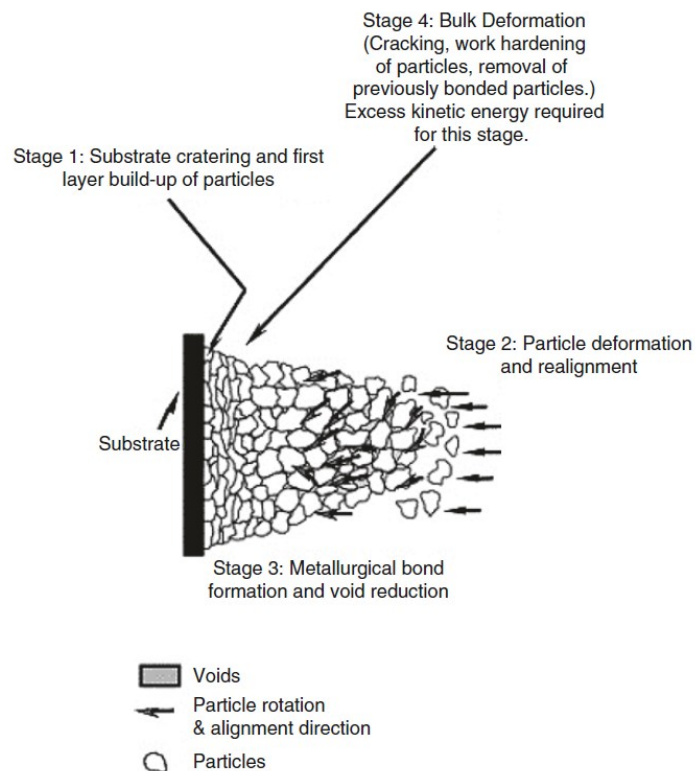


Figure 2.17 Different stages during the built-up coating by CGDS [25].

2.4.1 Bonding Mechanism

To achieve a successful bonding, it is necessary that the particles impacting the substrate exceed the associated critical velocity of the powder [26]. Bonding can be divided into two categories: metallurgical and mechanical, depending on the coating and substrate materials [27]. Mechanical interlocking is described as any physical connection between particles and substrate that has achieved adhesion [4]. Metallurgical bonding is a consequence of atomic diffusion between materials. Commonly metallurgical bonding shows a higher adhesion strength [28].

2.4.1.2 Metallurgical Bonding

Metallurgical bonding is only achieved when the native oxide film on the particles and substrate is broken and there is fresh metal-metal contact where highly localized contact pressure occurs; this is explained graphically in **Figure 2.18** [29].

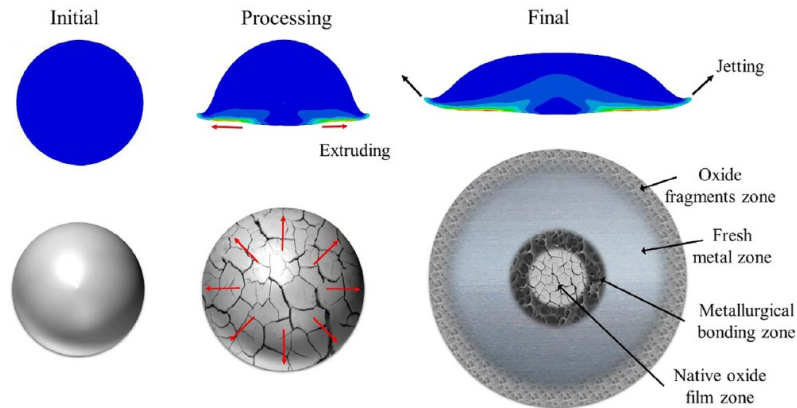


Figure 2.18 Diagram of the bonding process at the contact with the substrate [29].

The presence of this bonding type is often observed by the formation of an intermetallic phase at the interface, dimple like fractures [28], a small amorphous layer [30], and a recrystallization zone at the particle-substrate interface (RX) [31]. It can be difficult to observe this kind of bonding experimentally. One way is to detach single particles impacted on the substrate, as **Figure 2.19** demonstrates. This bonding can be observed by gluing the bottom of the substrate and the top of the particles to tensile test rods and then applying force to detach the particles from the substrate [28].

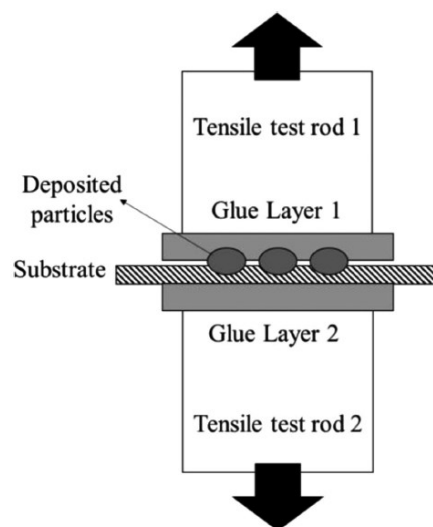


Figure 2.19 Representation of the experiment setup for detaching the particle from the substrate [28].

Once the particle is detached, dimple fractures, oxide film fragments, and micro-cracks can be observed, as shown in **Figure 2.20**, revealing the presence of metallic bonds prior to the test.

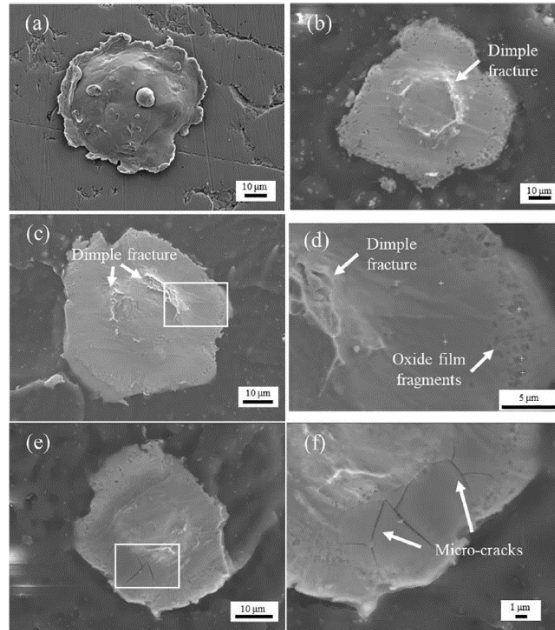


Figure 2.20 SEM images (a)Top view of single-particle impact, (b,c,e) bonding interface for different detached particle and (d,f) magnification of the images (c,e) [29].

Intermetallic phases can be formed by CGDS at the coating/substrate interface as long as there is localized melting at the nanoscale level. The localized melting is caused by the large deformation occurring at a high strain rate that increases local temperature, reaching the material's melting point or very close [32][33][34]. This allows for solid-state diffusion [32]. In other words, high kinetic energy conversion into heat and low volume of severe localized deformation can generate this localized fusion [35]. A factor that can enhance local melting is low thermal conductivity [35]. Interfacial melting was detected in the oxide-free zone only [29][30].

Some experiments have shown evidence of melting visible as long streaks or splashes that appear on the substrate around the Al-10Sn particle impacted on SAE 304 substrates, as shown in **Figure 2.21** [36]. Additionally, interfacial waves, ripple effects, roll-ups, and vortices are reported, likely a sign of an interfacial layer melting. Fluid flow can occur not only due to melting but typically in combination with the appearance of intermetallic layers as demonstrated in **Figure 2.22** [37].

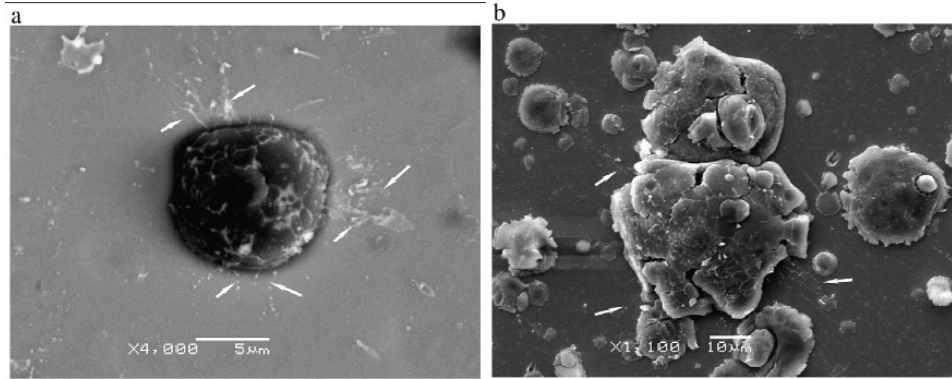


Figure 2.21 Evidence of melting like long streaks or splashes of Al-10Sn particle impacted on SAE 304 substrates. [36].

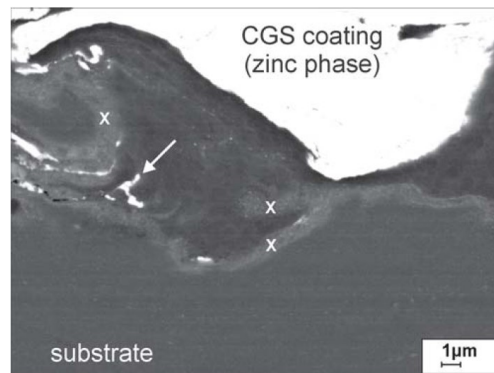


Figure 2.22 SEM image of Zn5Al coating and the AA7022 substrate that show vortices in the interface [37].

Another way to detect metallurgical bonding is by the observation of dimple-like features or cup and cones [29] [35][38][39][40]. Dimple-like fractures are typically observed to be around the central contact area where it is more straightforward to break the oxide layer due to the cleaning effect of the metal jets, as **Figure 2.23** shows. Evidence of micro-cracks is the result of the residual stress caused by the shrinkage during solidification from the local melting material [29].

Chen et al. [28] reported experimentally and with modeling that the angle at which the particles impact the substrate affects the amount of metallurgical bonding. Metallurgical bonding is more evident at 90° compared to the 75° and 60° spray angle, shown in **Figure 2.23**. Additionally, the creation of metallurgical bonding can be improved by annealing which promotes atomic diffusion and microstructure consolidation [27].

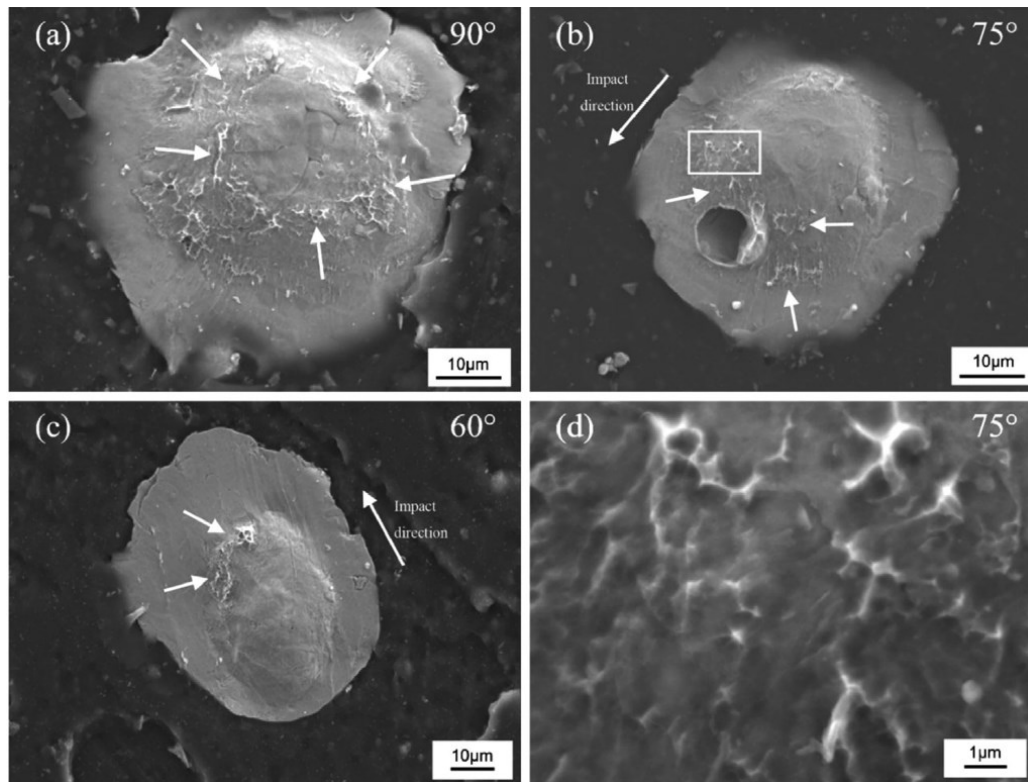


Figure 2.23 Evidence of metallurgical bonding by the dimple like fractures at different spray angles (a) 90°, (b) 75°, (c) 60°, (d) magnification of the image (b) [28].

2.1.1.2 Mechanical Bonding

Bonding can also be reached through mechanical interlocking. Mechanical interlocking is caused by the strong impact of particles on the substrate. This impact can form lips that envelope the particles [41], but with no atoms exchanged between the coating and substrate [42]. The mechanical bond is the physical connection between the particle and the substrate by the interlocking and mechanical anchoring. In some cases, adhesion strength can be stronger than metallurgical bonding [4], depending on the properties of the materials involved and spray conditions.

Hussain et al. stated that mechanical interlocking is created by the metal jet of particles during impacts that cause the lips of the substrate that envelop the particles [41]. Mechanical bonding or metal-metal anchoring increases with the increase of particle velocity [27]. Preparation of the substrate before a deposition can increase the levels of bonding using processes that may increase the surface roughness through methods including grit-blasting and forced pulsed waterjet (FPWJ) [4].

Grit blasting with Al_2O_3 is the most common substrate preparation process to increase the surface roughness necessary for bonding [43] and at the same time cleaning the surface. Grit blasting with

SiC may also be used for substrate preparation [44]. The two parameters important in this method are the pressure and the angle of grit-blast. The importance of each parameter depends on the material properties of the substrate resulting in different roughness and subsequently different adhesion strength between coating and substrate [44][45][46]. Regrettably, this technique has a limitation of the level of roughness that can be achieved, and sometimes residue can contaminate the coating process [47].

FPWJ was proposed as an alternative technique for creating higher surface roughness before coating deposition. This technique reduces the possibility of foreign particles that may produce contamination of the substrate [48]. FPWJ can increase mechanical adhesion due to enhanced anchoring as displayed in **Figure 2.24** [15][24][48].

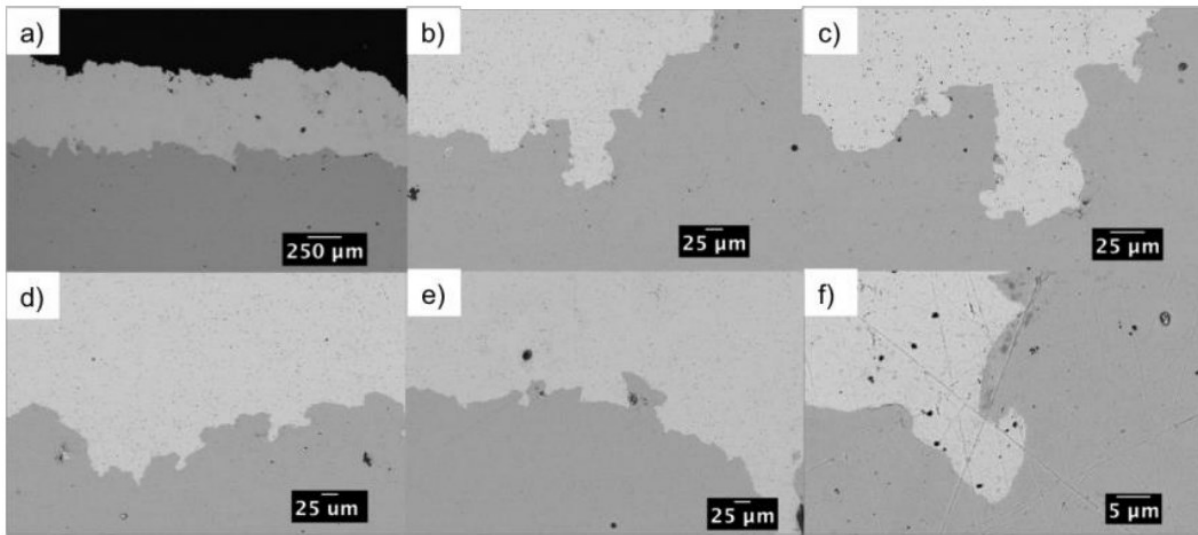


Figure 2.24 Mechanical anchoring demonstrated by a cross-section of coating-substrate, in which the FPWJ was used as substrate preparation [15].

2.4.2 Microstructure Upon Impact

The formation of the amorphous layer is a result of the rapid cooling because of the small amount of the melted particles. Then because of the quasi-stable microstructure, the recrystallization may begin the process of grain refinement, especially in the greatly elongated grains under the localized impact strain and experiencing severe plastic deformation [49].

Three factors play a role in the degree of amorphization on impact and atomic level mixing: the density of the particles colliding and the velocity at the impact, mechanical deformability, and hardness of the particle and substrate materials [50]. In other investigations, the amorphous layer was found to be formed upon the high-velocity impact of soft and highly deformed coating materials onto a hard deformed substrate [51]. However, other authors specify that the amorphous layer is the rapid quench of the extremely rapid heating and cooling in the adiabatic shear instability area [52]. For that reason, experiments commonly prove results with modeling. However, researchers found that the modeling did not achieve melting temperature but Transmission Electron

Microscopy (TEM) observation detected amorphous phases in the samples as **Figure 2.25** demonstrates [53].

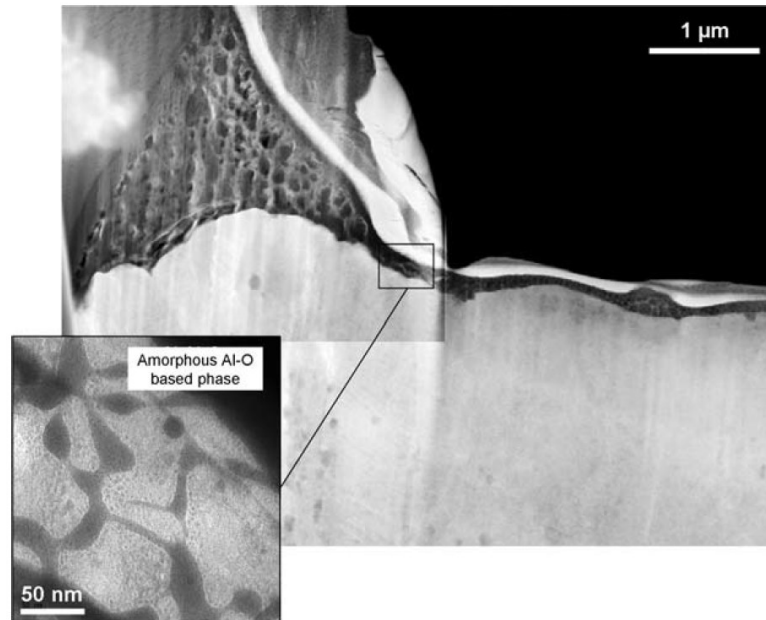


Figure 2.25 Image of an amorphous layer of Al-O from scanning transmission electron microscopy (STEM) high angle annular dark field (HAADF) [53].

The amorphous structure is retained down to room temperature due to the fast cooling by the thermal gradient acting normal to the interface [27]. Studies have demonstrated that metal at sufficiently high strain rates at temperatures of 27°C may experience a transformation to a homogeneous disordered state in strain-rate caused amorphization [27].

Researchers have found that the interface transitions into local amorphous volume fractions with the intermixing between substrate and coating resulted in the formation of vortices [50]. However, the researchers stated that it was difficult to maintain and experimentally observed the amorphization due to the fast crystallization at elongated time scales [52].

In summation, **Figure 2.26** demonstrates two types of processes for the development of nanograins at the particle-particle interface. The images on the side left of **Figure 2.26** (a-c) illustrate the particle impact with enough velocity on the coating surface and the massive deformation that results in the metal jetting as a result of adiabatic shear instability. The grains near the interface are elongated, accompanying the further deformation. The effect of tamping the successful impacts of particles results in the elongation of the interface grains. Likewise, through recrystallization, the dynamic refinement of the deformed grains is accomplished [49].

On the other side of **Figure 2.26** (d-f) the metal jetting is a result of the melting metal at impact due to the increase of the interface temperature. The splashing of this liquid appears to start the deposition of the fine particles on the curved surface of the deformed particles. Then the quick solidification of the fine particles forms the fine grains and amorphous layer. The subsequent

particle impacts are tamped to compress along the path of the interface, and the oriented lamellar structure is created.

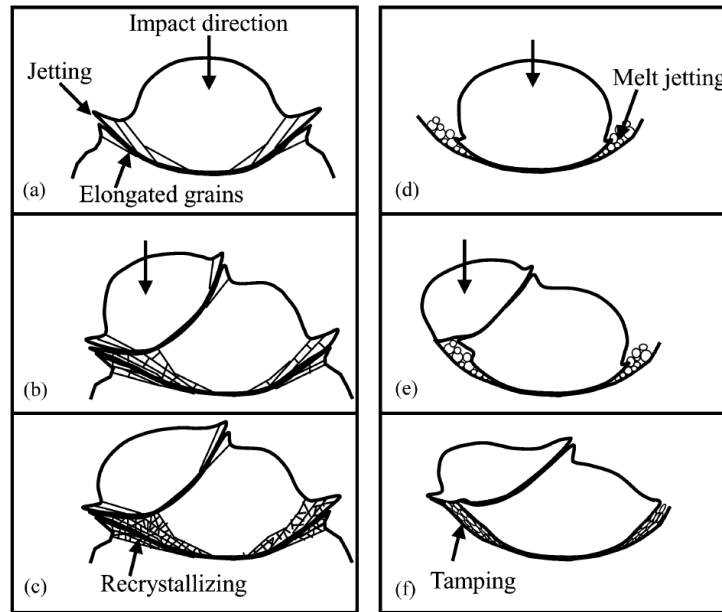


Figure 2.26 Illustration of the development of the particle interface microstructure in the cold-sprayed coating by recrystallization refinement mechanism (a–c) and tamping of melting-induced particulates to lamellae (d–f) [49].

Finally, B. Yu et al. [31] indicated that the degree of recrystallization (RX) is related to the metallurgical bonding appearance. In the CGDS process, there is evidence of Static recrystallization (SRX) and dynamic recrystallization (DRX) which depends on the thermal history at different areas of the coating. Likewise, the plastic deformation under high strain rate conditions induces a high amount of dislocations, dislocation wall formations, the formation of elongated sub-grains, break-ups of sub-grains, and recrystallization [54].

Additionally, Stoltenhoff et al. [55] identified that the DRX produced structures with fine-sized grains without voids or oxide presences that allow the particles to have a metal-metal bonding between them [13]. In **Figure 2.27**, the recrystallized inter-particle structure of the copper particles can be observed at the points shown by the arrows. The recrystallized structure smaller in size due to the rising temperature and strain rate that is evidence of DRX [54].

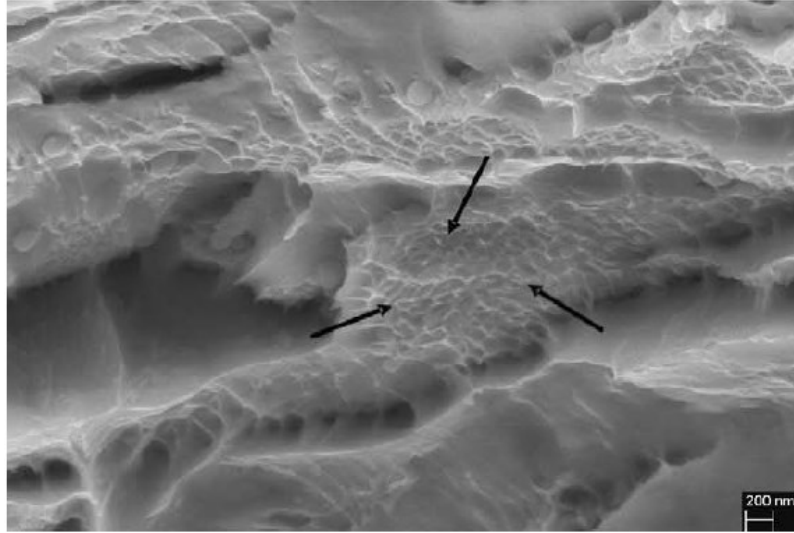


Figure 2.27 The recrystallized inter-particle structure indicated by arrows by Field Emission Scanning Electron Microscopy FESEM images [54].

Figure 2.28 illustrates the microstructural details from the top-view of the copper CGDS coating and demonstrates the fine-sized grains with an elevated amount of dislocations and the opposite case of dislocation free grains because of the DRX [54].

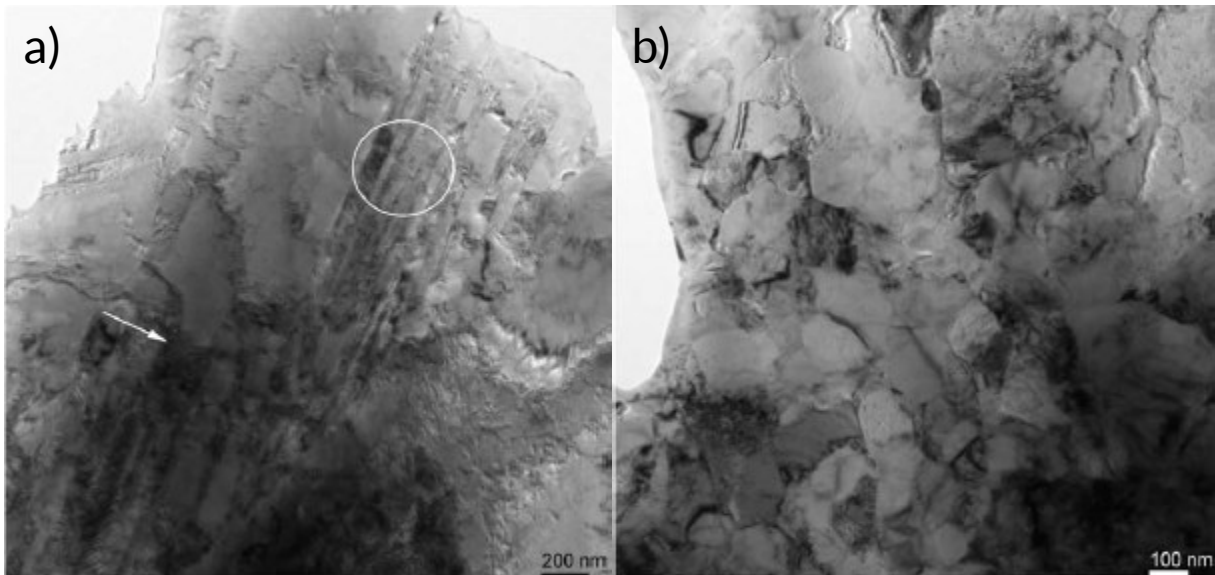


Figure 2.28 TEM Images of microstructural details from the top-view direction of cold-sprayed Cu coating a) shear bands (line-like structure, e.g., inside the circle) and high dislocation density (black areas, example showed by arrow) and B) grain structure with fine-sized grains. TEM images [54].

The annealing also encourages recovery, recrystallization, and grain growth through-out the coating because the strain gradient in the core of the splats of the deformed particles is reduced by the annealing [31]. As well, the atom diffusion is promoted by the annealing that modifies inter-particle bonding due to forming metastable microstructures such as dislocation cells and recrystallized fine grains at the inter-particle areas [55][56].

Recently, some studies were focused on the shot peening effect during the coating build up. The authors observed that the oxide layer that is necessary to break to allow the metallurgical bonding is not achieved completely with a single particle effect. Nevertheless, comparing this result with the finish and coating process in the same experiment they noticed that the oxide layer was completely ruptured by the effect of peening. By the shot peening effect, the interface coating/substrate is under high pressure that the metallurgical bonding is achieved as demonstrated in **Figure 2.29** through the modeling of the first and second layer of particles impacts at different pressures [57][58].

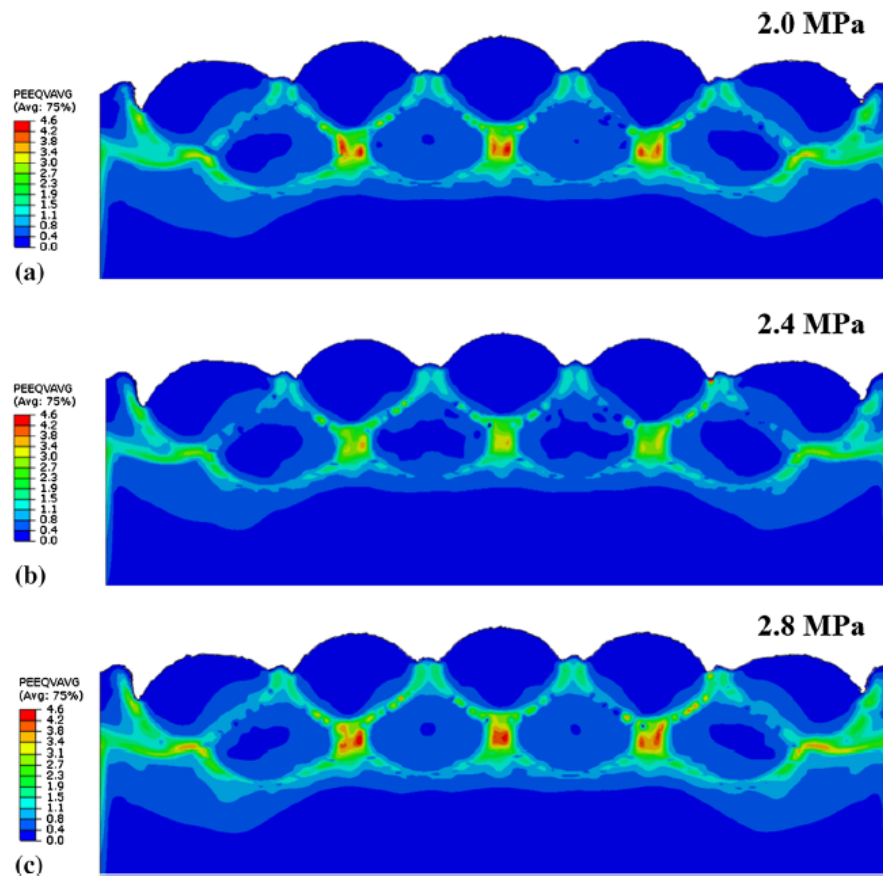


Figure 2.29 Modeling of first and second layer demonstrated the effective plastic strain evolution in different pressures [58].

2.4.3 Residual Stresses

The residual stresses are the stresses that continue in the coating/substrate in the absence of an independent mechanical or thermal force [4]. The distribution and quantity of residual stress is an important factor for the coating properties and coating adhesion such as bond strength [59][60][61]. The residual stresses depend on the plastic deformation, the strength level, and elastic modulus of the materials of the substrate and coating [59]. The residual stress can be compressive, neutral, or tensile depending on the particle density and deformation upon impact and coefficients of thermal expansion (CTE) of the substrate and coating materials [62][63].

The residual stresses are formed during two stages: a) particle deposition and b) cooling down after deposition [64][65]. During the deposition, the residual stress is due to the quench of a quick cooling and solidification of the particle upon impact [64]. Even that the CGDS process does not work with temperatures above the melting temperature, there is a heat transfer from the carrier gas to the powder and substrate [66] and in multi-passes deposition [60]. During the cooling down after the CGDS process, the residual stresses are developed due to the mismatch of CTE between coating and substrate [64][65].

Compressive residual stress may be produced during the CGDS by the high impact energy associated with the mass and the velocity of the particle and as well due to the peening effect of the CGDS [66][67][63] and because of that are the usual type of residual stresses on the CGDS as result of the plastic deformation [59][61][62][68]. The compressive are beneficial stresses on the enhance of the fatigue life [69] as these stresses delay the development and propagation of cracks so allows the application of a larger external load for a longer period of time [4][68]. Occasionally the compressive residual stress can introduce on the surface by hardening this surface such as it is the grit blasting technique as substrate preparation [66][70].

On the other hand, the tensile residual stresses are undesired as promote crack initiation and propagation [4]. After the CGDS deposition, the residual stresses have been demonstrated to range from compressive to tensile stresses. This is the most common negative effect or the residual stress that can be due to the accumulation of residual stress as coating thickness increases. Bonding can be achieved only in the case where the adhesive strength overcomes the internal residual stresses [20]. This effect can be generated by the mismatch of CTE of the material of the substrate and coating [64][67] that may towards the residual stress from compressive to tensile as the particles experience localized shrinkage [64].

The coating thickness is another aspect to consider in the adhesion strength due to the accumulation of residual stress [64]. The interfacial residual stress from compressive towards tensile with the increase of the thickness of the deposited layer. In other words, if the coating layer is thicker has a higher risk of debonding due to the accumulation of residual stress at the interface [60][71]. Additionally, a thick coating deposited with only one pass has a higher risk of debonding compared with another coating of the same thickness deposited of thinner layers at a small time interval [71]. This effect is due to the powder feeder is high or the nozzle spray speed is low that many particles are impacting over the substrate and consequently there is redundant residual

stress that can causing coating delamination or cracks due to the excessive particle bombardment per unit substrate area [72]. As well the stress distribution changes from compressive towards tensile with the increase in deposited layer thickness [71].

Suhonen et al. [62] states that the first layer of the coating is the most important on the effect of the residual stress on the properties and the bonding strength of the coating. Additionally, it is common that the nature of the residual stress of the first layer is different from the following layers.

One way to reduce residual stresses is through annealing [27]. Residual stresses begin to reduce through recovery and relaxation throughout the period of recrystallization [27]. The annealing temperature is an essential factor to analyze. Maintaining low-temperature annealing prevents the redistribution of residual stress or partial distortion. Additionally, it keeps the fine microstructure, hardness coating, and some other benefits of the as-sprayed material such as the absence of oxidation [27]. It has been shown that spraying a thin bond coat can have a positive change in the residual stress distribution [23].

2.4.4 Differences between Low and High-Pressure CGDS

One factor that can differentiate one CGDS system from another is based on the pressure of the propellant gas. In high-pressure cold spray (HPCS), the powder is injected in the high pressure section of the nozzle (upstream of the throat) while in low-pressure cold spray (LPCS) the particles are injected in the low pressure section (downstream of the throat) as **Figure 2.30** demonstrates. LPCS has the advantage that it is less expensive, as the powder feeder is not necessary to be robust and the system can have higher portability [4].

If the particles are injected in the converging area, the particles are in contact with a higher temperature gas. However, particles that are inserted in the diverging zone will contact only expanded lower temperature gas [73]. This can significantly affect the final temperature of the particle upon impact. In addition to the location where the particles are injected into the system, the particle deposition can be carried out in a coaxial or radial formation [21]. The coating structure of using the different CGDS systems can be observed in **Figure 2.31**.

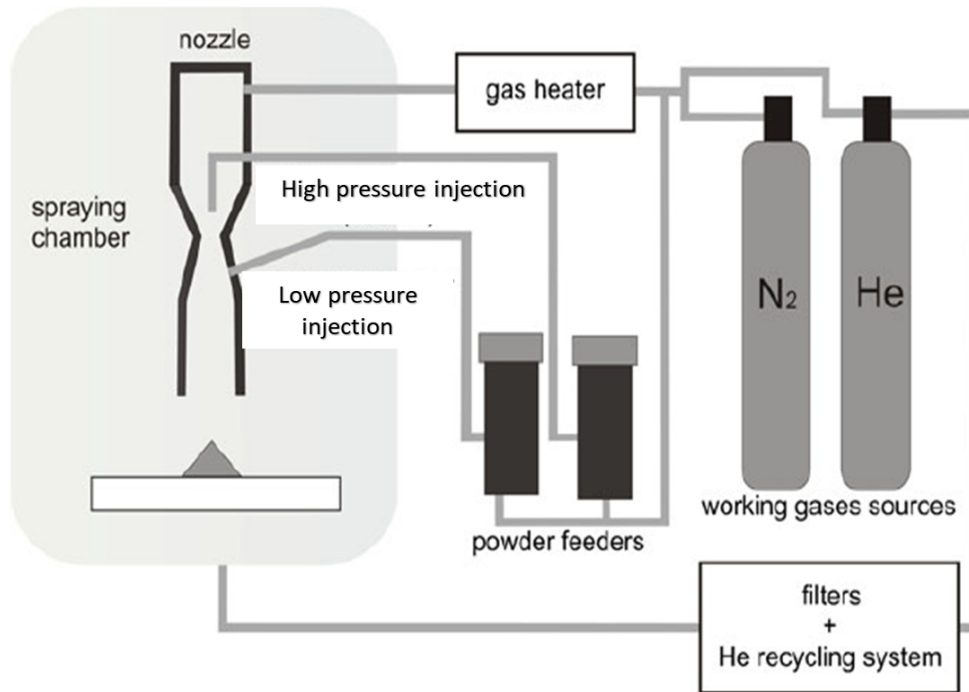


Figure 2.30 Representation of the CGDS process by two powder feeders and two carrier gas sources [21].

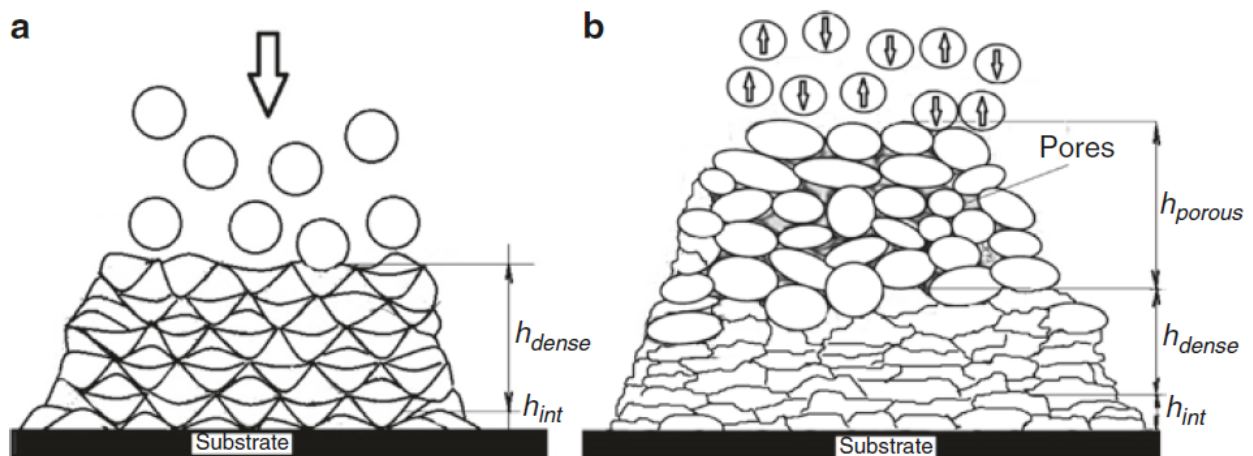


Figure 2.31 Schematic built-up coating in different systems a) High-Pressure System (HPCS) and b) Low-pressure System (LPCS) [27]

Commonly, when using the HPCS method, particles are deposited at a higher velocity compared to the LPCS method, therefore HPCS method usually has higher efficiency when comparing to the LPCS method [27].

Even though the particles usually have a lower velocity in the case of the LPCS method, particle consolidation occurs via the shot penning effect. When comparing the flattening ratio of particles, it is higher when observing the LPCS method than observed from the HPCS method where the

particles have a parachute-like shape. Additionally, **Figure 2.31**, shows that the densification of the coating is a result of the shot peening effect closer to the substrate, and near the top, the particles do not have enough kinetic energy to deform which results in a porous top coating [27].

2.4.5 Substrate Preparation

It has been stated that substrate preparation is not a necessary step in the CGDS process as the particles impact clean the substrate [4]. However, with further investigation substrate preparation can be found to be an important factor in achieving successful bonding. Commonly substrate preparation includes cleaning, chemical cleaning, polishing, or grit-blasting.

As noted previously, metallurgical bonding is often stronger than mechanical bonding [30]. Nonetheless, one way to improve adhesion levels of mechanical bonding is via improving the mechanical anchoring through the preparation of the substrate by increasing the roughness of the substrate [4]. Usually, grit-blasting is used as a substrate preparation method. As well as increasing surface roughness, the cleaning can break down the surface oxide layer [27]. Additionally, FPWJ can be used to increase the surface roughness to larger degrees when compared to the grit blasting, resulting in stronger adhesion of the coating [15][24][48].

Another method that is considered substrate preparation is shot peening in situ by introducing hard particles, such as Al_2O_3 , into the powder feedstock. This effect is because of the increased plastic deformation of the plastic particles expected to the further peening effect achieved through the hard and effectively nondeformable impinging particles [74][75]. However, the shot peening may result in contamination [76].

Chemical cleaning is not a very common substrate preparation method to employ due to the safety and environmental hazards introduced by the use of acids or bases including, but not limited to, sulfuric, nitric, or hydrochloric acid [4]. Despite this, Irissou [77] observed that metallurgical bonding was improved with the use of deoxidation using a solution containing 25% v/v of 85% H_3PO_4 (CE1) and also using a solution containing 50% v/v of 70% HNO_3 + 2% v/v of 40% HF. This substrate preparation eliminates the native oxide that is involved allowing metallurgical bonding to occur.

Differing from the methods described before, the laser ablation technique has recently been used to clean the surface, removing the oxide layer and adsorbed pollutant molecules. This occurs just before the particle deposition begins in the spray process where the pulsed laser irradiates the substrate [27][4][78][79][80]. **Figure 2.32** compares the surface morphology of the sandblasting process to the ablation laser process used as a substrate preparation method. It can be observed that the substrate with laser ablation preparation is more homogenous [78].

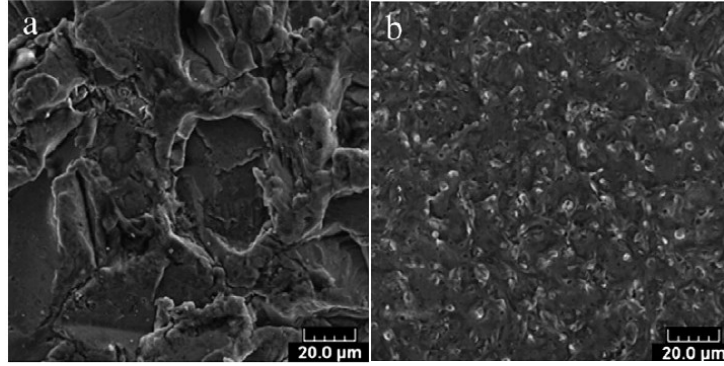


Figure 2.32 SEM images of Substrate surface finish after preparation by a) sandblasting and b) laser ablation [78].

Along with laser ablation, additional types of lasers are used to achieve substrate preheating and has been demonstrated as a factor for strong bonding and higher thickness of the coating. The substrate becomes softer as the temperature increases which allows deposition and the development of metallurgical and mechanical bonding [4] that is going to be explained in more detail in section 2.4.3 **Substrate temperature** of this document. Furthermore, sometimes the ablation and heating lasers can be combined in the CGDS process, **Figure 2.33** demonstrates this setup [78].

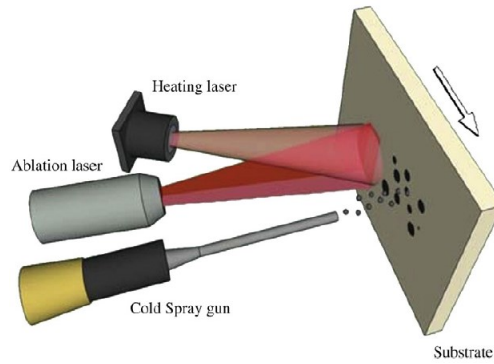


Figure 2.33 Set up of ablation and heating laser with the CGDS technique [78].

Nevertheless, adequate substrate preparation depends on the substrate material and strength, as well as the CGDS parameters. Different studies found suitable substrate preparation for some substrate materials but not all. It is necessary to perform proper investigations to find the appropriate substrate preparations for a given material.

Hussain et al. demonstrated that to achieve a durable bond through metallurgical bonding of spray aluminum onto aluminum alloy it is necessary to have a polished and annealed substrate compared to spraying onto a grit-blasted substrate [41]. As well, Yin et al. [30] found that polished and ground substrates improved atomic diffusion and increased the region of the intermetallic phase in contrast with the grit-blasted substrates. This may be a result of the work hardening responsible for the reduced plastic deformation ability of the spray coating to bond to the substrate [4]. In contrast, Makinen et al. found that for copper coatings, to achieve adhesion it is necessary to have a grit-blasted substrate [41].

2.4.3 Substrate Temperature

The substrate temperature is observed to be a factor that helps in coating bonding and in terms of achieving a quality coating in some particle/substrate material combination in the CGDS technique. Due to the gas preheating as a CGDS parameter, there is a heat exchange between the gas jet and the substrate that results in an increase of the substrate temperature during the spray[81]. This heat exchange is a result of the thermal conductivity properties, the speed of the nozzle or substrate during the process as a function of time and as well the thickness of the substrate, stand off distance, spray angle, and the number of passes to build up the coating [81][82][83][84].

Legoux et al. [85] demonstrated the effect of the heat exchange of the carrier gas and the substrate by measuring the substrate temperature using an infrared high-speed camera. In a) to d) of **Figure 2.34**, the substrate started at room temperature and when the gas is positioned in the center using the T gun inlet at different gas temperatures, the increase of substrate temperature can be observed as the gas temperature increases. However, in **Figure 2.34 e) to h)** the substrate started at different temperatures, in this case, the T gun inlet is at 500°C in all the cases and the result is that the heat transfer has an effect in increasing or decreasing substrate temperature.

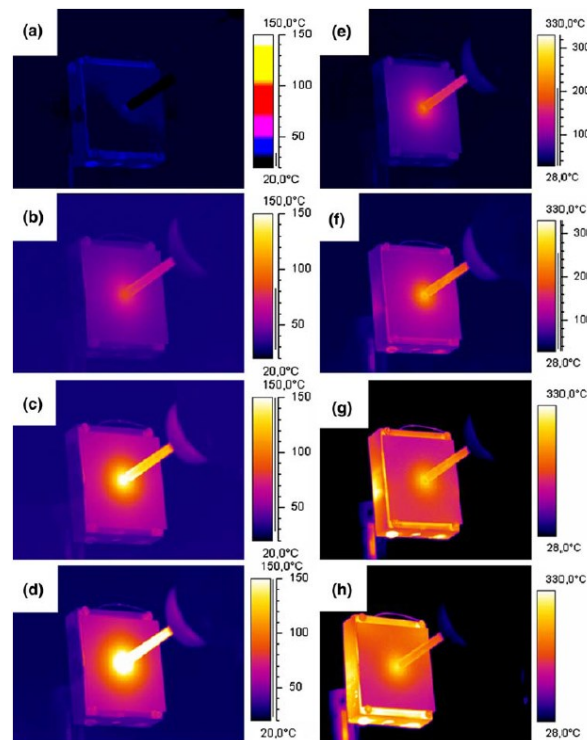


Figure 2.34 Infrared camera pictures of substrate and gun during CGDS at different conditions: left side substrate is at room temperature while the T gun inlet changes a) 33°C b)200°C, c)400°C and d)500°C. Right side T gun inlet at 500°C and substrate preheating at a) 33°C b)200°C, c)400°C and d)500°C [85].

The softness of the substrate can be achieved by raising its temperature to come to the conclusion that to achieve plastic deformation less kinetic energy is required [4]. The benefits of increasing the substrate temperature are that the deposition efficiency increases and consequently the amount of craters reduces in the first layer of the coating even without the preheating of the gas during the CGDS process [84][86], as **Figure 2.35** illustrates.

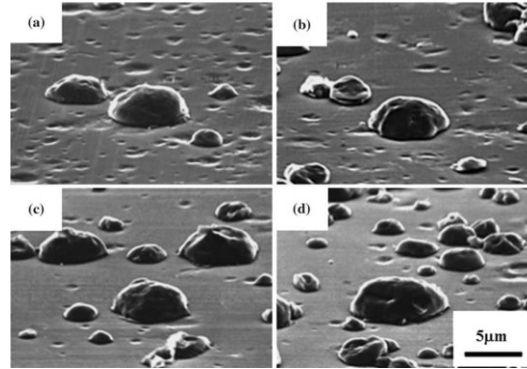


Figure 2.35 Single impact Cu particle at different substrate temperature a) 100°C, b) 200°C, c) 300°C and d) 400°C [86].

One more advantage of the substrate temperature increase is that it is easier to achieve mechanical bonding via interlocking [4]. The substrate deformation increase as a result of a decrease in yield strength and enhanced thermal softening [87]. This results in the achievement of the jetting from the substrate and particle that can be observed in **Figure 2.36** [88]. Moreover, **Figure 2.36** shows that as the substrate temperature increases the particles present less deformation and the substrate deformation rises even if an oxide layer at 700°C is present. In **Figure 2.36** (b) it is easy to identify the jets from the particle and the ones from the substrate.

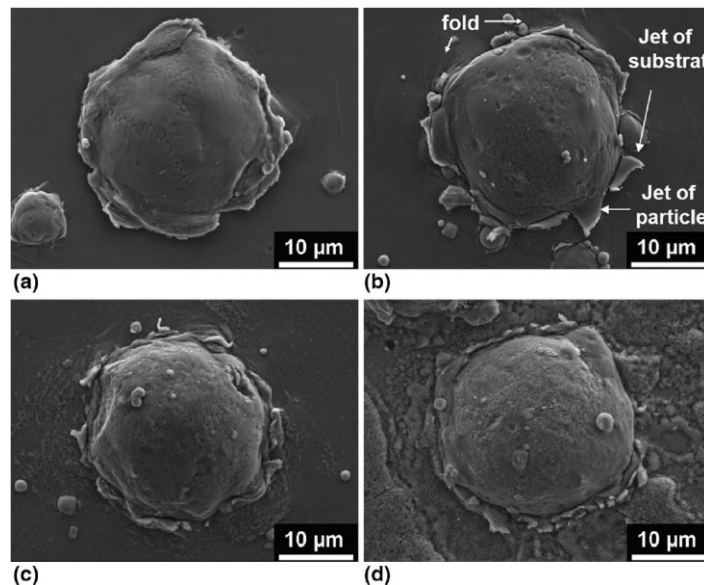


Figure 2.36 Single SS316L particle impact on a steel substrate at different temperatures a) 25°C, b) 400°C, c) 600°C and d) 700°C [88].

Additionally, metallurgical bonding is more easily achieved when a warmer substrate is used. This increase is a factor related to the interfacial melting because of the heat conduction [32]. As a result, the metal jet located at the substrate jet in the crater perimeter is more evident, and the atomic mixture results in a final outcome of stronger metallurgical bonding thus the bonding increases as can be observed in **Figure 2.37** [87][88]. Furthermore, temperature substrate increase results in more substrate deformation thus the oxide layer broke and a clean surface is available to achieve bonding. The characteristics of coating porosity and microhardness of the coating structure have minimal, if any, impact as a result of the substrate temperature [48][89][90].

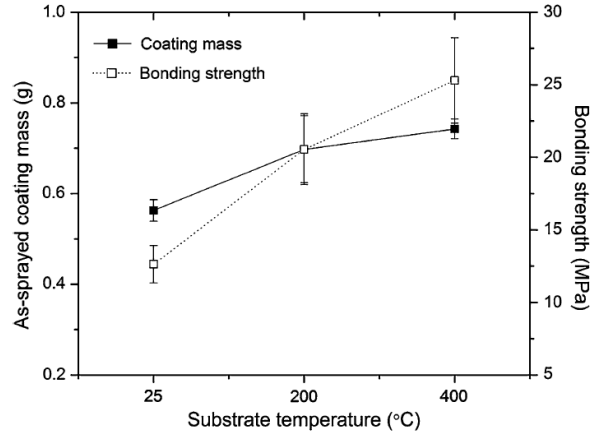


Figure 2.37 Bonding strength measurement at different substrate temperatures [87].

In **Figure 2.38** it can observe a modeling to confirm the experimental results when the substrate is preheated and in the case of the particle preheating. It can be observed that when the substrate is preheated the particles penetrate deeper and maintain a spherical shape while the substrate contains metal jetting [91][92]. In contrast, when the particle is preheated the particle deformation is massive resulting in splat shapes and it results in metal jetting when the penetration occurs at room temperature [91]. Furthermore, the substrate deformation has a positive effect on the particle adhesion due to the confinement of the adiabatic shear area with the splat/substrate interface heading to a successful metallurgical bonding [93].

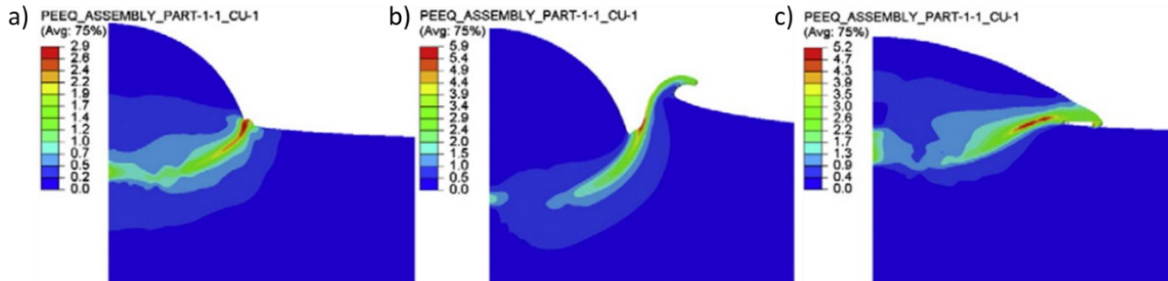


Figure 2.38 Deformation after particle impact in different temperatures of particle and substrate a) Particle and substrate temperature: 25°C, b) Particle temperature: 25°C and Substrate temperature: 700°C and c) Particle temperature: 700°C and Substrate temperature: 25°C [91].

The substrate preheating can affect the thermal expansion of the substrate and coating by altering the temperature distribution and thus release thermal stresses [90] [94]. The thermal stresses are caused by two factors: i) the mismatch in thermal expansion between the substrate and coating and ii) temperature distribution. These thermal stresses result in residual stresses [90] (as it was described in section **2.4.3 Residual Stresses**). Additionally, the thermal mismatched can turn the compressive residual stress that was developed under the peening effect into residual stress [66]. Besides, the substrate preheating maintains a more uniform substrate temperature during the spray and modifies the cooling rate [94] thus the reduction of residual stress [95].

Watanabe et al. [90] studied the effect of the A5083 substrate preheated effect by spraying Cu particles where the adhesion strength enhanced was observed. Their conclusion was that some thermal stress was relieved with the substrate preheated as the substrate temperature reduce the temperature difference between the inflight particles and the substrate and result in a decrease of the residual stress thus the adhesion strength enhances.

In other research of depositing SS304 particles onto SS304 substrate showed a coating without cracking due to the use of the laser preheating before the deposition. The researchers explained that the SS304 had a high CTE that results in large thermal gradients and tensile residual stress. However, with this laser pre-heating of the substrate reduced the thermal gradient thus a coating developed without cracks [96]. Furthermore, the author stated that the laser preheating can be controlled and thermal cycles could be established that can minimize residual stresses in the coating and substrate [96].

In contrast, one consequence of the substrate preheating is the growth of the oxide layer. Though, researchers confirmed that the intensive deformation of hard particles at high substrate temperature results in high adhesive strength of the interface coating/substrate even if the substrate contains a thick surface oxide layer [88][90].

2.4.3.1 Laser Heating

Laser assistance was described as a method of cleaning the substrate surface; nevertheless, the laser can also act to preheat the substrate just before the particles impact. The first time Laser Assisted Cold Spray (LACS) was presented was by Bray in 2009 [97] illustrated in **Figure 2.39**, where the laser is situated next to the nozzle and an infra-red pyrometer that measure the substrate temperature.

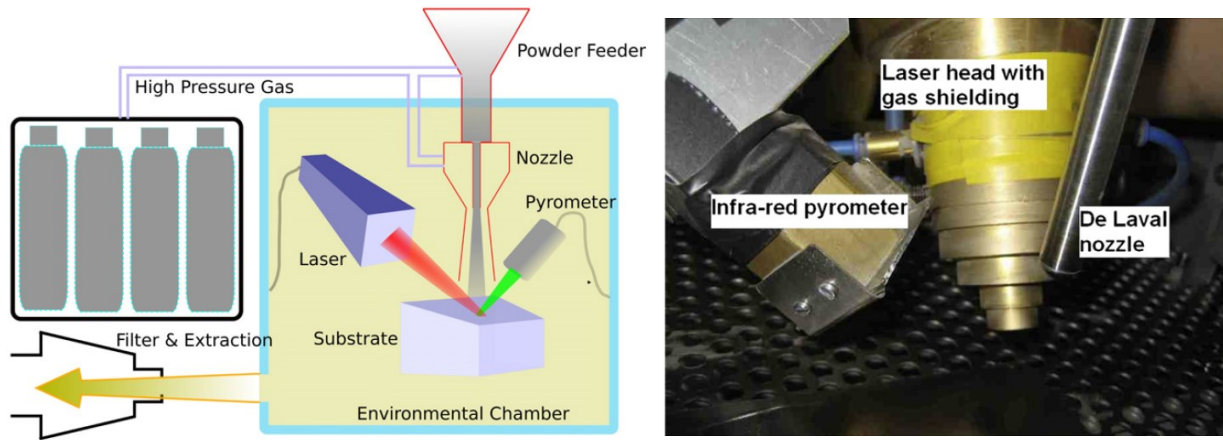


Figure 2.39 Laser Heating Cold Spray (LACS)Set up [97].

2.4.3.2 Induction Heater

Induction heating is one of the most powerful and common ways to heat metals because it is reliable, repeatable, non-contact, and energy-efficient heat that reduces the time required to achieve required levels of heat [98]. The components necessary to achieve induction heating are the induction coil, an alternating current (AC) power supply and the material to heat.

The principle involves an alternating voltage applied to an induction coil resulting in an alternating current in the coil. This alternating current will produce a magnetic field with the same frequency of the coil that will stimulate eddy currents in the material to heat in the opposite direction of the coil frequency. At the same time, these eddy current emit their magnetic field but in the opposite direction of the magnetic field of the coil that finally produces heat by the Joule effect [98].

3. Research Objectives

3.1 General Objectives

The principal objective of this work is to study the effects of substrate temperature on coating formation and properties at the fundamental level: the single particle impact. This is part of the work conducted to evaluate substrate heating as a sustainable solution for the elimination of helium in the copper CGDS coating process for the closure weld zone of the UFC. The substrate temperature has been demonstrated to have beneficial effects during the CGDS process such as an increase in deposition efficiency and coating bonding strength. However, these studies only partially establish fundamental knowledge on the modifications to the bonding mechanism resulting from the heated substrate due to the lack of studies focused on the impact phenomena at the particle scale.

Consequently, the objectives of this work were: 1) achieve deposition of individual copper particles through the use of the CGDS process, 2) characterize craters from bounced off particles, bonded particles and pulled out particles, 3) characterize the differences between methods of substrate preheating, 4) evaluation of the effect of the substrate temperature on bonding along with the effect of particle velocity/temperature/size and 5) model mechanical anchoring adhesion strength.

3.2 Deposition of individual copper particles by CGDS

Single copper particles were deposited over A516 Grade 70 steel preheated substrate (using induction heating) with the objective of studying the deformation levels of particles and substrates using CGDS with only nitrogen as the carrier gas. Tests were performed starting with a substrate surface at room temperature. Then the substrate surface was preheated with the use of an induction heater at 100°C and then increasing the temperature at 100°C intervals up to 600°C. The copper particles were divided into three different size ranges: large ($d > 45 \mu\text{m}$), medium ($45 \mu\text{m} > d > 20 \mu\text{m}$), and small ($d < 20 \mu\text{m}$).

After a thorough analysis of the impact tests performed and used as a guide to determine the best substrate temperature, a second series of deposition tests were carried out with a laser attached to the CGDS system in order to preheat the substrate before particle impact. This deposition test was completed with the substrate at room temperature and 600°C. This test was characterized in the same way as the tests carried out using induction heating. The two tests were compared and contrasted to fully understand the effects of substrate temperature during the CGDS process.

3.3 Characterization of craters (from bounced off particles), bonded particles and pulled off particles

First, craters resulting from bounced off particles were studied in order to evaluate the substrate deformation level upon particle impact and the effect of substrate temperature on the geometry of the resulting crater. This study consisted of crater depth, diameter, and volume measurements. Secondly, copper bonded particles were analyzed by measuring their diameter and height as well as particle compression ratio to observe the effects of substrate temperature on these geometric deformation parameters. This examination was accomplished using Optical Microscopy and Scanning Electron Microscopy. Finally, the characterization of pulled out particles was performed to investigate the bonding mechanisms in relation to the substrate temperature.

3.4 Substrate preheating methods

Two methods were used to achieve a preheated substrate and studied in order to identify the different effects of the preheating method on the bonding process. The first method used an induction heater that preheated the substrate before the start of the CGDS process. The second method involved a laser attached to the CGDS nozzle to preheat the steel substrate just before particle impact.

3.5 Effect of substrate temperature in relation to the particle velocity/temperature/size

The single-particle CGDS process was used to deposit particles at three different sets of particle velocity/temperature/size; results were then analyzed to understand the effect of substrate temperature on the bonding process. The parameters of particle velocity and temperature were obtained from the two deposition tests carried out at the University of Ottawa and the NRC. These particle parameters can be modified through the spray process parameters used.

3.6 Mechanical anchoring simulation

A finite element analysis was performed using ABAQUS/Explicit to understand the level of mechanical anchoring of the coating that contributes to adhesion strength. This analysis was carried out using two coatings. The first coating was developed with a helium bond layer and then built up the rest of the coating with nitrogen as the carrier gas. The second coating is with a substrate preheated with the laser with only nitrogen as the carrier gas.

4. Experimental Procedures

This section presents the experimental procedures which include the description of substrate surface preparation, feedstock powder, and CGDS system. Additionally, this section will detail the equipment required for the data collection, characterization tools, and steps taken for the analysis of craters and particles.

4.1. Substrate

A516 Grade 70 Steel with one inch of thickness is the UFC material and is utilized as the substrate material in this research. The initial dimensions of the substrate were 38.1mm x 76.2 mm x 25.4mm of thickness; this thickness was selected with the objective of being the same thickness as in the UFC. However, the thickness was reduced to allow for a reduced time in preheating and cooling down the substrate, to minimize the possible oxide growth before and after spraying.

Figure 4.1 illustrates the received substrate cross-section in the secondary electron and BSD modes. This oxide layer is between 8 to 11 μm and might be a mill scale from the hot rolling manufacturing process. However, it is necessary to remove it to ensure a clean contact between the sprayed particles and substrate surface.

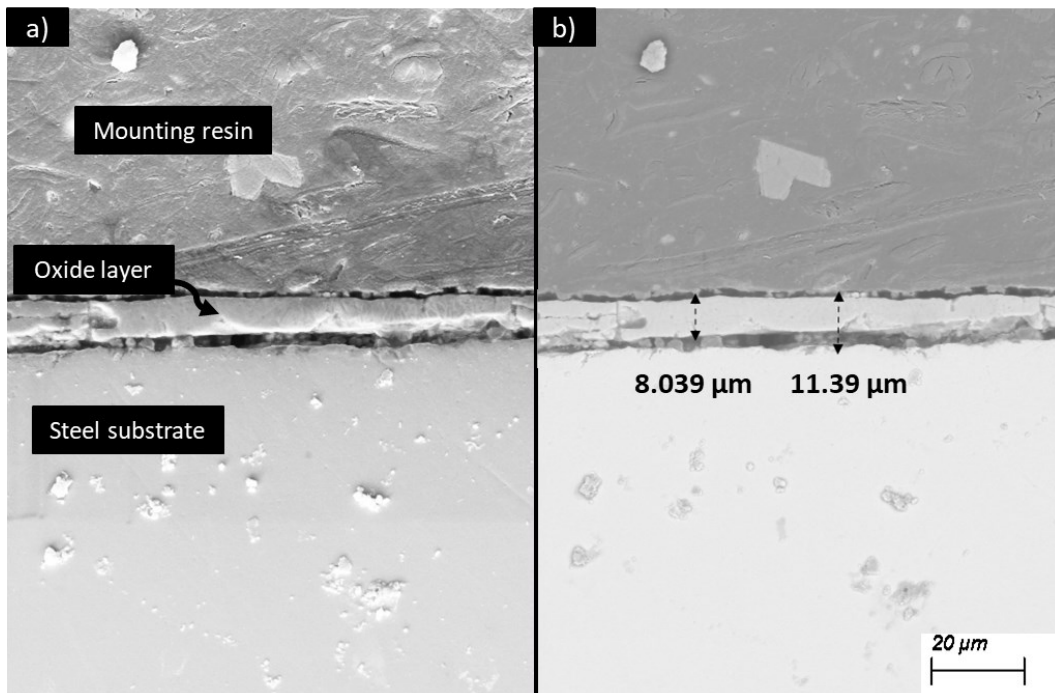


Figure 4.1 SEM image of A516 grade 70 steel as received a) Secondary electron b) BSD.

4.1.1. Substrate Preparation

Elimination of the thin oxide film to obtain a polished surface finish is performed. This surface is achieved using a polishing machine that is described later in this chapter. The polished surface reduces the surface roughness to $0.7 \pm 0.2 \mu\text{m}$. **Figure 4.2** illustrates the cross section of the polished substrate where it can be observed that the oxide layer is reduced comparing with the layer observed in Figure 4.1.

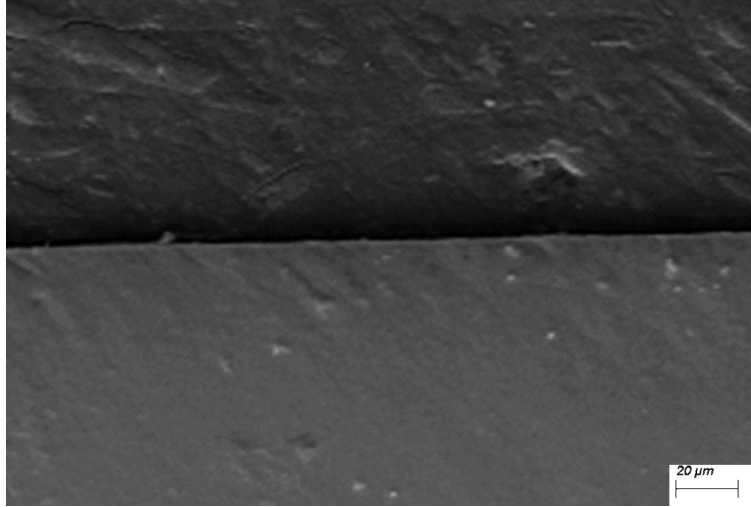


Figure 4.2 Cross-Section SEM image of the polished substrate.

Table 4.1 describes the surface polishing procedure to achieve the mirror-like surface finish during the research.

Table 4.1: Procedure for polish surface finish

Time	Plate	Suspension/Lubricant	Suspension size (μm)
1.5 min	Piano	Water	N/A
4 min	Largo	Largo	9
3 min	Mol	Mol	3

4.2. Feedstock Material

Studies were previous carried out on different Cu powders with different morphology and particle distribution by NWMO and NRC. The optimal Cu powder selected was PG-PMP-1016 Cu Powder by Plasma Giken Co., Ltd. Japan, produced by inert gas atomization, is displayed in **Figure 4.3**. It can be observed that the powder is spherical, and it has a broad particle size distribution.

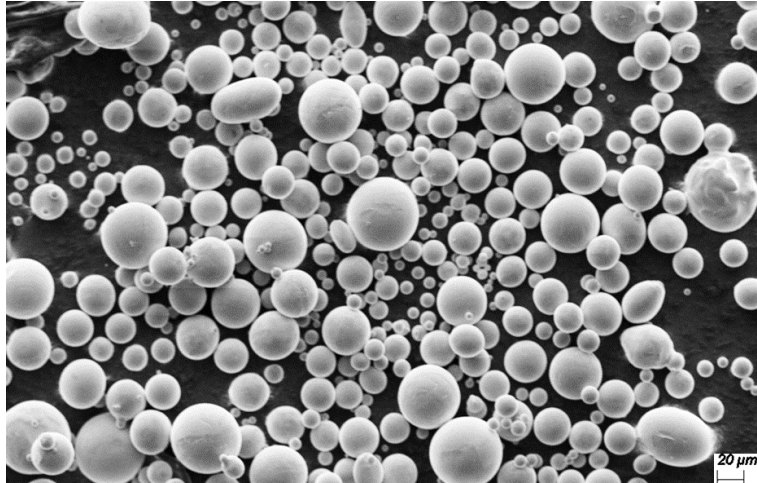


Figure 4.3 SEM images of Cu powder by Plasma Giken Co., Ltd.

As mention before, the deposition efficiency depends on the particle impact velocity. This impact velocity is required to be higher than the critical velocity, which changes depending on the material and particle size. In **Figure 4.4**, the morphology of the as-received Cu particles can be observed. Measurements reveal a broad diameter distribution, where the minimum diameter is approximately 7 μm to a maximum diameter of approximately 55 μm.

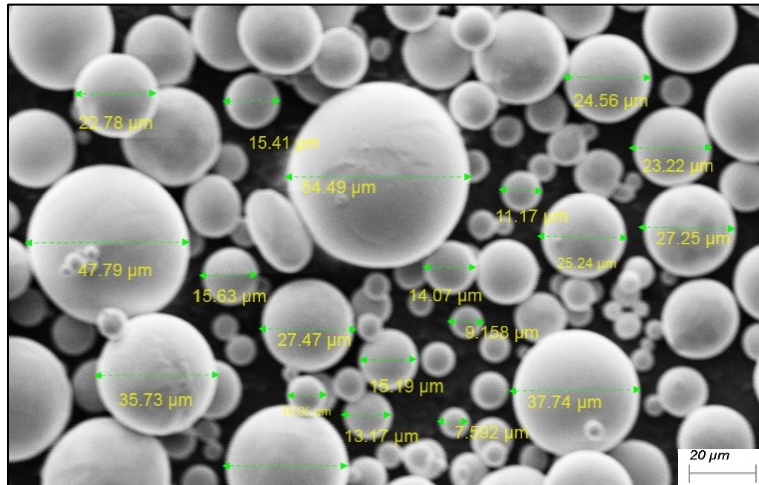


Figure 4.4 Diameter distribution of Cu particles.

Due to the broad size distribution, it was decided to sieve the particles in three different size ranges. The size ranges can be observed in **Table 4.2** and displayed in **Figure 4.5**.

Table 4.2: Particle distribution according to its diameter

Particle	Diameter size
Small	$d < 20\mu\text{m}$
Medium	$20\mu\text{m} < d < 45\mu\text{m}$
Large	$d > 45\mu\text{m}$

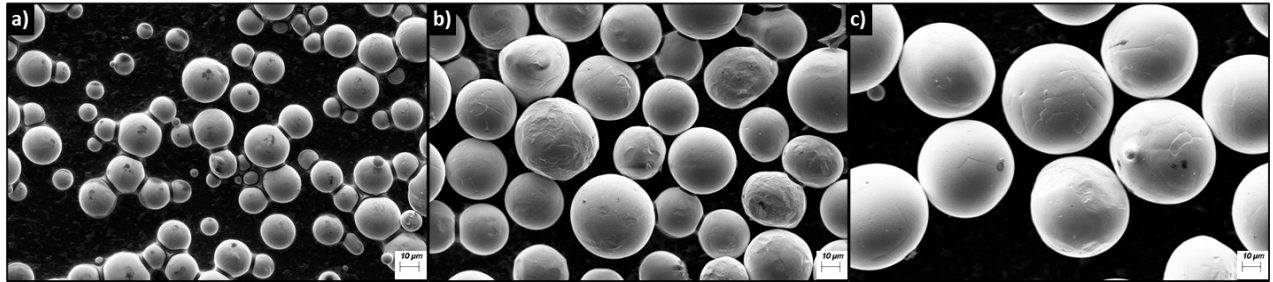


Figure 4.5 SEM images of Particles size distribution: a) Small Particles $d < 20\mu\text{m}$, b) Medium Particles $20\mu\text{m} < d < 45\mu\text{m}$, c) Large Particles $d > 45\mu\text{m}$.

4.3 Inert Environment

Oxidation growth was observed at the substrate surface as its temperature increased during preheating. To prevent this situation, as it is unlikely to occur to that extent when using the laser as a heating source, substrate preheating, and particle deposition were carried out under an argon environment. A 3D-printed box to be filled with argon, shown in **Figure 4.6**, was designed to accommodate the setup of the CGDS system, the induction system, and the tools for temperature measurements. This box was designed to allow the nozzle movement through it.

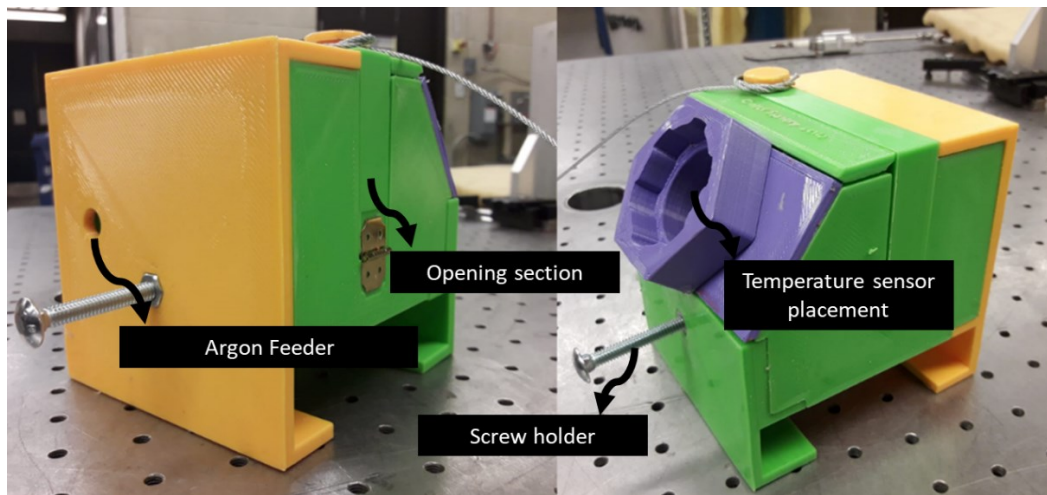


Figure 4.6 3D printing box for an argon environment, front part (left) and back part (right).

Figure 4.7 a) displays a cross section of a substrate preheated under normal atmospheric conditions, while **Figure 4.7 b)** illustrates the case under the argon conditions. The oxide thickness is reduced from $\sim 8\mu\text{m}$ to $\sim 1\mu\text{m}$ in an argon environment.

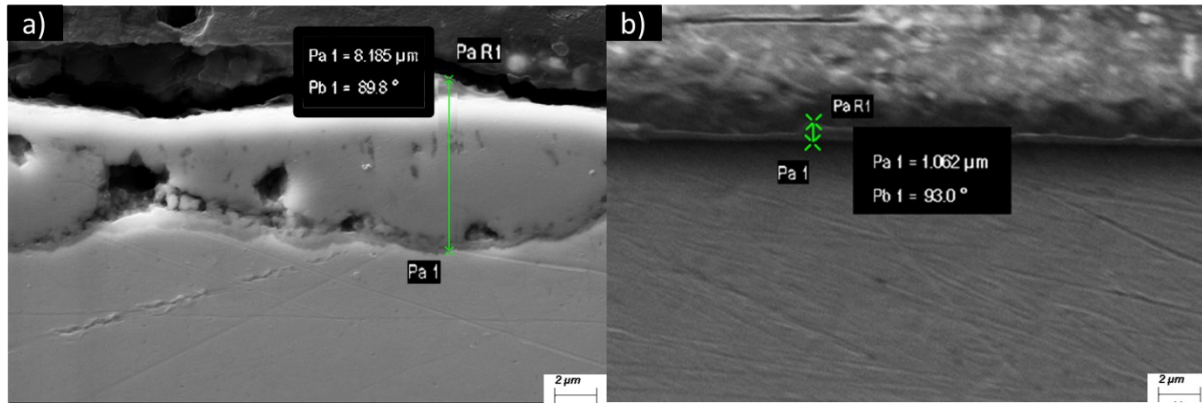


Figure 4.7 Cross-Section SEM images of substrate preheating at 660°C in a) natural environment b) argon environment.

Another purpose of the argon environment is to reduce the substrate cool downtime, minimizing the oxidation after particle deposition, as the oxide layer starts to grow at 200°C. As mentioned previously, the substrate thickness is a factor that influences the cool downtime. **Figure 4.8** plots the substrate surface temperature evolution for an initial substrate thickness of 25.4 mm versus a substrate thickness modified to 3.175 mm. This is the reason that the thinner substrate was used.

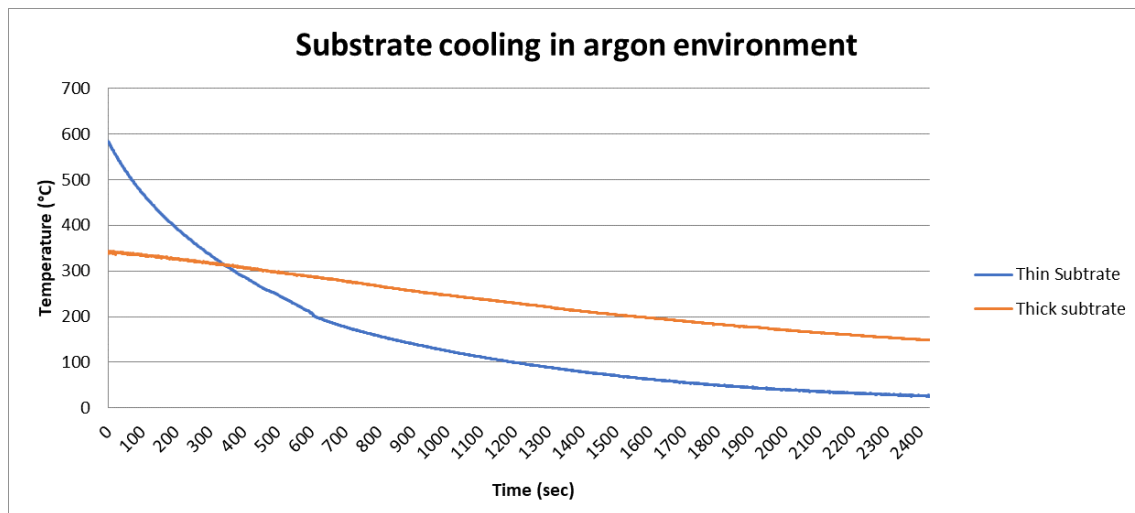


Figure 4.8 Substrate temperature during cooling in argon environment.

4.4. Cold Gas Dynamic Spray Equipment

Single Particle impact deposition was carried out using the commercially available SST Series EP CGDS system from Centerline Ltd., Windsor, ON, Canada (shown in **Figure 4.9**). This system consists of a control cabinet, spray chamber, gas heater, robot (controlled by computer), spray gun, and ventilation system with water filtering. Additionally, a separate powder feeder is connected to the system with its gas connection. The maximum stagnation pressure of the system is 3.4 MPa and the maximum temperature of 500°C. Its temperature and pressure are verified each week and calibrated regularly with a Centerline (Windsor) Ltd. calibration kit.

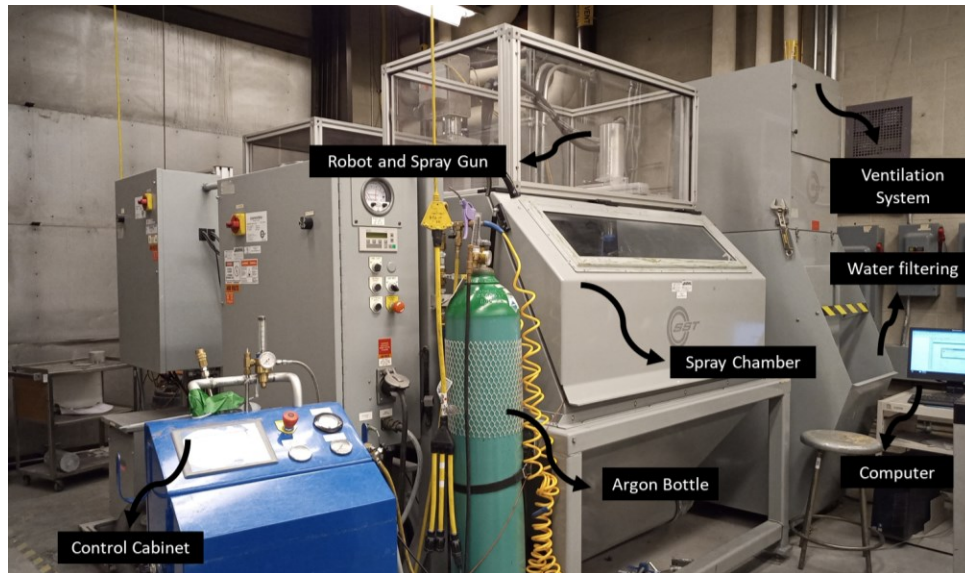


Figure 4.9 CGDS System.

4.4.1. Control Cabinet

The control cabinet with a touchscreen display (shown in **Figure 4.9**) allows for control of the temperature and pressure of the carrier gas.

4.4.2. Nozzle Assembly

The nozzle selected for this research work was the UltiLife nozzle assembly, which is commercially available from Centerline Ltd. (Windsor, ON, Canada). The nozzle requires separate parts to be assembled and attached to properly connect the powder feeder, the converging-diverging portion, and the nozzle holder. A picture of the nozzle assembly is seen in **Figure 4.10**.

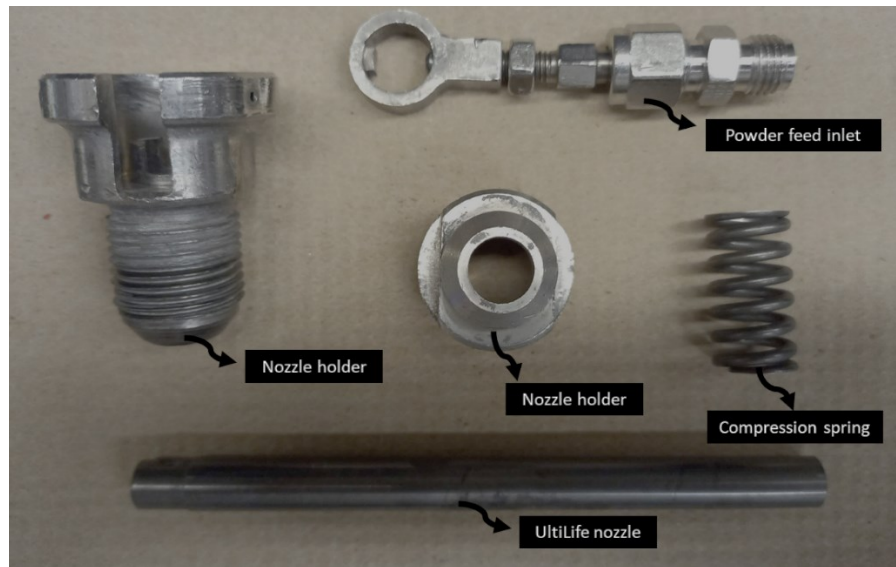


Figure 4.10 Nozzle Assembly.

The nozzle holder attaches the nozzle to the gas heater exit and integrates the converging-diverging nozzle section that accelerates the carrier gas coming from the heater. The nozzle section is designed with a 2 mm throat diameter. Also, this holder is the conduit into which the powder inlet is inserted. The powder inlet lets the powder into the supersonic gas and helps to keep the nozzle centered in the holder.

As previously mentioned, the nozzle employed during this research was the Centerline Ltd. UltiLife nozzle (illustrated in **Figure 4.10**). The diverging nozzle section is 120 mm in length with a 6.3 mm exit diameter. The material of this nozzle is tungsten-carbide in a cobalt matrix. The nozzle selection was made according to prior research carried out using copper powder.

4.4.3. CGDS Spray Gun, Heater and Robot

The CGDS system includes a vertical piece presented in **Figure 4.11** that connects the spray gun, gas heater, robot transverse system, and powder preheater. The latter was not used in this work.

The gas heater, as shown in **Figure 4.11**, has the characteristics of 15 kW, 480 Volt, 3PH, and has a maximum stagnation temperature of 500°C for the carried gas. The carrier gas was heated to the chosen temperature with the use of electrical resistance contained within an insulated frame. The CGDS X-Y movement is controlled by an automated robot that has a maximum speed of 200 mm/s. Additionally, the thermocouple used for system verification and calibration can be observed in **Figure 4.11**.

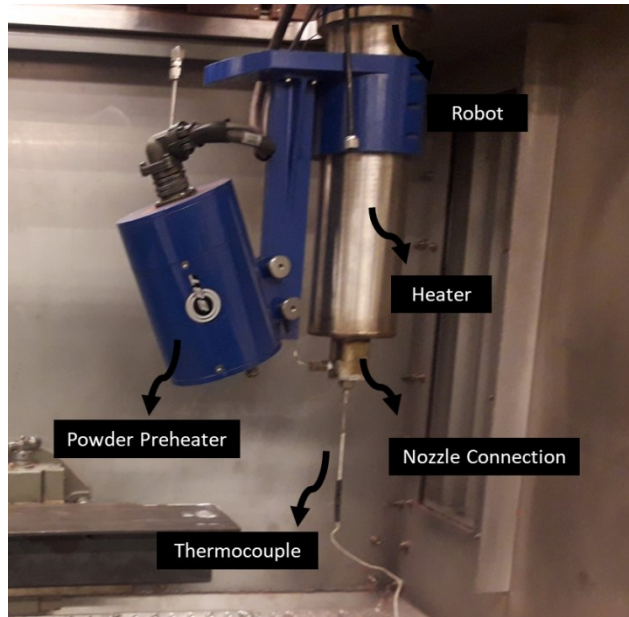


Figure 4.11 CGDS Spray gun, gas heater, powder preheater and robot.

4.4.4. Powder Feeder

The powder feeder used during this research was a AT-1200HP, Thermach Inc., Appleton, WI, USA, as shown in **Figure 4.12 a)**. It consists of a pressurized canister where the feedstock material is stored and where pressure is built up to propel the powder into the feeder outlet. The volumetric flow rate of nitrogen supplied to the canister was set to 14.16 l/s.

During this study, a small feeding wheel (320 holes), as shown in **Figure 4.12 b)**, has been used with the objective of reducing the amount of powder that will be fed at once. This investigation requires the impact of single particles, so it is important to limit the powder fed into the system. The powder feeding rate is controlled by the speed at which this wheel rotates. The speed was kept as low as possible. The wheel holes align with the powder feeder outlet as the wheel is rotating which allows the carrier gas to carry the particles into the nozzle inlet. Additionally, the periodical movement of a hammer that is installed at the top of the wheel helps to prevent agglomeration and achieve a consistent feeding rate.

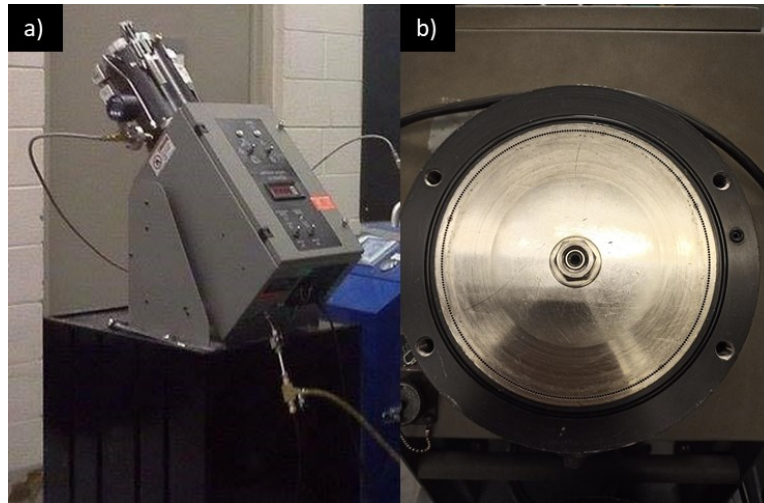


Figure 4.12 a) CGDS powder feeder b) small wheel.

4.4.5. Spray Chamber

The main goal of the CGDS spray chamber displayed in **Figure 4.13** is to create a safe environment to carry out the spray process. The chamber is equipped with a collector for particles that are not deposited during the process. The powder is pulled through a water filter, after which the remaining air then travels through a HEPA filter before being released.



Figure 4.13 CGDS spray chamber.

4.4.6. Gas Storage

The carried gas employed during the investigation was nitrogen and it is provided from a bottle pack unit that consists of eleven industrial high-pressure cylinders connected with a total pressure of 18 MPa. This unit is shown in **Figure 4.14**.



Figure 4.14 Nitrogen bottle packs.

4.4.7 Induction heater

Substrate preheating was accomplished by the use of an induction heater (Tucker Induction Sys. Inc., Shelby Township, MI, USA). The selection of this method was based on the fact that the induction heater can induce high substrate temperatures in a short period of time. As well, with the selection of adequate coil design, it can be integrated easily with the CGDS system. In this case, the best option was a pancake coil, as presented in **Figure 4.15**.



Figure 4.15 Pancake coil.

Figure 4.16 shows a schematic of how the coil is positioned inside the 3D printed box and the position of the substrate and the infrared sensor.

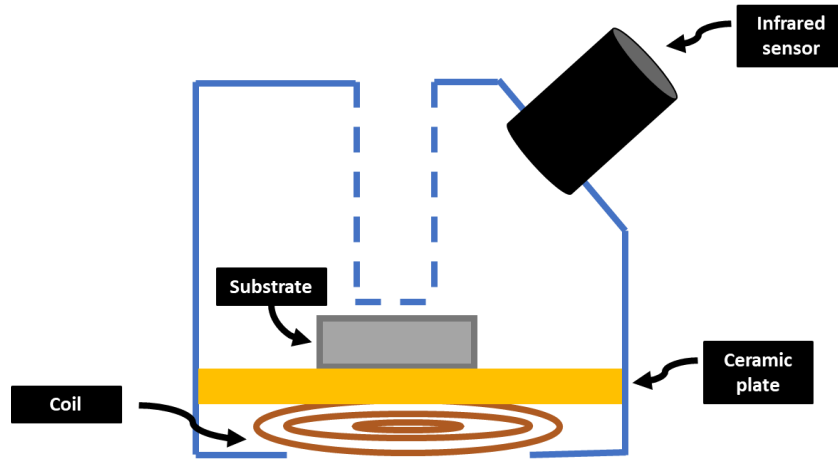


Figure 4.16 Schematic of the set up of the substrate, coil inside of the 3D printed box.

Figure 4.17 (left) presents the induction heater machine for this study that was adapted into the back of the spray chamber. The coil passes through the spray chamber wall avoiding metal material contact with the coil which can result in the machine short-circuiting. To simplify the connection, the pancake coil was designed, as shown in **Figure 4.15** and **Figure 4.17 (right)**.



Figure 4.17 Induction heater machine (left) and final coil set up inside the CGDS chamber (right).

The induction preheating method was compared to two strip heaters (TEMPCO, Wood Dale, IL, USA) rated at 300 W that were connected in parallel and used to preheat the substrate. **Figure 4.18** presents the time required for induction heating to achieve a temperature of 600°C at the substrate surface versus the time needed for the strips heater to reach 300°C (their maximum temperature). It can be observed that the induction heater has significantly better preheating performance when compared to the strip heaters.

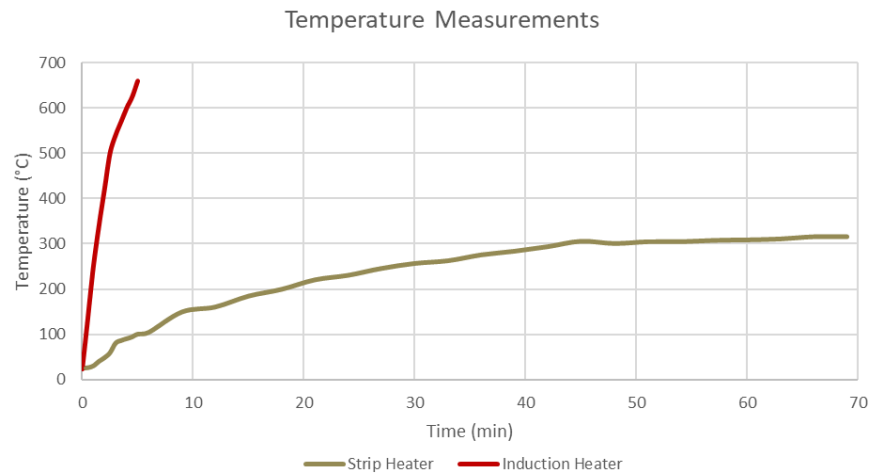


Figure 4.18 Induction heater rate compared with strip heater.

4.4.8 Substrate Temperature Measurement

The substrate surface temperature was measured using two thermal infrared sensors because of the temperature reading limitation of both sensors. For temperature measurements below 300°C, the thermal infrared sensor RAYGPRSF (Raytek, Thermalert GP Series, Santa Cruz, CA, USA) was used and for temperatures above 300°C the thermal infrared sensor OptCT3MH2SF (Optris, Portsmouth, NW, USA) was used. Both thermal infrared sensors are illustrated in **Figure 4.19**.

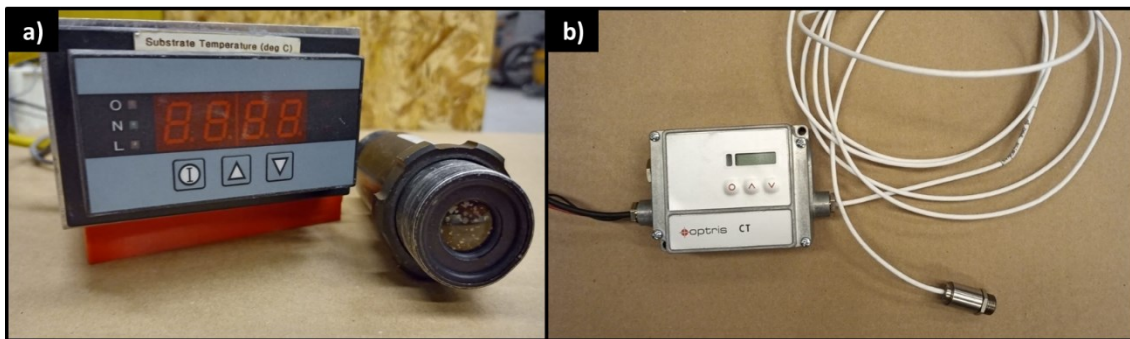


Figure 4.19 a) thermal infrared sensor RAYGPRSF (Raytek, Thermalert GP Series, Santa Cruz, CA, USA), b) OptCT3MH2SF (Optris, Portsmouth, NW, USA).

Emissivity is an essential factor in order to read the correct substrate temperature during the test; for that reason, both infrared sensors were calibrated with a thermocouple type k to find the correct emissivity at each temperature. The emissivity data obtained are presented in **Table 4.3**. The large difference in the emissivity between substrate temperature ranges is due to the oxidation of the steel substrate, additionally, the temperature reading ranges are different between the sensors.

Table 4.3: Emissivity at different substrate temperatures for the different sensor employed

Substrate Temperature	Sensor	Emissivity
RT	RAYGPRSF infrared thermometer	0.16
100°C		0.16
200°C		0.16
300°C	OptCT3MH2SF infrared thermometer	0.55
400°C		1
500°C		1
600°C		1

4.4.9 Spray Final Set up

An image of the final setup for single impact deposition at different substrate temperatures is presented in **Figure 4.20**. To reduce the oxide layer growth as much as possible, the flow of argon is opened up before beginning to preheat the substrate and is only closed after the sample is cooled to room temperature. **Figure 4.20** shows the nozzle's path through the 3D printed argon environment box, indicated by the dotted arrow-ended line. The door of the box is opened just before the nozzle starts to pass through the box and closed as soon as the nozzle is outside of the box.

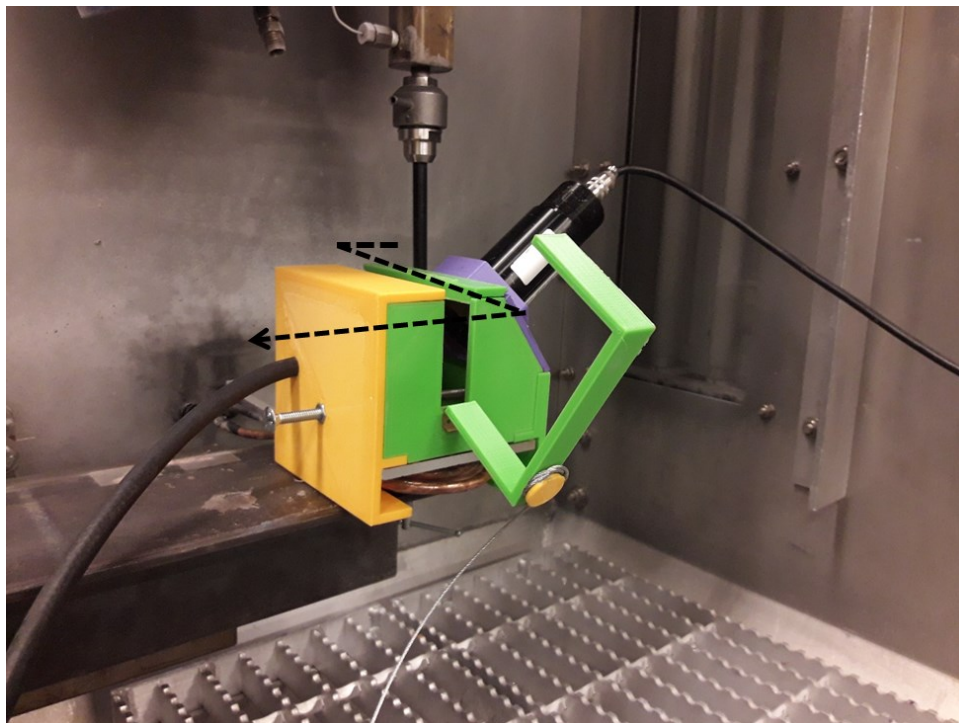


Figure 4.20 Final set up of spray with nozzle movement path.

The steel samples were placed inside the box, secured with two screws onto a ceramic plate to avoid any sample movement during the spray process. Additionally, fiberglass insulation is between the ceramic and steel sample (as shown in **Figure 4.21**) to prevent any heat transfer. The ceramic plate prevented the steel from having contact with the coil.

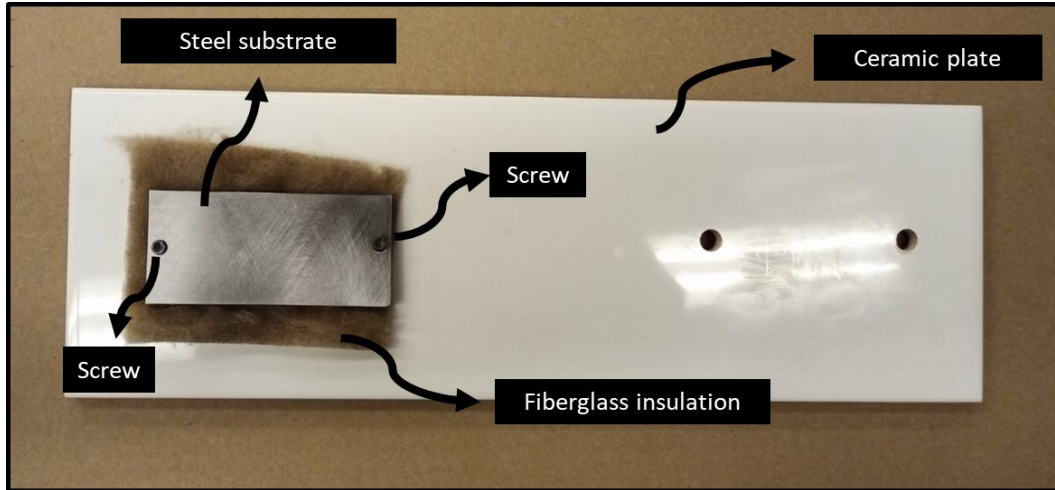


Figure 4.21 Steel Substrate secured with two screws onto a ceramic plate with fiberglass insulation between them.

Furthermore, the argon flow helps to reduce the cool-down time and reduce the possibilities of the effect of heat treatment. For this reason, the effect of the argon volumetric flow rate was tested, as illustrated in **Figure 4.22**. It can be observed that at $1.42 \text{ m}^3/\text{h}$ the time that the sample requires to cool down to room temperature is approximately 41 minutes compared to 53 minutes at $0.71 \text{ m}^3/\text{h}$. Based on the results, the higher volumetric flow rate was selected for this research.

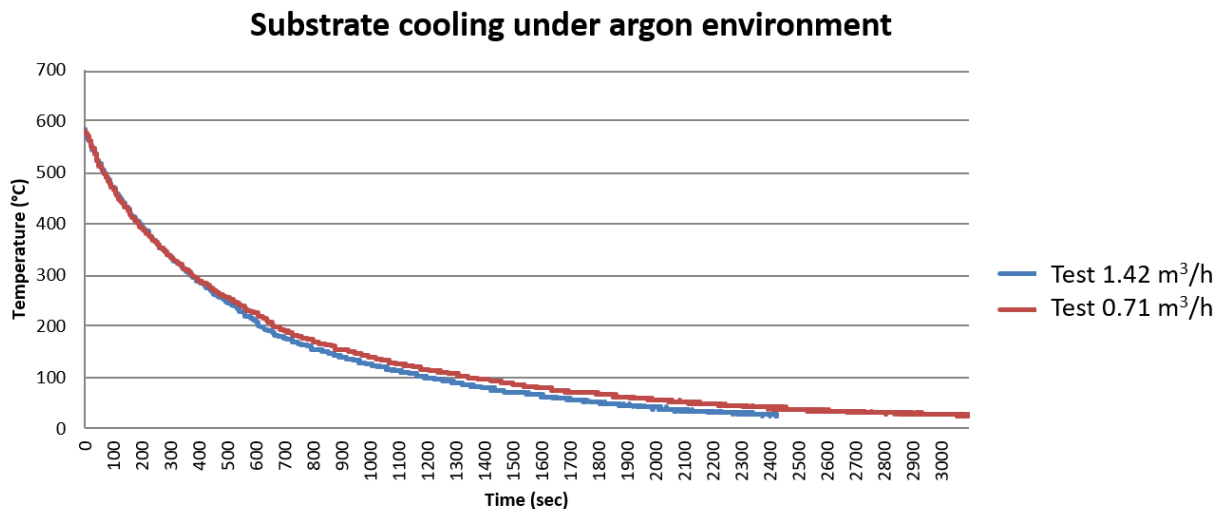


Figure 4.22 Comparison of argon flow between 25 vs 50 CFH.

4.4.10 CGDS Parameters

Table 4.4 shows the CGDS parameter employed in this research at the CGDS in the uOttawa equipment spray.

Table 4.4: CGDS Parameters in the uOttawa equipment spray

CGDS Parameter	Large Particle	Medium Particle	Small Particle
Gas pressure	3.44 MPa		
Gas temperature	400°C		
Nozzle Speed	150 mm/s		
Powder feeder speed	1.5 rpm	1 rpm	

4.5 Laser-Assisted Spray Set up

A second deposition of individual particles was performed in the NRC facilities with other CGDS systems. The CGDS system at NRC is shown in **Figure 4.23**, it can be seen that this system has a laser placed right next to it and that it moves together with the system since it is attached to the same robot with the purpose of preheating the substrate just before impact of the particles.

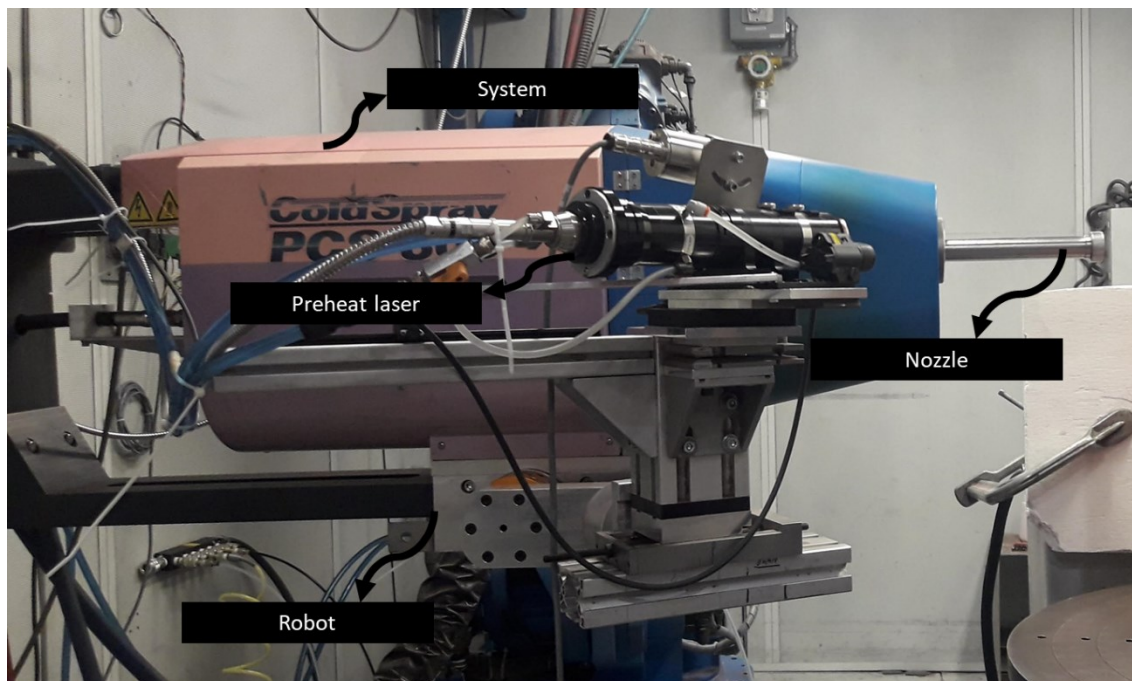


Figure 4.23 CGDS system at NRC.

The biggest difference from this deposition is that the heating of the substrate will be carried out by means of a laser. Furthermore, the NRC CGDS system differs from the system in uOttawa mainly in that it is a high-pressure system. Another difference is that the particles are inserted in the convergent section so that the temperature of the particles increases because the carrier gas is at a high temperature and the contact time between the carrier gas and the particles increases.

In **Figure 4.24** it can observe a portion of the nozzle and the spot laser that preheats the substrate just before the particle hits, this system also contains a pyrometer sensor attached to the laser for the measurement of temperature during the spraying process.

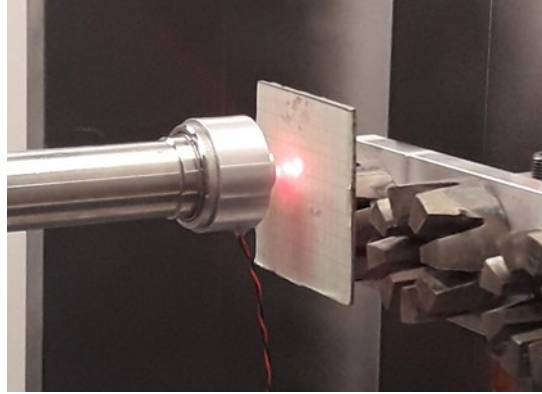


Figure 4.24 Portion of the nozzle of the CGDS system and the spot laser that preheats the substrate.

Furthermore, the NRC system allows using higher gas stagnation pressures and temperatures. The spray conditions used for each condition (NRC or uOttawa) are shown in **Table 4.5**.

Table 4.5: Spray parameter for the laser-assisted (NRC) for the laser-assisted (NRC) parameter and the induction heater (uOttawa)

System/Parameters	NRC	uOttawa
Pressure	4.9 MPa	3.44 MPa
Temperature	800 °C	400 °C
Stand of Distance	30 mm	
Nozzle speed	100 mm/s	

Additionally, the particle velocity and temperature were simulated based on the research done by A. Nastic et al. [99]. This CGDS modeling was based on the measurement obtained using high-speed, high-definition infrared (IR) camera to infer the suitability and precision of Nusselt number and drag coefficient correlation. The objective of this modeling is to have a comparison between the two sprays at different systems as they have different parameters and in that way the sprays can be compared.

4.5 Analysis Equipment

4.5.1 Sample Preparation for Microscopic Analysis

Some samples needed to have a cross-section cut for microscopic analysis. The samples were cut using a Struers Secotom-10 precision saw (shown in **Figure 4.25**) equipped with a 50A20 aluminum oxide cut-off wheel. The wheel speed selected was 2200 rpm with a feed rate of 0.005 mm/s. These values were chosen to achieve a smooth cut of the copper coatings and steel substrates.



Figure 4.25 Struers Secotom-10 cutting machine.

The next step to prepare the samples was the mounting process with the Struers LaboPress-3 machine, as displayed in **Figure 4.26**. The powder selected for this process was a phenolic plastic that is inserted into the automatic hot mounting press. The parameters for this powder are 20 KN uniaxial compressive force, 6 to 8 minutes of heating at 150°C, and 2 to 3 minutes of cooling time.



Figure 4.26 Struers LaboPress-3 mounting machine.

The final step is the grinding and polishing process using a Struers TegraPol-31 automatic grinder-polisher, as displayed in **Figure 4.27**. The sample is polished in this step until it reaches a mirror-like finish. It is essential to mention that between steps in the polishing process, cleaning was carried out with pure ethanol only. This is because it was observed that when water was used in the cleaning process, oxidation occurred in the sample. After cleaning the samples were dried using compressed air.



Figure 4.27 Struers TegraPol-31 polishing machine.

4.5.2 Optical Microscopy

Particles and craters from the wipe test were analyzed using an optical microscope (VHX-2000E, Keyence, Canada). This microscope, as shown in **Figure 4.28**, has the unique function of image-stitching and fine depth composition with a maximum magnification of 1000X to create 2D and 3D images. This allows for the characterization of particles and craters caused by particles that failed to bond.

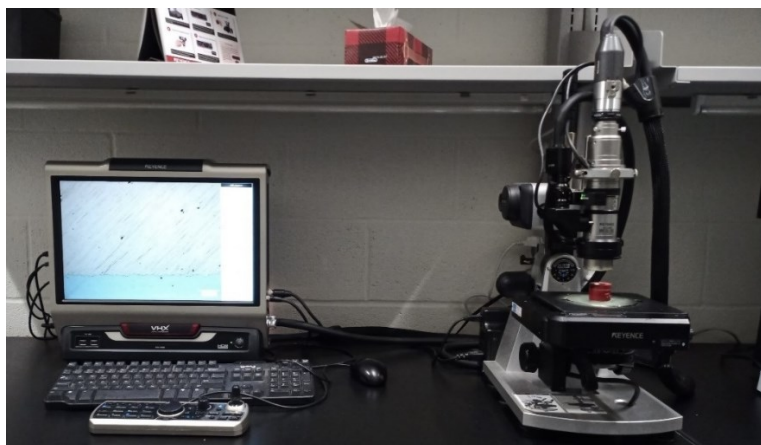


Figure 4.28 VHX-2000E digital optical microscope.

4.5.3 Scanning Electron Microscope (SEM)

A Scanning Electron Microscope (SEM) was used for microstructure observations and characterization. The SEM (EVO-MA10, Zeiss, UK), displayed in **Figure 4.29**, is equipped with an imaging mode that has detectors of secondary electrons (SE) and Backscattered electrons (BSE). As well, the SEM is able to characterize depth with the detectors of energy dispersive X-ray spectrometer (EDS), electron backscatter diffraction (EBSD), and X-ray computed tomography (CT). In this research, the detectors used were SE and BSE for high-quality images of the single-particle impacts and detached particles. Additionally, EDS analysis was made for particle/substrate study.

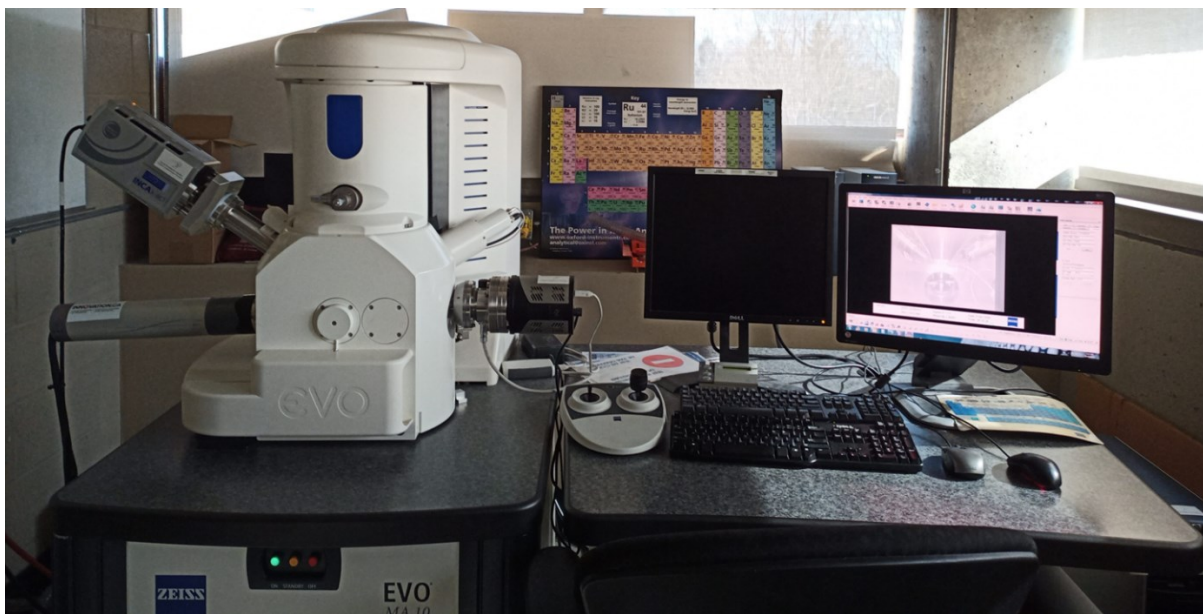


Figure 4.29 Scanning electron microscope (EVO-MA10, Zeiss, UK).

Before the SEM analysis, all the samples have been gold-sputtered (Denton Vacuum), shown in **Figure 4.30**. This gold film prevents charging of the samples once electrons bombard the samples inside the SEM. As well, the gold film reduces thermal damage and improves the signal to noise ratio.



Figure 4.30 Denton Vacuum Desk IV gold sputtering machine.

4.6. Characterization Procedures

In this section, the characterization procedures are going to be explained. The characterization is classified in non-destructive and destructive methods.

4.6.1. Non-Destructive Method

The non-destructive method of sample characterization was for the measurement of craters produced from particles that failed to bond to the surface. However, even without successful bonding, the particles leave a trace in the form of a crater that is useful to examine to understand the parameters required to achieve successful deposition as the substrate temperature increases. The depth, diameter, and volume of the craters were measured, as **Figure 4.31** displays.



Figure 4.31 Crater measurements of depth (left), diameter (middle), and volume (right).

In addition, the particles which achieved successful deposition were analyzed. The height and diameter of these particles were examined (illustrated in **Figure 4.32**). The height of the particle extends from the substrate to the top of the particle and the particle diameter does not include the jetting region surrounding the impacted particle.

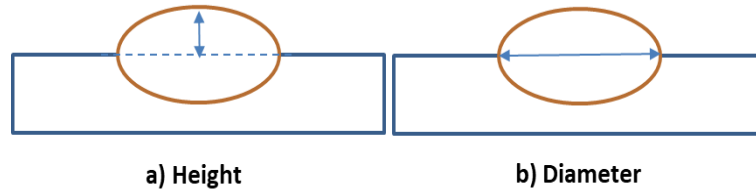


Figure 4.32 Particle measurements of a) depth and b) diameter.

All the measurements for the non-destructive methods were carried out using the digital optical microscope, described in section **4.5.2 Optical Microscopy**. The image-stitching function provides a 3D view of the sample that contains the particles and craters. The next section explains step by step how the analysis of these images was carried out.

4.6.1.2.1 Non-Destructive Procedure: crater volume measurements verification

Acrylic tools were manufactured (shown in **Figure 4.33**) with the purpose of verifying the volume measurements obtained from the optical microscope and to evaluate the error percentage of each measurement.

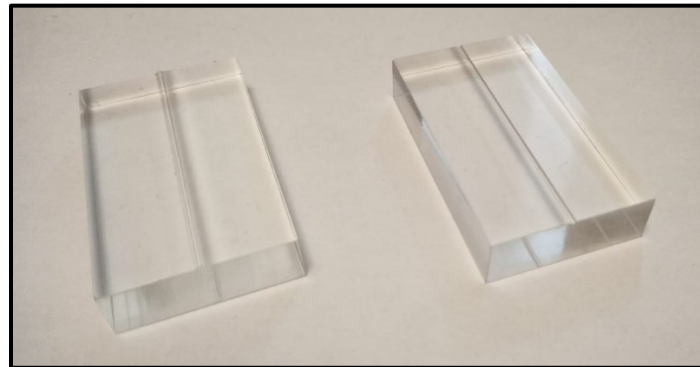


Figure 4.33 Volume Verification tools.

Figure 4.34 shows the design renderings of the tools with a diameter of 1 mm which is not as easily observed in **Figure 4.33**. However, the manufacturing process cannot produce the ideal design, as a result, **Figure 4.34 b)** shows the real manufacturing for this tool, which can be observed during the optical microscope measurements. The tools are to measure the positive and negative (craters) volume from the surface.

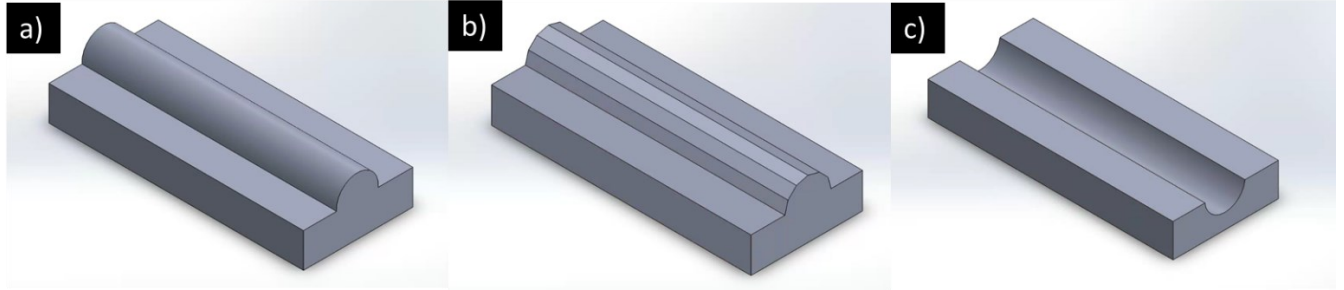


Figure 4.34 a) Ideal design for positive volume b) Realistic manufactured for positive volume c) Ideal design for negative volume.

The volume measurements of the machined parts are shown in **Figure 4.35**. It can be noticed in the figure that the tool for negative volume has the shape displayed in **Figure 4.34**. The following theoretical equation was compared with the real-life direct volume measurement which the microscope shows.

$$V = \frac{\pi r^2 h}{2} \quad \text{Eq. 4.1}$$

The error for the positive volume is 14.70%; where on the other hand, the error for the negative volume is 1.82%. The difference in the errors is a result of the machining process required in the case of the positive volume tool. In this research, the volume measurement is only taken for the craters; therefore, the best tool to verify the volume is the one for negative volume.

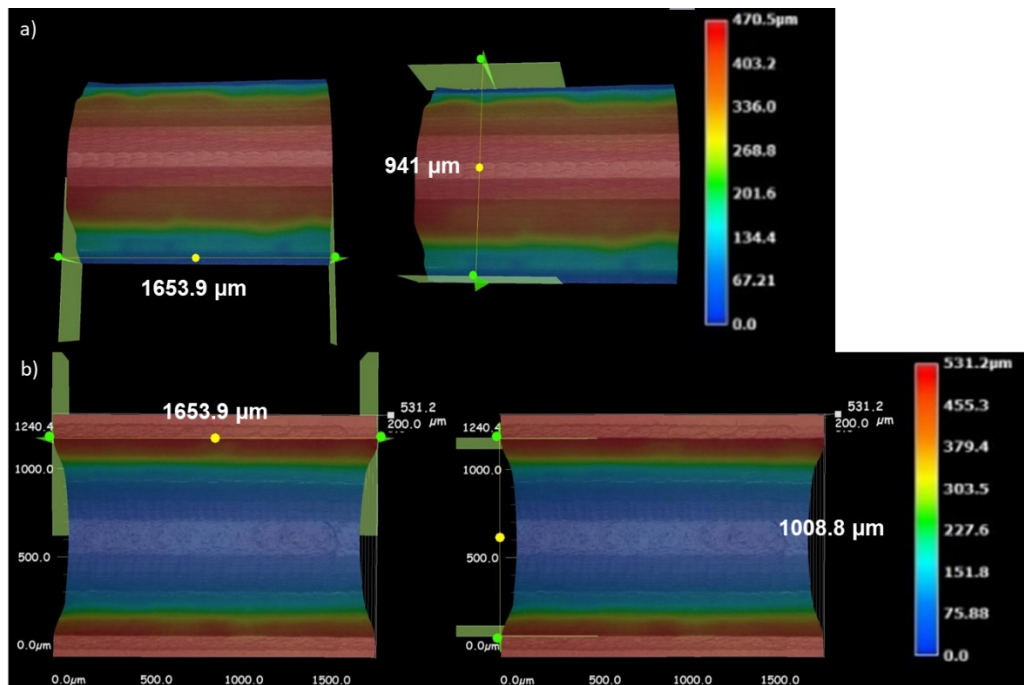


Figure 4.35 Optical microscope measurements: a) grow volume and b) crop volume.

4.6.2. Destructive Method

The purpose of the destructive measurement method is to determine the penetration depth of the copper particles into the steel substrate as its temperature increases. Additionally, this method aims to determine the bonding mechanisms as a result of the substrate preheating. In this case, two alternative methods were employed to achieve these objectives: laser micromachining to develop cross-section cuts of the particles and detaching deposited particles for measurement. However, laser machining turned out to not be an optimal method for this study; consequently, the analysis was only carried out by measuring the detached particles.

4.6.2.1 Laser Micromachining

Laser micromachining is an alternative process that was used to try to produce cross section cut precisely in the center of a single particle. This process can be compared with cuts made by a Focused Ion Beam (FIB) used in many other studies of CGDS coating. FIB is a slow and local procedure that results in very clean cuts so that it is possible to observe grains and microstructure. In contrast, laser micromachining is done fast, resulting in clean-cut surfaces, and long lines can be cut so that it is possible to have multiple measurements. Using this method, it is possible to see the location of the cut. **Figure 4.36** shows FIB and laser micromachining cuts. It can be observed that both cuts provide a clean surface.

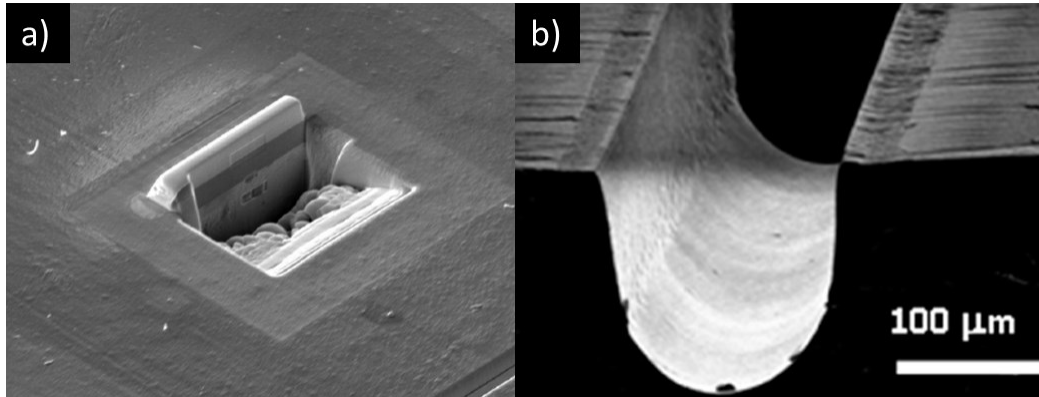


Figure 4.36 a) FIB cut of a thin layer of platinum [100] b) Laser micromachining cut of Pyrolytic Graphite Sheet [101].

The characterization of particle cuts was carried out using a Yb:KGW femtosecond laser (PHAROS from Light Conversion, Inc.), generating a linearly polarized Gaussian beam with a pulse duration of 300 fs (shown in **Figure 4.37**). Femtosecond lasers are usually employed on a small scale due to the advantages of short pulses, which produce a minimal heat affected zone (HAZ) and minimal dislocations and defects after the laser cuttings. Nevertheless, there are no studies in the CGDS area using femtosecond for cross sectional cutting. Observation of the cross section cut will be made using SEM where the substrate will be placed at an inclination of 30° from the horizontal in order to clearly observe the perimeter of the particle and measure its penetration depth.

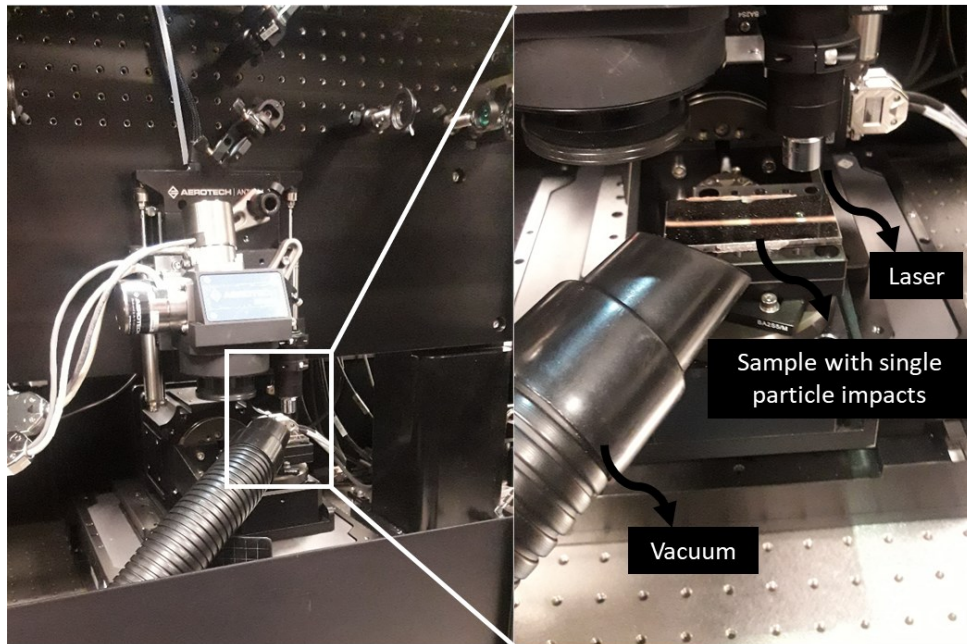


Figure 4.37 Yb:KGW femtosecond laser (PHAROS from Light Conversion, Inc.).

4.6.2.2 Detached particles method

The second method used for the analysis of the penetration depth is a method where the deposited particles are detached based on the procedure developed by Chen et al. [28]. **Figure 4.38** describes the method where glue is placed between the impacted particles and a metal piece.

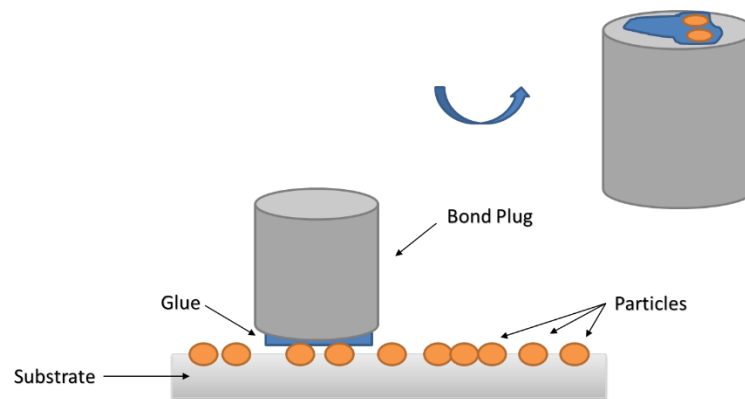


Figure 4.38 Detached particles process.

The procedure for this method is:

1. Grind the bond plug with a 200-grit sandpaper in a figure eight pattern.
2. Heat the FM1000 glue in the oven at 90°C for 45 minutes to reduce the humidity.
3. Place a small piece of glue in the test zone.
4. Put the bond plug on the glue area applying downward pressure with a clamp.
5. Place in oven at 190°C for 4 hours.
6. Leave the samples in the oven overnight to cool.
7. Apply upward force carefully to remove the bond plug from the sample.

Figure 4.39 shows the images taken by an optical microscope after detaching particles using the procedure described above, both the bond plug and substrate surface can be observed. The zoom enhanced the vision of both the top and bottom image is from the bond plug with glue and the substrate respectively and confirm that the particles have been detached as expected. Looking at the 3D images in figures b) and d) one can be observed that the three particles have been detached by the glue and left craters where the particles were.

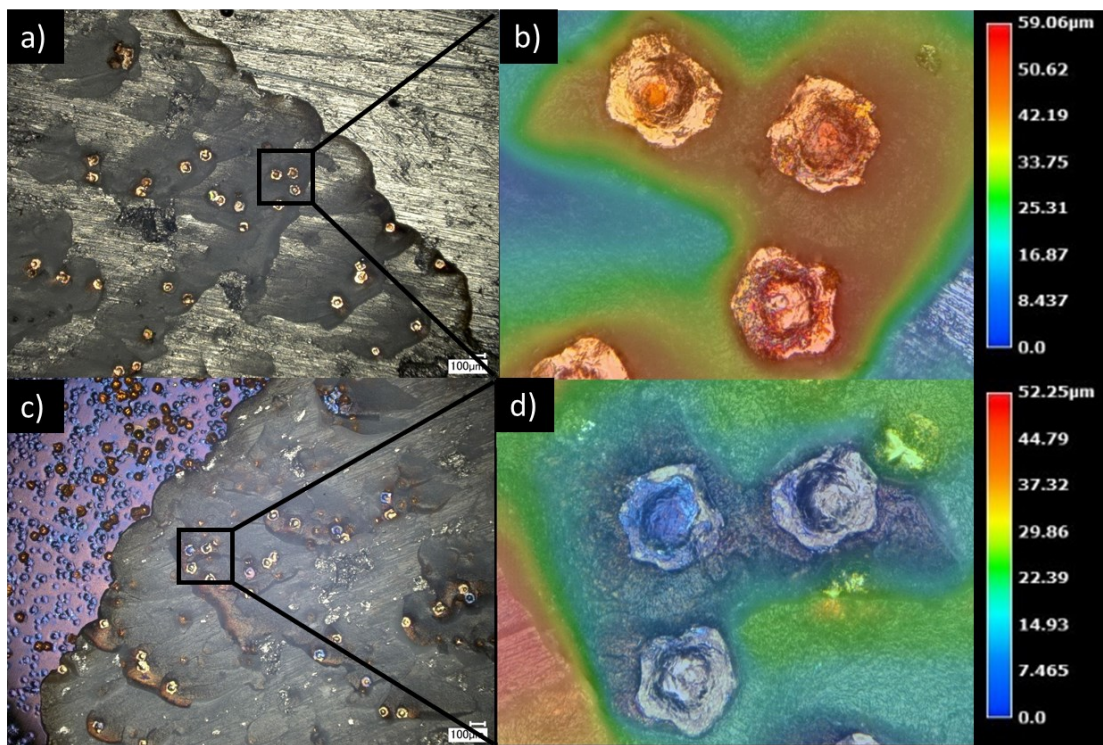


Figure 4.39 Optical Microscope images after detaching particles a) Bond Plug with glue. b) zoom in of glue zone c) Substrate d) zoom in of substrate.

4.7 Metallurgical Bond Measurements

The presence of dimple features at the detached particles surface is a sign of metallurgical bonding; consequently, it is important to measure and compare these as a function of the substrate temperature. **Figure 4.40** shows a particle detached and the substrate area where the particle was detached from. Additionally, a zoomed image of the dimple features in both cases can be observed. Through these images, it can be noted that the dimple features are more noticeable in the detached particle in contrast to the substrate crater left by the detached particle; thus, the bonding measurements were carried out on the detached particles. The metallurgical bonding measurement was carried out using Adobe Photoshop CS5, as described in **Appendix B Metallurgical Bonding Measurement Procedure**.

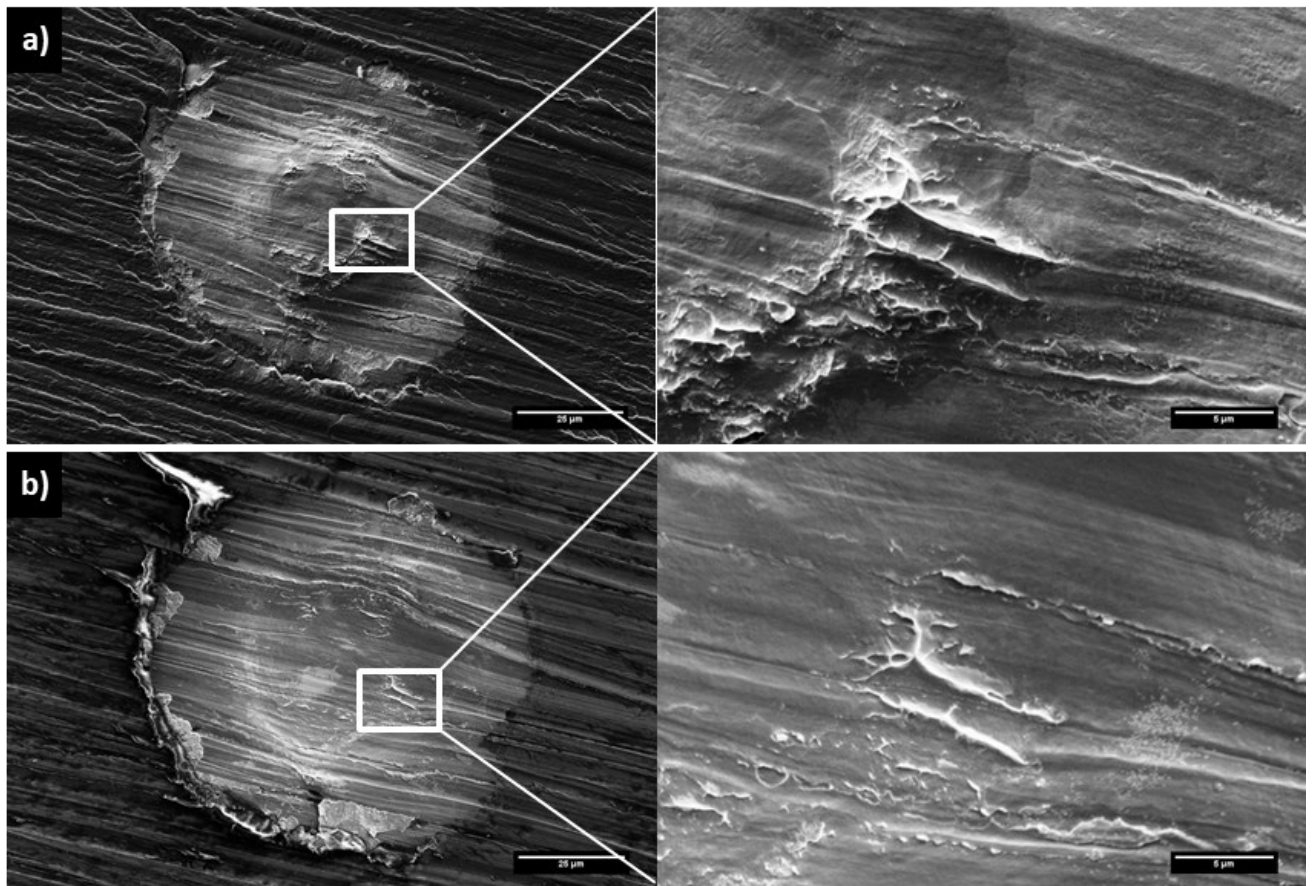


Figure 4.40 SEM images: a) detached particle b) substrate area where the particle was detached.

4.8 Mechanical anchoring prediction

The simulation made in this research is based on the interface and the mechanical anchoring points between the coating and the substrate taken from the Optical Microscope and then processed by Image J software, as **Figure 4.41** illustrates. The profile extraction consists of getting the XY coordinates of the interface to transfer to Abaqus in order to predict the mechanical anchoring strength.

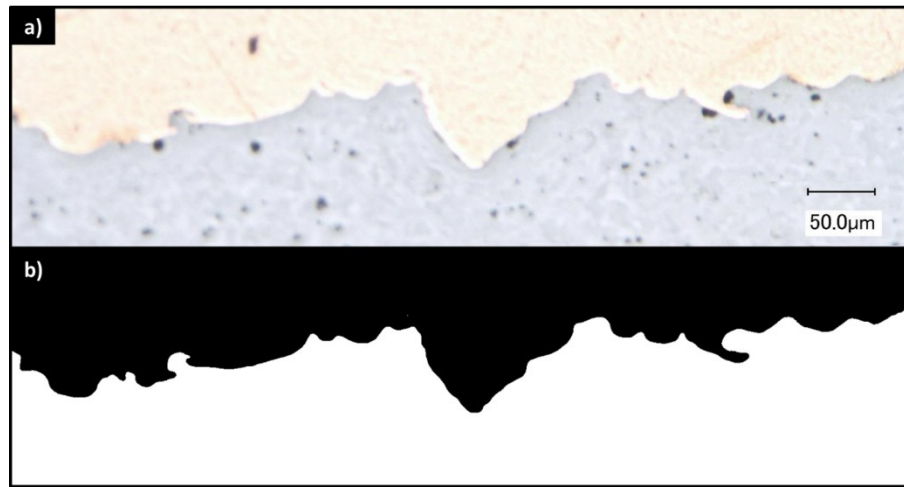


Figure 4.41 a) Optical Microscope cross-section of copper coating b) Profile processed by Image J from the cross section image.

A quad-dominated mesh was used with a four-point strain element type (CPE4R) and in order to reduce the simulation time the parts (coating and substrate) were divided into two approximated 0.14 mm further from the interface (as shown in **Figure 4.42**).

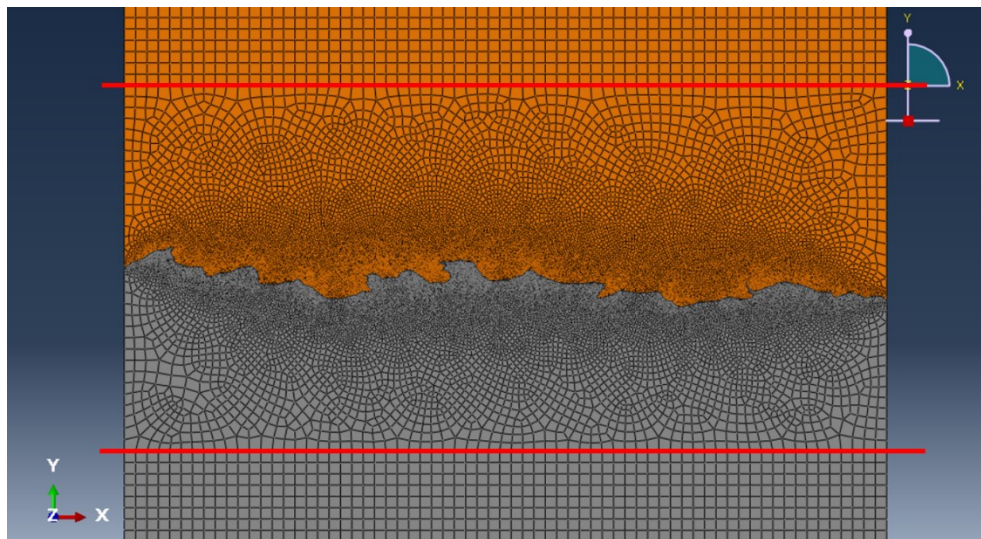


Figure 4.42 Quad-dominated mesh with a four-point strain element type (CPE4R) of the substrate and coating. The division of the mesh is shown with the red lines in both parts.

Figure 4.43 shows the mesh of the part near to the interface is finer with an approximate size of 0.00075 mm at the interface and coarser as it moves away from the interface until 0.01 mm and the second part with a mesh uniform of 0.01 mm size.

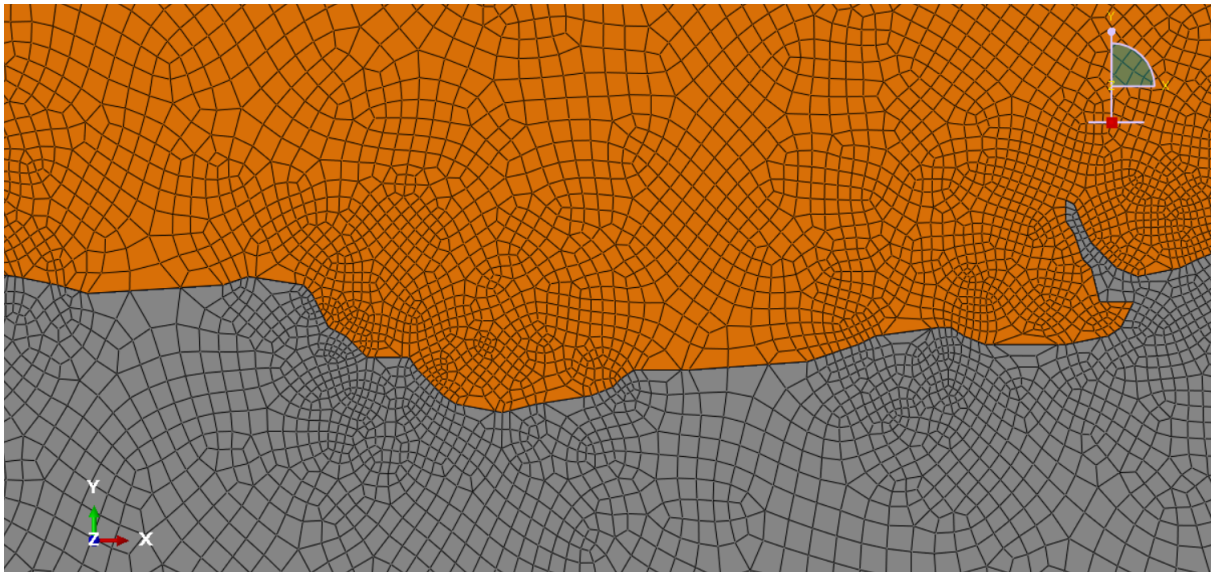


Figure 4.43 Quad-dominated mesh with a four-point strain element type (CPE4R) of the interface between the coating and substrate.

The boundary conditions employed were: a) the sidewalls of the substrate and coating only permit vertical movement, b) the base at the bottom of the substrate was fixed, c) the top of the coating permits a vertical speed of 0.02 mm/s as ruled by the ASTM 633-C and d) the coating and substrates were supposed to be at room temperature. Additionally, a hard contact interaction property was employed at the interface with a fiction of 0.5. In this research, the copper coating and low carbon steel properties are based on the simulation made by Fernandez et al. [24] and are represented in **Table 4.6**:. The properties of the A516 Grade 70 steel are replaced with Steel A36 which has the same amount of carbon content thus similar mechanical properties.

Table 4.6: Material properties for copper and steel A36

Properties	Copper	Steel A36
$\rho(\text{Kg/m}^3)$	8960	7830
E (GPa)	124	200
ν	0.34	0.26
k (W/m K)	386	45
C_p (J/kg K)	383	477

The plasticity model used in the simulation was that of Johnson-Cook and is shown in **Eq. 4.2**:

$$\sigma_{eq} = [A + B\varepsilon_p^n] \left[1 + C \ln \left(\frac{\dot{\varepsilon}_p}{\dot{\varepsilon}_{ref}} \right) \right] \left[1 - \left(\frac{T - T_{ref}}{T_m - T_{ref}} \right)^m \right] \quad \text{Eq. 4.2}$$

Where, A, B, C, n, m, $\dot{\varepsilon}_{ref}$, T_{ref} are the Johnson-Cook parameters, ε_p is the plastic strain, T is the material temperature and T_m is the melting temperature. The parameters employed in this simulation are shown in **Table 4.7**: based again on the simulation by Fernandez et al. [24]

Table 4.7: Johnson-Cook parameters for copper and steel A36

Properties	Copper	Steel A36
A (MPa)	90	146.7
B (MPa)	292	896.9
C	0.025	0.03
n	0.31	0.32
m	1.09	0.323
$\dot{\varepsilon}_{ref}$	1	1
T_m (K)	1356	1810
T_{ref} (K)	293	293

The coatings are expected to have a more prominent hardness when compared to the bulk material. This is because of the deformation that the particles have during the CGDS procedure caused by work hardening, due to this the hardness of the coatings is determined by the method of the accompanying condition:

$$H \approx c \times \sigma_y \quad \text{Eq. 4.3}$$

Where H is the hardness of the coating material, c is a material constant, and σ_y the yield strength. The coating hardness obtained is employed in order to calculate the strain value at the moment of adhesion simulation that is represent by the predefined strain field for the coating as a value of $\varepsilon_p=0.29$ obtained by **Eq. 4.4**.

$$\varepsilon_p = \left(\frac{H}{c \times B \left[1 - \left(\frac{T - T_{ref}}{T_m - T_{ref}} \right) \right]} - \frac{A}{B} \right)^{\frac{1}{n}} \quad \text{Eq. 4.4}$$

Finally, the adhesion strength prediction was assumed as the maximum value of the calculation of the stress values calculated with the average vertical stress (S22) of the elements at the base of the substrate.

5. Results

Single particle depositions (wipe test) were done using the as-received powder thus the particle size is between approximately 7 μm to a maximum diameter of approximately 55 μm . **Figure 5.1** shows individual particles impacted at different substrate temperatures. It can be observed that in all the cases, small, medium, and large particles are deposited, and the particles that bounced off left craters on the substrates. However, the number of craters is reduced while the substrate temperature is increased as the number of deposited particles is increased with the increase of substrate temperature. However, this large size distribution results in difficulties in concluding in detail the effect of substrate temperature in terms of particle deformation.

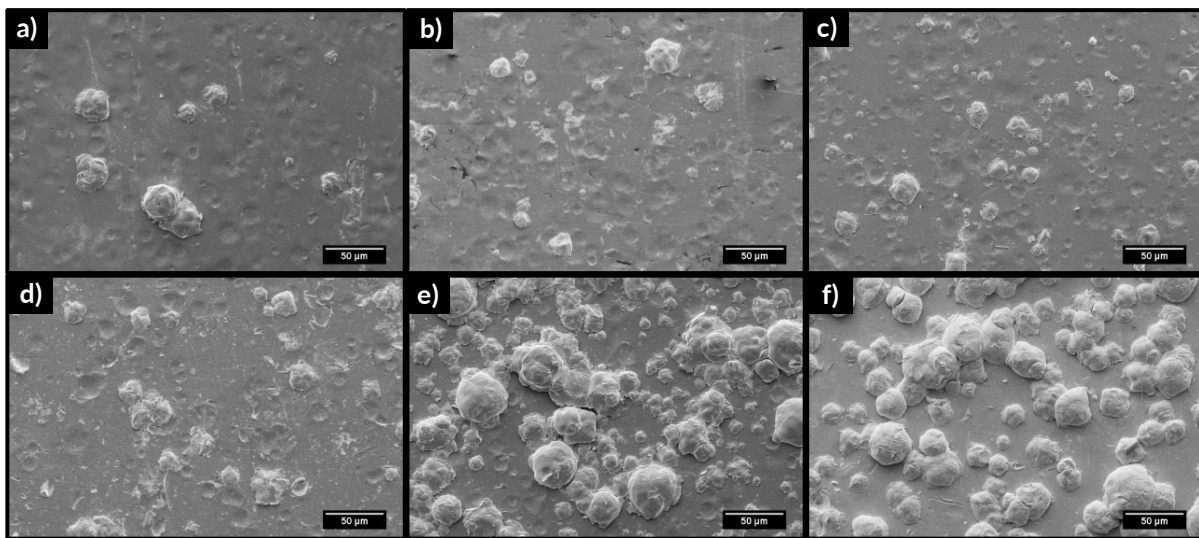


Figure 5.1 Wipe test at different substrate temperatures: a) 25°C, b) 50°C, c) 75°C, d) 100°C, e) 200°C, f) 300°C.

Figure 5.2 shows images from the same wipe test, although the focus is on single particles deposited at different substrate temperatures. The feedstock powder's large particle size distribution makes it difficult to observe particles from the same particle size range between the various test and to compare and conclude about the effect of the substrate temperature. Furthermore, the deformation level is not constant throughout the tests as particles with high and low deformation levels can be observed in the same test.

Additionally, the critical velocity is known to be a function of the particle size [4]; consequently, the deformation is different for each particle size under the same spray conditions, and the deposition efficiency is also affected the same way. The deposition efficiency for the large particles is lower in comparison with the smaller particles: **Figure 5.2** shows a large number of small particles at some substrate temperatures.

Another effect of the large particle size distribution of the feedstock powder is that it is common that small particles hit on larger particles already deposited, resulting in different deformation (as shown in **Figure 5.2 c)**); thus, this particle combination cannot be characterized to investigate the substrate temperature effect on particle deformation. In addition, particle characterization is to be conducted only for particles that do not show an impact over a crater already formed by a previous particle impact.

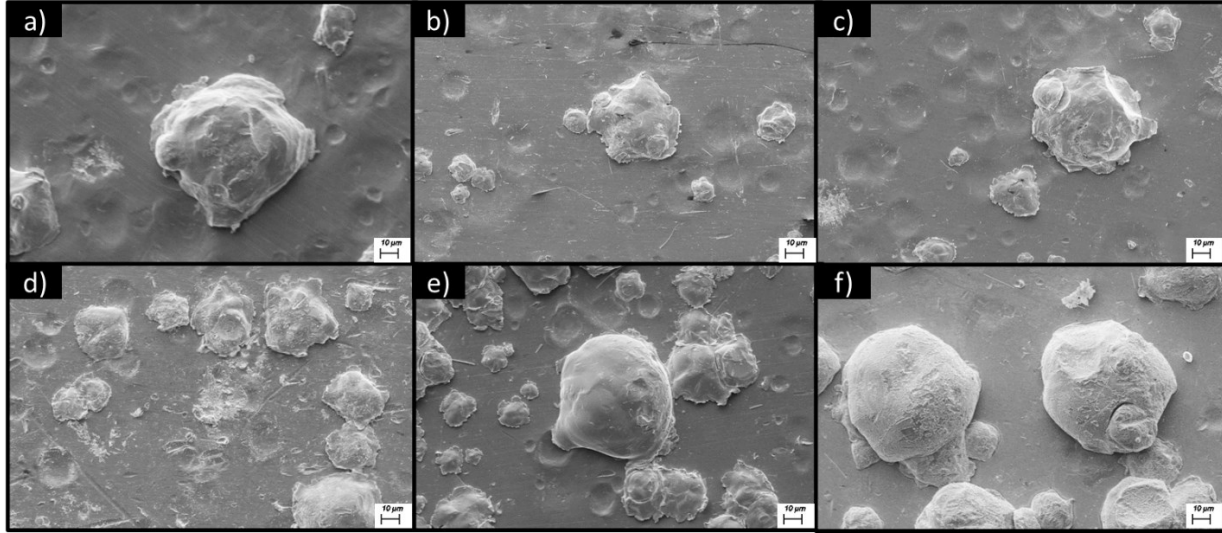


Figure 5.2 Wipe test (zoomed images) at different substrate temperatures: a) 25°C, b) 50°C, c) 75°C, d) 100°C, e) 200°C, f) 300°C.

For all these reasons, the particles were separated (as shown in **Figure 4.7** and **Figure 4.8**) into three different diameter sizes: large, medium, and small, to reduce the size distribution and avoid the above-mentioned effects that can hinder the understanding of the substrate temperature effect as well as particle impact velocity and temperature. Thus, in this chapter, the results are presented for the different particle size ranges. In the last section, only the large particle size range was used to perform the comparison with the laser-assisted wipe tests performed at the National Research Council Canada, Boucherville. The decision to only select this particle size to perform at NRC is because the large particles show the most noticeable trend through the change of substrate temperature.

Figure 5.3, Figure 5.4 and Figure 5.5 show typical optical microscope images from large, medium, and small particle size range at substrate temperatures of 25°C, 100°C, 200°C, 300°C, 400°C, 500°C, and 600°C. The only parameters that were changed during the tests are the powder feed rate and the nozzle transverse speed, to ensure a limited number of particles on the substrates while ensuring a statistically significant number for the analysis, depending on the particle size and the substrate temperature. The process gas temperature and pressure were always kept the same and thus it is expected that the particles were always impacting the substrate with the same velocity distribution within each powder size range. Only the number of particles impacting the substrates was affected by the powder feed rate and nozzle speed. This kind of image was performed in order to analyze the wipe test in the section followed.

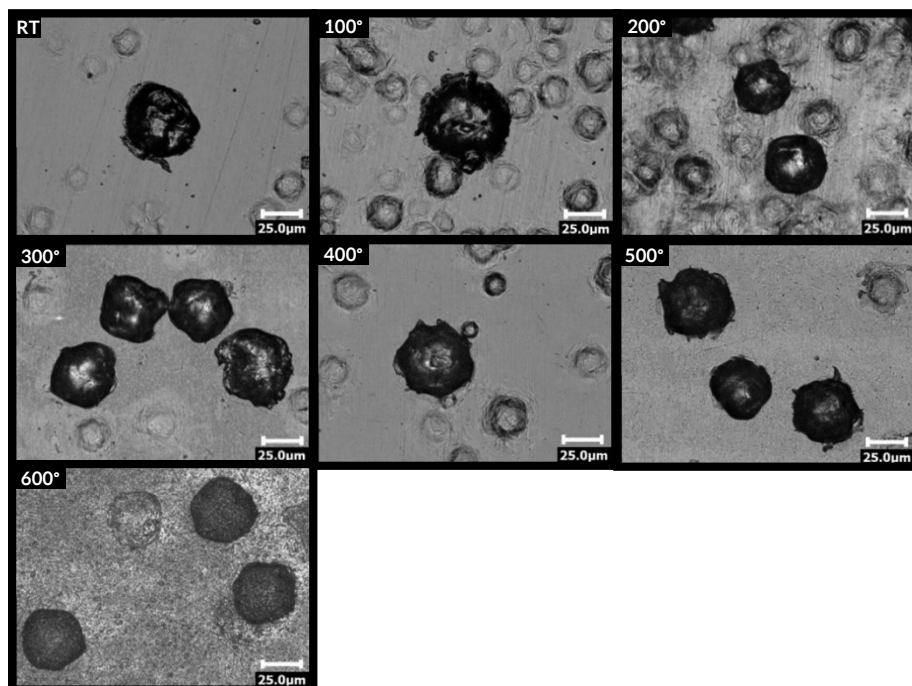


Figure 5.3 Optical microscope images of large particles ($d > 45 \mu\text{m}$) wipe tests at different substrate temperatures.

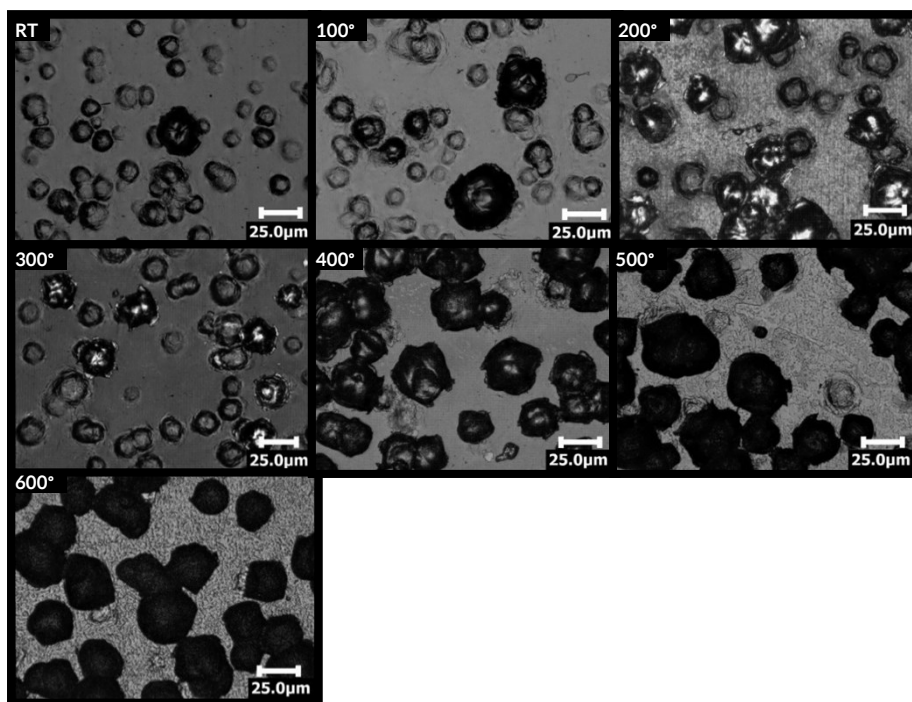


Figure 5.4 Optical microscope images of medium particles ($20 \mu\text{m} < d < 45 \mu\text{m}$) wipe tests at different substrate temperatures.

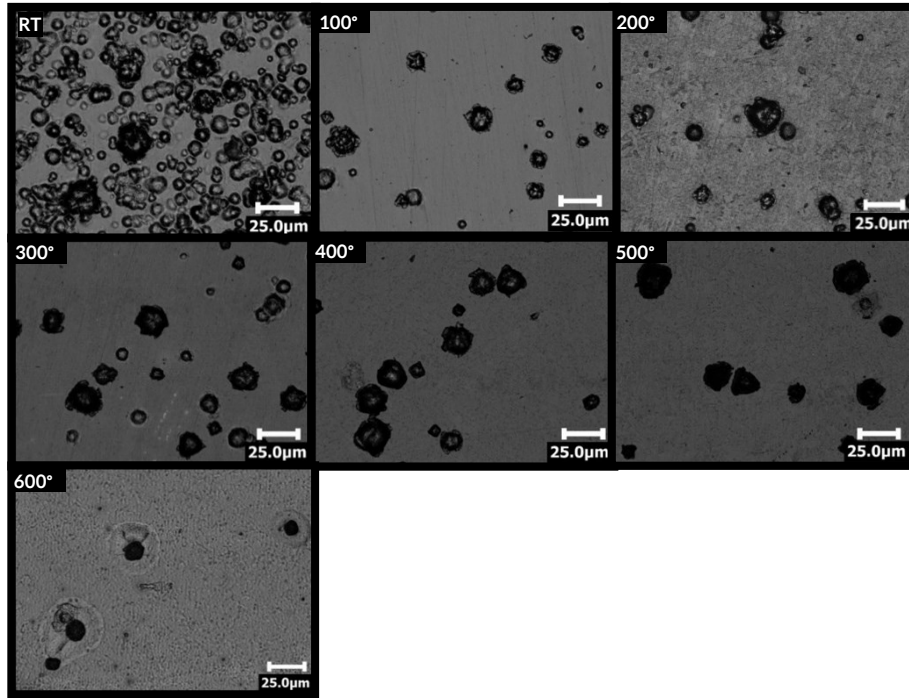


Figure 5.5 Optical microscope images of small particles ($d < 20\mu\text{m}$) wipe tests at different substrate temperatures.

5.1 Non-Destructive Measurements

For the non-destructive measurements, the wipe test samples (such as those shown in **Figure 5.3**, **Figure 5.4** and **Figure 5.5**) were used without any modification during the non-destructive examination/characterization procedures. These measurements are divided for craters created from the particles that did not reach the critical velocity so bounced off and particles with successful deposition. The crater characterization includes its diameter, depth, and volume. The particle characterization involves the height (distance from the substrate to the top of the deformed particle) and the diameter (which does not include the jetting caused by the impact deformation). Additionally, different background color contrasts can be overserved in **Figure 5.3**, **Figure 5.4** and **Figure 5.5** at different substrate temperature are due to the oxide layer and for the light from the optical microscope.

5.1.1 Craters

5.1.1.1 Crater diameter

Figure 5.6 shows the evaluation of the crater diameter (left by the bounced off particles) at the different substrate temperatures for the three different particle sizes. The crater diameter generally slightly increases as the substrate temperature increases for the three different particle

sizes, but this increase is not very significant for the smaller size range. This increase is more noticeable for the large particles that the crater diameter is from 32 μm to 55 μm when the substrate temperature is increased from 25°C to 600°C, with a large increase noticed at 500°C while limited to and no large increase at any temperature. For the medium particle size, the increase of crater diameter is from 25 μm at the substrate temperature of 25°C to 32 μm at the substrate temperature of 600°C with no large increase at any temperature. For the small particles, there is not a significant trend.

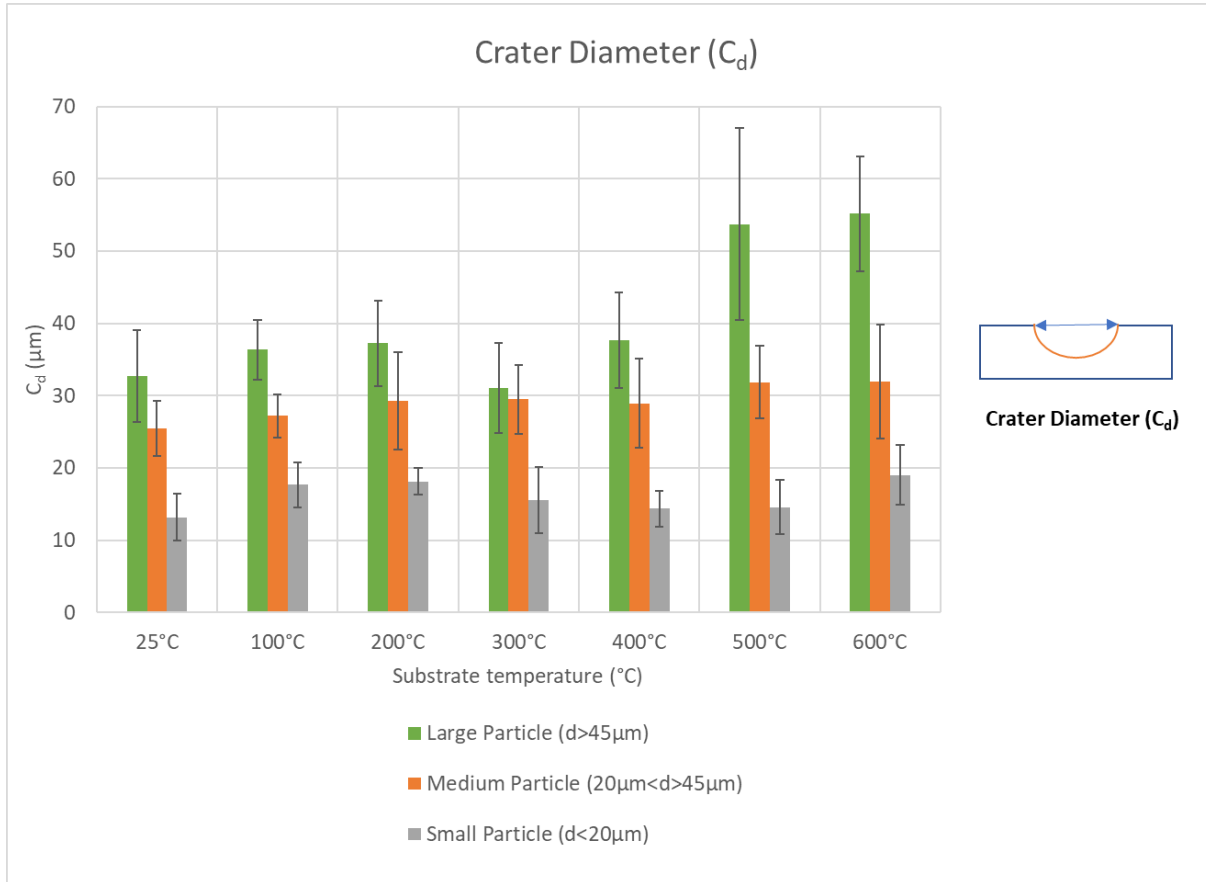


Figure 5.6 Crater diameter left by bounced off particles as a function of substrate temperature and particle size range.

5.1.1.2 Crater depth

The characterization of crater depth as a function of substrate temperature for the various particle size ranges is illustrated in **Figure 5.7**. Similar to the crater diameter analysis, the crater is deeper as the substrate temperature rises, with a more substantial/significant increase around 400°C for the large particle size range, 500°C for the medium particle size range, and around 600°C for the small particle size range.

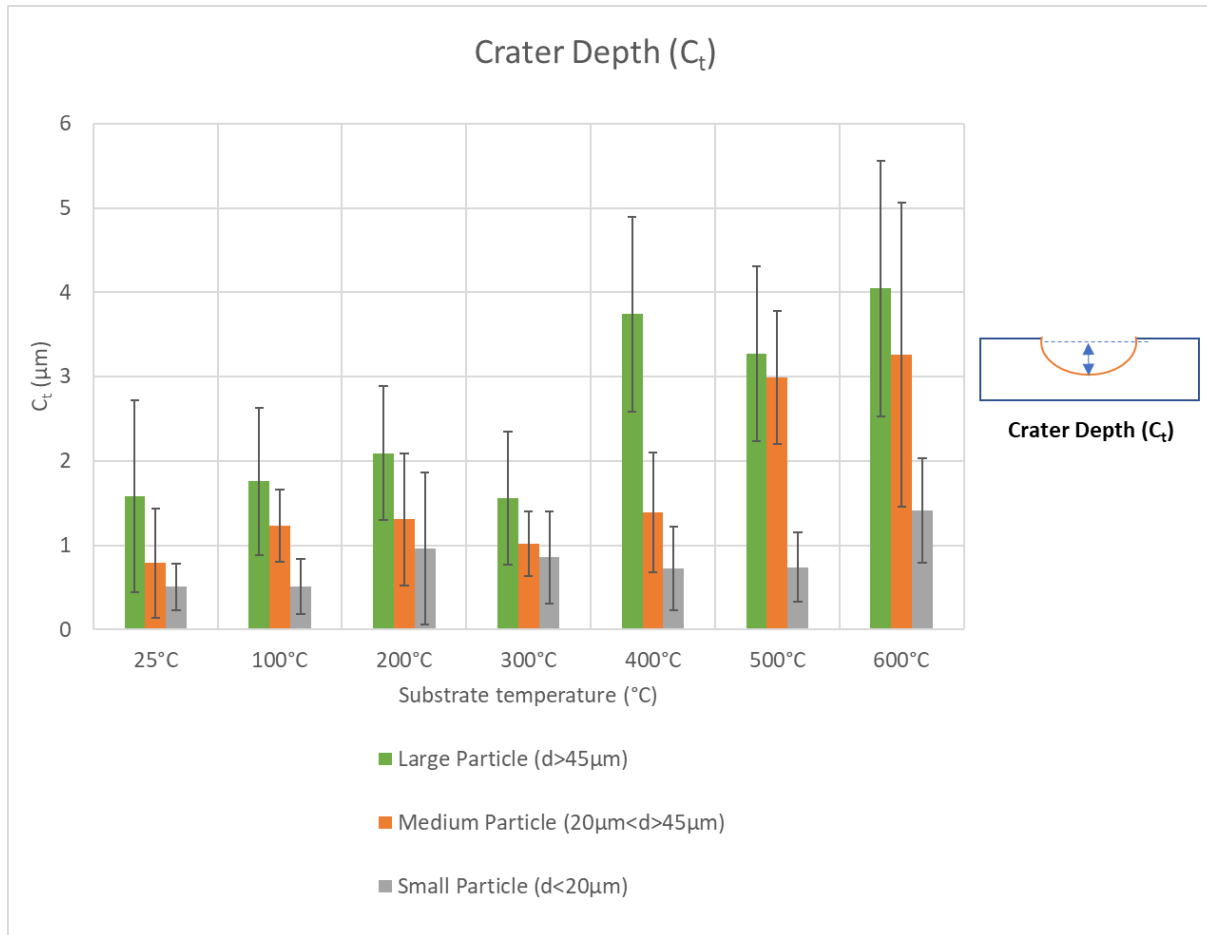


Figure 5.7 Crater depth left by bounced off particles as a function of substrate temperature and particle size range.

5.1.1.3 Crater volume

The crater volume analysis is generated by using the crater diameter and depth and measurement by the optical microscope, which is supported by the observed craters. The results are shown in **Figure 5.8**. The main observation is that the volume increases as the substrate temperature increases, while limited in the case of the smaller particle size range. One can also observe a more significant increase at 500 $^{\circ}\text{C}$ for the large and medium particle size range.

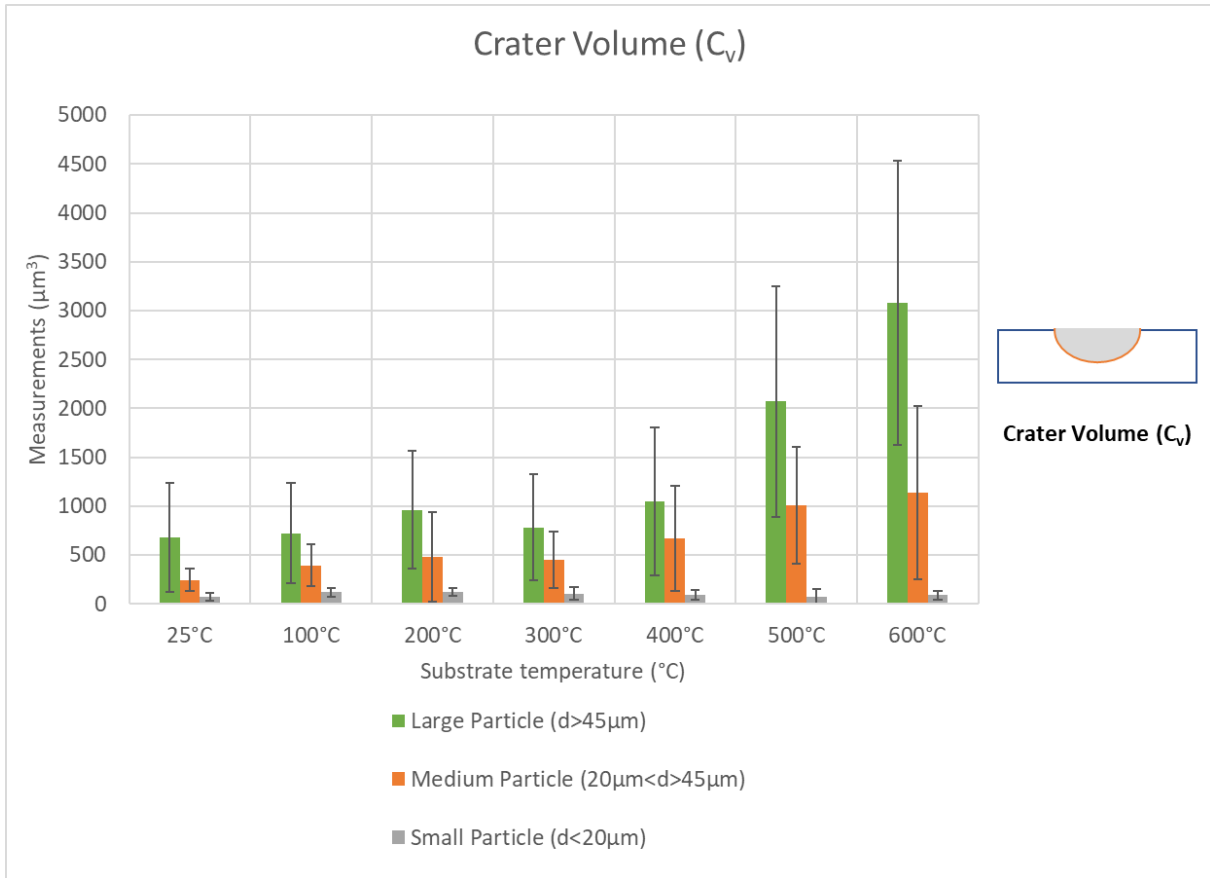


Figure 5.8 Crater volume of bounced off particles as function of substrate temperature and particle size range.

5.1.2 Particles

5.1.2.2 Particles diameter

Figure 5.9 presents the results of the particle diameter that was successfully deposited during the wipe tests as a function of the substrate temperature, for the three particle size ranges. It is essential to remember that the diameter measurements do not include the jetting area but exclusively the particle core and if it is not clear it is assumed to have a circular shape with the help of the microscope measurement tools. The effect of the substrate temperature rise is that the deformed particle diameter core slightly decreases for all size ranges, but not in a significant way. This could be that as the substrate temperature increases, there is less particle core deformation and more substrate deformation; in other words, the particle remains in its spherical shape from before impact. However, the particle diameter decrease is minimum, if observable for the medium

and small particle size ranges so one may conclude that this geometric parameter might not be of significant value to conclude anything.

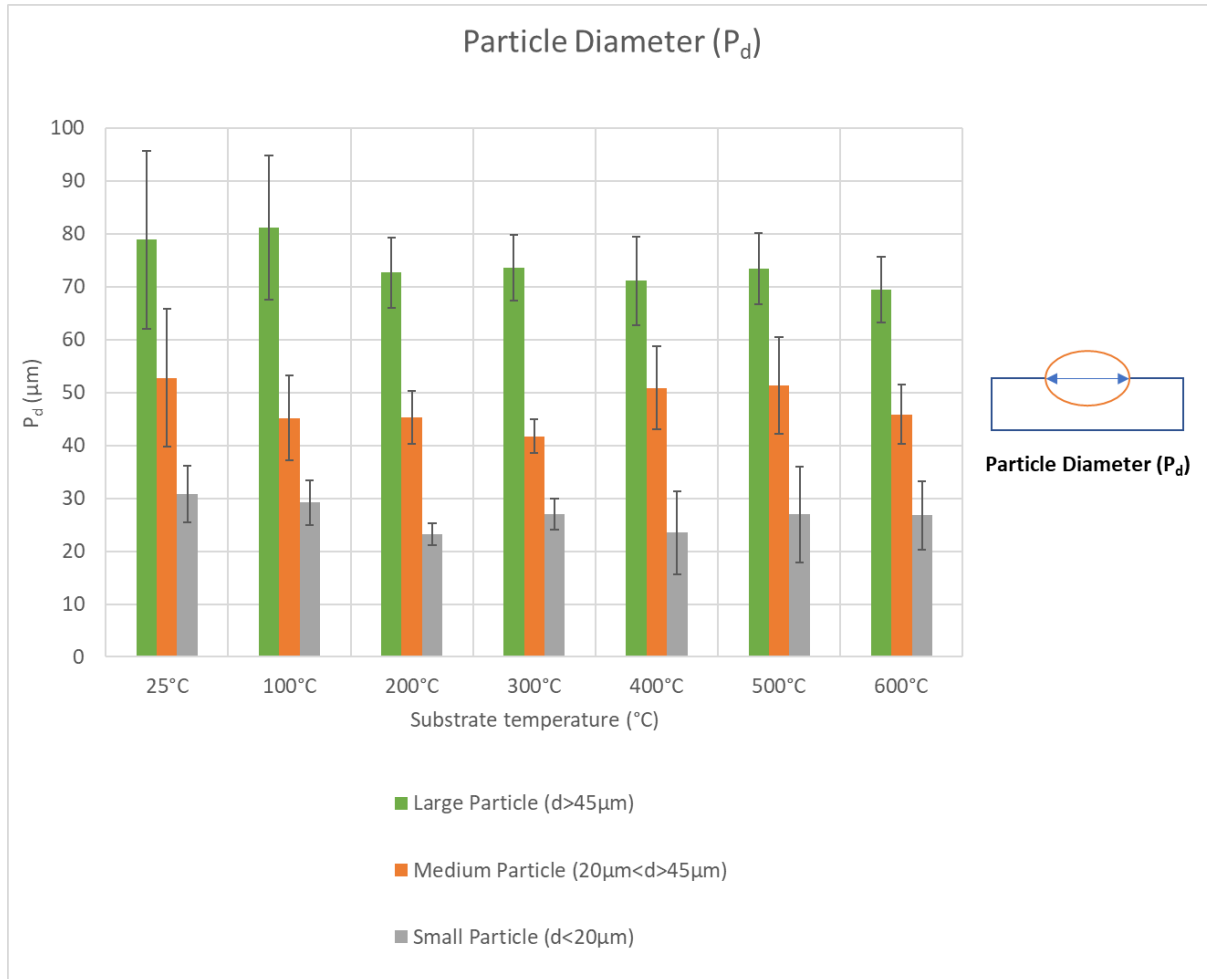


Figure 5.9 Deposited particle diameter as a function of substrate temperature and particle size range.

This particle diameter measurement is a sign of the particle core deformation; however, the jetting is probably a better sign of the overall particle deformation. The jetting analysis confirms that as the substrate temperature increases, the particle deformation decreases (presented in section **2.4.3 Substrate Temperature**).

5.1.2.2 Particle height

The particle height measurements presented in **Figure 5.10** for each particle size range as a function of substrate temperature is highly variable, with potentially an increase with the temperature above 200°C for large particles and 400°C for medium particles. However, it is difficult to be confident in a general trend beyond these two localized increases.

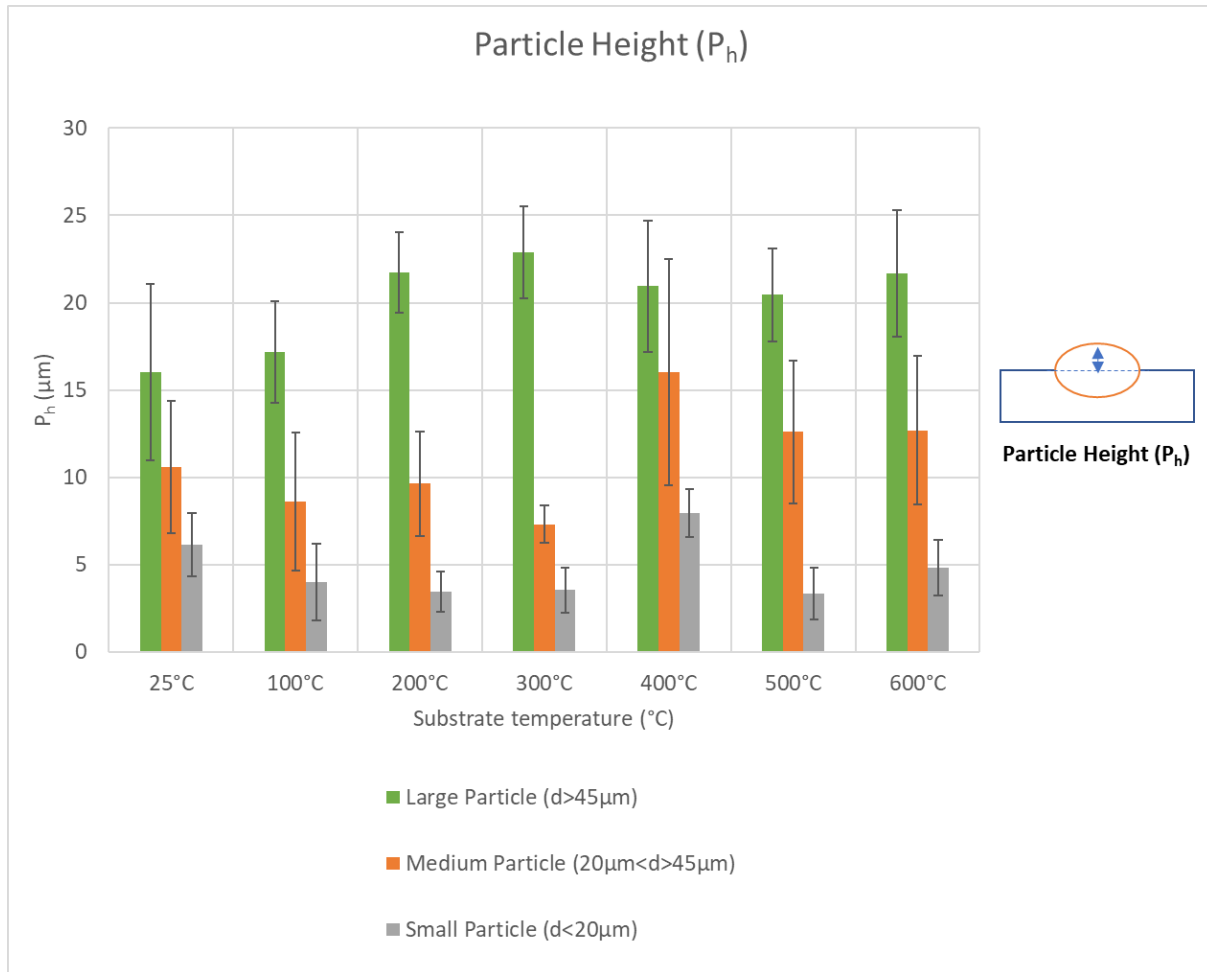


Figure 5.10 Deposited particle height as function of substrate temperature and particle size range.

5.1.2.1 Particle deformation

One consequence of the substrate temperature is the change in particle plastic deformation level of the different particle size ranges. As the critical velocity increases with decreasing particle size, different particle deformation levels are expected for the same impact velocity. However, it is essential to mention that the particle deformation is unique for each particle, due to the impact velocity and angle, and particle temperature prior to impact.

Figure 5.11 shows SEM images of single bonded particles from the large particle size range sprayed on substrates at different temperatures. It can be observed that at 25°C the impact generated jetting of material at the particle periphery. However, as the substrate temperature increases, the jetting is reduced and is completely absent at temperatures of 500°C and above. Additionally, it can be observed that the substrates at 500°C and above have a thin oxide layer; nevertheless, the particles break it upon impact, leaving signs of this around the particle as the image shows.

However, the oxide layer in the substrate can be grown before or after the particle impact, which is difficult to determine. The evidence that the oxide layer is broken (shown in **Figure 5.11** with white arrows) suggests indicating that it was there before the impact and got broken due to the particle impact. **Figure 4.7** shows the oxide layer of approximately $1\mu\text{m}$ when the sample is preheating at 600°C and with the particle impact, this oxide is broken. Furthermore, the particle on the 500°C and 600°C substrates manifest signs of oxide layer growth, which can be possible as a result of the heat transfer from the substrate to the particle, after the impact.

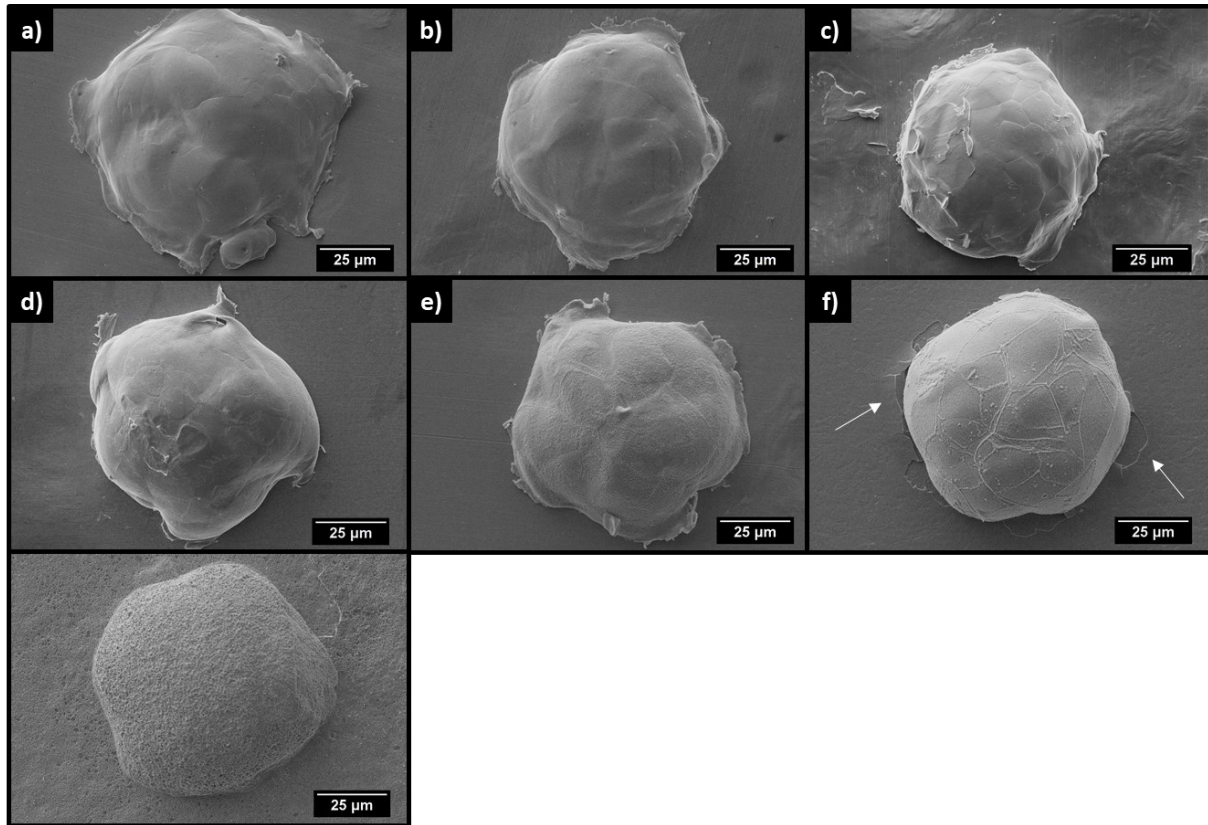


Figure 5.11 Single particle SEM images of bonded particles from the large particle size range at different substrate temperatures: a) 25°C , b) 100°C , c) 200°C , d) 300°C , e) 400°C , f) 500°C and g) 600°C .

The particle deformation for the medium particle size range is shown in **Figure 5.12**, with the preheated substrate at different temperatures. The particle deformation as the substrate temperature increases is similar to the large particle size range, whereas the substrate temperature increase leads to a reduction of the particle jetting and the particles remain spherical. However, for the medium size range particles, the formation of jettings is more noticeable.

Similarly to the case for large particle size range, when the substrate is preheating at 500°C (**Figure 5.12 f**) the particle breaks the oxide layer (shown with white arrow) that did grow on the substrate. Another similarity of the medium and large particle size ranges is that at 500°C the particle shows some oxide growth on its surface.

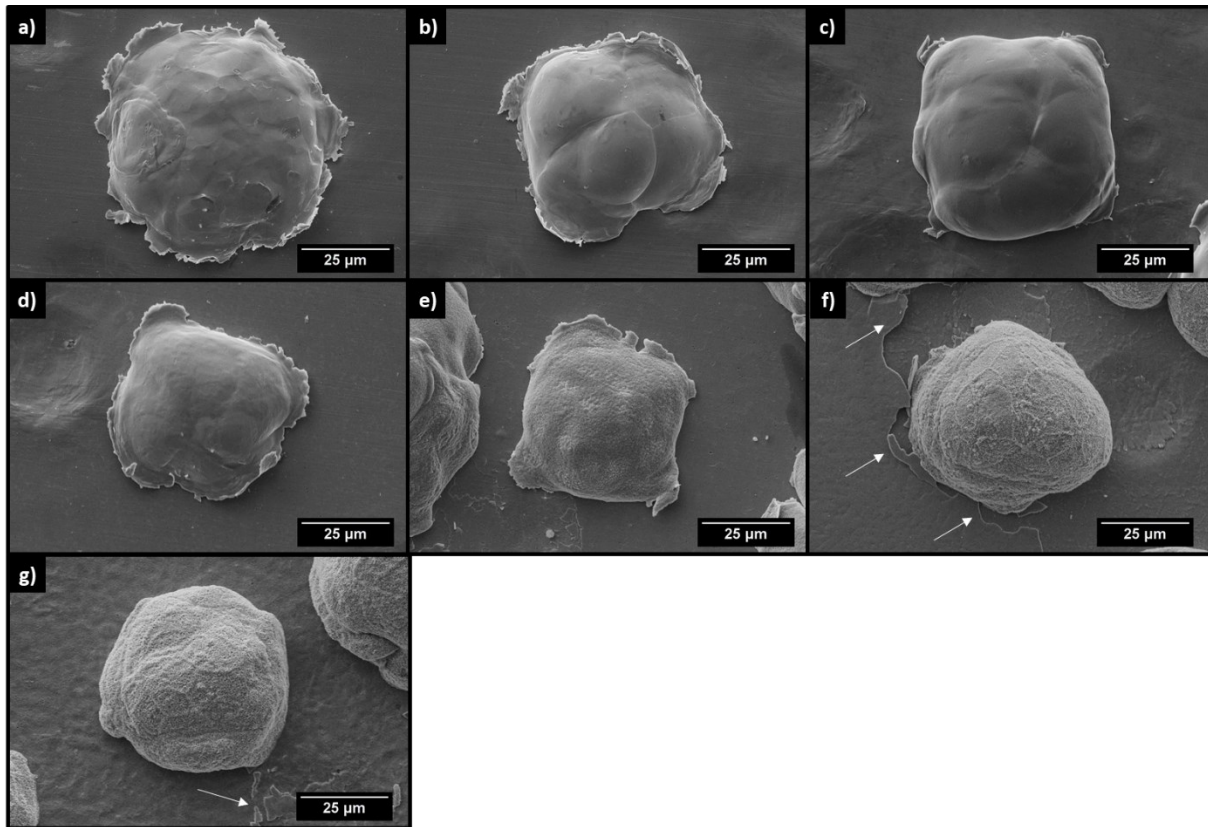


Figure 5.12 Single particle SEM images of bonded particles from the medium particle size range at different substrate temperatures: a) 25°C, b) 100°C, c) 200°C, d) 300°C, e) 400°C, f) 500°C and g) 600°C.

Lastly, **Figure 5.13** evidences the deformation for the small particle size range. In this case, for all the substrate temperatures, there is evidence of jetting; however, comparing the jetting from 25°C and 600°C, the jetting at 25°C is more pronounced. Furthermore, for the substrate temperature of 500°C (**Figure 5.13 g**) similar to the other particle size ranges, the small particle size range shows just slight evidence that particles break the oxide layer, though, at 600°C the oxide breakage is more evident. Nevertheless, the indication of oxide growth in the particle is more evident in the small particle size.

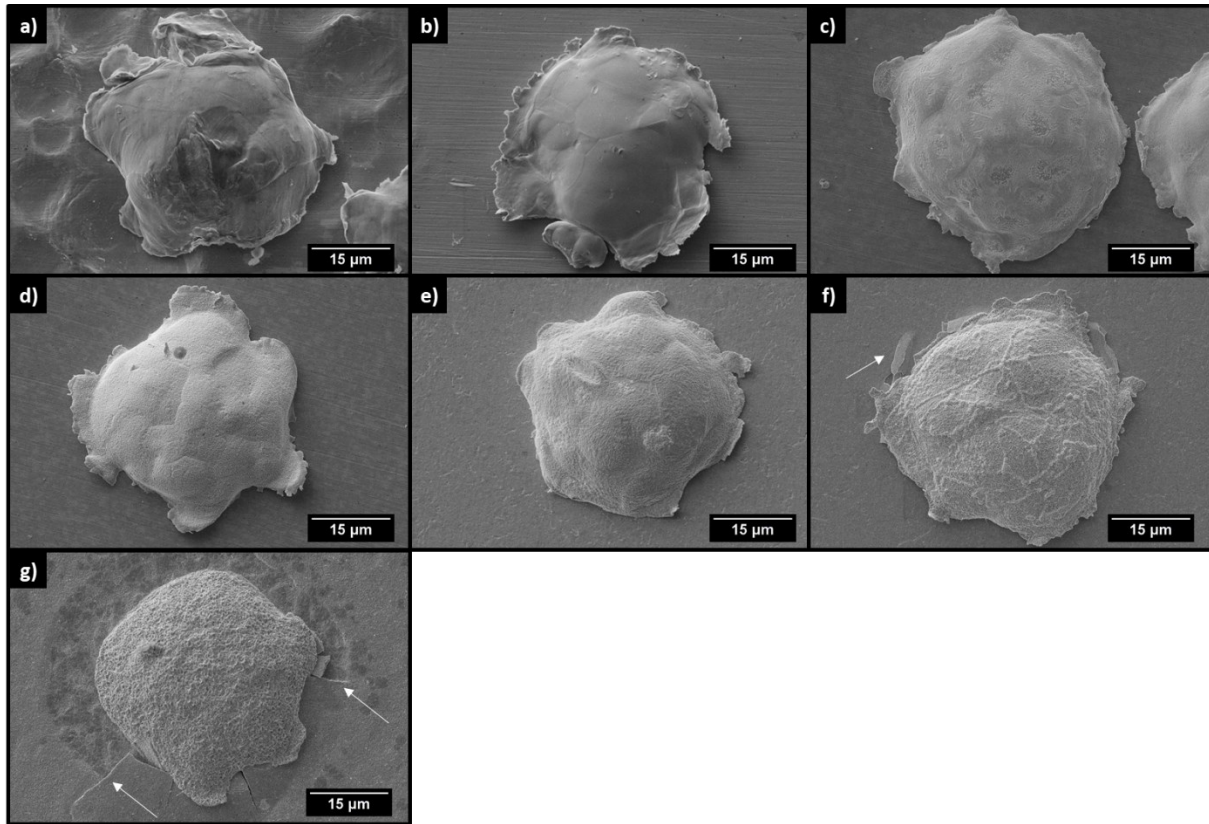


Figure 5.13 Single particle SEM images of bonded particles from the small particle size range at different substrate temperatures: a) 25°C, b) 100°C, c) 200°C, d) 300°C, e) 400°C, f) 500°C and g) 600°C.

Figure 5.14 illustrates the single particle at 300°C where it can be seen that oxide layer growth occurred on the particle at 300°C as a possible result of heat transfer from the substrate to the particle. The copper starts to form a thin layer of Cu_2O between room temperature and 100°C and then around 150°C a complex oxide forms Cu_3O_2 and finally at 200°C to 300 °C CuO forms which is the most significant oxidation [102].

Furthermore, in the magnification of the marked area of **Figure 5.14**, the jetting can be observed without an oxide layer at the external perimeter pointed with a white arrow. It is hypothesized that this can occur because the jetting area is not in direct contact with the substrate, thus minimizing heat transfer between this particle location and substrate. Another possible reason can be that the thin edge of the jetting not in contact with the substrate cools rapidly, thus the oxide does not form. Those possible reasons can be used to confirm that the oxidation layer on the particle occurs during the cool downtime after the impact and not during the particle flight.

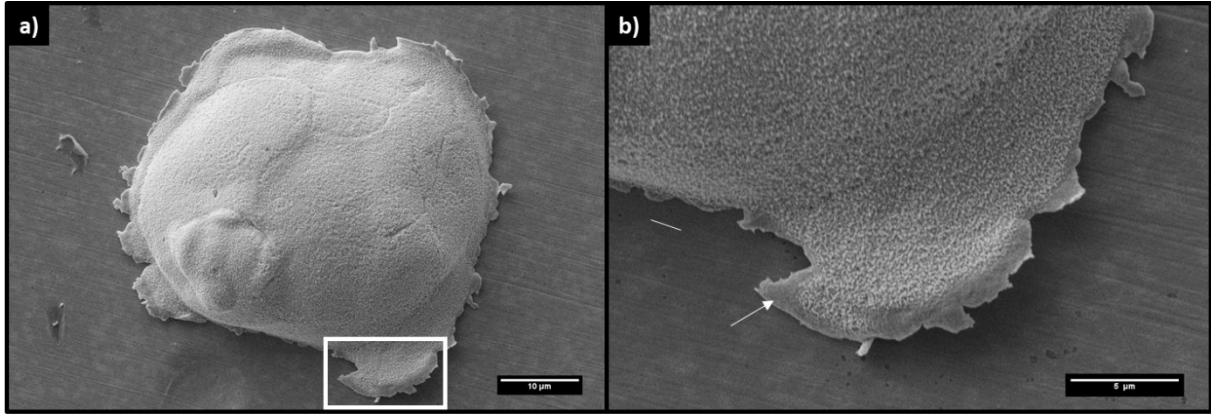


Figure 5.14 a) Single particle SEM image of particle from small particle size range at substrate temperature of 300°C, b) magnification of the marked area of image a).

The particle deformation can be quantified with the compression ratio or flattening parameter, and it can be determined by the equation [103][104]:

$$R_c = \frac{P_{d_0} - h}{P_{d_0}} \quad \text{Eq. 5.1}$$

where h is the height of the deformed particle and P_{d_0} is the diameter of the spherical particle before impact. It can be calculated from the deformed particle geometry using the following equation [103][104]:

$$P_{d_0} = \sqrt[3]{\frac{3}{4}\omega^2 h} \quad \text{Eq. 5.2}$$

where w is the particle diameter and h the particle height, both measured after particle impact. The particle diameter before the particle impact is shown in **Figure 5.15**.

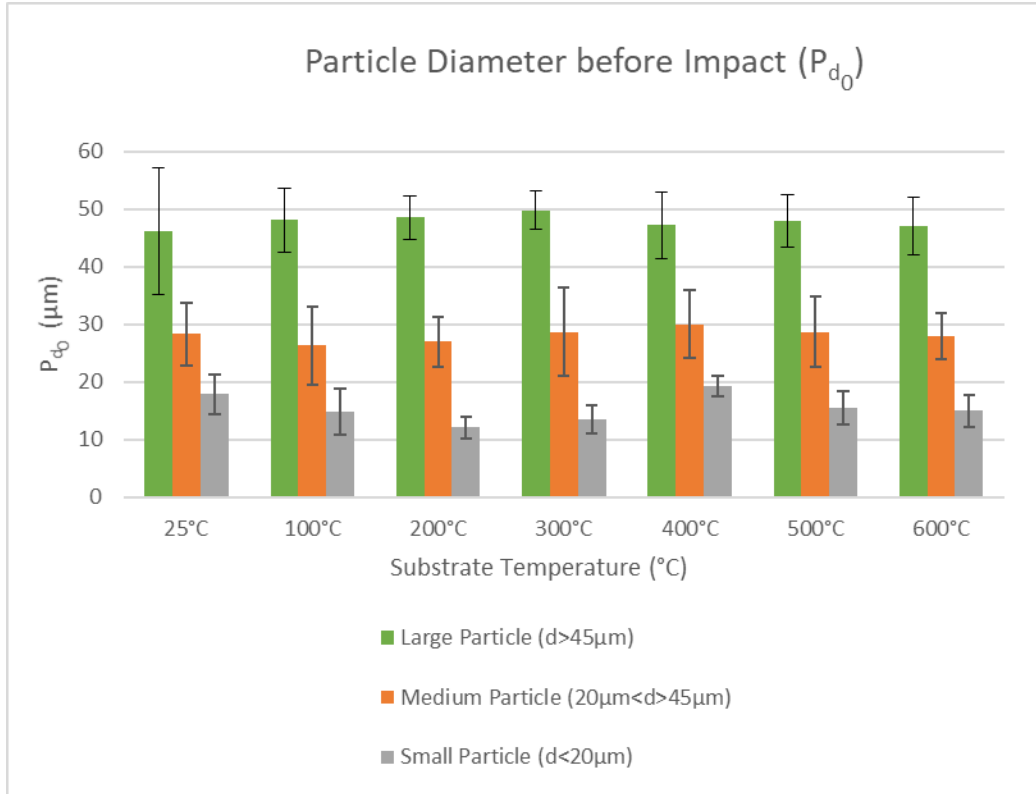


Figure 5.15 Particle diameter before impact for the different particle size range at each substrate temperature.

These equations can be used because the copper particles are initially spherical. **Figure 5.15** shows the particle diameter before impact as determined with equation 5.2. Comparing these results with the particle size diameter that it is determined before the spray, the calculated average diameters match ideally between the range for large ($d > 45\mu\text{m}$), medium ($20\mu\text{m} < d < 45\mu\text{m}$), and small size ($d < 20\mu\text{m}$). Hence, the compression ratio equations can be used in this investigation.

Figure 5.16 provides the compression ratio (R_C) from the different particle size ranges as a function of the substrate temperature. The R_C for the three particle sizes at 25°C is the same; however, as the substrate temperature increases, the R_C starts to change differently for each particle size. For the large particle size range, the R_C is reduced as the temperature rises and is the lowest R_C of the three particle size ranges at each substrate temperature, as observed qualitatively from the SEM images. Particles from the medium particle size range show the same trend; however, the reduction is not as important. The small particle size range reveals a considerable variation between each temperature but is not reduced as in medium and large particles.

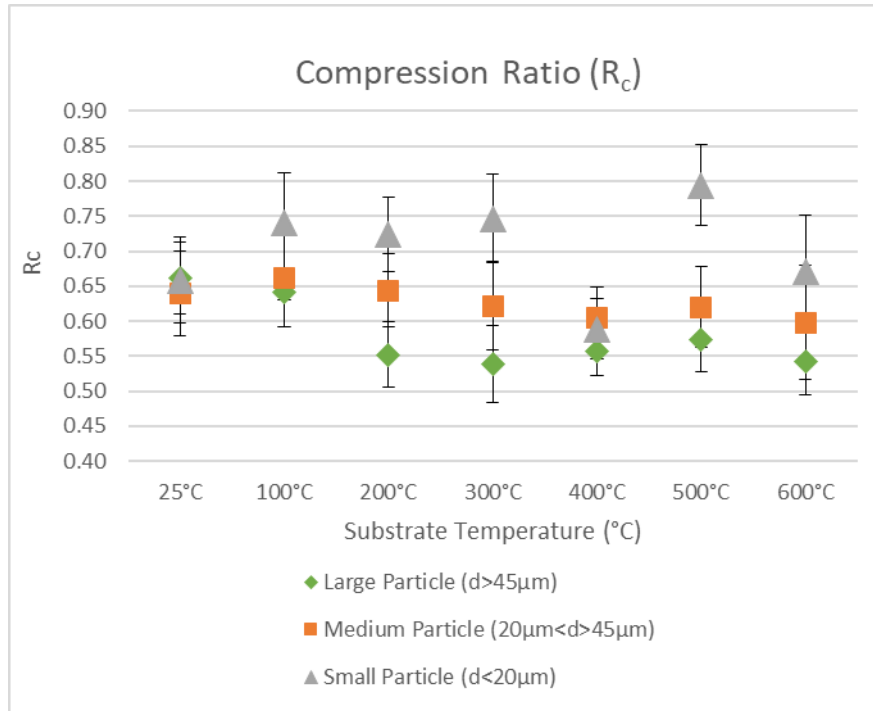


Figure 5.16 Compression ratio (R_c) for the different particle size ranges as a function of the substrate temperature.

Furthermore, the small particle size shows to experience the most particle deformation as the substrate temperature decreases, then the medium size range and finally large size range that shows the less deformation. A possible explanation of these results is as the substrate is preheated, its yield strength is reduced, and the thermal softening is increased, which enhances the substrate deformation instead of the particle deformation.

5.2 Destructive Measurements

5.2.1 Laser Cut

The cross-section examination of single CGDS particle impact has been studied by many researchers. The most common way is the use of a focused ion beam (FIB) to obtain a clean cross-section [105][106][107]. However, FIB is a very time consuming procedure. In this research, the need to characterize a large number of particles to get statistically meaningful results lead to the introduction of the idea of performing cross-section cuts using an Yb:KGW femtosecond laser. The laser generates a linearly polarized Gaussian beam with a pulse duration of 300 fs at a wavelength of 1030 nm and 200 uJ pulse energy.

One of the advantages to perform cuts using the femtosecond laser is the ability to select accurately the cut position, in this case in the middle of the particle. This would allow the exact measurement of the particle diameter and depth, for each cut particle, with the purpose to link the particle/substrate deformation for different particle size range at the different substrate temperatures.

The selection of the correct laser parameters combination is a challenge because the laser needs to cut the copper particles and the low carbon steel substrate that have different properties. The laser parameters that can be modified with the purpose to obtain a clean cut surface are:

- Laser output power (mW- W)
- Laser repetition rate (kHz)
- Laser trace velocity (mm/s)
- Laser polarization
- Number of passes

It is important to mention that the laser output power is measure by an Ophir Vega power meter at the exit of the laser. The laser power is measure at the exit because the input power is lost though as it travels between lenses and it is hard to have the same output power again once the laser set up is changed.

Figure 5.17 shows the result of a laser cut using the optical microscope. It can be observed the laser cuts through the copper particles and craters from particles that bounced off. The 3D stitching with a depth scale shows the Heat Affected Zone (HAZ) caused by the fact that the pulse duration is longer than the thermalization time of each metal [108]. The HAZ can be represented by a Gauss distribution cut (as shown in **Figure 5.17**) that results in an unclear particle interface and the inability to cut precisely in the middle of a particle, consequently leading to an incorrect penetration depth measurement. Additionally, it is noticed that the quality surface of the sidewalls and the depth can result in different surfaces finished [109].

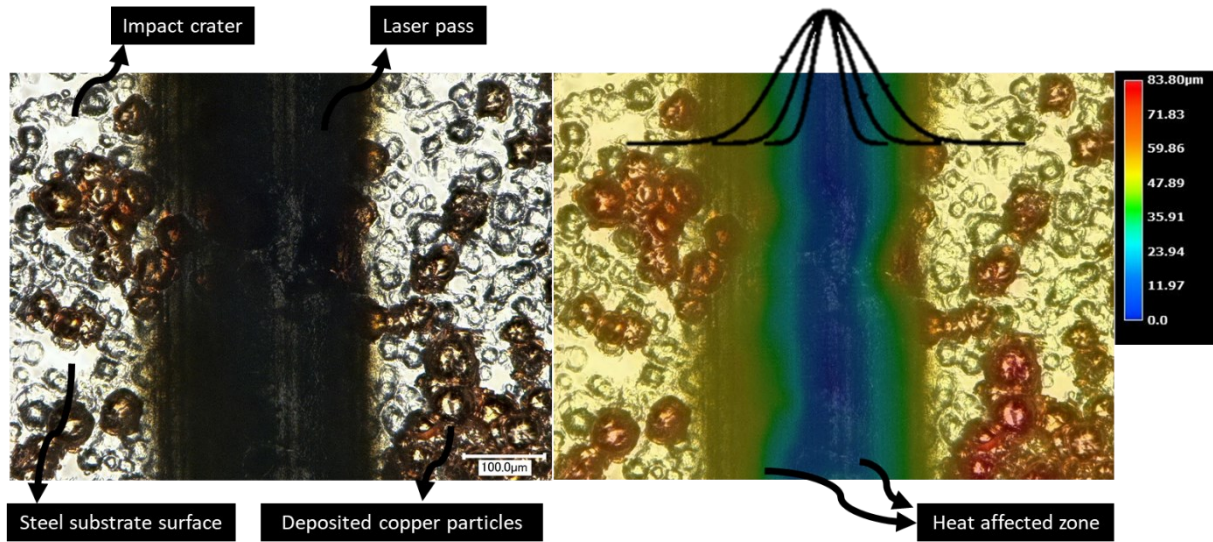


Figure 5.17 a) Optical microscope of a laser-cut over the wipe test, b) 3D stitching with depth scale.

Several wipe tests (as illustrated in **Figure 5.18**) were subjected to laser cuts to test and determine the necessary parameters to achieve the best quality of cuts. A quality cut allows identifying the particle interface to measure the penetration and diameter of the particle and also to make relationships between particle deformation and penetration. All cuts were carried out at room temperature in air perpendicular to the wipe test and then analyzed in SEM to observe the cut quality. All the images were taken with the tilt of the sample at 30° with respect to the horizontal to observe the particle interface and know that the cut is deep enough.

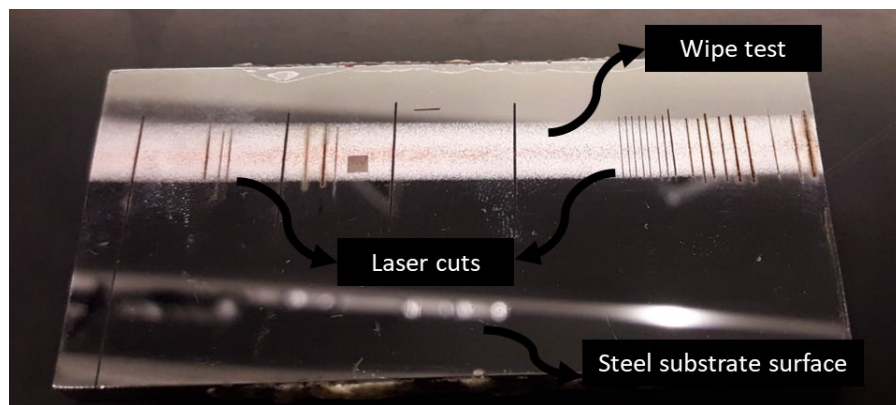


Figure 5.18 Laser cuts of the wipe test.

The first parameter studied is the repetition rate. **Figure 5.19** illustrates five different repetition rates (1, 5, 10, 30, and 200 kHz) at the same laser output power (148 mW) and laser trace velocity (1 mm/s), using linear polarization and a single pass. At the lower repetition rate of 1 kHz, the cut is not deep enough to cut all the cross section of the particle and a HAZ can be noticed. The increase of the repetition rate resulted in shallow cuts at 30 kHz and 200 kHz, where the cuts are superficial. Additionally, at 5 kHz, different microstructure starts to appear, called laser induced periodic surface structures (LIPSS) or ripples that result in an obstacle to look at the particle interface. At 10kHz LIPSS is still slightly observed. At 30 kHz, melting material resulting from the cut causes splashes over the top surface. The best cut in this test is the one with 200 kHz which is the parameter for the next test.

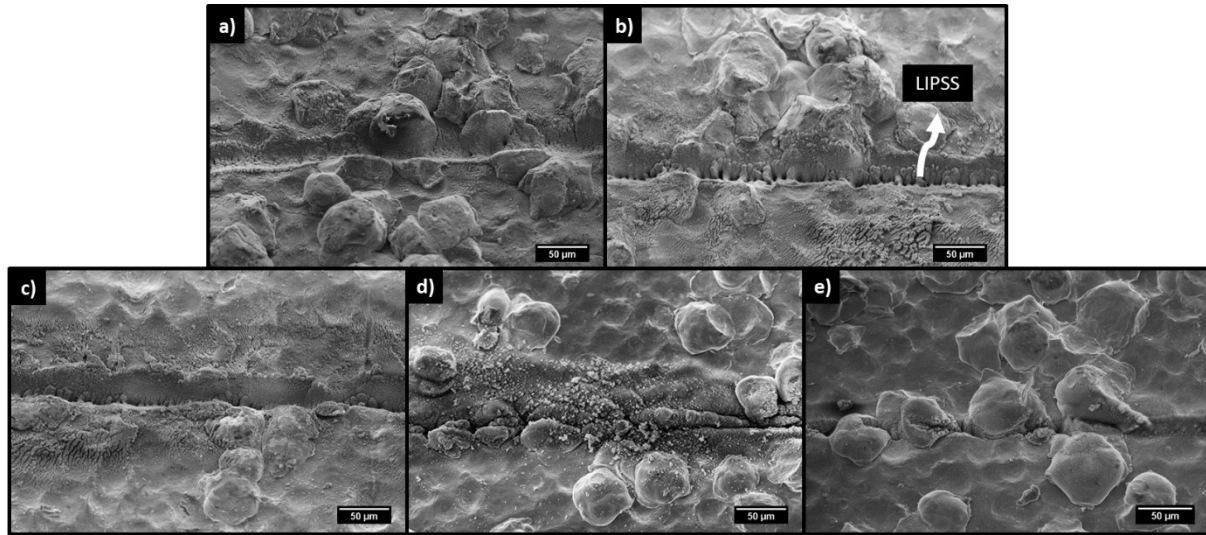


Figure 5.19 SEM image of laser cut with parameters of laser output power: 148mW, laser trace velocity: 1 mm/s, linear polarization, single pass and varying repetition rate: a)1kHz, b) 5kHz, c) 10kHz, d) 30kHz and e) 200kHz.

The LIPSS is an outcome of the interaction of the scattered light and the incident laser light on the surface [109]. The morphology of the LIPSS is related to the material properties, the energy density, and the laser optical setup (modifying the polarization) [110]. These structures can be prevented with the specific parameters' combination for each metal. In this case, the parameter combination needs to satisfy both materials, copper, and low carbon steel.

Figure 5.20 shows the outcome of the cuts keeping the repetition rate at 200 kHz and using a laser output power of 2.8 W. The laser trace velocity is varied from 0.2 mm/s to 30 mm/s. In these conditions, there is no evidence of splashes on the top surface. The lowest velocities result in unclear cuts with the presence of HAZ and LIPPS. For velocities between 15 mm/s to 25 mm/s the cut is clear, however, the particle/substrate interface is not easy to identify. At 30 mm/s the cut is not deep enough, and a Gaussian cut distribution is detected.

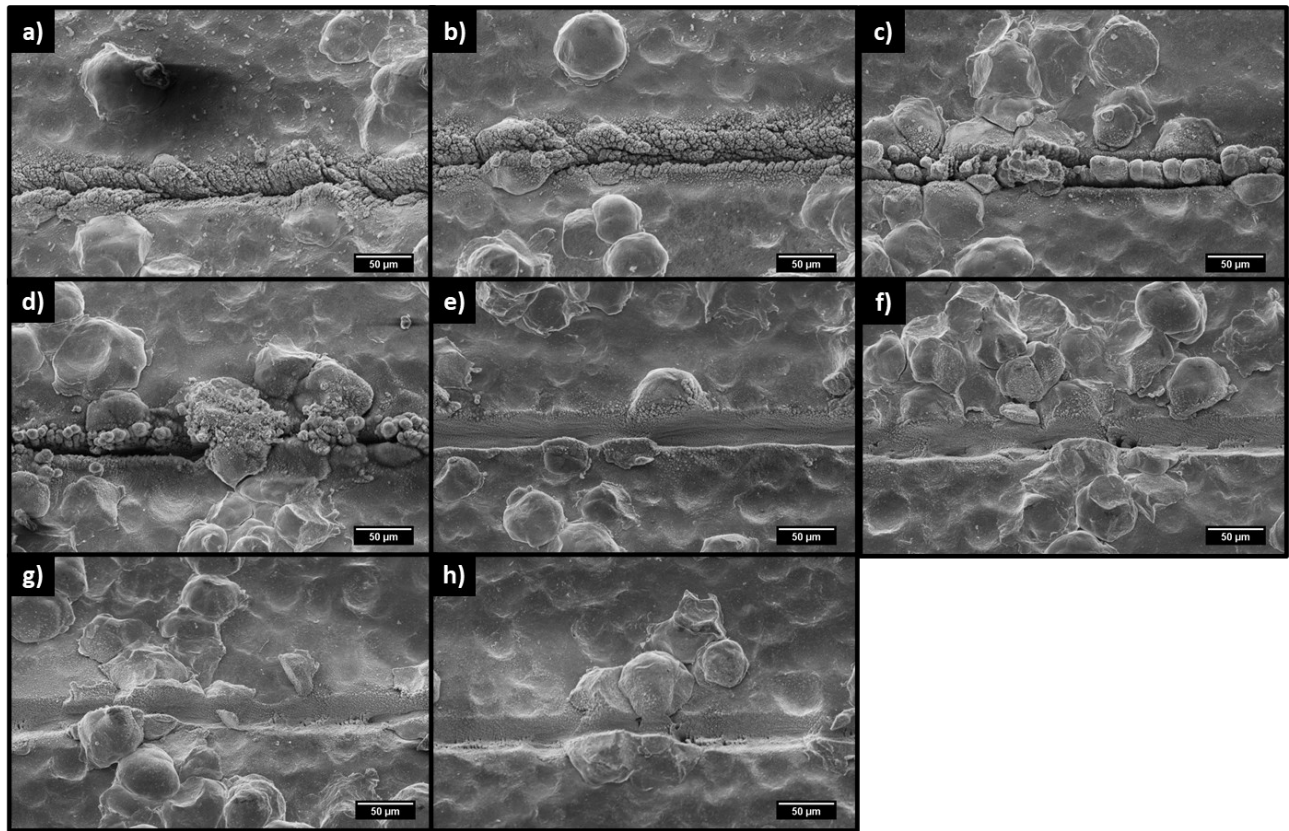


Figure 5.20 SEM image of laser cut with parameters of repetition rate: 200 kHz, laser output power: 2.8W, linear polarization, single pass and varying the laser trace velocity: a) 0.2 mm/s, b) 1 mm/s, c) 5 mm/s, d) 10 mm/s, e) 15 mm/s, f) 20 mm/s, g) 25 mm/s, h) 30 mm/s.

Considering the previous results, the repetition rate was reduced to 100 kHz (as presented in **Figure 5.21**) while the other parameters were kept constant except the laser trace velocity. At the laser trace velocity of 5 mm/s, splashes of the melting material are noticed at the top surface. As the trace velocity is increased, the splashes are eliminated; nevertheless, LIPSS started to appear. As the trace velocity is increased, the depth of the cut is reduced, such that at 40 mm/s only part of the particle is cut.

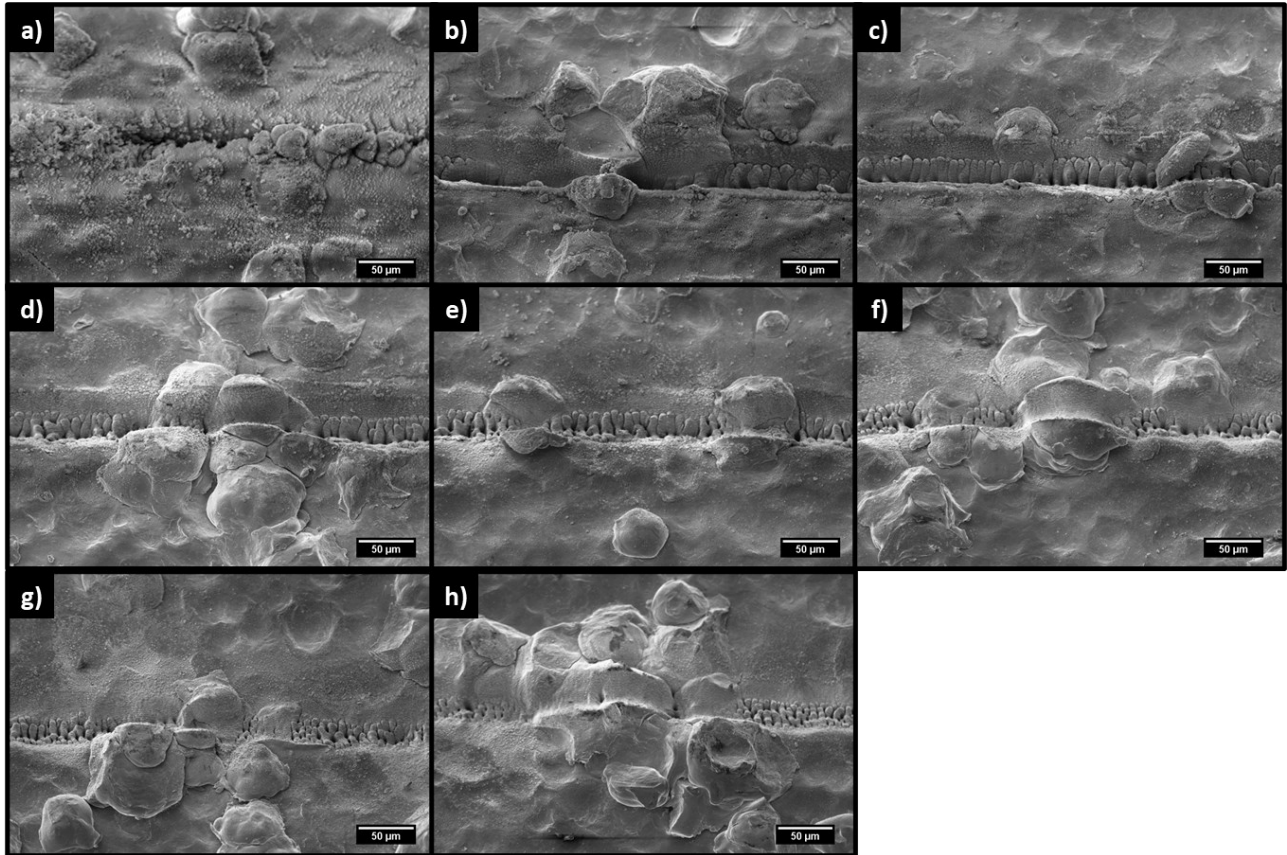


Figure 5.21 SEM image of laser cut with parameters of repetition rate: 100 kHz, laser output power: 2.8 W, linear polarization, single pass and varying the laser trace velocity: a) 5 mm/s, b) 10 mm/s, c) 15 mm/s, d) 20 mm/s, e) 25 mm/s, f) 30 mm/s, g) 35 mm/s and h) 40 mm/s.

The laser output power was increased to 4.6 W. **Figure 5.22** illustrates the results. At lower trace velocities the quality of the cuts is low with the melting material covering the cut. Increasing the trace velocity up to 20 mm/s increases the cut quality; however, a HAZ appears. In addition, as the trace velocity increases the cut is getting narrower that results in difficulties in observing the interface.

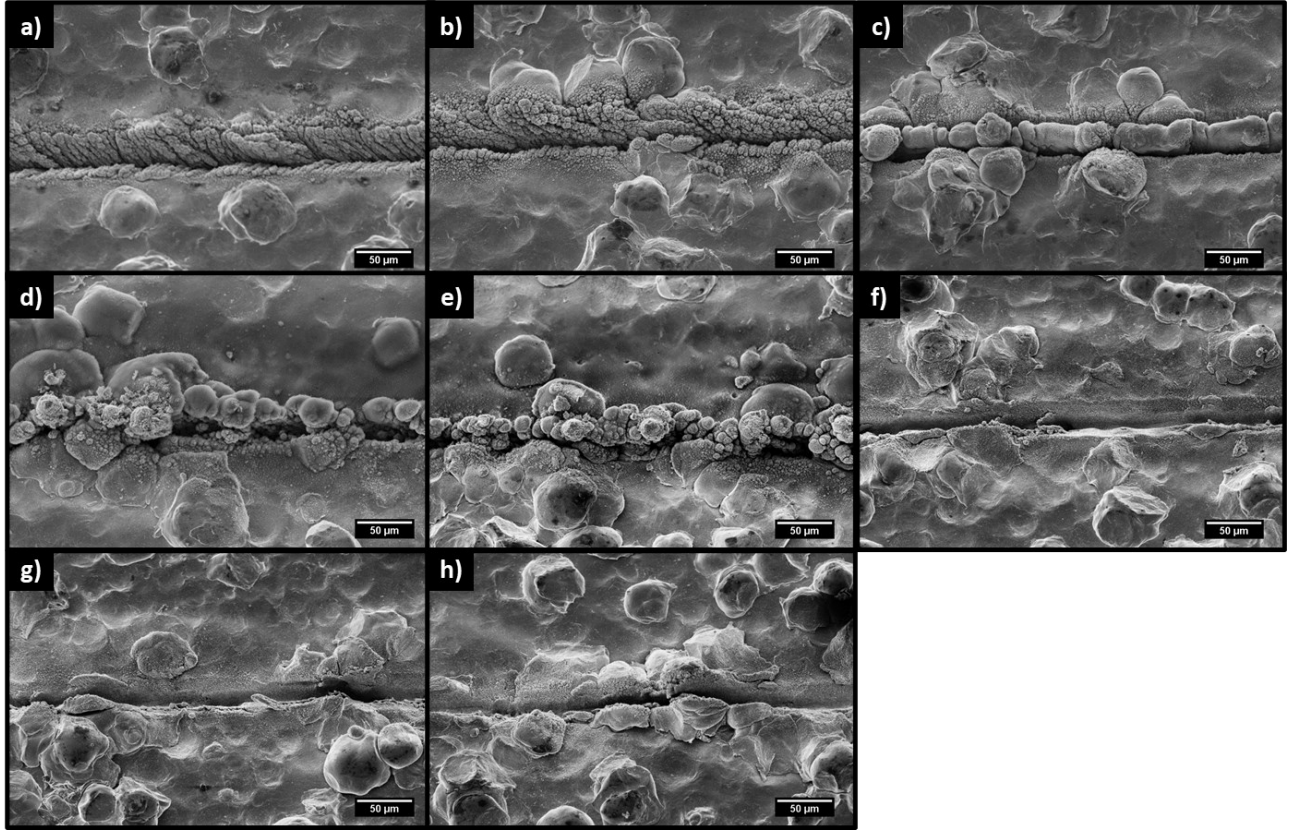


Figure 5.22 SEM image of laser cut with parameters of repetition rate: 200 kHz, laser output power: 4.6 W, linear polarization, single pass and varying the laser trace velocity: a) 0.2 mm/s, b) 1 mm/s, c) 5 mm/s, d) 10 mm/s, e) 15 mm/s, f) 20 mm/s, g) 25 mm/s, h) 30 mm/s.

From all tests performed, the best cut quality is the one with the following parameters: 200 kHz, 2.8W, 15 mm/s, single pass. However, the polarization is another parameter that can be modified. **Figure 5.23** demonstrates the same parameters at different polarization: horizontal (HP) linear (LP), linear scramble (LSP), and circle scramble polarization (CSP). It can be noticed that the best quality cuts are the ones with LP and CSP, where the cut is wide and depth enough. However, the particle interface is clearer in the case of the CSP. Moreover, there is no evidence of LIPSS for these parameter sets, no matter the polarization type.

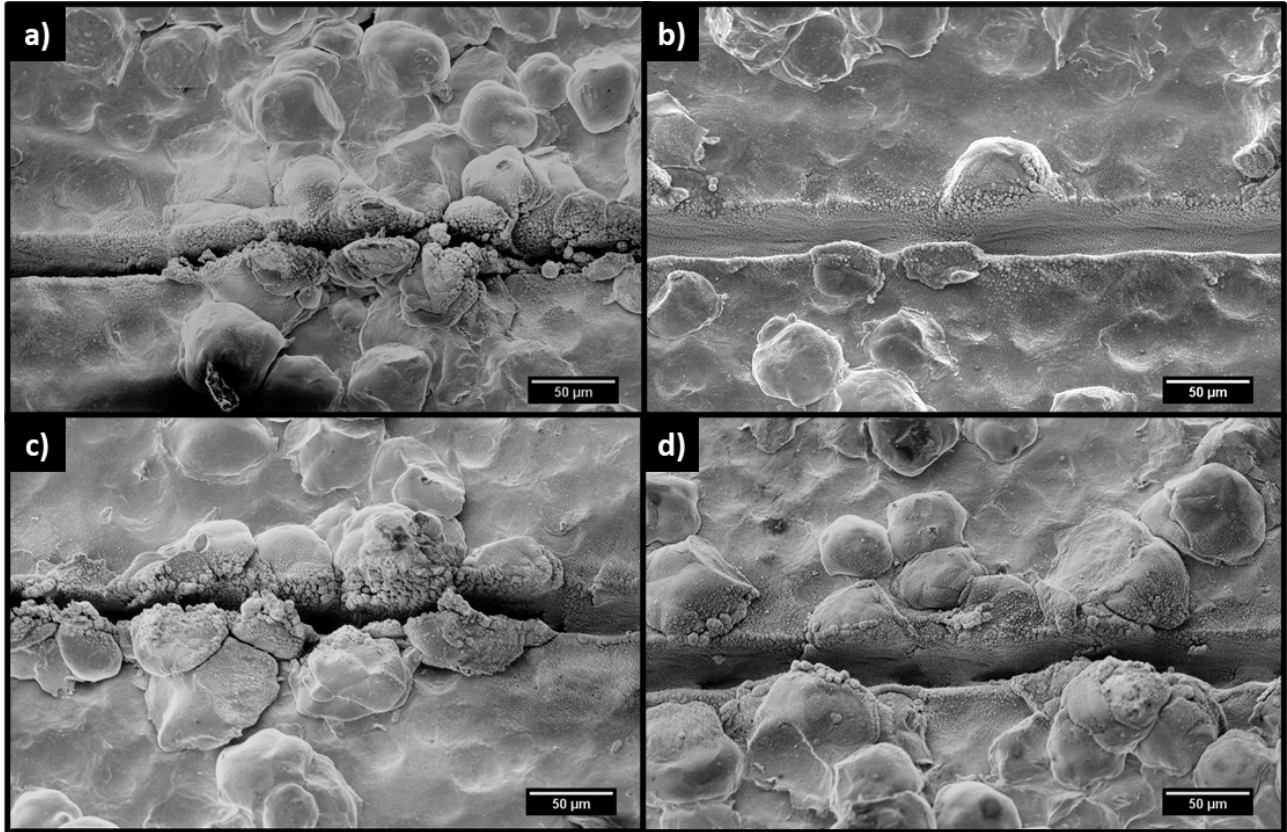


Figure 5.23 SEM image of laser cut with parameters of repetition rate: 200 kHz, laser output power: 2.8W, laser trace velocity: 15 mm/s, single pass and varying the polarization a) horizontal (HP), b) linear (LP), c) linear scramble (LSP) and d) circle scramble polarization (CSP).

Knowing that the circular scramble polarization is one of the best quality results, **Figure 5.24** shows the results of cuts using this type of polarization. The number of passes was explored, reducing the parameters to 10 kHz as repetition rate, the laser output power of 100 mW, and trace laser velocity of 20 mm/s. The reduction of the parameters is to reduce as much as possible the damage to the sample. According to the images at one single pass, the damage is very low; however, as the number of passes increases, a HAZ can be noticed. The image of the higher number of passes shows that LIPSS started to form, and it is evident that the HAZ results in a Gaussian distribution cut.

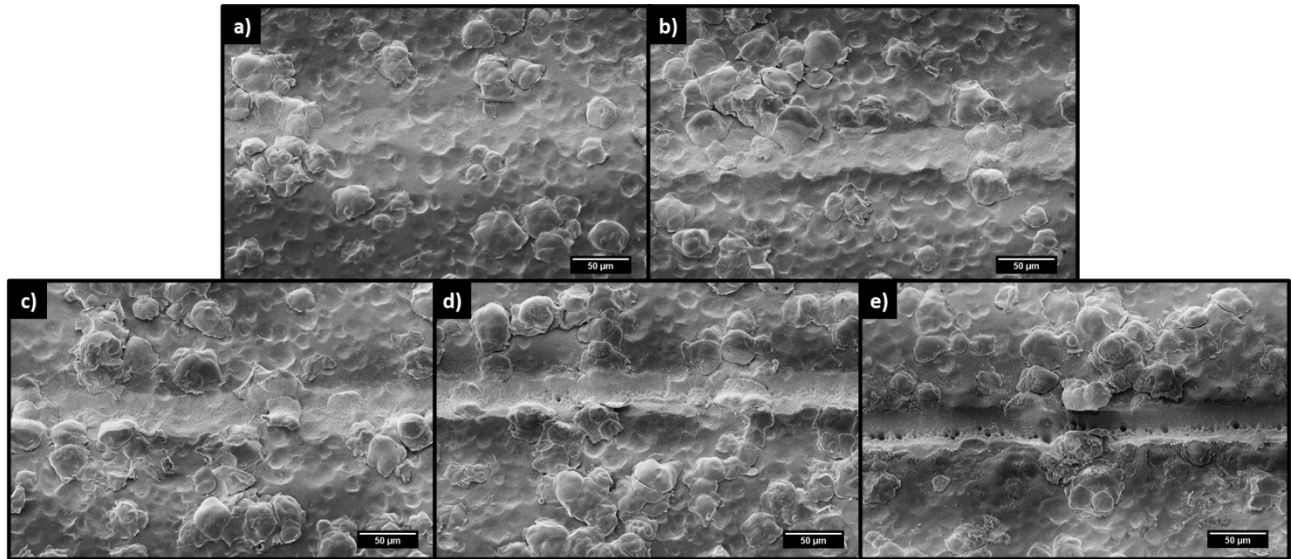


Figure 5.24 SEM image of laser cut with parameters of repetition rate: 10 kHz, laser output power: 100mW, circular scramble polarization (CSP), laser trace velocity: 20 mm/s and varying the number of passes a) 1 pass, b) 3 passes, c) 5 passes, d) 10 passes and e) 20 passes.

While increasing the number of passes with the circular scramble polarization results in low-quality cuts compared with the findings with a single pass, the results of a single pass were reanalyzed. **Figure 5.25** shows cuts based on the outcomes of **Figure 5.23** that demonstrated that the parameter set gives a good quality (repetition rate: 200 kHz, laser output power: 2.8W, laser trace velocity: 15 mm/s, single pass, and circular scramble polarization). The laser speed used was 15, 20, and 25 mm/s. LIPSS are formed at a higher velocity of 25 mm/s in the bottom of the cut, and the quality is not enough, even though it is possible to detect partially and mark the particle interface.

At the end of all the cuts analyzed, the best result is presented in **Figure 5.25 a)**, where it can be observed the particle/substrate interface is clearer and no LIPSS formation is observed. However, if the copper particle is not perfectly aligned when cut; the measurements for penetration depth can be affected because the cut will not be in the middle of the particle. As a result, it was determined that these parameters are not adequate for their purpose.

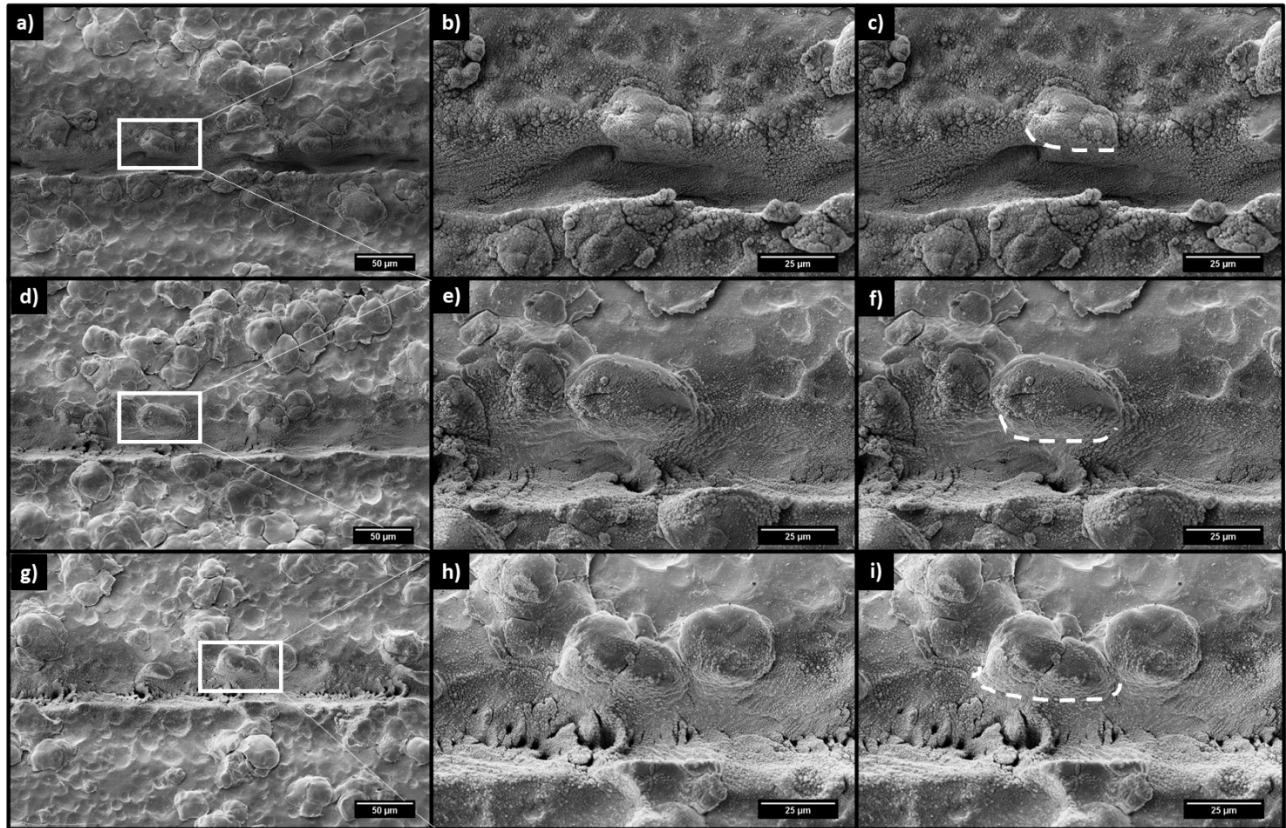


Figure 5.25 SEM image of laser cut with parameters of repetition rate: 200 kHz, laser output power: 2.8 W, circular scramble polarization (CSP), single passes: 20 mm/s and varying the laser trace velocity: a) 15 mm/s, b) increase magnification of zone a), c) highlight interface particle of image b), d) 20 mm/s, e) increase magnification of zone d), f) highlight interface particle of image e), g) 25 mm/s, h) increase magnification of zone g), i) highlight interface particle of image h).

To conclude this section, this technique can be extremely useful but proper development is crucial and requires time. The laser cutting process through two different metals is very irregular as copper and iron react differently to laser pulsation micromachining, which adds variables to find the correct parameter set in order to come up with a good quality cut. Copper has a higher thermal conductivity that creates less LIPPS or ripples, although the parameters must cut enough through steel with the purpose of identifying the particle interface. However, a very specific set of parameters can lead to clean surfaces but requires an exhaustive study. For that reason, the laser micromachining process was not used for particle penetration depth measurements. Instead, the characterization of detached particles was developed and used.

5.2.3 Detached Particles

The purpose of the characterization of the detached particles is to evaluate the penetration depth, penetration diameter, and observe signs of metallurgical bonding (mostly as dimples features) at the particle surface. **Figure 5.26** shows the surface of the detached particles that were in contact with the substrate prior to removal. **Figure 5.26 a)** of the large particle size at room temperature substrate shows a localized dimple feature. The sign of dimple features as metallurgical bonding was only observed in the large particle at room temperature substrate.

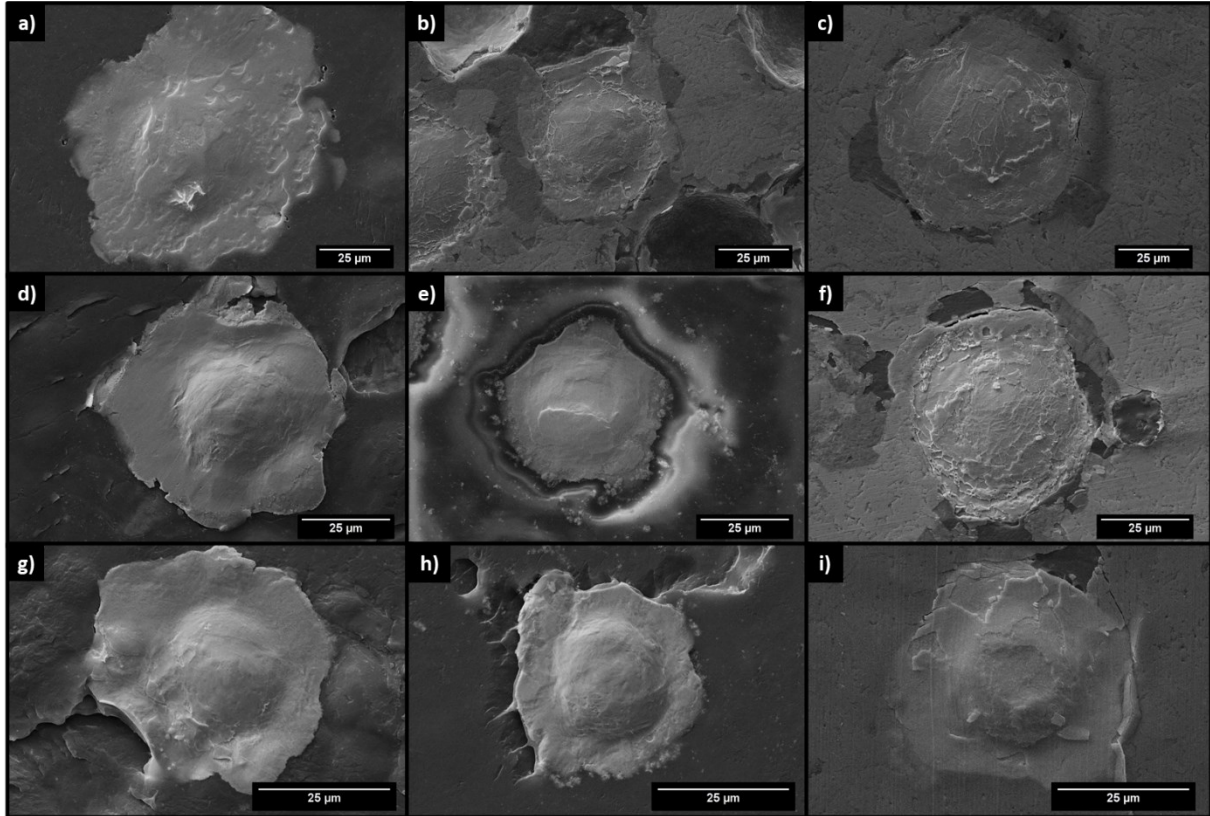


Figure 5.26 SEM images (bottom of particles that were bonded to the substrates) of detached particles for large particle size range at various substrate temperatures : a) 25°C, b) 300°C, c) 500°C, medium particle size range : d) 25°C, e) 300°C, f) 500°C and small particle size range: g) 25°C, h) 300°C, i) 500°C.

Furthermore, an oxide layer in the particle can be observed when the substrate is preheated at 500°C this layer is visible in **Figure 5.26** for all the particle sizes, however, in the case of large and medium particles the layer appears to be broken around the center of the penetration depth, and it is surprising that the layer is adhering to the particle. Additionally, it is difficult to determine if the oxide layer growth occurred before or after the particle impact. However, the indication that the

oxide layer is broken with the particle impact (shown in **Figure 5.11**, **Figure 5.12** and **Figure 5.13**) suggests that the oxide layer was growing before the particle impact.

One characteristic of the detached particle method is that some particles remain attached after each pull-off test which has different features between them. This calls into question the veracity of the measurements for penetration depth and diameter by the reason of being a biased method that consists of only particles that are detached. However, different tests were done in order to clarify if the measurements are adequate to determine an average per sample. **Figure 5.27** presents the results of the penetration diameter for three pull-off tests of large particles. The first and second pull-off test was performed in the same area of the wipe test surface, meaning that the second pull-off test detached particles that did not detach during the first pull-off test, and the third pull-off test was performed in a different surface area. The results provide evidence that there is not a large variation between the various tests, with similar values and standard deviations.

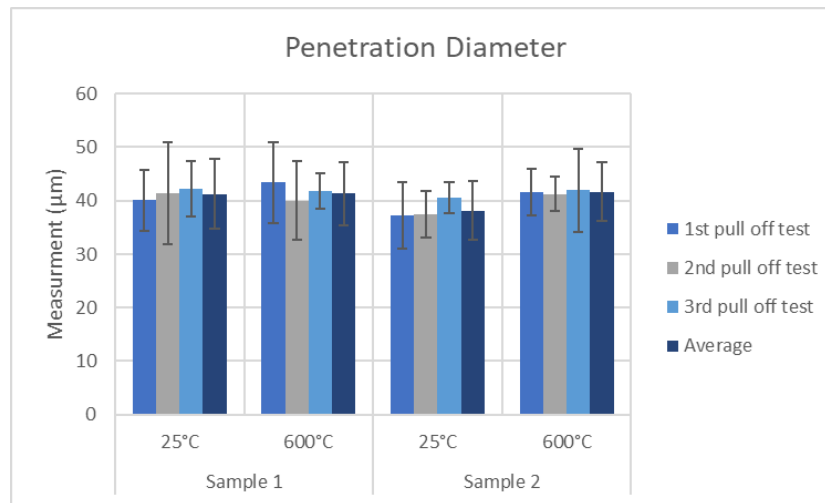


Figure 5.27 Penetration diameter from three different pull-off tests of large particles range.

Additionally, **Figure 5.28** illustrates the results for the three pull-off tests for the case of the penetration depth measurements. For these measurements, the results from the different tests are slightly different according to the location and test repeat, however, the penetration depth averages are all within the same range. It is important to remember that each particle is unique (different size, impact velocity, impact temperature, and impact angle), justifying the need to measure enough particles to be representative (a minimum of thirty particles per sample were used in this work).

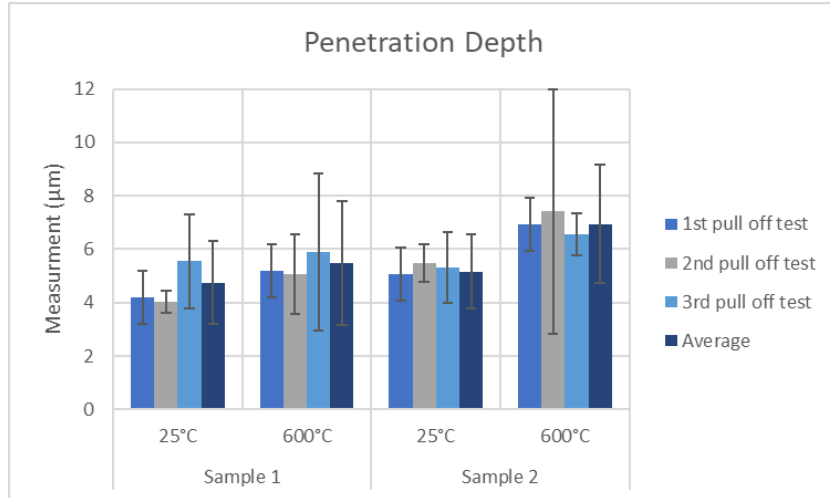


Figure 5.28 Penetration depth from three different pull off test of large particle range.

For the samples for the medium and small particle size ranges, with the substrate preheated to 600°C, pull-off tests were carried out many times without resulting in any detached particle, indicating a stronger adhesion than all the other cases studied. For that reason, the results for the medium and small size range at the substrate temperature of 600°C is not provided in the following figures.

The penetration diameter was analyzed, and the results are shown in **Figure 5.29**. The large and medium particle size ranges show a penetration diameter increase between 25°C and 100°C and stay constant after that for all substrate temperatures. However, the large particle size range exhibit a significant increase when the substrate is at 500°C, similar to the observed behavior of the craters. The small particle size range presents a constant penetration diameter up to 400°C where it increases more abruptly.

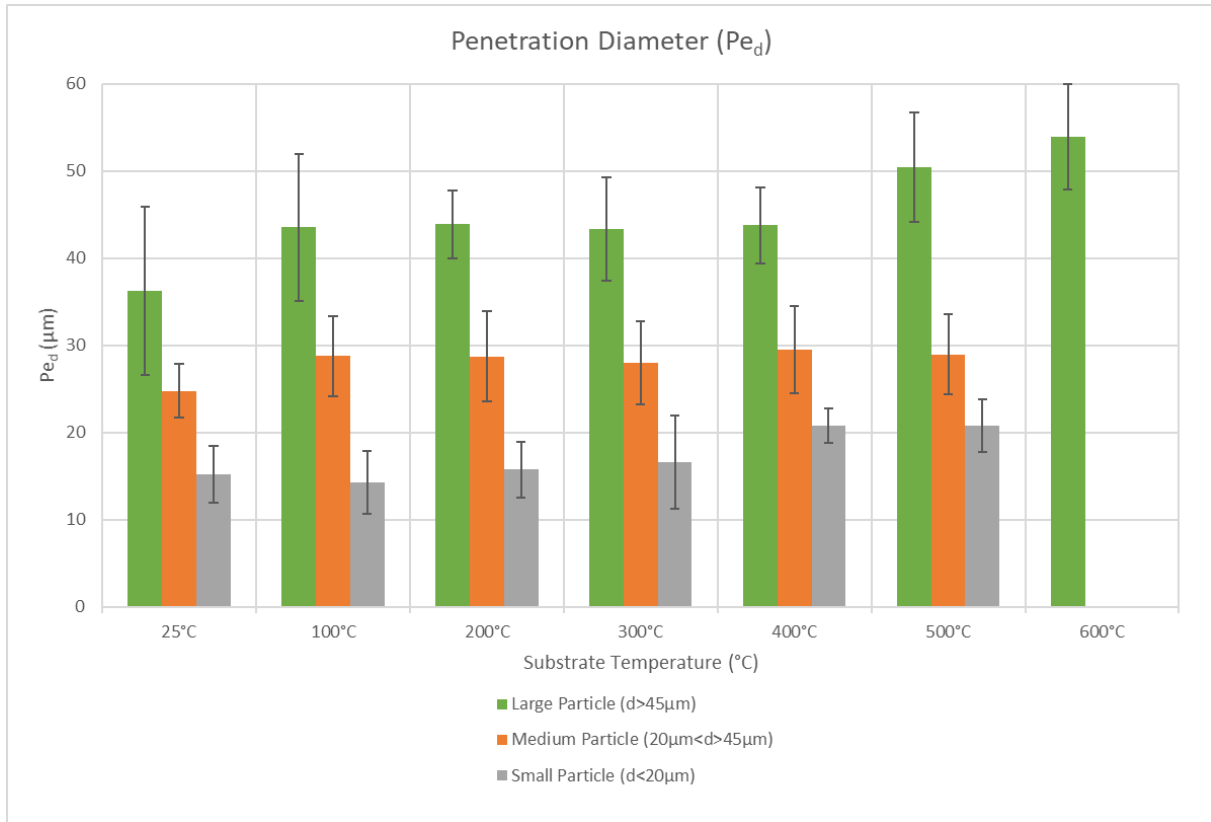


Figure 5.29 Penetration diameter as function of the substrate temperature for the various particle size ranges.

Additionally, the penetration depth was measured, and the results are illustrated in **Figure 5.30**. As opposed to the penetration diameter, there is no significant change in the penetration depth for the medium and large particle size range between substrate temperatures at 25°C and 100°C. However, the small particle size range shows a slight increase between these two substrate temperatures while remaining constant for all other temperatures. The medium and large particle size range shows an increase in penetration depth once the substrate temperature reaches 500°C, similar to the crater depth behavior previously observed.

One can observe that for the large particle size range, the particles penetrated 2 μm deeper when the substrate is at 600°C compared to 25°C. For medium and small particle size ranges, they penetrated 1 μm deeper at 500°C compared to 25°C due to the decreased substrate yield strength and enhanced thermal softening. The large particles show a higher difference by the reason that large particle impact with higher kinetic energy than the medium and small particle range. Additionally, the large particle range has less oxygen content because as the particle surface area to volume ratio decreases thus the oxygen content decreases [27].

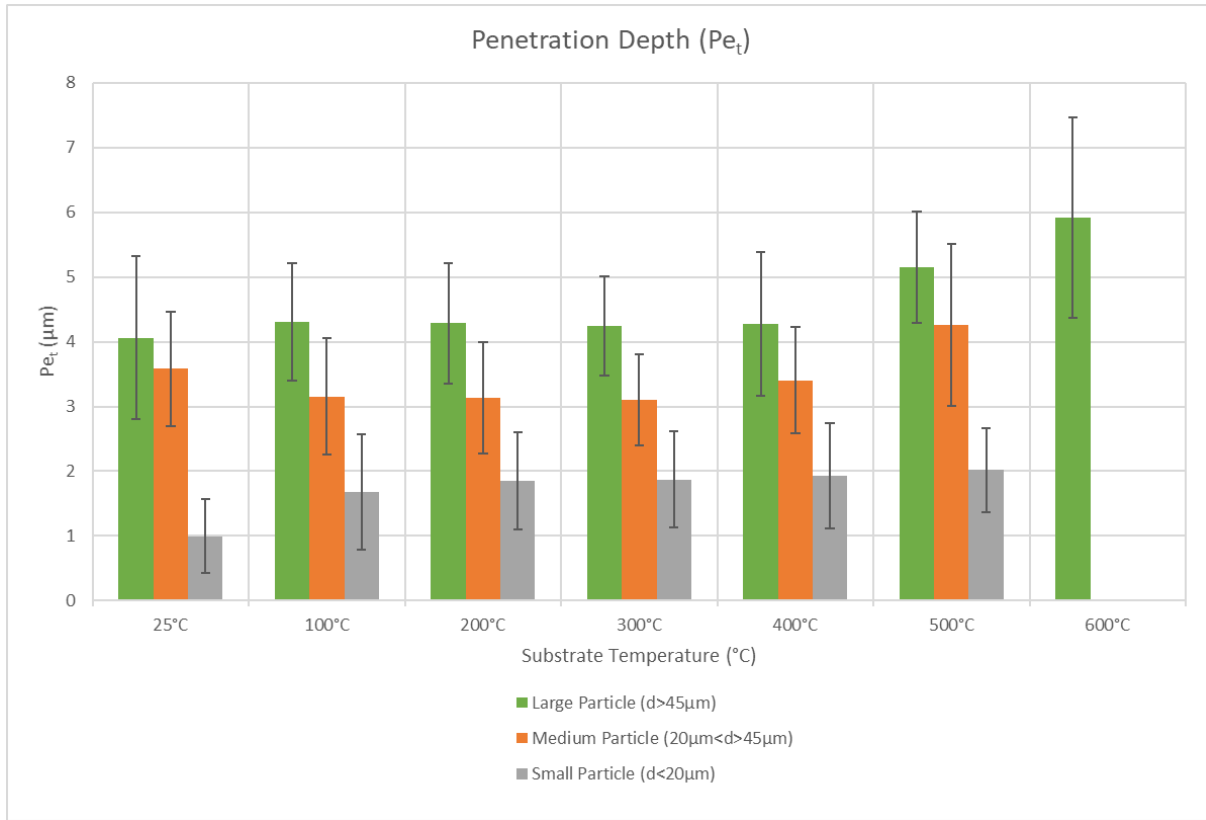


Figure 5.30 Penetration depth as function of the substrate temperature for the various particle size ranges.

The penetration depth can be compared with the crater depth with the purpose of knowing if there is any relation between the particles that have successful deposition with the ones that bounced off. **Figure 5.31** shows both results one next to another per particle size at each substrate temperature. For the large particle size analysis, the maximum crater depth is $4 \mu\text{m}$ on average at 600°C of substrate temperature while the minimum penetration depth is the same average at 25°C substrate temperature. This correlation implies that there is a critical depth to have successful particle deposition. This relationship happens as well for the medium particle size where the critical depth average is $3 \mu\text{m}$ and for the small particle size around $1 \mu\text{m}$; however, this particle size is hard to make the hypothesis as the measurement is small and this size has a lot in variation for all the past results.

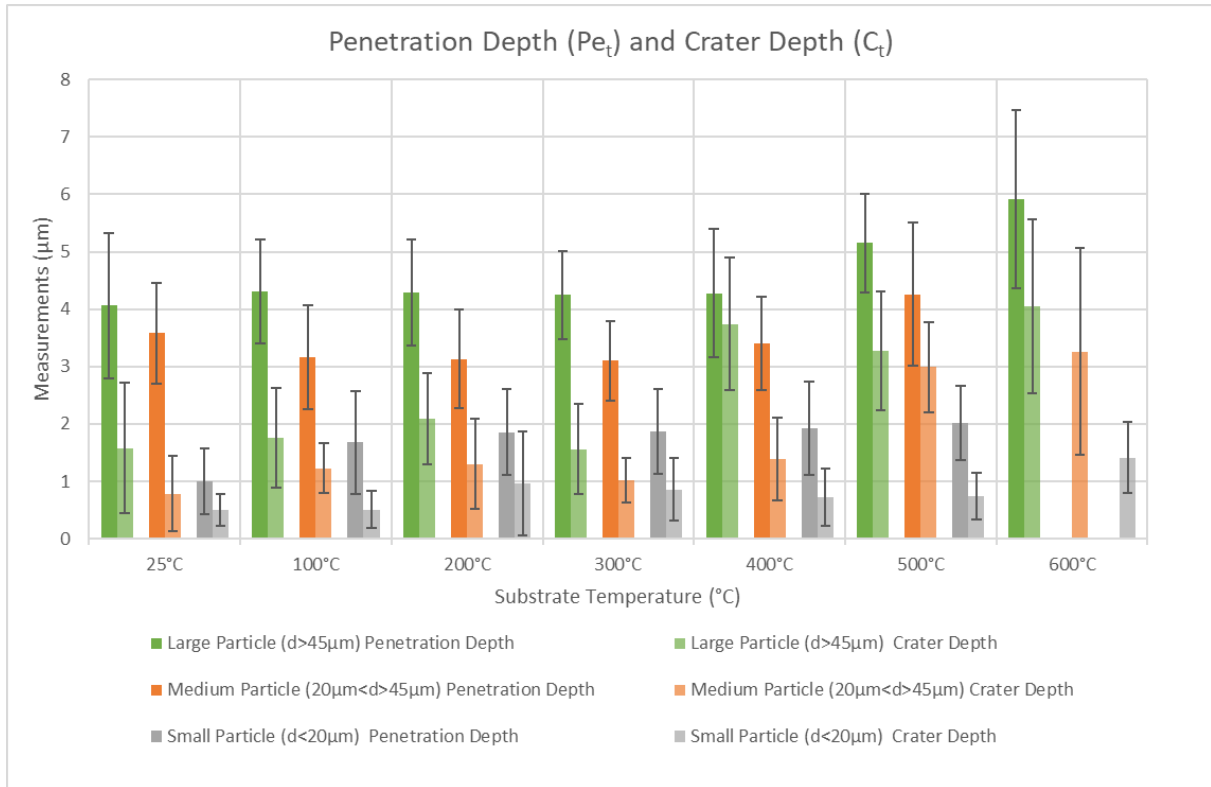


Figure 5.31 Penetration depth and crater depth as function of the substrate temperature.

Furthermore, in **Figure 5.31**, the standard deviation can be observed when we compare the penetration of the particle with the penetration of the crater. The standard deviation of the penetration measurements did not overlap until the substrate was preheated to 400 °C. What is striking is that yield strength begins to be modified by temperature. **Figure 5.32**, shows the behavior of yield strength with the change in temperature of A36 steel [111]. This steel is not the same as the one used in this investigation, however, it contains the same carbon content, so the behavior can be assimilated to the A516 steel grade 70 that was used [24].

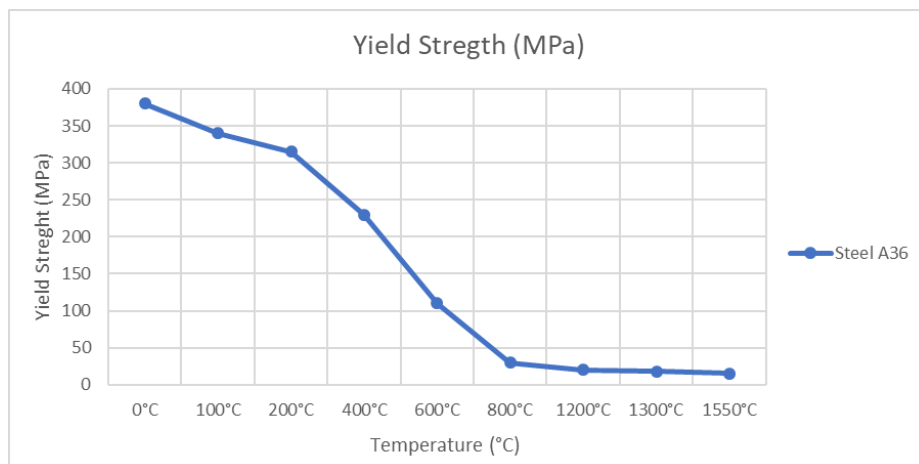


Figure 5.32 Yield strength behavior of steel A36 at different temperature [111].

5.3 Laser-assisted single copper particle deposition

According to the crater and particle results from the wipe tests carried out using the CGDS system installed in the uOttawa and the induction heating substrate pre-heater, the large particle size range was shown to be the most affected by the substrate temperature. For that reason, wipe tests were accomplished for the large particle size range using the laser-assisted CGDS system located at NRC-IMI, as it is planned to use laser heating for the commercial large-scale application. The installation uses a laser next to the CGDS nozzle with the purpose of preheating the substrate locally just before the impact.

For comparison purposes, as the spray nozzle geometry for both systems is different as well as the powder injection methods, the nozzle used for the laser-assisted trials was also operated with the spray parameters used for the uOttawa nozzle. For simplicity and clarification, three cases were studied, as shown in **Table 5.1**.

Table 5.1: CGDS System and Parameters for each wipe test case

Case	System	Parameters
A	Laser-Assisted (NRC) CGDS	NRC
B	Laser-Assisted (NRC) CGDS	uOttawa
C	Induction heated (uOttawa)	uOttawa

For each case, the particle velocities were measured and particle temperatures were evaluated by modeling and are presented in **Table 5.2**. The particle velocity and temperature were calculated with the objective to have a comparison between the different wipe tests.

Table 5.2: Particle Velocity and Temperature for each wipe test case

Case	Particle Velocity	Particle Temperature
A	673 mm/s	472 °C
B	536 mm/s	232 °C
C	461 mm/s	31 °C

Wipe test was performed with the different conditions at a substrate temperature of 25°C and 600°C. The laser power was set up at 1.5 kW in order to preheat the substrate at 600°C. The results and the discussion will be presented in the next section in the same path as the results presented in the previous section.

5.3.1 Non-Destructive Method

5.3.1.1 Craters

Figure 5.33 shows the results for the crater volume for cases A, B and C at 25°C and 600°C, and also at every 100°C intervals for case C, presented already in the previous section. The crater volume when the substrate is not preheated is similar for cases A and B, and is lower for case C. These results are explained by the fact that even if the particle impact velocity is larger for A compared to B, the particles for case A are softer than B (due to the higher temperature) and this creates similar crater upon impact prior to bouncing off. Lower values for case C are attributed to the lower particle impact velocity.

When the substrate is preheated at 600°C, there is only a small increase of crater volumes for cases A and B. In contrast, for case C the increase is over fivefold despite the fact that the particle impact velocity is substantially lower than for the other two cases.

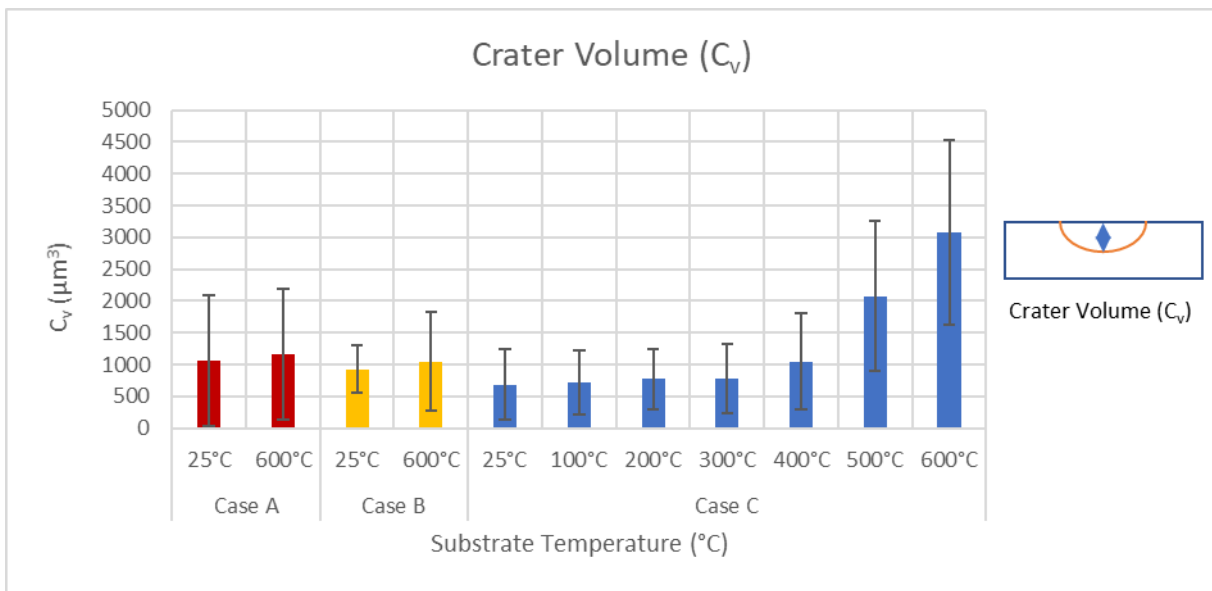


Figure 5.33 Volume crater of bounced off from for each case as function of substrate temperature.

This large difference in crater volume is possibly attributed to the substrate preheating method. While induction heating likely preheated the entire thickness of the substrate, laser as the substrate preheated method only preheated at best a few μm , however, further research needs to be done. Another factor that could have affected the results is the low particle temperature for case C, thus reduced particle ductility compared to cases A and B, however, when the substrate has not preheated the case C has the lowest crater volume value so this possibility is ruled out.

5.3.1.2 Particles

The values for particle heights and diameters are illustrated in **Figure 5.34**. For the measurements of both particle height and diameter, it can observe that there is not a noticeable effect of the substrate temperature for the three cases as the particle height remains around 20 μm and particle diameter around 75 μm .

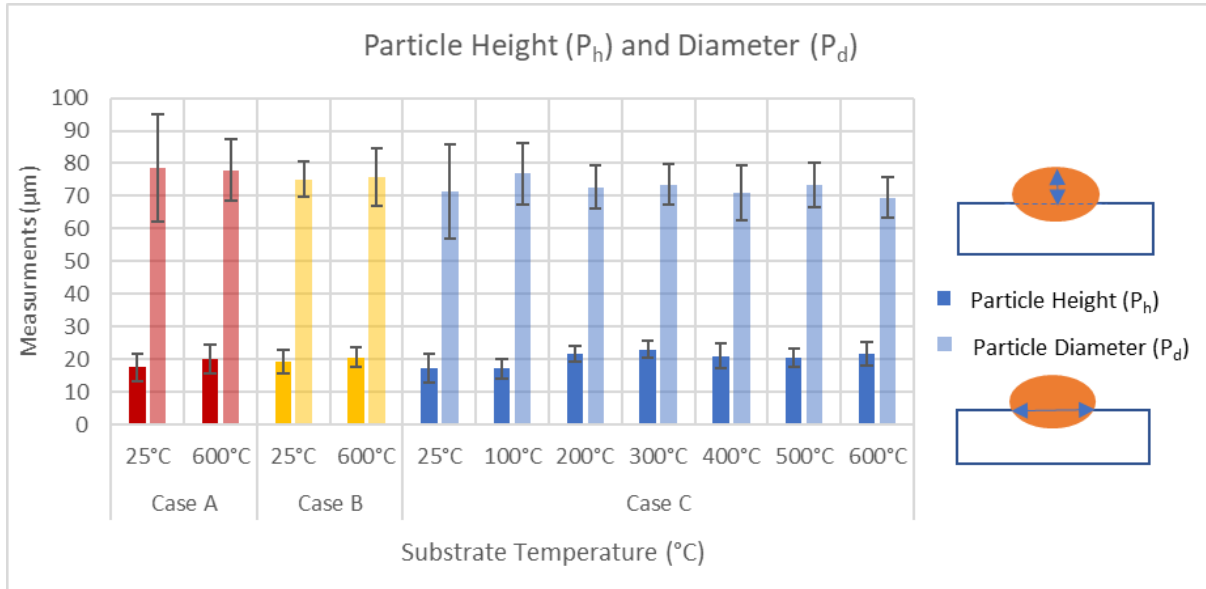


Figure 5.34 Particle height and diameter for as function of substrate temperature.

Additionally, R_c was calculated using the results of the particle height and diameter measurements, as shown in **Figure 5.35**. The three cases show a reduction of R_c which means that the particle deformation decreases as the substrate temperature increases. This effect might be due to the reduction of the yield strength of the substrate as the temperature increases. Additionally, the kinetic energy at the impact when the substrate is preheated might be as result in more substrate deformation as the crater volume increased as the temperature increased (shown in **Figure 5.33**) Case C has the highest change of R_c . Cases A and B almost have the same R_c when the substrate temperature is 600 °C, however, without substrate preheating case A has higher R_c compared to that of case B.

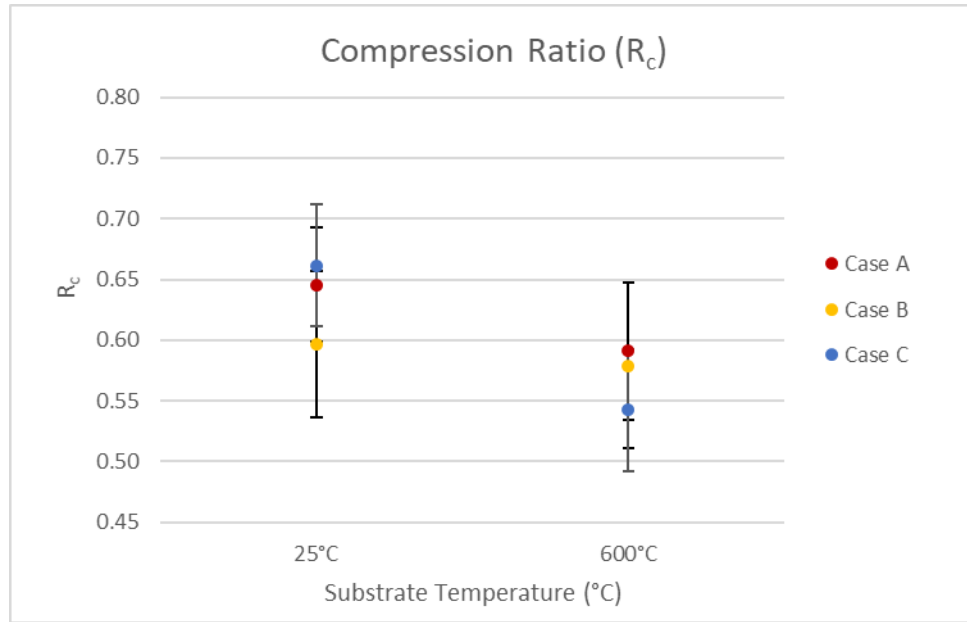


Figure 5.35 Compression ratio (R_c) for each case without and with substrate temperature.

Figure 5.36 shows SEM images of single particle impacts for each case with and without substrate preheating. It can be observed that without preheating there is more particle jetting compared to when the substrate is preheated to 600°C for each case. For case C there is no evidence of jetting when the substrate is preheated. As was demonstrated with the R_c when the substrate temperature increases there is less particle deformation. Additionally, **Figure 5.36** shows that for cases A and B there is no oxide layer when the substrate is preheated as opposed to what can be observed in case C.

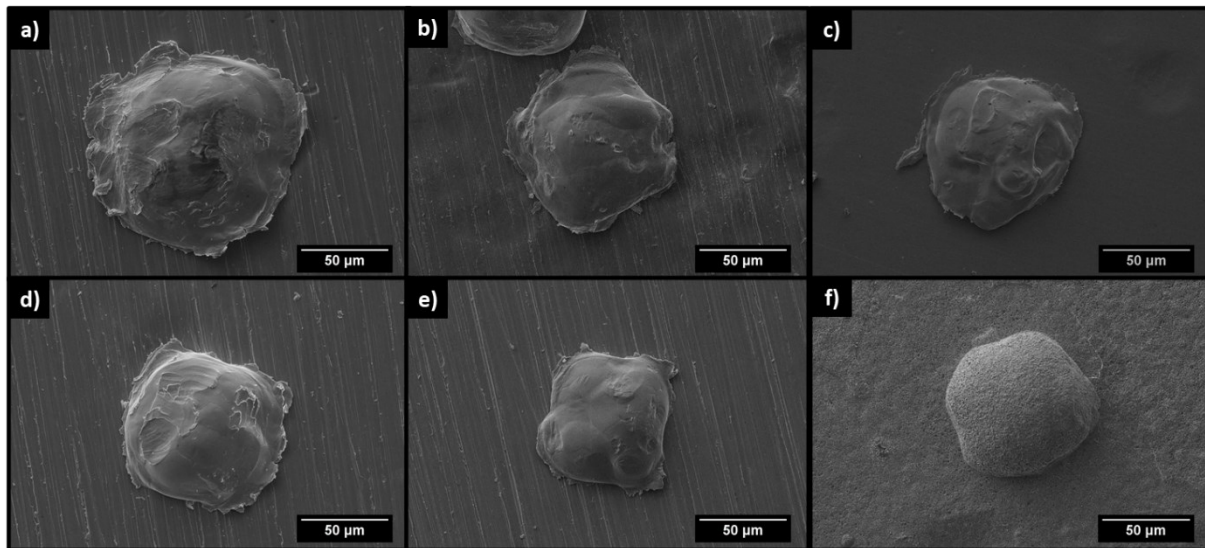


Figure 5.36 Single particle SEM image without substrate preheating : a) case A, b) case B, c) case C, and with substrate preheating d) case A, e) case B, f) case C.

5.3.2 Destructive Method

5.3.2.1 Detached Particles

Figure 5.37 illustrates the penetration depth and additionally the crater depth is added. Substrate preheating to 600°C results in a deeper penetration depth for all cases compared to the substrate at 25°C.

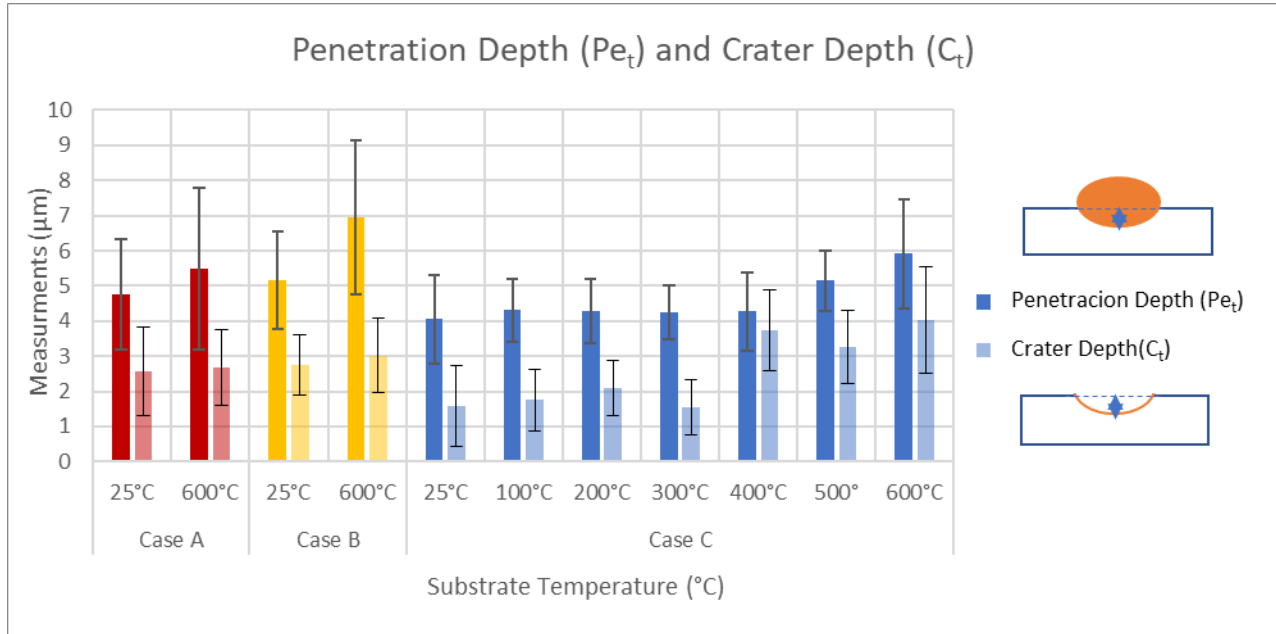


Figure 5.37 Penetration depth vs crater depth for each case as function of substrate temperature.

Furthermore, case B provides the greatest depth of penetration. The possible reason is related to the temperature of the particle and the melting temperature (T_m) of copper. In this case, the temperature of the particles (232°C) is below 0.3 T_m of copper (325°C), this means that the plastic deformation is considered as cold work. This is due to the fact that energy only remains in a crystal if the temperature is low for that the atoms are effective without movement [112]. On the other hand, in case A, the temperature of the particle (472°C) exceeds 0.3 T_m , which means that it does not consider as cold work and the deformation is different from the one of cold working and cannot penetrate deeper even if the particle is of higher speed. For that possible reason, case B proves to have a deeper insight.

Likewise, comparing case B and C where the particle temperature is considered to be that of a cold working process the only remaining difference is the particle velocity. The particle velocity of case B is larger than that of case C, thus case B results in a larger penetration depth. However, when the substrate temperature increases to 600 °C both cases show an increase of 2 μm in penetration

depth which represents the same substrate temperature effect. In contrast, the crater depth comparison does not follow the same effect, which case C shows the larger crater depth.

Figure 5.38 illustrates the detached particles with and without substrate preheating for the three cases. Dimple features as a sign of metallurgical bonding can be observed in all samples. However, for case C when the substrate is preheated, the detached particle shows the oxide layer that was detached from the substrate and remained bonded to the particle.

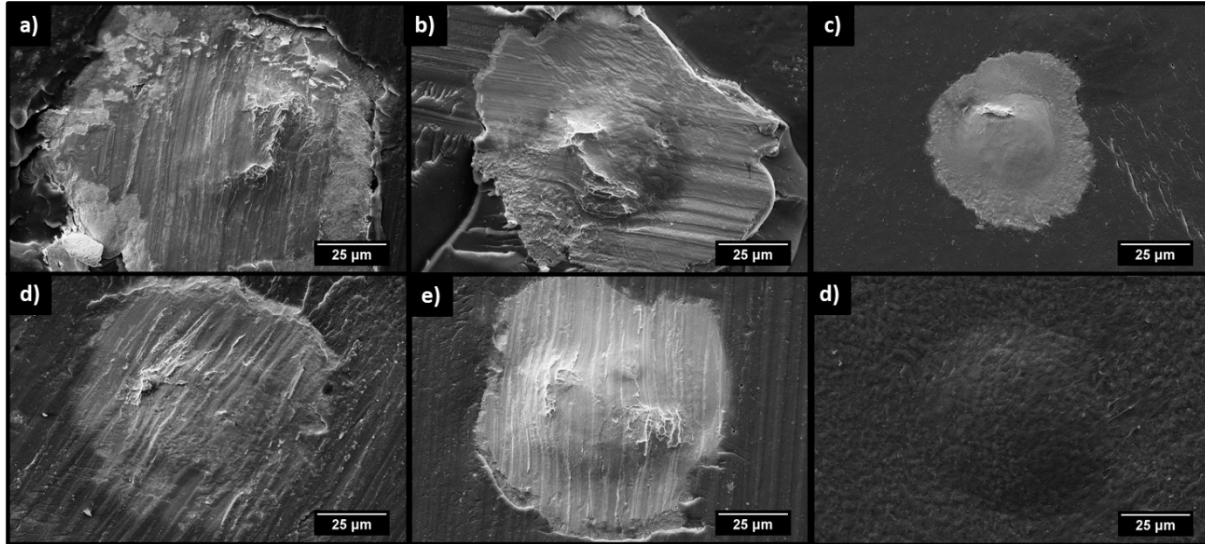


Figure 5.38 SEM images of detached particles without substrate preheating: a) case A, b) case B, c) case C, and with substrate preheating d) case A, e) case B, f) case C.

5.3.2.2 Metallurgical bonding

One of the theories found in the literature review is that when the substrate is preheated the coating adhesion increases due to the increase of metallurgical bonding. Metallurgical bonding is difficult to demonstrate, requiring complex microscopy techniques that are not always easy and fast to perform and thus unsuitable for looking at a large number of particles. However, one way that it can be used is to identify the dimple features on the surface of the detached particles.

Laser assisted cold spray was used with the same spray parameters as the ones used for case A to spray particles of all sizes (as-received powder without sieving to particle size ranges). The particles were then detached to see the effect of the substrate preheating at 600°C. **Figure 5.39** illustrates typical large, medium, and small detached particles resulting from that spray. Evidence of dimple features can be observed in all the detached particles, however, by observation alone, it is hard to state any conclusions. For that reason, the zone where the metallurgical area (dimples) can be observed was measured from approximately thirty detached particles per sample for the three different particle size ranges. Additionally, the penetration area was measured from the same

detached particles to represent the measurements of the metallurgical area as a ratio with the penetration area.

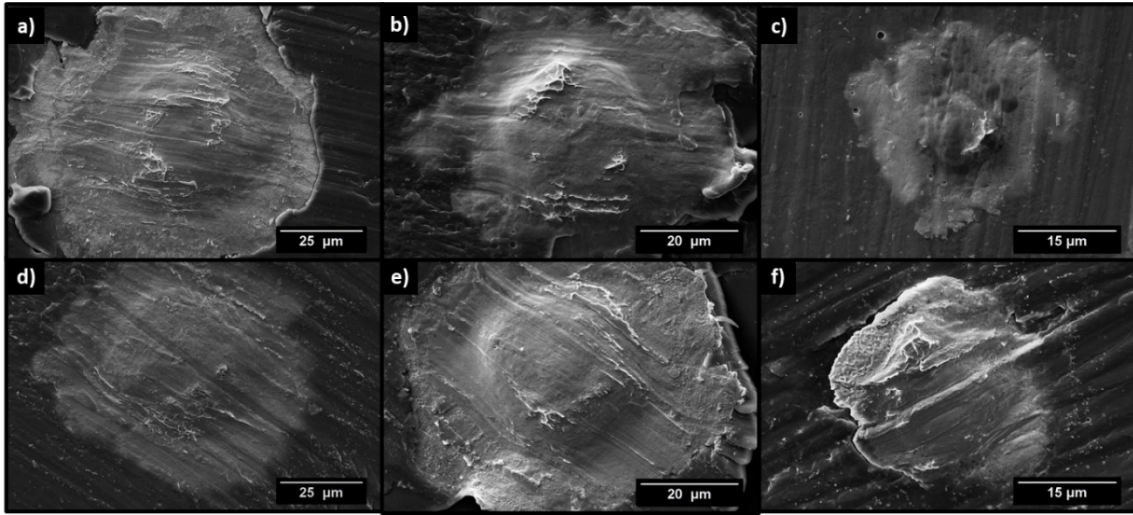


Figure 5.39 SEM images of detached particles without substrate preheating: a) large, b) medium, c) small particle size and with substrate preheating d) large, e) medium, f) small particle size.

Figure 5.40 presents the results of the ratio between the metallurgical and penetration area (shown in **1)Appendix B Metallurgical Bonding Measurement Procedure**). It can be observed that in the case of the large particle size the ratio decreases as the substrate is preheated, however, the standard deviation is large for this size. On the other hand, the medium and small particle size shows the same ratio at both substrate temperatures; despite this, the small size appeared to have more dimples features area than the medium particles size.

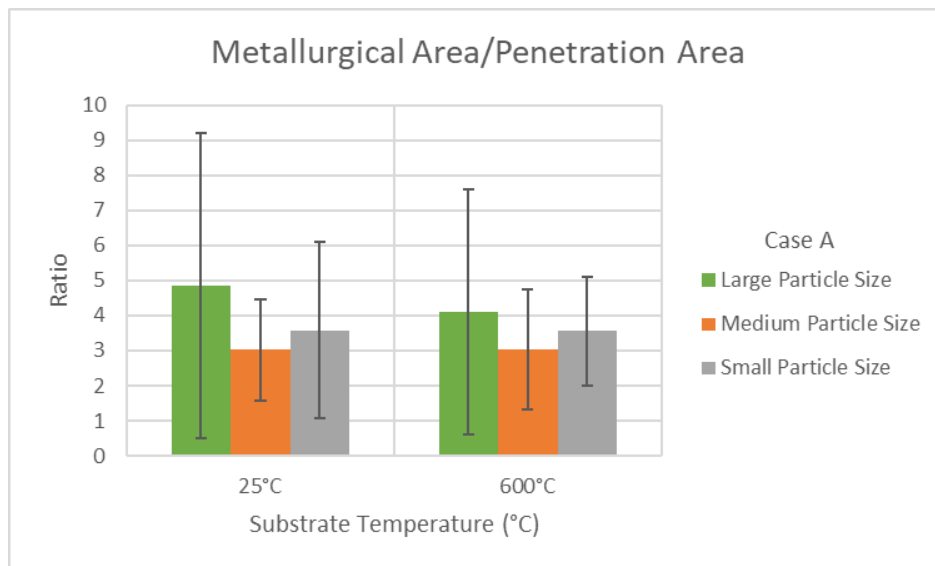


Figure 5.40 Ratio between metallurgical area and penetration area for the three particle size of the case A.

5.4 Mechanical Adhesion Strength Prediction

Figure 5.41 shows the profile of a cross section cut of two copper coating with the same CGDS conditions of 800°C and 4.9 MPa. The difference is that in **Figure 5.41 a)** the coating has a helium bond coat and then the rest of the coating is built up with nitrogen as the carrier gas. On the other hand, **Figure 5.41 b)** the coating is built up only using nitrogen as the carrier gas and with the substrate preheated just before the particle impact using the laser at a power of 3.5 kW. As it can be observed the coating with the helium bond coat shows noticeable mechanical anchoring comparing with the coating where the substrate was preheated. However, the substrate preheating was able to develop enough bonding that prevents coating delimitation only using nitrogen as the carrier gas.

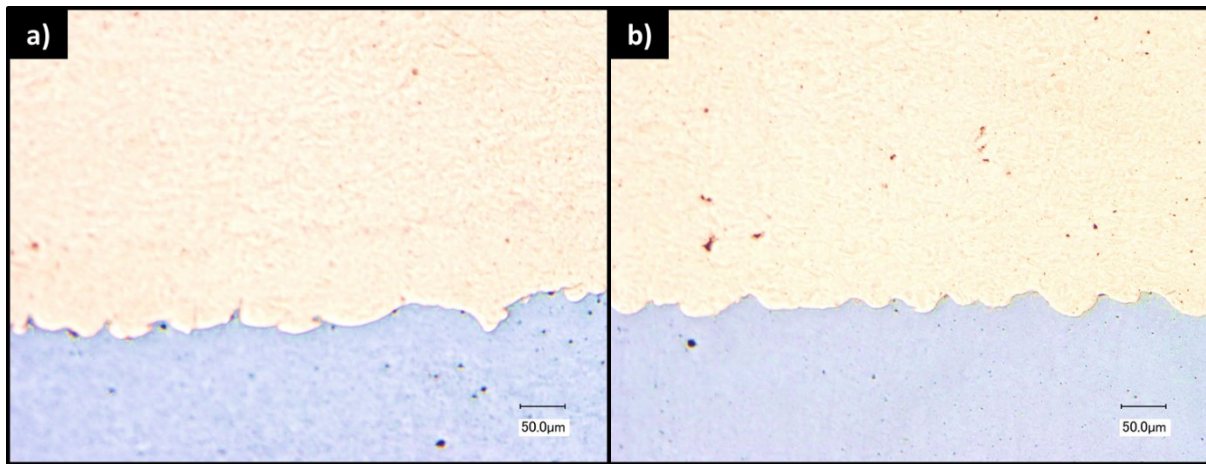


Figure 5.41 Cross section cut of copper coating over low carbon steel a) with a helium bond coat b) with substrate preheated by laser just before the particle impact.

For the mechanical adhesion strength prediction, ten profiles of each coating were taken with the optical microscope with a magnification of 500x, similar to the ones shown in **Figure 5.41**. Half of the ten profiles of each sample were taken from the cross section cut in the same direction that the CGDS coating was built and the five other profiles were taken from the cross section in the perpendicular direction. The modeled values of mechanical adhesion strength are compared with the experimental pull test that includes the contribution to adhesion strength of mechanical anchoring and metallurgical bonding.

Figure 5.42 shows the stress (S_{22})-displacement curve of the coating profiles with the helium bond coat. Additionally, images of all the profiles are also shown on the right side, to compare the results with the visual mechanical anchoring. The maximum prediction of adhesion strength of this coating is approximate 25 MPa from profile 1 while the minimum prediction is 2.5 MPa from the profile 5. The profiles images of these predictions can clearly show that the profile 1 has a predominant mechanical anchoring in contrast with the profile 5. The measured adhesion strength of coatings produced under the same conditions was 76 MPa (adhesive failure in a previous study), which far from the maximum value of the adhesion strength prediction of the mechanical anchoring. This

suggests that mechanical anchoring is not the main bonding mechanism and suggests that metallurgical bonding is predominant.

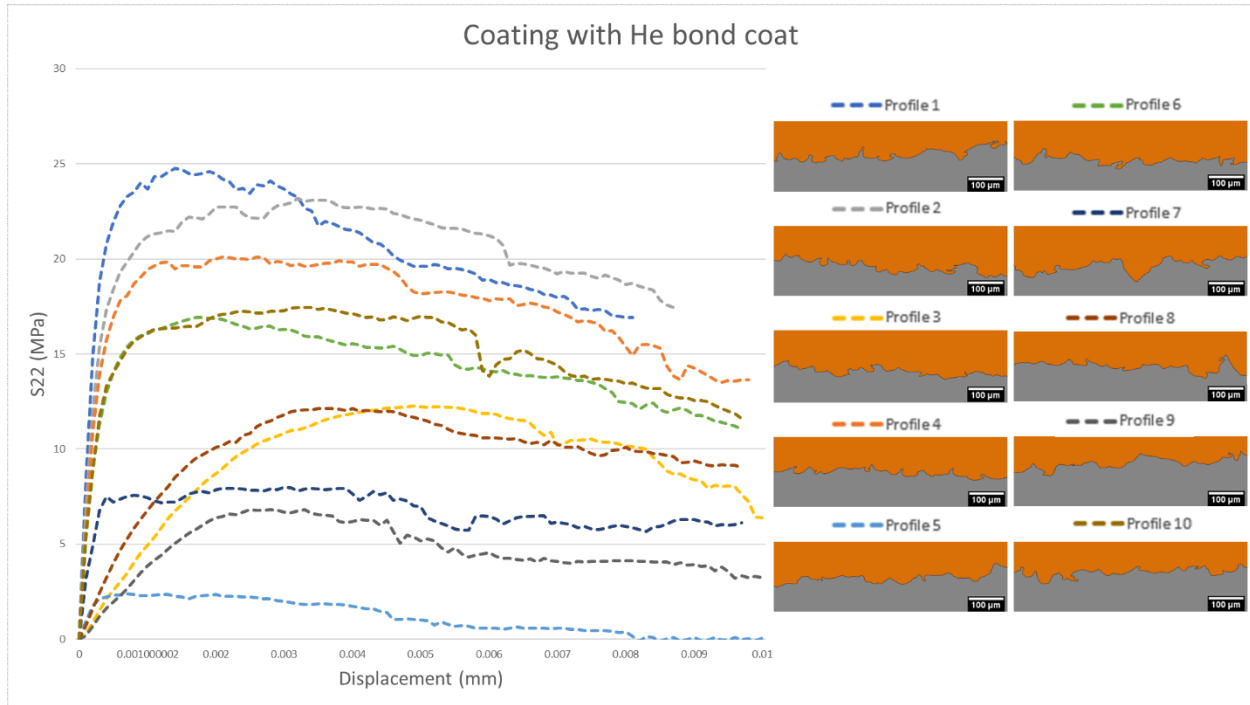


Figure 5.42 Stress-displacement curve of the copper coating profiles with helium bond coat and then built up with nitrogen as the carrier gas.

Figure 5.43 shows the stress-displacement curve of the coating sample sprayed with the laser-assisted system as well as the profiles that were analyzed. The experimental adhesion value was 87 MPa (glue failure) while the maximum model prediction is 12 MPa from the profile 5. Profile 4 and profile 7 have a prediction of 0 MPa, indicating that there is no noticeable mechanical anchoring for these profiles. Comparing the two different coatings (with helium bond coat vs laser-assisted), it can be noticed that the prediction of the adhesion strength resulting from the mechanical anchoring reduces with the substrate preheating. However, the experimental results reveal that when the substrate is preheated the coating does remain attached to the substrate as opposed to the case when no substrate preheating is used (with only nitrogen as process gas) and thus substrate preheating increases the adhesion strength. This means that potentially metallurgical bonding increases when the substrate is preheated as mechanical bonding is not sufficient to allow reaching the measured adhesion strength. This also indicates that the measure of dimples as a sign of metallic bonds is not a reliable method to assess the level of metallurgical bonding as it is too macroscopic.

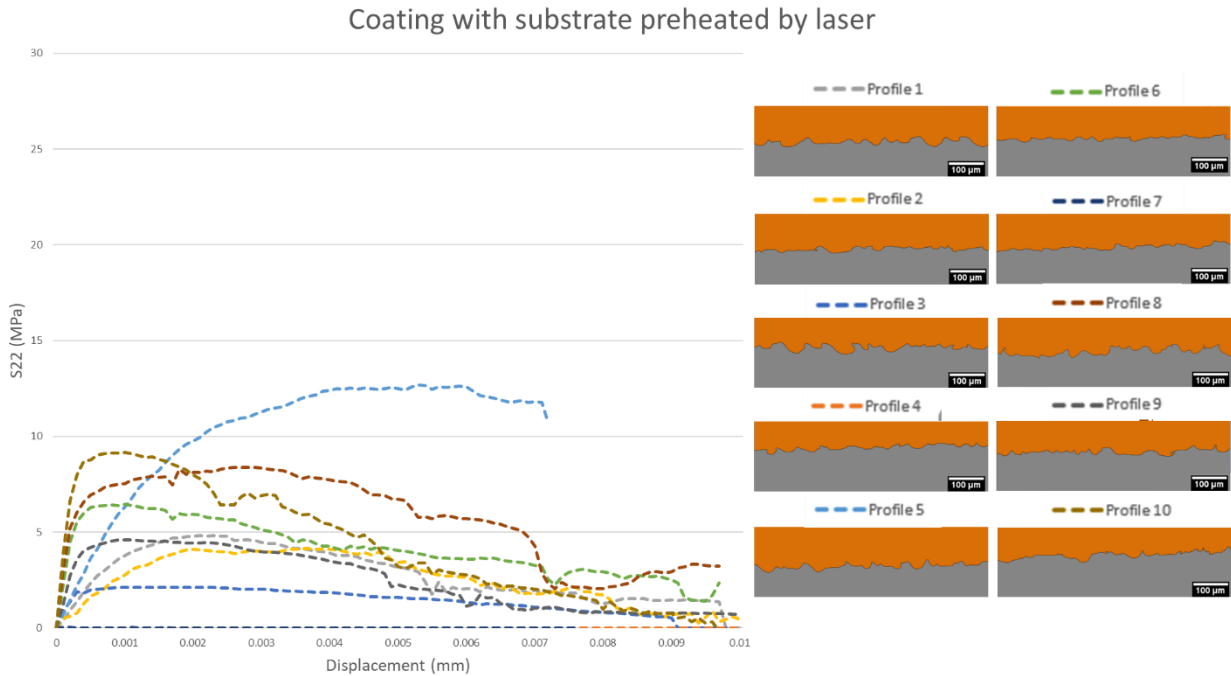


Figure 5.43 Stress-displacement curve of the copper coating profiles with substrate preheated by laser and only nitrogen as the carrier gas.

5.5 Discussion

The first benefits of preheating the substrate during the CGDS process were observed as a result of the heat transfer of the working gas to the substrate during the deposition of the particles. Wong et al. [84] and Legoux et al. [85] noticed that a slower gun traverse speed increased the substrate temperature which improves the CGDS process by increasing the adhesion strength and deposition efficiency. The following are some factors to explain what is occurring when the substrate is preheating based on the results presented in this thesis.

Intermetallic phases

It might be possible for the material to melt in at the interface, as a result, i) of the very local heat transfer from substrate preheating to the particle and ii) of the transfer of energy from kinetic energy at particle impact, which can create intermetallic phases. Additionally, it was observed by Yin [87] spraying nickel onto copper substrates, he demonstrated that the high-temperature substrate significantly promotes temperature rise in the interface between the particles and substrate during impact. However, in this research investigations were not focused on determining if there are intermetallic phases in the interface, this could be the topic of a future study.

Particle behavior

One observation of this research was that as the substrate temperature increases the penetration of the particles increases as a result of the substrate softening (as shown in **Figure 5.44**). The same result was found by Yu et al. [91]. Yu states that the deformation patterns transfer to be a method of penetration because the particle comes close to retaining its original shape prior to the CGDS process. The same particle behavior can be observed in **Figure 5.11**, **Figure 5.12**, and **Figure 5.13** where the particles sprayed onto a preheated substrate retain a more spherical shape compared to the ones that make an impact onto a substrate at room temperature where particles jettings are intensified. This was also observed by Yu et al. [92] with the spray of copper particles onto an IN718 substrate. He states that the copper particle has a pancake shape when the substrate is not preheated. However, when the substrate is preheated, the particle penetrates deeper and the particle maintains a more spherical form.

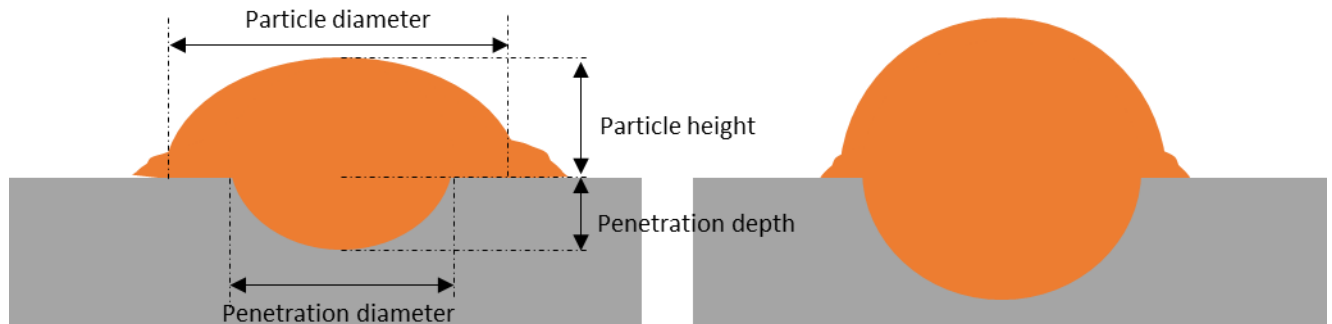


Figure 5.44 Cross section diagram of differences of particle diameter/height and penetration diameter/depth on a substrate is not preheating (left) and preheat substrate (right).

Deposition efficiency

Figure 5.1 illustrates that the deposition efficiency increases as the substrate temperature increases. This was also detailed by Fukomoto et al. [86] where an increase in the deposition efficiency from almost zero to 55% was observed when the substrate temperature was increased from 25°C to 427°C. Additionally, Fukomoto suggested that the deposition efficiency increased for the heated substrate even without using heated particles to achieve the modified temperature of the working gas. However, it was found that the pressure of the working gas also has an effect on the deposition efficiency. In other research by Yin [87], it is stated that the deposition efficiency of the first layer improves and subsequent coating mass grows with the substrate temperature.

Mechanical anchoring

In addition, another benefit of the substrate preheating is the formation of mechanical anchoring due to substrate deformation between the particle and substrate as stated by Suo [89], Yu [91], and Yin [87]. It can be observed in **Figure 5.41** from the profile that was used for the simulation that

anchoring is possible with only nitrogen as the carrier gas in the CGDS process. This might be a result due to the fact that the preheated substrate experiences more intense plastic deformation because of a reduction in yield strength and improved thermal softening. However, in **Figure 5.41** the mechanical anchoring was also compared to the interface where a bond layer was formed with helium as the carrier gas, and then the remainder of the coating formed with the carrier gas of nitrogen. The interface of the coating with a helium bond coat exhibited more clearly an example of mechanical anchoring compared to the coating develop with the substrate preheated. Nevertheless, with the substrate preheated was able to form a thin coating comparing with the one without a heated substrate that it was not able to build up the coating only using nitrogen as the carrier gas.

Metallic bond

The finding that a preheated substrate may promote metallurgical bonding was stated by Xie et al. [88]. Another finding by Goldbaum et al. [93] explains why the metallic bonds are more successful when the substrate is preheated and states that confinement of the adiabatic shear region within the splat and substrate due to the deformation of the substrate. Metallic bonds are complicated to identify experimentally; one of the clearer ways to identify this type of bond is by the dimples which are formed. However, dimple development can be affected if the particle impact is at an angle with the substrate surface resulting in a lower area of dimples in the particle [28].

Adhesion strength

The adhesion strength was compared through physical experiment and simulation of the coatings with only nitrogen as the carrier gas in the CGDS process. If the substrate is preheated by the laser, the adhesion strength is 87 MPa while if the substrate is not preheated delamination occurs so the adhesion strength is considered to be 0 MPa. This increase of adhesion was also noticed by Xie et al. [88] and suggests that is due to the intensive deformation at high temperatures even if the substrate contains a thick surface oxide layer.

The simulation results suggest that the adhesion strength generated by the mechanical anchoring is approximately 7 MPa. These results suggest that the remainder of the adhesion strength is can be attributed to metallic bonds. The increase of the adhesion strength might be due to the increase of material interlocking, especially metallurgical bonding [88][89][90][87], as a result of the preheated substrate.

Residual Stress

One cause of the delamination of the copper coating during the CGDS process without substrate preheating and while using nitrogen as the carrier gas is the accumulation of the residual stress at the interface between the two components: coating and substrate due to plastic deformation and the thermal stresses.

The thermal stress is caused by the gap of thermal expansion between the substrate and the coating particularly in the interface between them; therefore, the volume of this expansion is different for

the two components. When the CGDS process is completed both components were contracted in different ratios as a result of the cooling which resulted in higher stresses. However, when the substrate is preheated the temperature distribution changes and the thermal stress in the substrate can be mitigated according to Watanabe et al. [90].

On the other hand, Shim et al. [94] explains that the reduction of residual stresses developed at the interface of the components during the CGDS process is caused by an increase of the tensile strength due to the preheating of the substrate. In his research, the substrate was preheated with an induction heater, which is the same method used in this research. He explains that the residual stress in the interface was tensile and was decreased by slowing the cooling rate of the preheated substrate. Finally, it was concluded that substrate preheating relieves internal stresses generated by the phase transformation and steep temperature gradients.

Peening Effect

Another possible reason for the increase in adhesion might be the result of the peening effect. This effect is introduced as the coating is formed because the following particles impact with higher kinetic energy, this is beneficial for the metallic bonds as there is no oxide layer at the interface [58]. Xie et al. [57] concluded that single particle impacts cannot successfully achieve a clean surface to produce metal to metal contact. However, a clean interface could be accomplished with complete coating deposition which would then result in metallurgical bonding between the substrate that increases the adhesion strength.

This could be one explanation for the increase of adhesion strength; however, in this study, there is not a second impact that could explain the peening effect. This effect can be beneficial for the preheated substrate as the contact with the particle at the interface increases and the laser can result in a more oxide free surface in the interface which could, in turn, result in greater metallic bonding.

6. Conclusions

6.1 Summary of Results

Single copper deposition tests were successfully carried out using two different CGDS systems (induction heating and laser-assisted heating) at various substrate temperatures ranging from room temperature to 600°C. These tests were completed with the purpose of understanding the effects of substrate temperature at the fundamental level on bonding mechanism, in order to find a sustainable solution for the elimination of helium in the copper CGDS process used to seal the weld zone of the UFC.

Characterization of craters (created by bounced off particles), bonded particles, and pulled out particles that did stick to the substrate was carried out for three different particle sizes. The findings from this characterization were that large particles ($d > 45\mu\text{m}$) are more noticeably (positively) affected by the increase of substrate temperature during the CGDS process. This finding influenced the decision to investigate and characterized large particles only on the second set of single copper deposition tests using the laser-assisted spray system.

From the observations of the craters, it can be concluded that as the substrate temperature increases, and the volume of the crater also increases. This aspect of the research suggested that a preheated substrate experiences more intense plastic deformation because of the reduction of the yield strength and improved thermal softening.

This leads to the theory that the particles partially maintain the shape which they had prior to the CGDS process and jettings are less prominent as the substrate temperature increases. Furthermore, results have shown that the compression ratio reduces as the substrate temperature increases. The pull out particle tests demonstrated that as the penetration diameter and depth increases, the particle surface contact with the substrate also increases. In addition, these findings provide additional information relating to the reduction of substrate yield strength and improved thermal softening.

When comparing the crater depth from the bounced off particles to the penetration depth of the bonded particles of the CGDS process carried out at the University of Ottawa the existence of a critical depth of the particles to achieve successful bonding was observed. These basic findings are consistent with research showing that in the case of large particles the critical penetration depth is $4\mu\text{m}$, for medium and small particles it is $3\mu\text{m}$ and $1\mu\text{m}$ respectively. Additionally, the standard deviation does not overlap the measures of penetration and crater depth until 400°C. This might be by the reason that the yield stress of the substrates starts to show a reduction that might soften the substrate and the kinetic energy transform into the particle and substrate deformation. However, some particles do not have sufficient kinetic energy to bond even if the substrate is soft as some of the kinetic energy is employed for broke the oxide layer. The remaining kinetic energy is not enough to bond so bounced off and leave a deeper crater.

Furthermore, characterizations of pull out particles were carried out for deposition tests using the laser-assisted cold spray system. The pull-out particles showed dimple features associated with metallic bonds between the copper particles and the substrate. This was deemed as a possible indicator of an increase in coating adhesion strength. The quantity of dimple features exhibited at the bonding area remained almost constant as the substrate temperature increases.

The effects of substrate temperature on bonding depending on particle velocity/temperature were demonstrated by observing the differences between the results of cases A and B. In these cases, the spray parameters were modified but the substrate preheating method remained constant. Overall, the results demonstrate a strong effect of particle temperature on bonding as case B achieved a higher penetration depth through the velocity of the particle is lower than that of case A. This provides the hypothesis that the deformation of case A is not considered cold work as the particle temperature is higher than the $0.3T_m$ of copper. This is reflected in the decrease in the particle penetration depth as the substrate temperature increases. Therefore, in case B, although the particle traveled at a slower speed and a lower temperature, it results in deeper penetration.

Finally, the results of the mechanical anchoring simulations suggest that the coating adhesion strength when the substrate is preheated at 600°C can primarily be attributed to metallurgical bonding. This realization comes from the comparison of the simulation results to those of the experimental pull-out test that involved both elements of the adhesion strength: metallurgical bonding and mechanical anchoring. The simulation also compared the mechanical anchoring between a coating with a helium bond coat to that of a coating with only nitrogen as the carrier gas onto a preheated substrate. The outcomes were that the coating with a higher substrate temperature was not able to achieve the same level of deformation of the substrate. However, the mechanical anchoring achieved with the substrate preheating was higher than that achieved without preheating as the coating delaminated only using nitrogen as the carrier gas in both sprays.

6.2 Future work

This research was focused on single copper particles impacted over a heated substrate with the goal of understanding the effects on the first level of the coating. Furthermore, one analysis with a full coating was carried out in order to understand the difference in mechanical anchoring between the coating formed using a helium bond coat with a preheated substrate. However, there are still many unanswered questions about all the effects of preheating the substrate before the CGDS process so future work might be done to fully understanding these effects such as:

- Study other ways to identify metallic bonds including intermetallic phases at the interface between the substrate and the coating in single particle impacts and with the complete coating deposition over a heated substrate.
- Study the effects of the second impact on top of the particle that is already deposited in the heated substrate to determine if there is an increase of metallic bonds. In other words, understand the peening effect over a preheated substrate to determine if there is a reason for the increase of adhesion strength due to the mechanical anchoring and/or metallic bonds.
- Study and measure the residual and thermal stress in the interface between the coating and the heated substrate as it can change the cooling rate and the stress can be lowered.
- Further study of how deep the laser preheats the substrate just before the impact when using the laser preheating method in the CGDS process.
- Identify the parameters of the laser with the purpose to develop a clean and clear cross section cut of bonded particles with the purpose to have an exact relation between the penetration depth and particle diameter, height and compression ratio.

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Appendix A Non-Destructive Procedures

Height/Depth Measurements Procedure

- 1) On the main menu of the Optical Microscope go to the image stitching section and select the “3D image stitching” as displayed in **Figure A.1**.

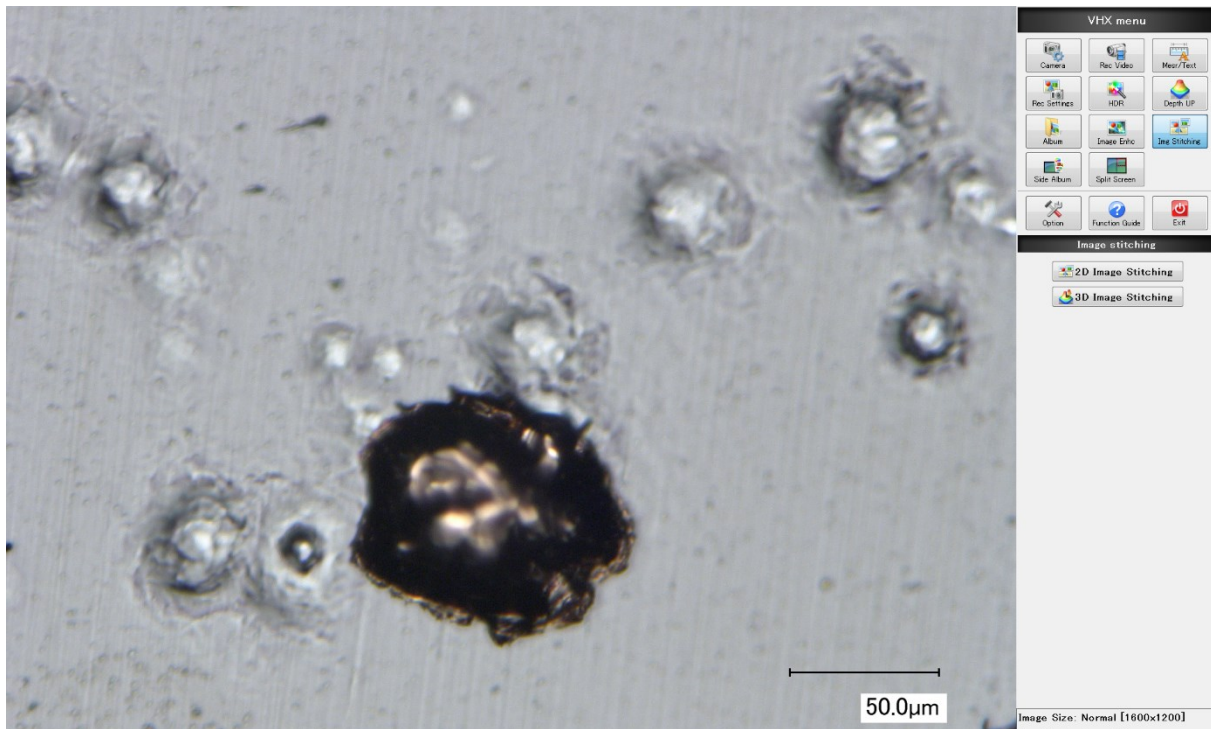


Figure A.1 Digital Optical Microscope: main menu.

- 2) **Figure A.2** shows the 3D image stitching menu that is divided into sections for each step, the buttons that need to be clicked are circled. The options in the Step 1 section are usually not modified.

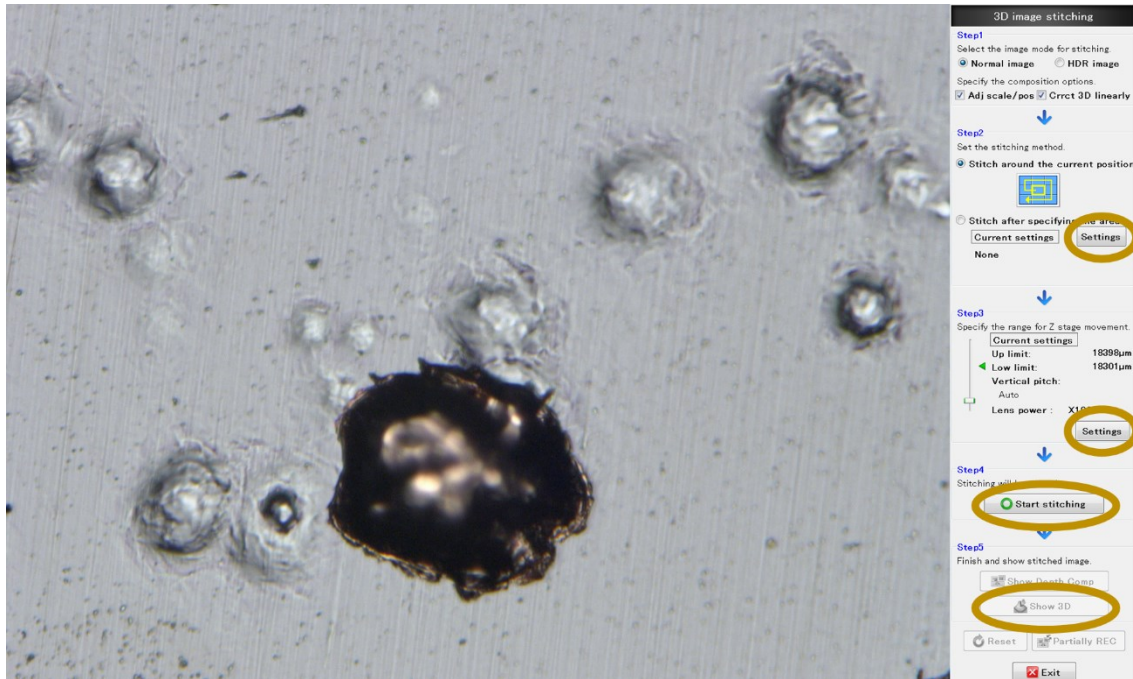


Figure A.2 Optical Microscope 3D image stitching section.

- 3) The settings panels, which appear when selecting the circled buttons are displayed in **Figure A.3**. In step 2 (**Figure A.3 a**) settings panel the size of the 3D image is selected by moving the stage of the microscope with the control panel and clicking the buttons: up end, lower end, left end and right end. A preview of the image size is displayed in the yellow square in the “confirm the area” section. The image size that is displayed in **Figure A.3** is the minimum and it is the image size selected for this research.

The step 3 settings panel provides options to select the Z stage setting as **Figure A.3 b**) demonstrates. It can be observed that the image is not as clear as in **Figure A.3 a**), both images are showing the same position. In this step the objective is to select the high and low limit circled in **Figure A.3 b**), by moving with the arrows until the image is not clear in both limits.

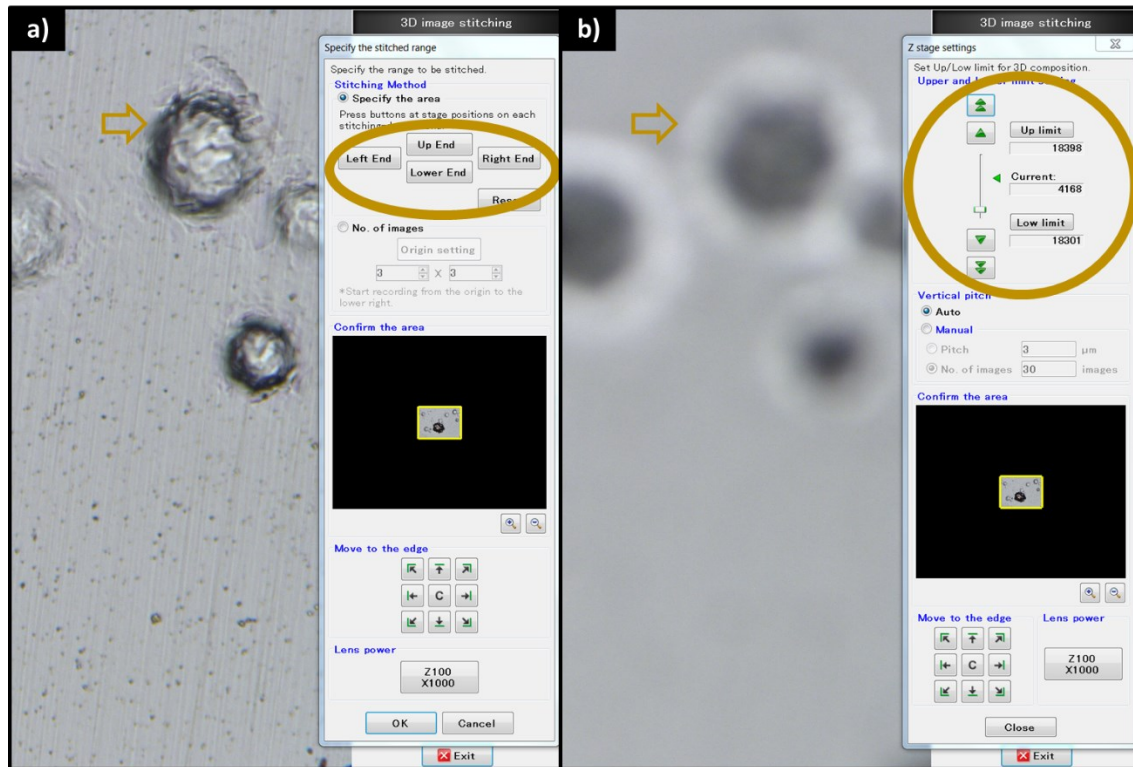


Figure A.3 Optical Microscope 3D image stitching section a)Step 2: image stitching range and b)Step 3: Z stage settings.

- 4) Once the 3D display screen, shown in **Figure A.4**, appears, the 3D image appears. The first option that can be modified is the height of the figure. As the image is in 3D, for better measurements it is recommended to reduce the magnification of the height image to zero. In addition, it is important to do a 3D tilt correction because the figure may have some minimal tilt error which is important to correct before continuing with the crater depth or particle height.

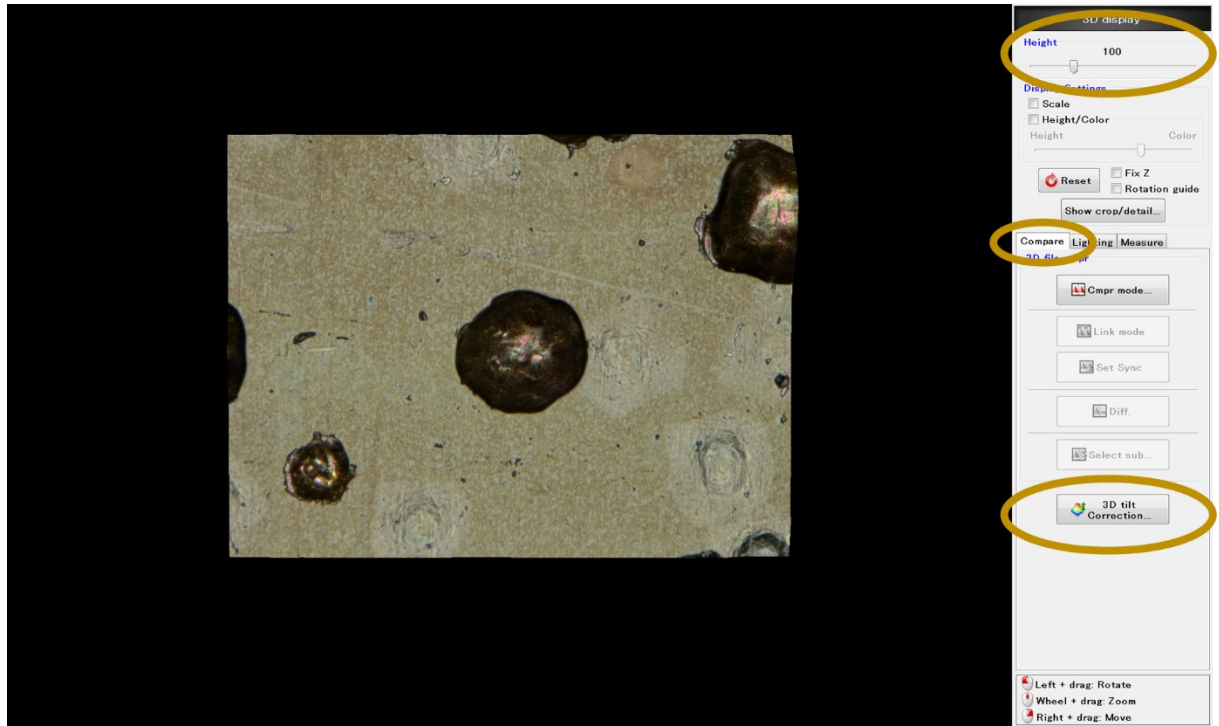


Figure A.4 Digital Optical Microscope: 3D Display screen.

- 5) In the 3D tilt correction view, the configuration options are indicated on the right side (illustrated in **Figure A.5**). The first step is to select three points to specify the plane, in this case, the points need to be placed on the substrate. Once the three points are positioned correctly, the next step is to click correctly. If the tilt correction does not appear adequate, the last step can be repeated until the tilt correction is appropriate. The final step is clicking the button “Show 3D”, once this button is clicked, a window will appear to accept the changes and return to the 3D display.

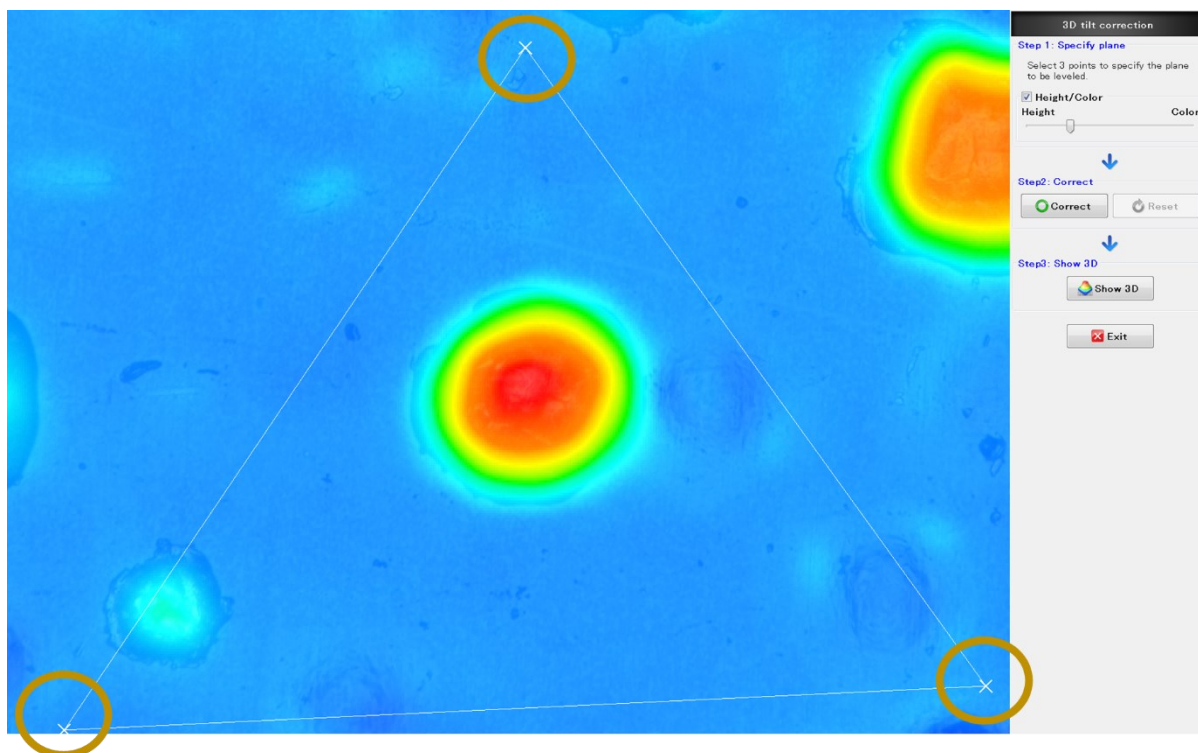


Figure A.5 Digital Optical Microscope: 3D tilt correction display.

- 6) The next step is to click on the “Measurement” tab in the middle right of the 3D display panel. The following step is to activate the “Profile” option in the 3D measurements menu. The Measurements and Profile window will appear containing a red and white dot on the 3D image and a profile graph below. The red dot represents the left start point of the graph illustrated in the profile window while the white dot represents the right endpoint of the profile graph, as marked in **Figure A.6** with a green and orange circle respectively. Next, the dots from the profile line need to move in a manner that the line which they make up crosses just through the middle of the particle or crater. The dots need to be on the same level to have a precise measurement, if this is not possible the tilt correction step needs to be carried out once more.

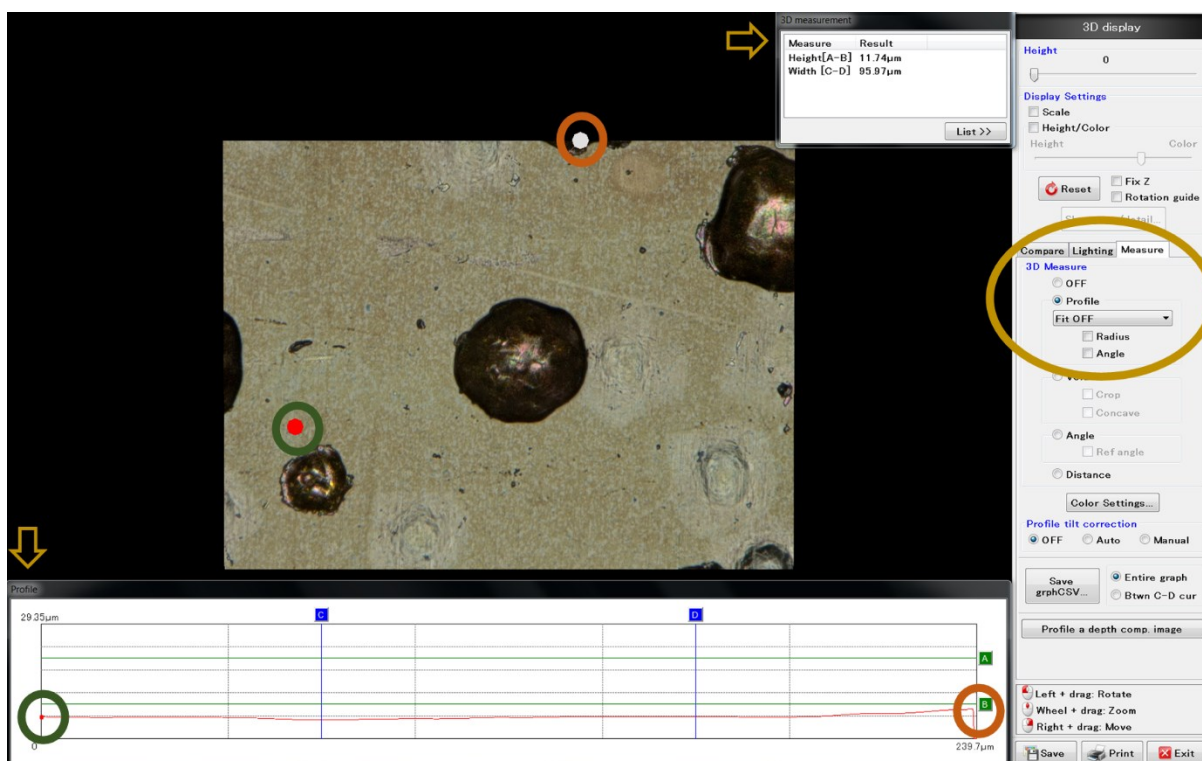


Figure A.6 Digital Optical Microscope: 3D Measurement display #1.

- 7) Once the dots of the profile line are placed correctly, the option below the “Profile” button needs to be changed from “Fit Off” to “Fit height mode”, so that the profile line graph shows at the correct scale in the Profile Window, as **Figure A.7** shows. Once the profile graph is displayed at the correct scale, the green lines with letters A and B need to move so that A is at the top of the plot on the profile graph and B is at the bottom. Once moved appropriately these cursors will mark measure the height and the value will be displayed in the 3D measurement window. As well, the width measurement can be taken by moving the blue lines C and D; however, this is not the way that the diameter was studied. Using this method, it would be hard to be consistent in avoiding the jetted regions. The particle diameter will be explained later in this section.

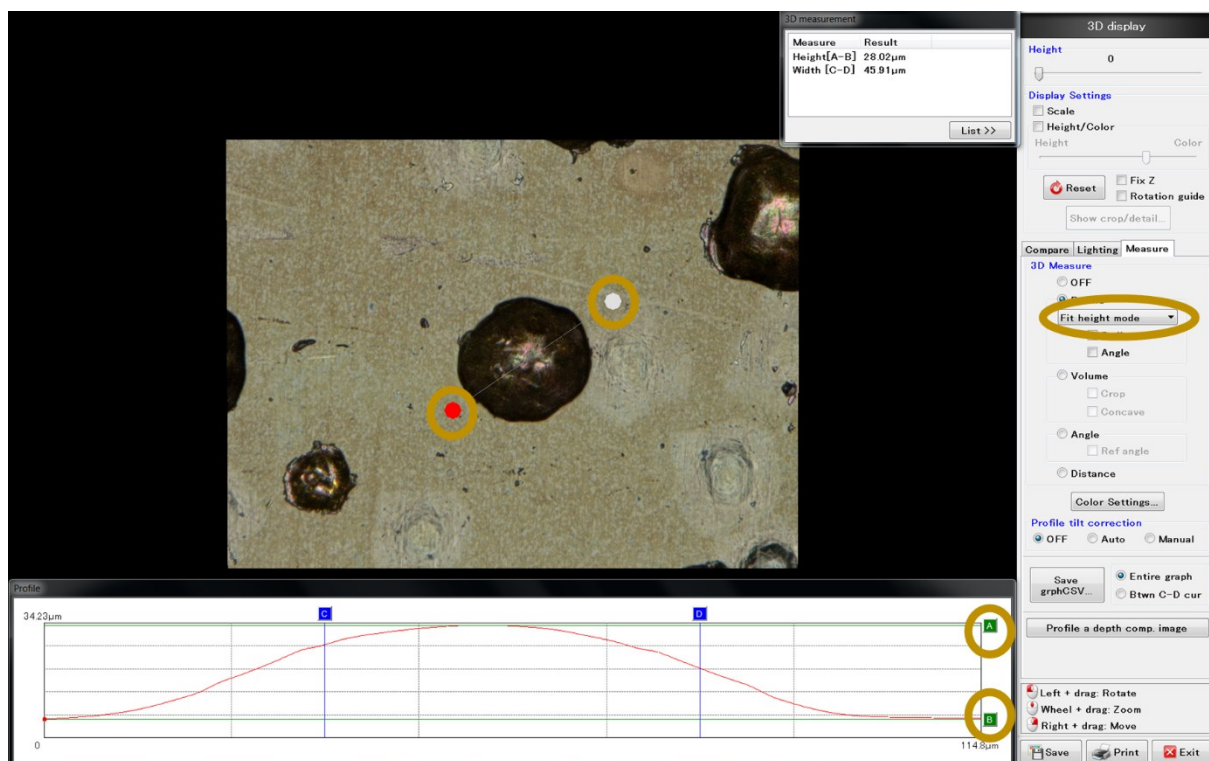


Figure A.7 Digital Optical Microscope: 3D Measurement display #2.

Crater Volume Measurements Procedure

- 1) Once the “VHX-6000_950F communication software” is open, the folder containing the images needs to be selected on the left side of the menu (as shown in **Figure A.8**). This software can open both 3D and 2D images. The 2D/3D images can be differentiated by a small icon in the bottom right of each image preview. For particle diameter measurements it is necessary to open a 2D image file, doubling clicking on the selected image will open a small window where the “Captured image” button should be clicked.

It is important to mention that a 2D version of a 3D image can be opened, however, when the measurements are made using a 3D image the software does not apply the conversion correctly resulting in incorrect measurement results.

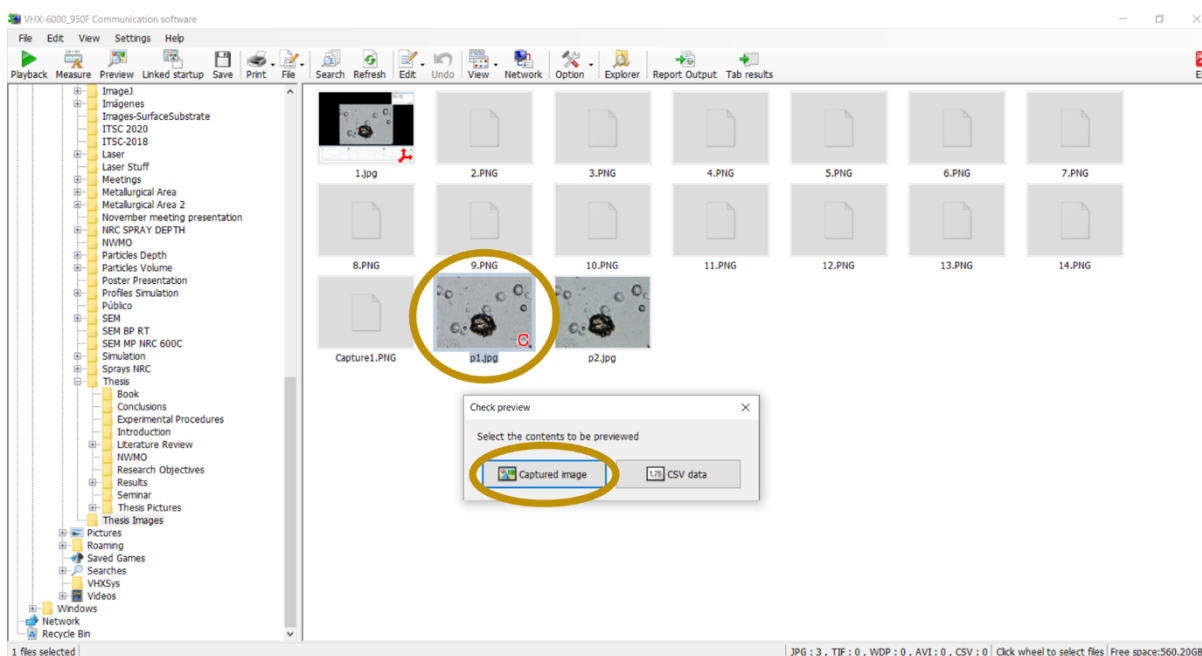


Figure A.8 Main menu screen of VHX-6000_950F communication software.

- 2) Once “Capture image” is clicked, another window is opened, as **Figure A.9** shows, which displays the options available for the 2D image. To start measurement the button “Measure/Comment” needs to be clicked. In this next window the first option “Measure the source without changes to size” is selected, as Figure A.9 demonstrates.

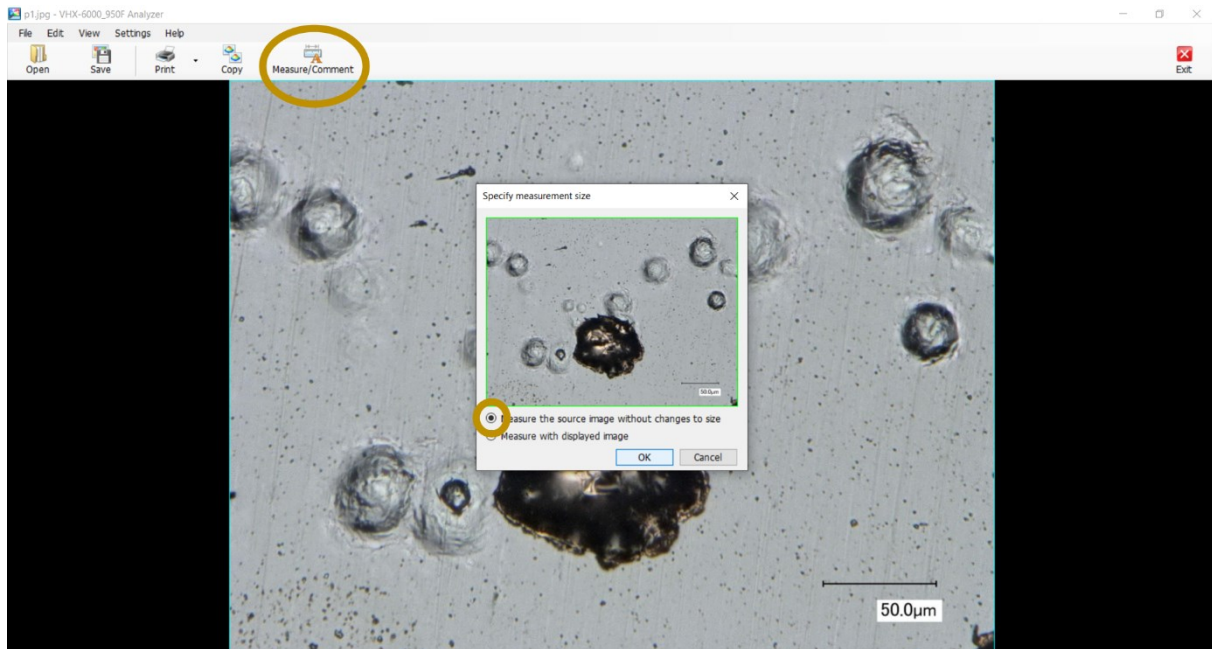


Figure A.9 2D file options of VHX-6000_950F communication software.

- 3) **Figure A.10** shows the resulting window, which has measurement options for the image. In the main tab, the diameter option is selected. Clicking the image will increase the zoom in the area selected. The next click will place a cross on the image; this marks the first point that will be used for taking the diameter measurement. Once the first point is selected the image will return to its original scale, the next point is then selected by clicking again at a perimeter point of the particle that does not contain jetting.

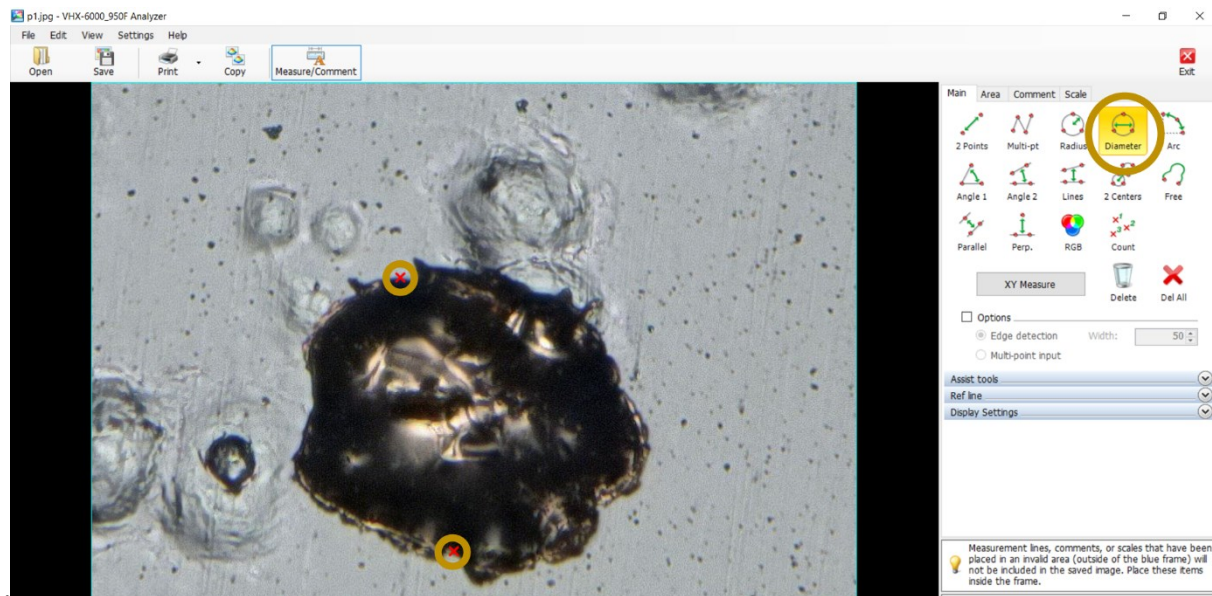


Figure A.10 Measure/Comments section of VHX-6000_950F communication software.

- 4) Once the two points have been selected, a circle with measurements to select the third cross will appear (shown in **Figure A.11**). This point should be selected in the best possible way to cover the entire perimeter of the particle without covering the jettings.

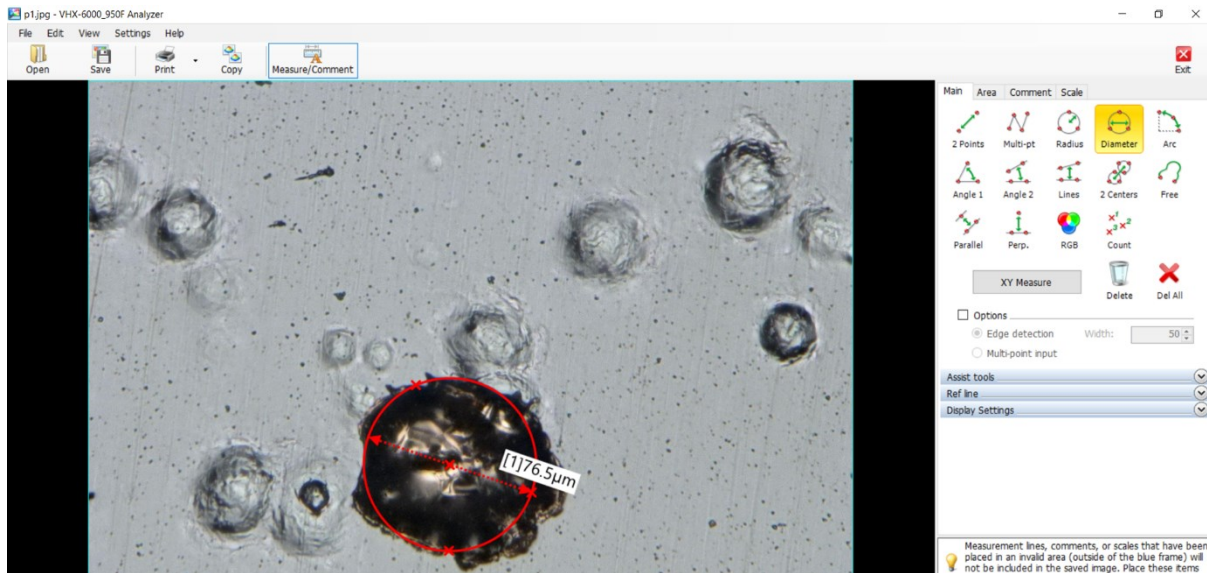


Figure A.11 Particle diameter by VHX-6000_950F communication software.

Appendix B Metallurgical Bonding Measurement Procedure

- 1) Open the image taken from the SEM, where the scale line is provided on the image by the SEM software. With the ruler tool (as shown in **Figure B.1**) draw a line over the scale of the image, and the measurement of the line shows in the panel above the image, as illustrated in **Figure B.1**. For this step be sure that the option “Use Measurement Scale” is selected.

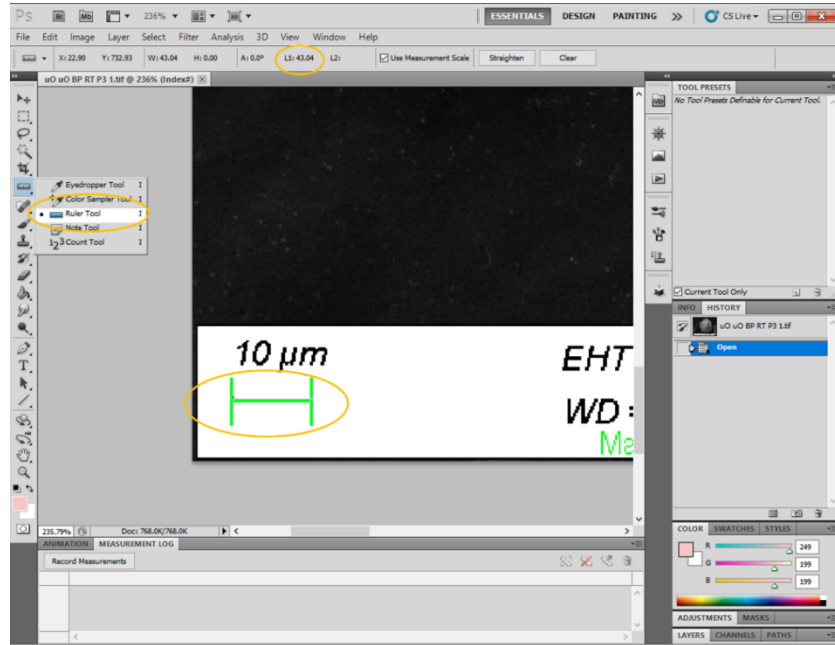


Figure B.1 Photoshop software: ruler tool.

- 2) Knowing the measurement of the line, the scale can be readjusting by opening the scale window, described in **Figure B.2**, to open the scale window is necessary to click on Analysis>Set Measurement Scale>Custom. The measurement of the tool and the known scale are then inserted in the window.

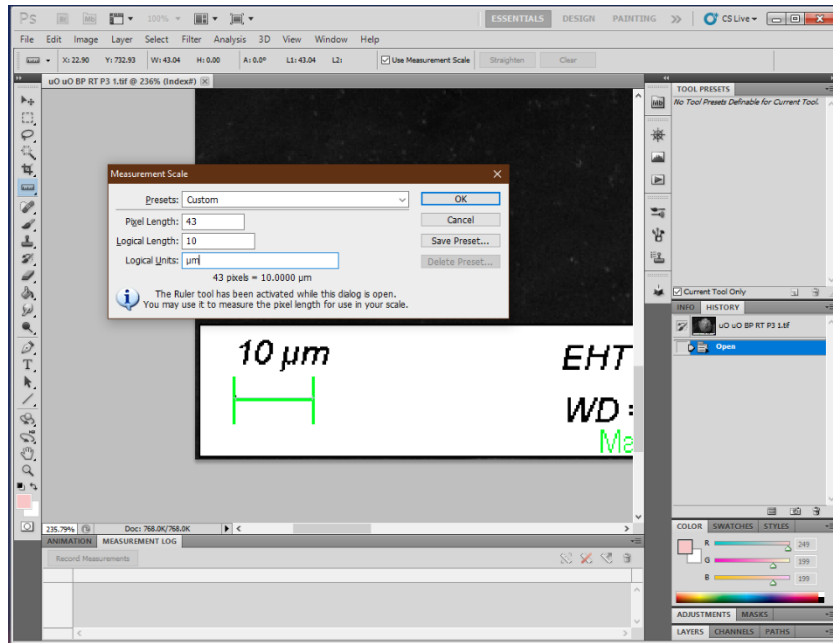


Figure B.2 Photoshop software: Scale window.

- 3) Select the bonding area with the Lasso tool; this area is determined by observation of where the penetration starts, as **Figure B.3** displays, then measure the area by clicking “Record Measurement,” if the measurement log does not appear, it is necessary active it in the “Window” menu. This area measurement is used to obtain the metallurgical bonding ratio.

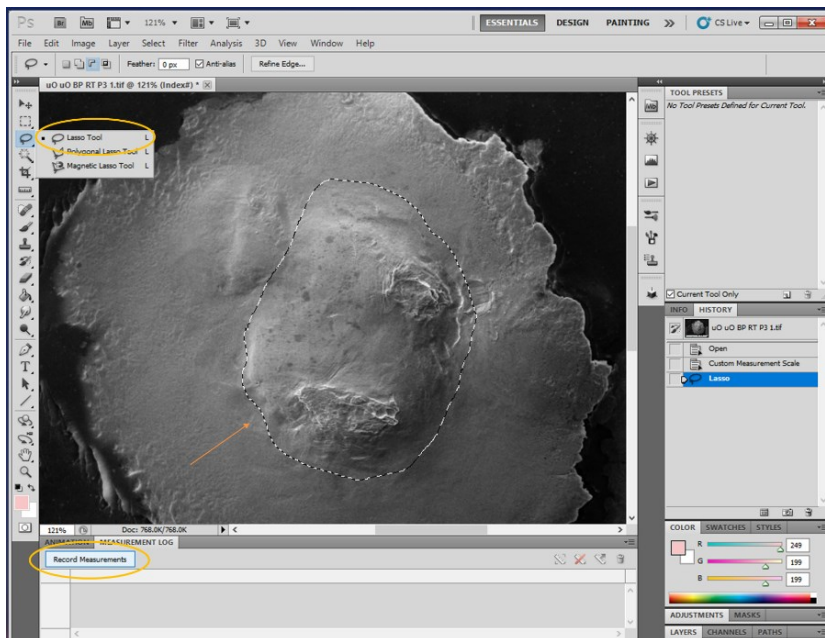


Figure B.3 Photoshop software: Selected area.

- 4) Press the combination of “CTRL+SHIFT+I” keys to inverted the area and delete using the “Delete” key, as **Figure B.4** demonstrates; the rest of the area is not of interest for these measurements.

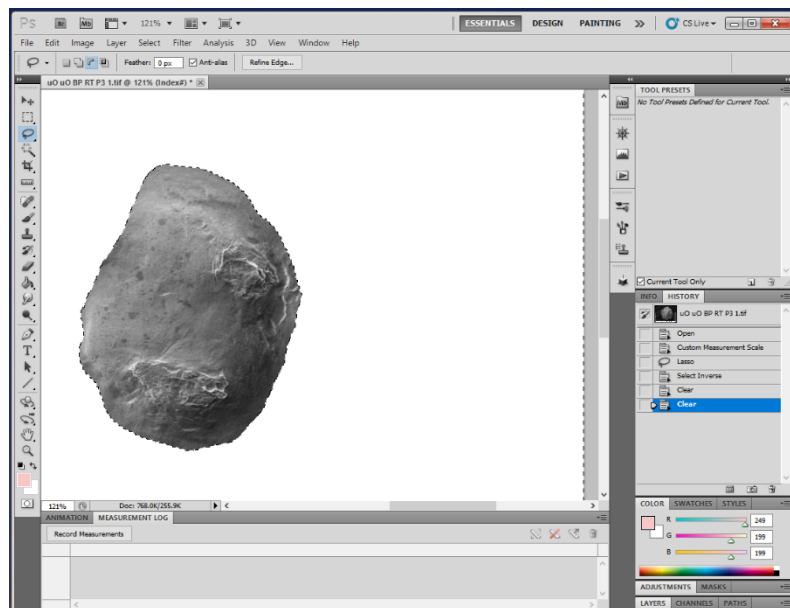


Figure B.4 Photoshop software: Inverted and delete area.

- 5) Using the paint bucket tool start to paint the area, as **Figure B.5** illustrates. The paint bucket tool works based on pixel colors thus by clicking an area where there is no metallurgical bonding the tool will fill in all area which does not contain bonding. Continue clicking until the area painted does not change and covers all the non-metallurgical bonding area, as **Figure B.5** demonstrates all the metallurgical areas not painted with blue.

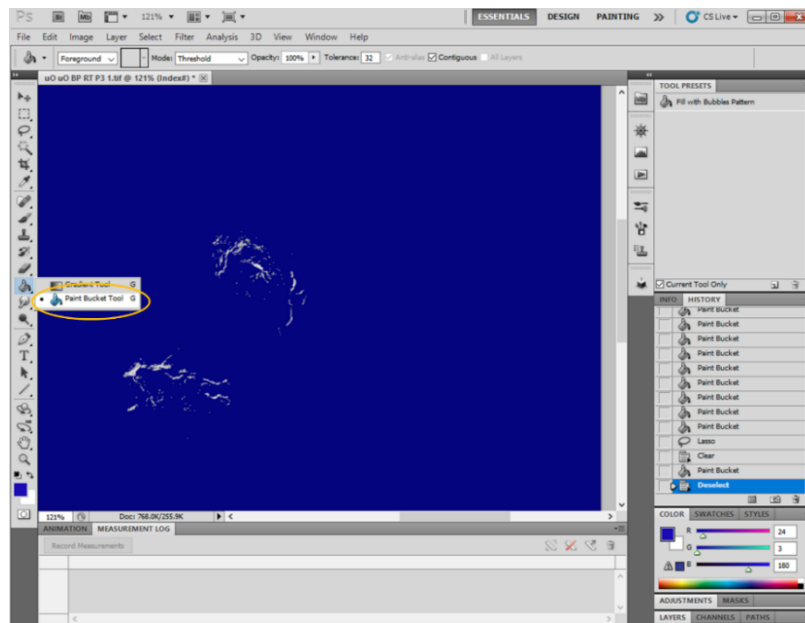


Figure B.5 Photoshop software: painted area.

- 6) Select the “magic wand tool” (as shown in **Figure B.6**) for easy metallurgical bonding area measurement. Once selected select the painted area by clicking anywhere in the painted area and then invert the area with the key combination “SHIFT+CTRL+I.” Selecting the metallurgical area is harder because the area is divided into different segments due to the difference of color in the area. Finally, measure the selected area by clicking “Record Measurements” in the measurement log. The first line of the measurement is the sum of each segment of metallic bonds the area and the rest of the lines are the areas of each segment of the metallurgical area.

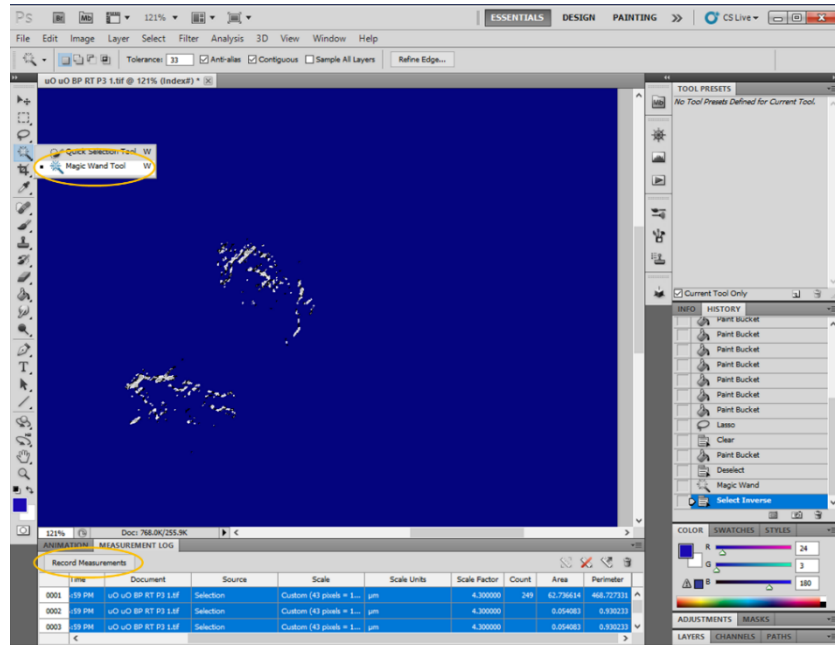


Figure B.6 Photoshop software: Metallurgical bonding area selection and measurement.

- 7) Finally, to get the ratio of the metallurgical bonding is calculated by the division of the total of the metallurgical area obtained in the last step by the total of the penetration area obtained in step number three.

Appendix C Mechanical Anchoring Prediction Procedure

Profile Extraction Procedure

- 1) Once the image is opened in the Image J software, the first thing to do is set the scale in the “Analyze” section, as **Figure C.1** demonstrates. To properly set the scale it is necessary to create a straight line over the scale line. Once this line is created the length of this line will appear in the “Distance in pixels” field of the “Set Scale” window. In this same window the known distance is applied as well as the unit of length; in this case μm .

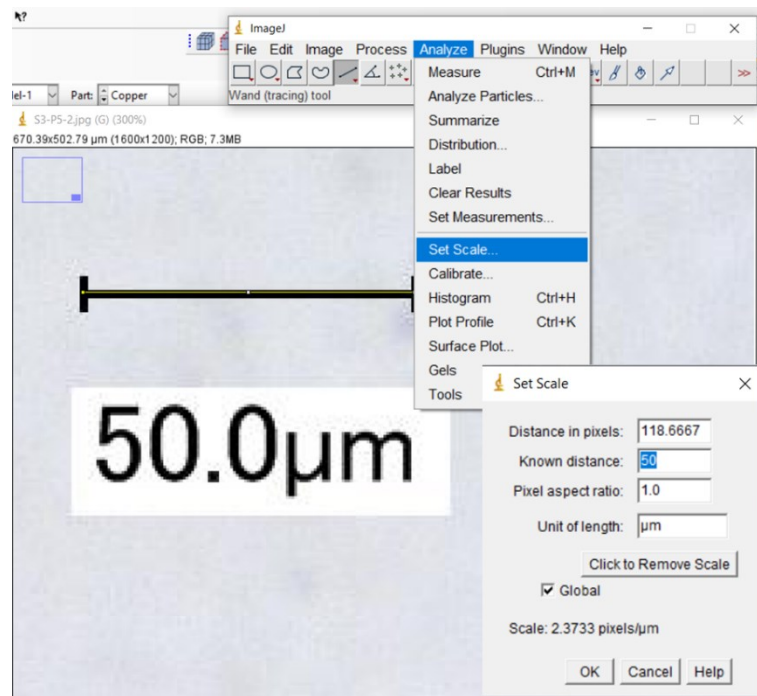


Figure C.1 Image J software: set scale image.

- 2) Since the simulation is focused on the interface of the cross section, it is faster to process if the image is cropped to only the interface. For that, a rectangular area needs to be selected with the crop tool. The area which desired to work with is selected and then select crop in the Image menu, as indicated in **Figure C.2**

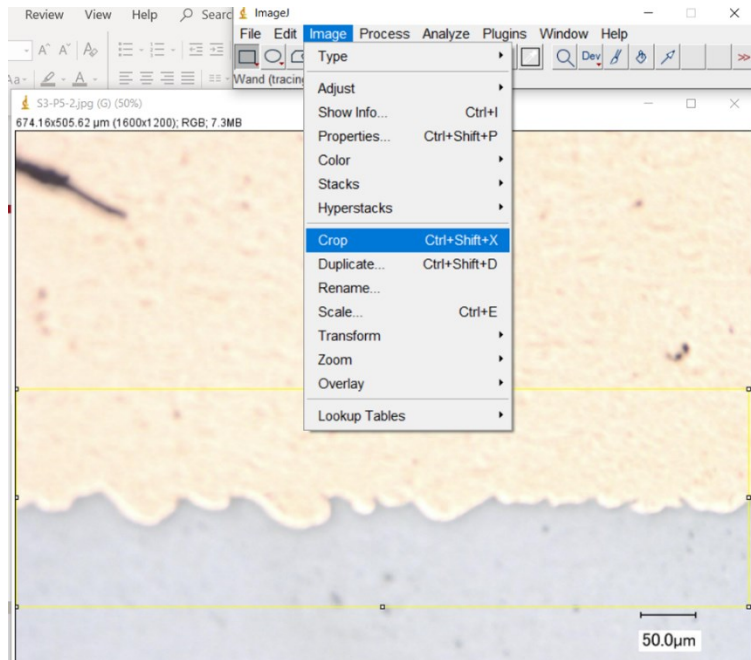


Figure C.2 Image J software: crop image.

- 3) Next, it is necessary to change the image type to 8-bit, as displayed in **Figure C.3**, with that, the image will change to 8-bit grayscale.

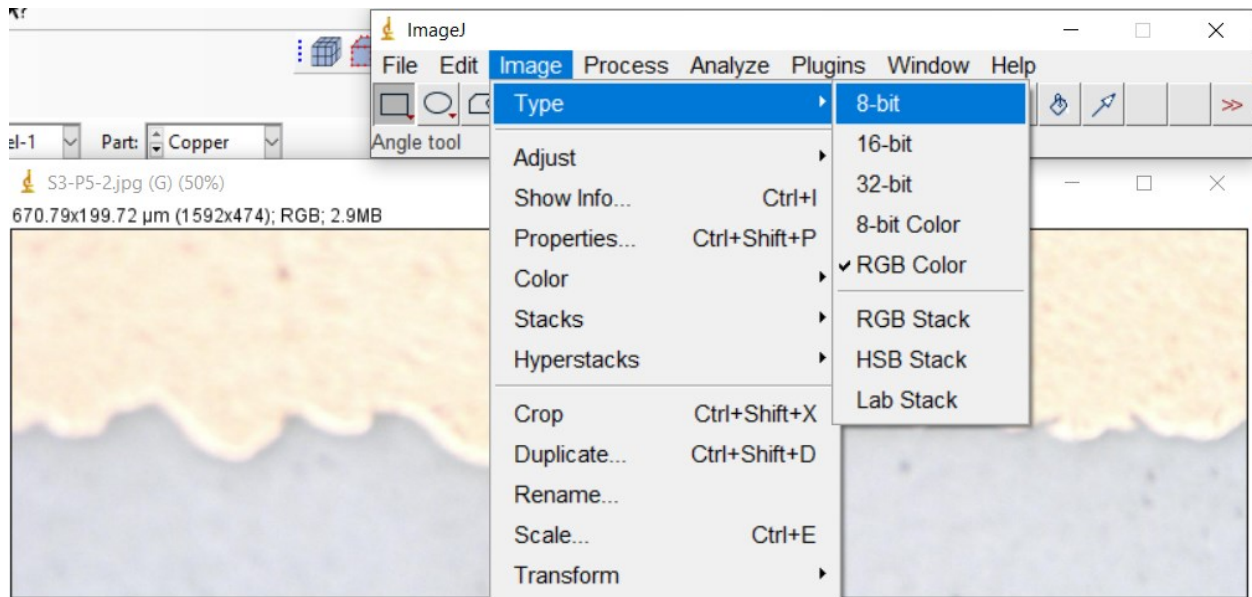


Figure C.3 Image J software: type of image section.

- 4) The brightness/contract can be adjusted under the Image menu to achieve a better profile section, this is pictured in **Figure C.4**.

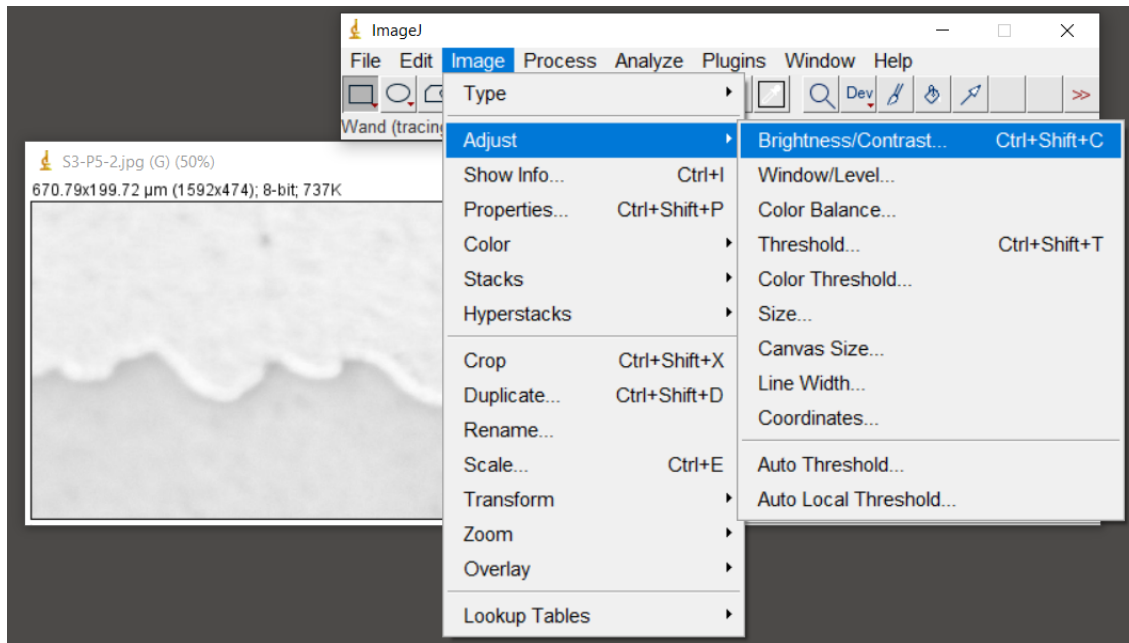


Figure C.4 Image J software: bright/contrast option.

- 5) Modify the brightness/contrast options so that the image changes from grayscale to black and white as **Figure C.5** illustrates. Each image is different so there is no exact configuration to reach this point.

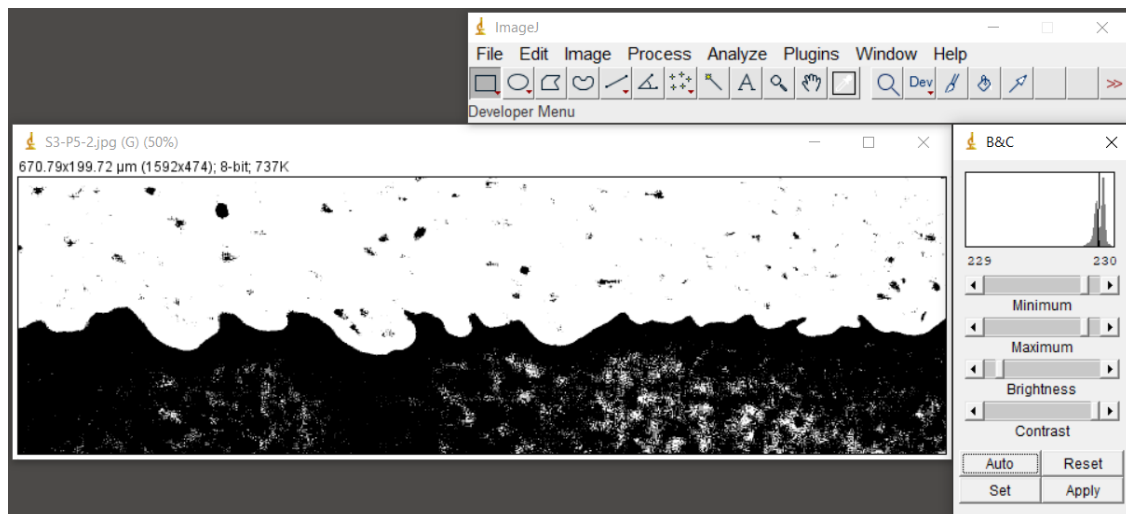


Figure C.5 Image J software: bright/contrast option.

- 6) To achieve an even clearer profile, the image must be converted to binary; this is done using the binary option in the process menu, as **Figure C.6** demonstrates. For this specific image eroding option worked best. To make it easier to determine the best configuring the preview option can be activated on the window. If the clarity of the profile has not yet improved the number of iterations or count can be modified or the Erode setting can be modified to Dilate.

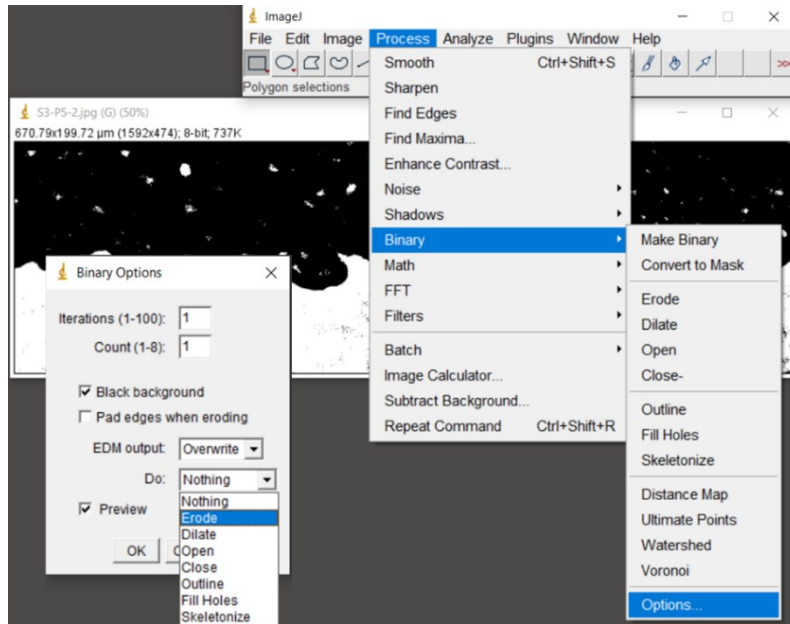


Figure C.6 Image J software: Binary process options.

- 7) Another option to refine the profile is using the Median filter under the process menu, as displayed in **Figure C.7**. For this filter the radius can be modified to achieve better results, it is also important here to have the preview option activated in order to see the changes in the image in real-time.

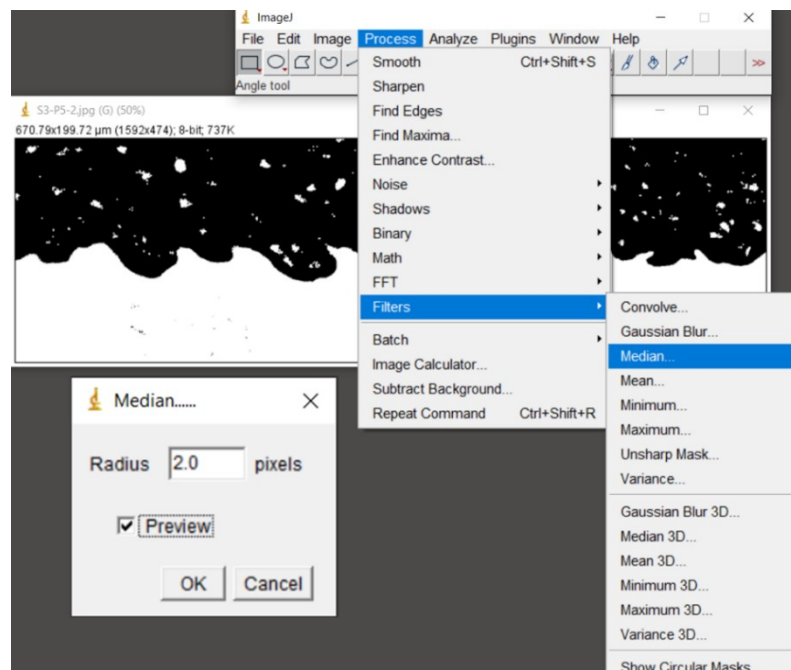


Figure C.7 Image J software: median filter in the process options.

- 8) The binary and median filter options can be adjusted until the profile is clear. Once the profile is ready, the profile is selected with the wand tool such that it appears as shown in **Figure C.8**.

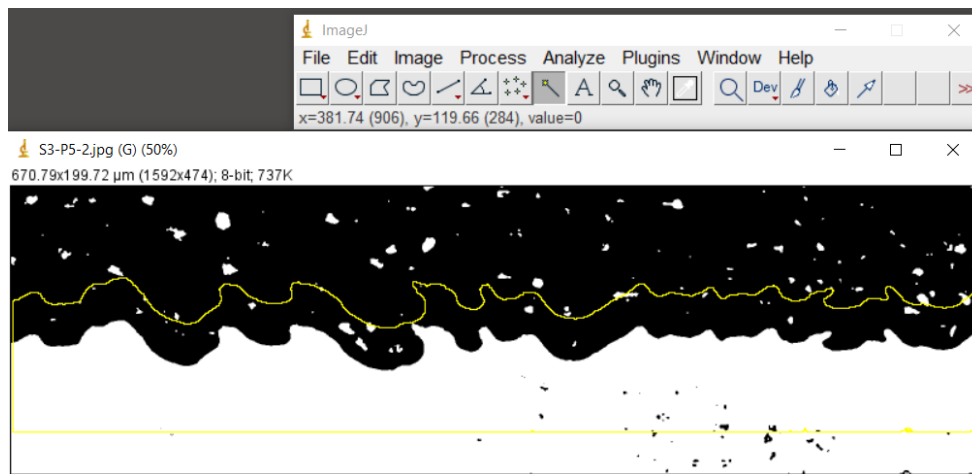


Figure C.8 Image J software: profile selected with the wand tool.

- 9) **Figure C.9** demonstrates the last step which is to save the profile as XY coordinates. This will save the data in a plain-text script format and will be used to transfer the profile data into the Abaqus software.

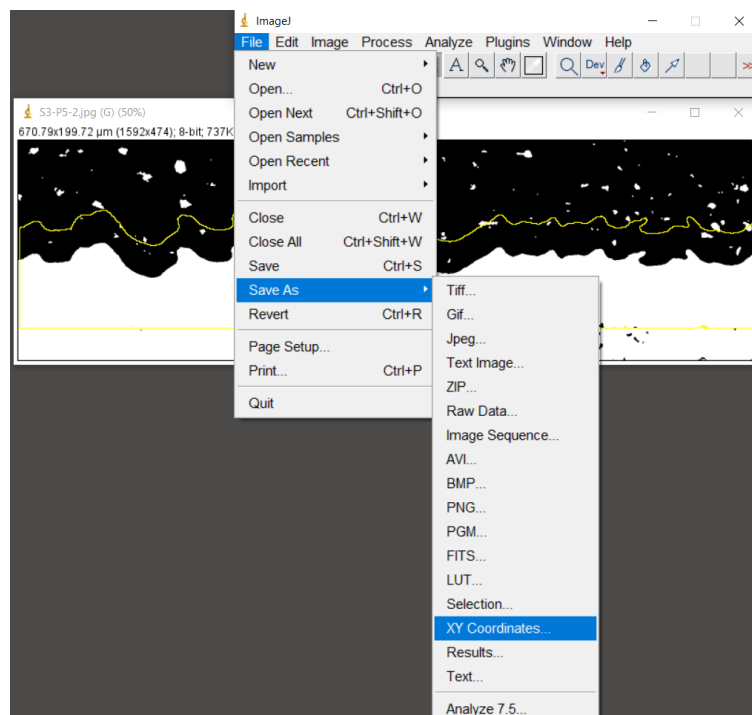
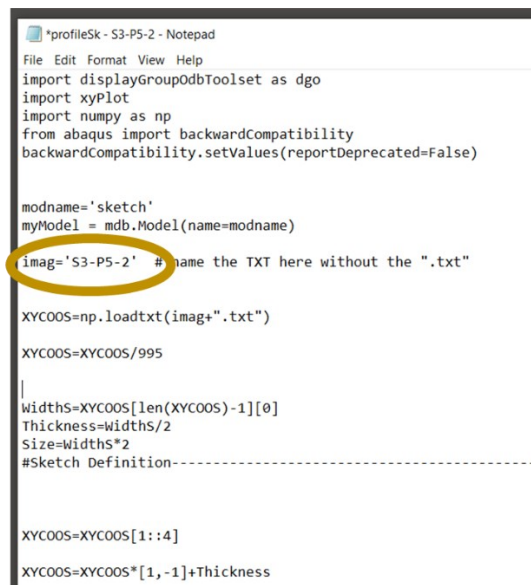


Figure C.9 Image J software: save as XY coordinates option.

10) Finally, the name of the XY coordinates file needs to be inserted in the line that starts with “imag=” to properly extract the profile, as **Figure C.10** demonstrates.



```
*profileSk - S3-P5-2 - Notepad
File Edit Format View Help
import displayGroupOdbToolset as dgo
import xyPlot
import numpy as np
from abaqus import backwardCompatibility
backwardCompatibility.setValues(reportDeprecated=False)

modname='sketch'
myModel = mdb.Model(name=modname)
imag='S3-P5-2' # name the TXT here without the ".txt"

XYCOOS=np.loadtxt(imag+".txt")

XYCOOS=XYCOOS/995

|
WidthS=XYCOOS[len(XYCOOS)-1][0]
Thickness=WidthS/2
Size=WidthS*2
#Sketch Definition-----

XYCOOS=XYCOOS[1::4]

XYCOOS=XYCOOS*[1,-1]+Thickness
```

Figure C.10 Code for profile extract.

Profiles

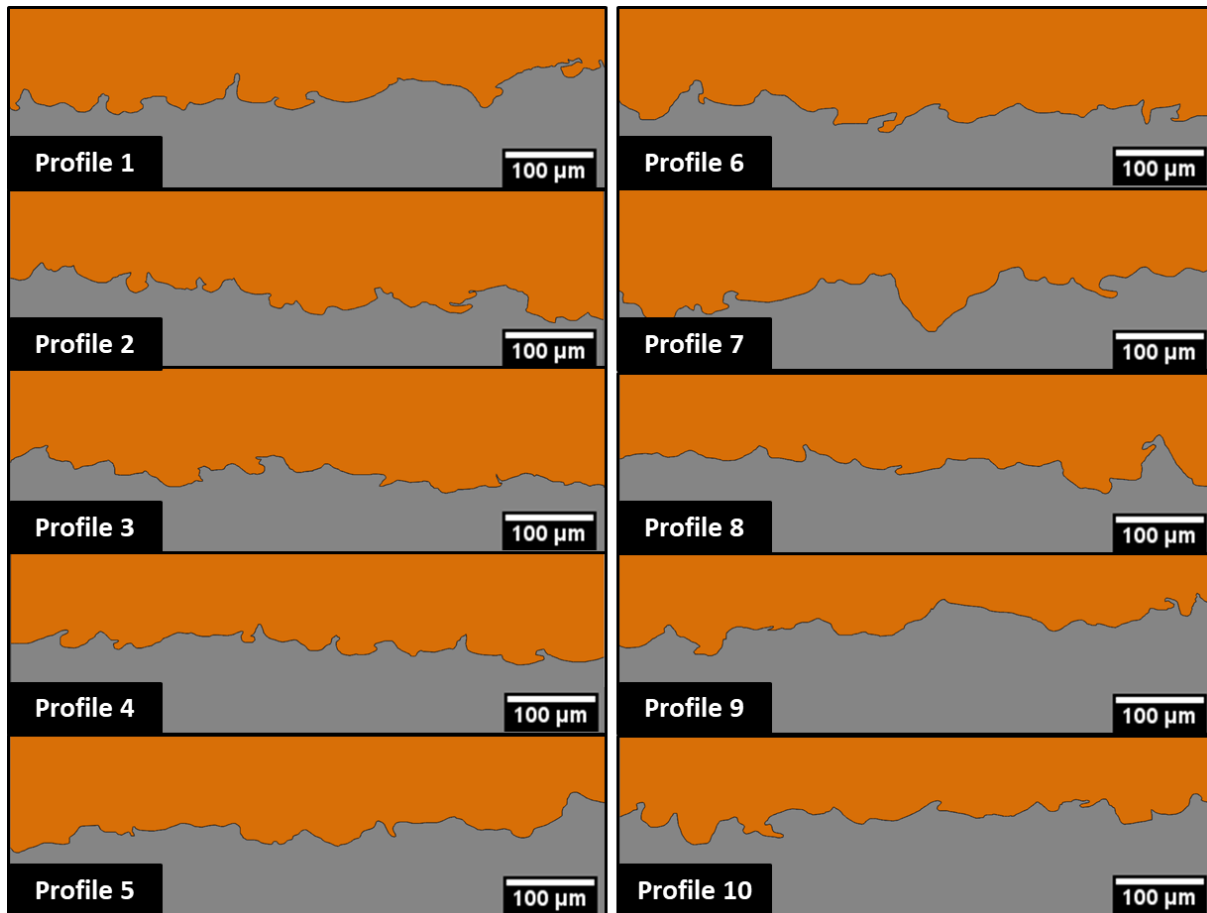


Figure C.11 Coating profiles of copper coating over low carbon steel with a helium bond coat around 100µm and then built up with nitrogen as carrier gas .

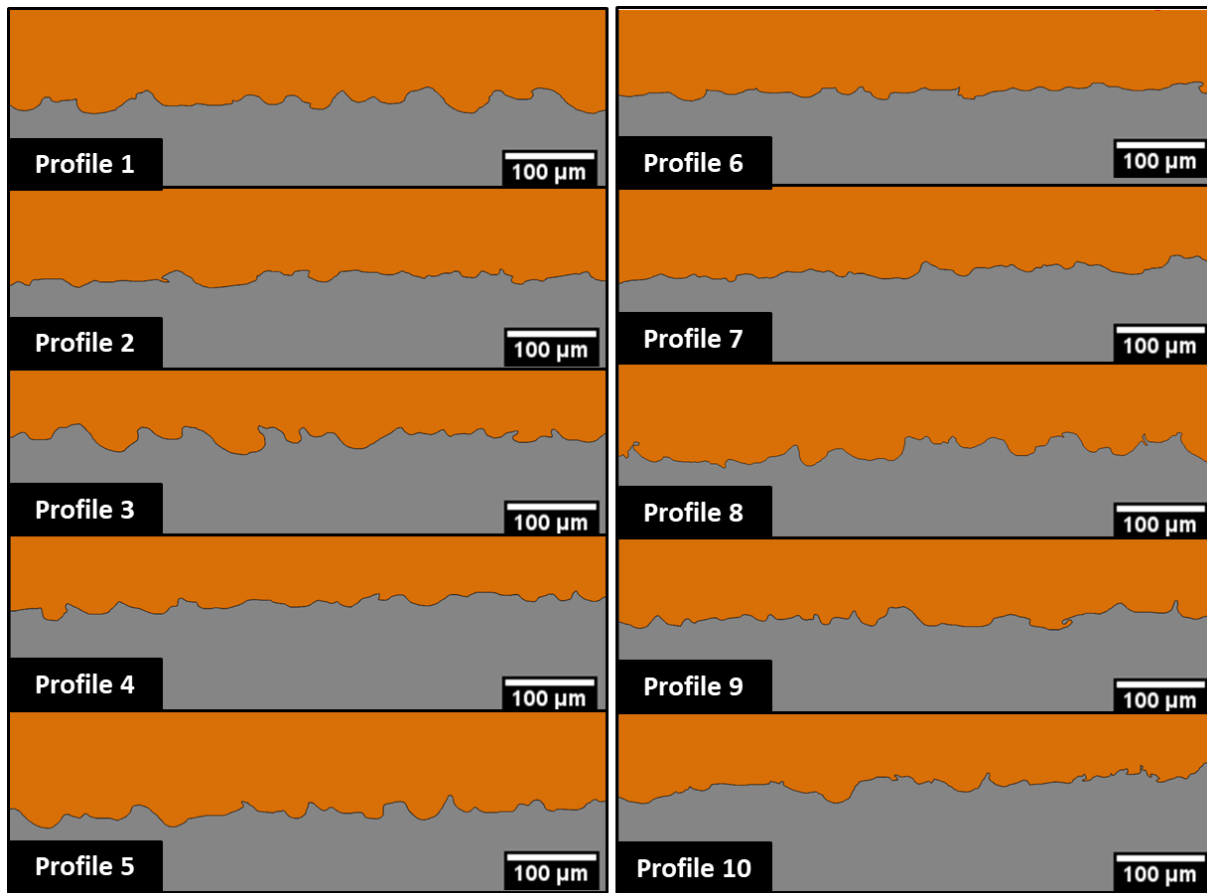


Figure C.12 Coating profiles of copper coating over low carbon steel with substrate preheated at 600°C by laser just before the particle impact.

Simulation Procedure

- 1) **Figure C.13** illustrates the first step which is to set the working directory in order to select the folder in which Abaqus will save all the files created by the simulation.

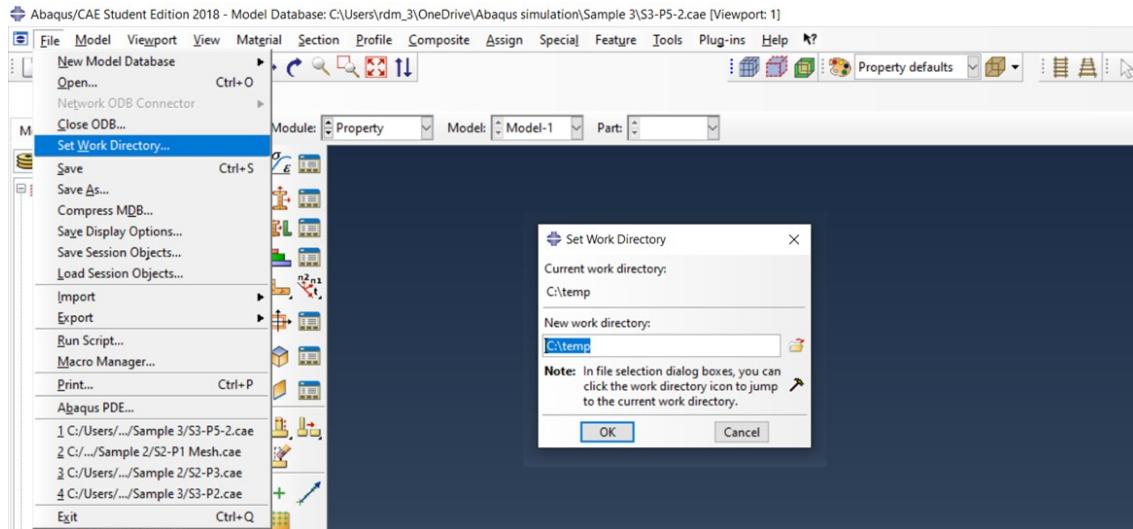


Figure C.13 Abaqus software: set work directory.

- 2) To import the profile coordinates exported from Image J software it is necessary to click “Run Script...” in the file menu, as **Figure C.14** demonstrates.

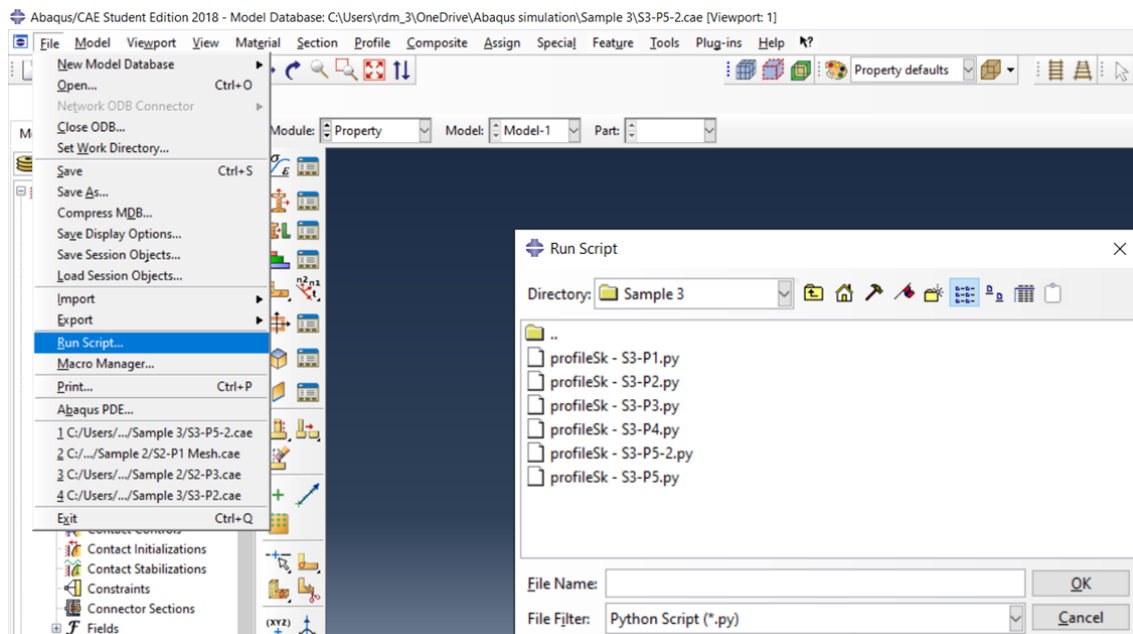


Figure C.14 Abaqus software: run script.

- 3) The next step, once the profile is inserted, is to verify that all the points of the profile are connected. If all the points of the profile are not connected it is necessary to connect them

with the “Create connected lines” tool that is circled in **Figure C.15**. Additionally, using the same tool, create the shape of the substrate by creating the lines from end points of the profile coordinates in a rectangular shape. **Figure C.15** shows the final sketch of the substrate that was done.

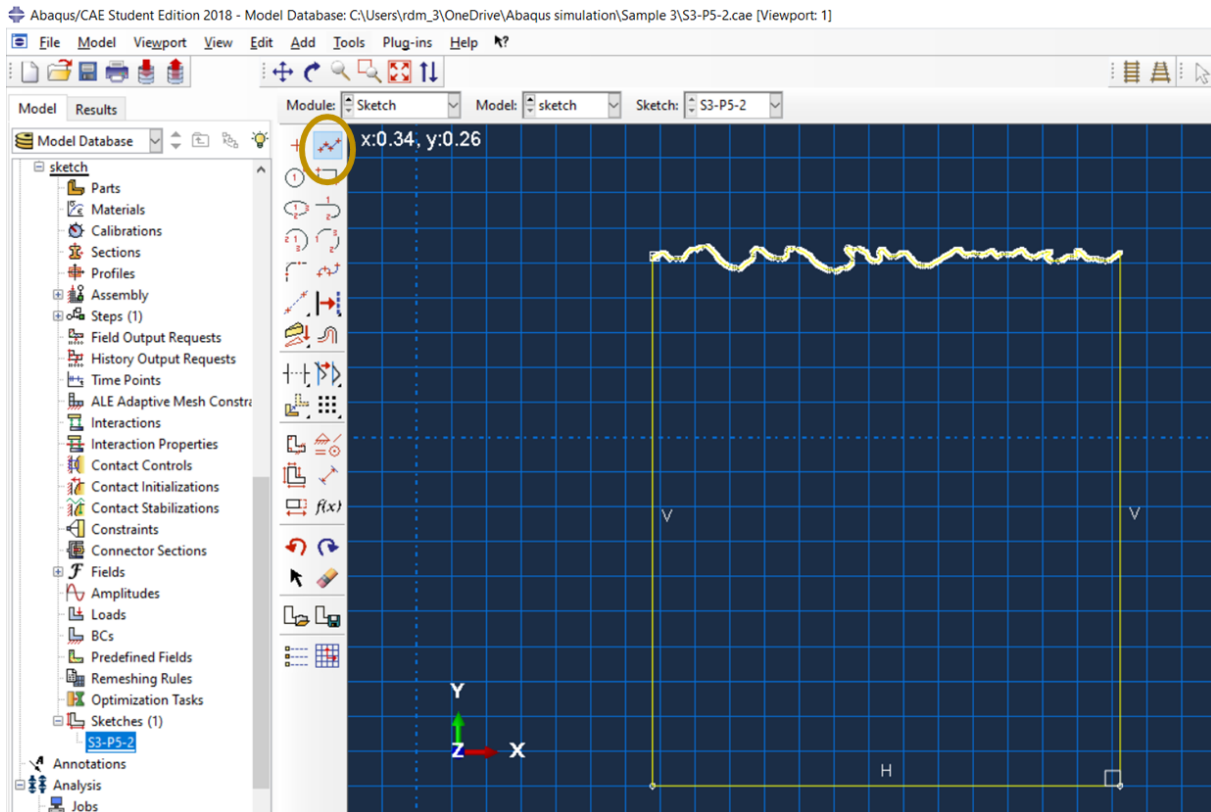


Figure C.15 Abaqus software: Sketch modifications.

- 4) As seen in the previous figure the profile is located inside a sketch that is separate from the model, it must be moved to the model. To achieve this the copy objects option in the model menu must be used, this is demonstrated in **Figure C.16**. Following the instructions of the copy objects window from **Figure C.16**, the sketch must be selected and moved to the model and then applied.

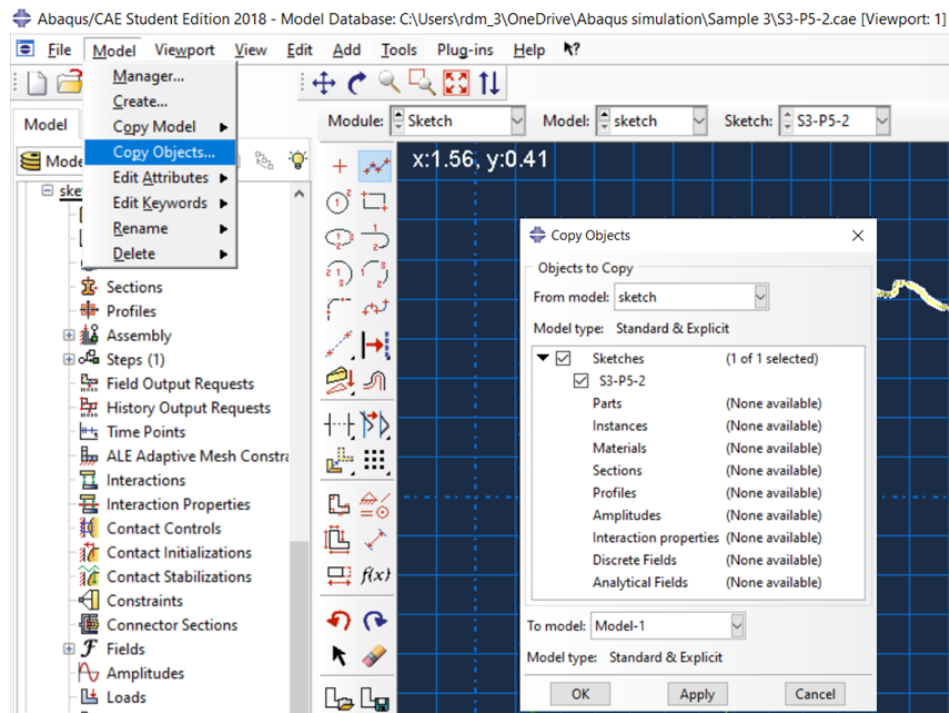


Figure C.16 Abaqus software: copy objects.

- 5) Next, the parts are created by right clicking on the Parts selection (as displayed in **Figure C.17**) in the model panel to the left of the screen and selecting create. Then in the create part window select a 2D planar modeling space, deformable part type, shell base feature, and modify the approximate size in mm which will depend on the size of the sketch. After space was created, add the profile sketch using the option circled in **Figure C.17** then select the sketch and the part will be created.

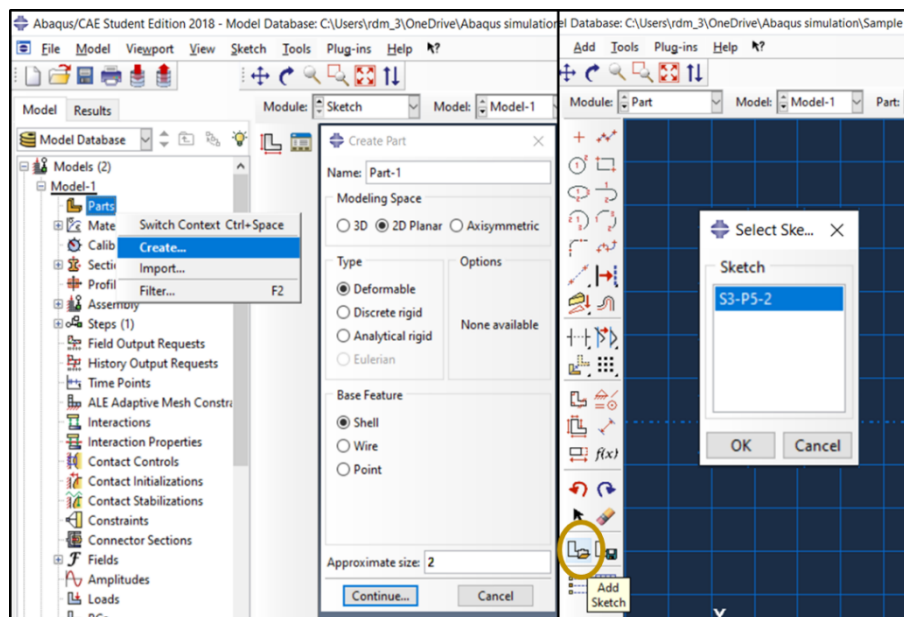


Figure C.17 Abaqus software: create parts.

- 6) **Figure C.18** illustrates how the materials are created, to create a material it is necessary to right click on the materials selection in the model panel to the left. This will bring up the edit material window where various properties of the materials may be selected.

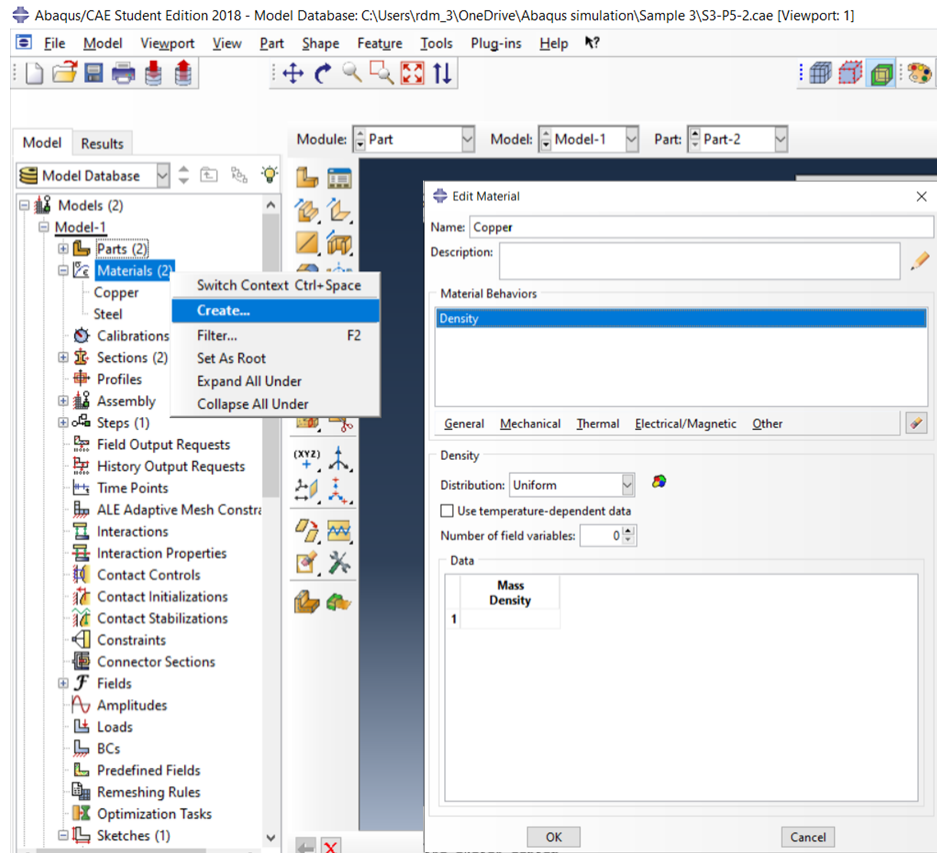


Figure C.18 Abaqus software: material properties.

In this research, the copper coating and low carbon steel properties are based on the simulation made by Fernandez et al. [24] and are represented in **Table C.1**:. The properties of the A516 Grade 70 steel are replaced with Steel A36 which has the same amount of carbon content.

Table C.1: Material properties for copper and steel A36

Properties	Copper	Steel A36
$\rho(\text{Kg/m}^3)$	8960	7830
$E \text{ (GPa)}$	124	200
ν	0.34	0.26
$k \text{ (W/m K)}$	386	45
$C_p \text{ (J/kg K)}$	383	477

The plasticity model used in the simulation was that of Johnson-Cook and is shown in **Eq. C.1**:

$$\sigma_{eq} = [A + B\varepsilon_p^n] \left[1 + C \ln \left(\frac{\dot{\varepsilon}_p}{\dot{\varepsilon}_{ref}} \right) \right] \left[1 - \left(\frac{T - T_{ref}}{T_m - T_{ref}} \right)^m \right] \quad \text{Eq. C.1}$$

Where, A, B, C, n, m, ε_{ref} , T_{ref} are the Johnson-Cook parameters, ε_p is the plastic strain, T is the material temperature and T_m is the melting temperature. The parameters employed in this simulation are shown in **Table C.2**: based again on the simulation by Fernandez et al. [24]

Table C.2: Johnson-Cook parameters for copper and steel A36

Properties	Copper	Steel A36
A (MPa)	90	146.7
B (MPa)	292	896.9
C	0.025	0.03
n	0.31	0.32
m	1.09	0.323
ε_{ref}	1	1
T_m (K)	1356	1810
T_{ref} (K)	293	293

- 7) After creating the materials with the appropriate properties, it is essential to create homogeneous solid sections in each of the materials as shown in **Figure C.19**.

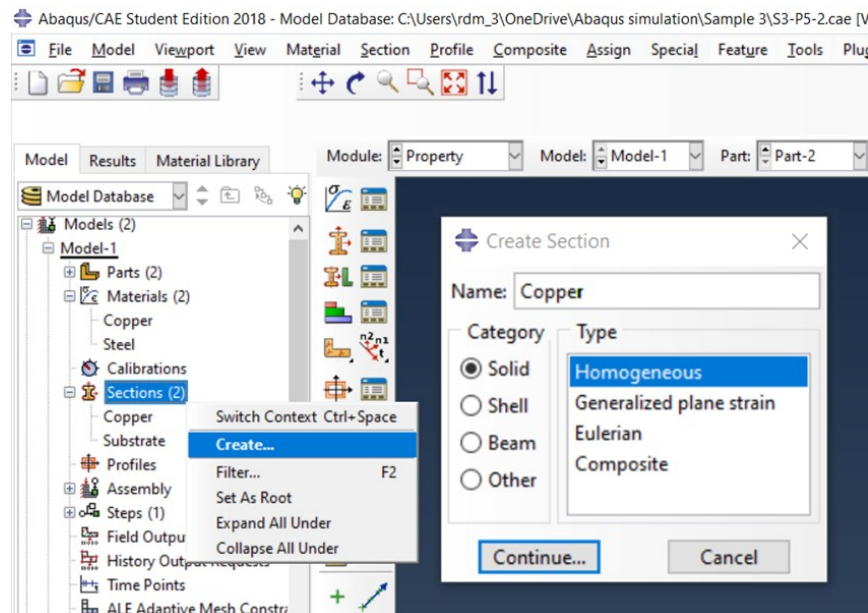


Figure C.19 Abaqus software: create section of each material created.

- 8) Once the sections are created it is necessary to assign them to the appropriate parts. To do that go to the parts section in the model panel and then right click section assignment and click create. The edit section assignment window will appear allowing to configure an appropriate section for each part (shown in **Figure C.20**).

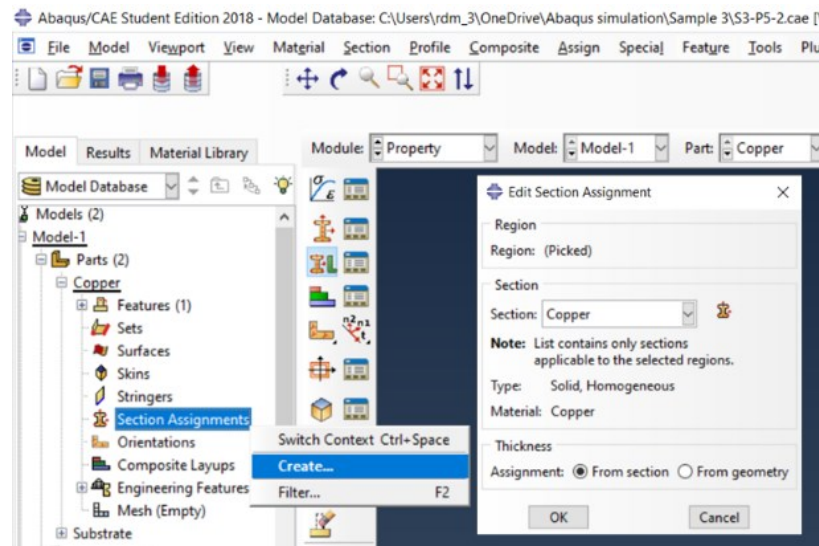


Figure C.20 Abaqus software: section assignments for the part.

- 9) The next step is to create the assembly of both parts (coating and substrate) with the instances option in the assembly section of the model panel, as **Figure C.21** shows. To create it first select one part and then click on "Apply" at the bottom of the create instance window. Then select the "Auto-offset from other instance" option so the next part is not connected to the previously instanced part, the connection between parts needs to match exactly with the profile which will be done in a future step. Finally, select the other part and then apply it. **Figure C.21** shows how the parts were inserted.

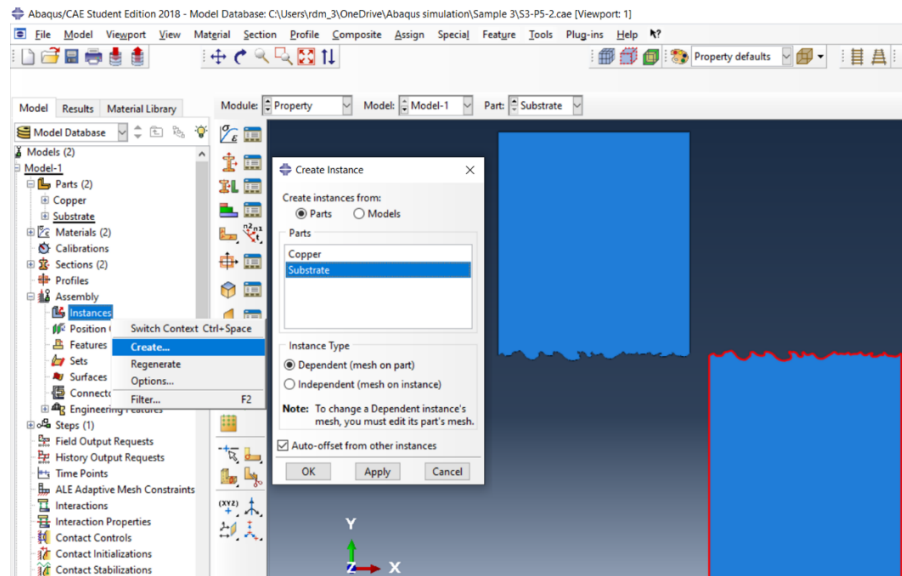


Figure C.21 Abaqus software: Instance create for the parts assembly.

10) **Figure C.22** shows the creation of the surfaces for the profile of one part, to do that the entire profile needs to be selected. This tool is located in the assembly menu and it will be required for a future step. Additionally, **Figure C.22** shows how the profile needs to be selected, one part of the profile that is not selected is circled in the figure. The selection of the entire profile is crucial in this simulation as these surfaces are where the adhesion occurs between the copper coating and the substrate.

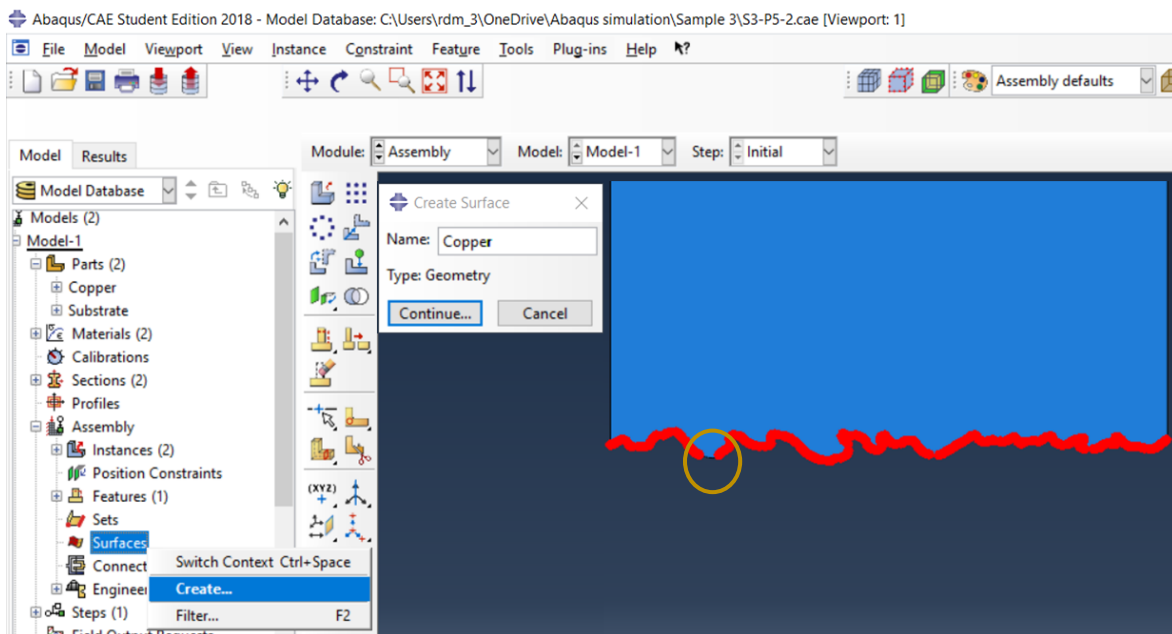


Figure C.22 Abaqus software: surface creation and selection for the parts.

- 11) The next step is to move or translate one of the parts to be connected to the other part. To achieve this the translate option in the instance menu needs to be selected (as shown in **Figure C.23**). The part that is going to move needs to be designated and then select one point of the interface of this part and then select the exact point selected of the interface on the other part in order to have the interface perfectly match.

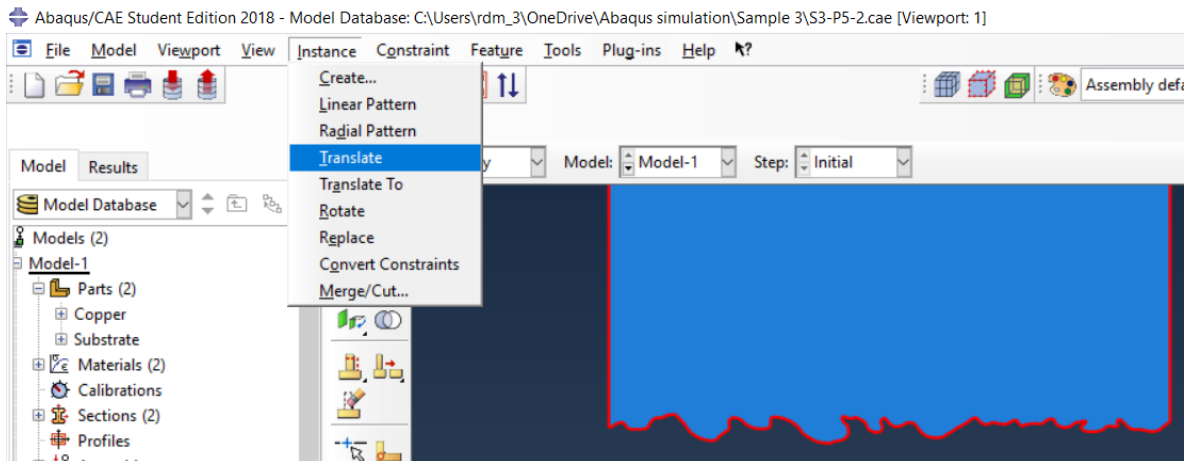


Figure C.23 Abaqus software: translate tool to move the parts.

- 12) **Figure C.24** shows the creation of a simulation step, in this case of this specific simulation the type is Dynamic explicit. The time period in this research is 0.001 seconds.

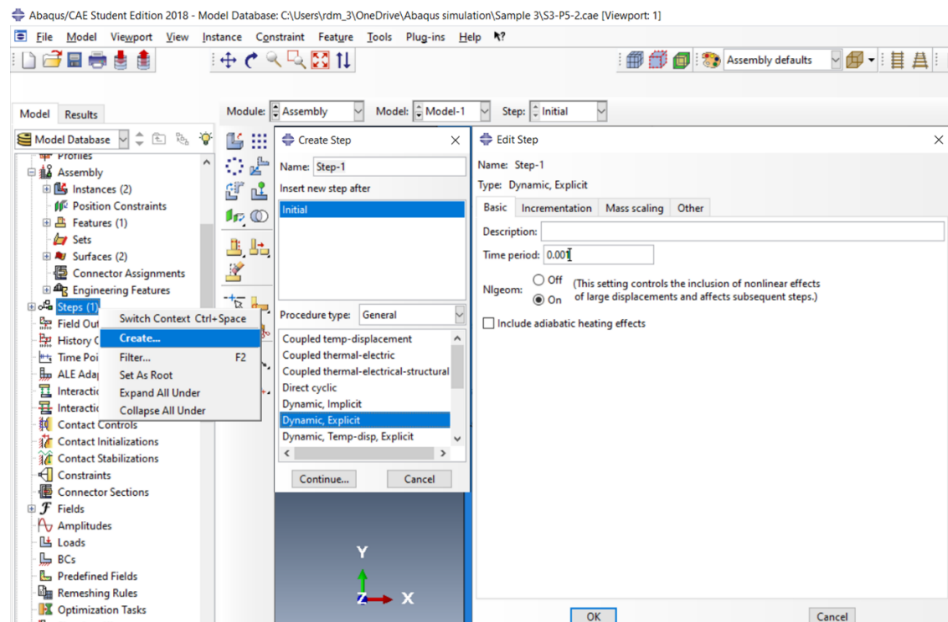


Figure C.24 Abaqus software: Step creation of Dynamic explicit.

- 13) Once the step is created the field/history output request sections are going to be created in the model panel. **Figure C.25** shows that the interval needs to be modified to 100 in the field output request.

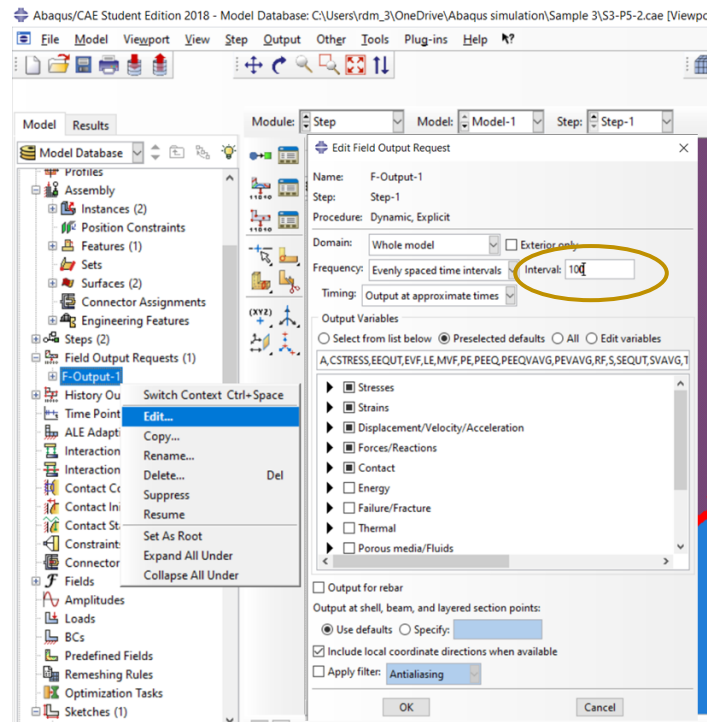


Figure C.25 Abaqus software: field output request edition.

14) Then **Figure C.26** demonstrates the creation of the interaction properties. The type of interaction property is contact and then the options must be modified for the three contact properties. The first option is tangential behavior, with friction formulation set to penalty and the friction coefficient is set to a value of 0.5 based on the simulation by Fernandez et al. [1]. The next property is normal behavior where there are no modifications to the options required. And, the third and last property is heat generation that also required no modifications to the options.

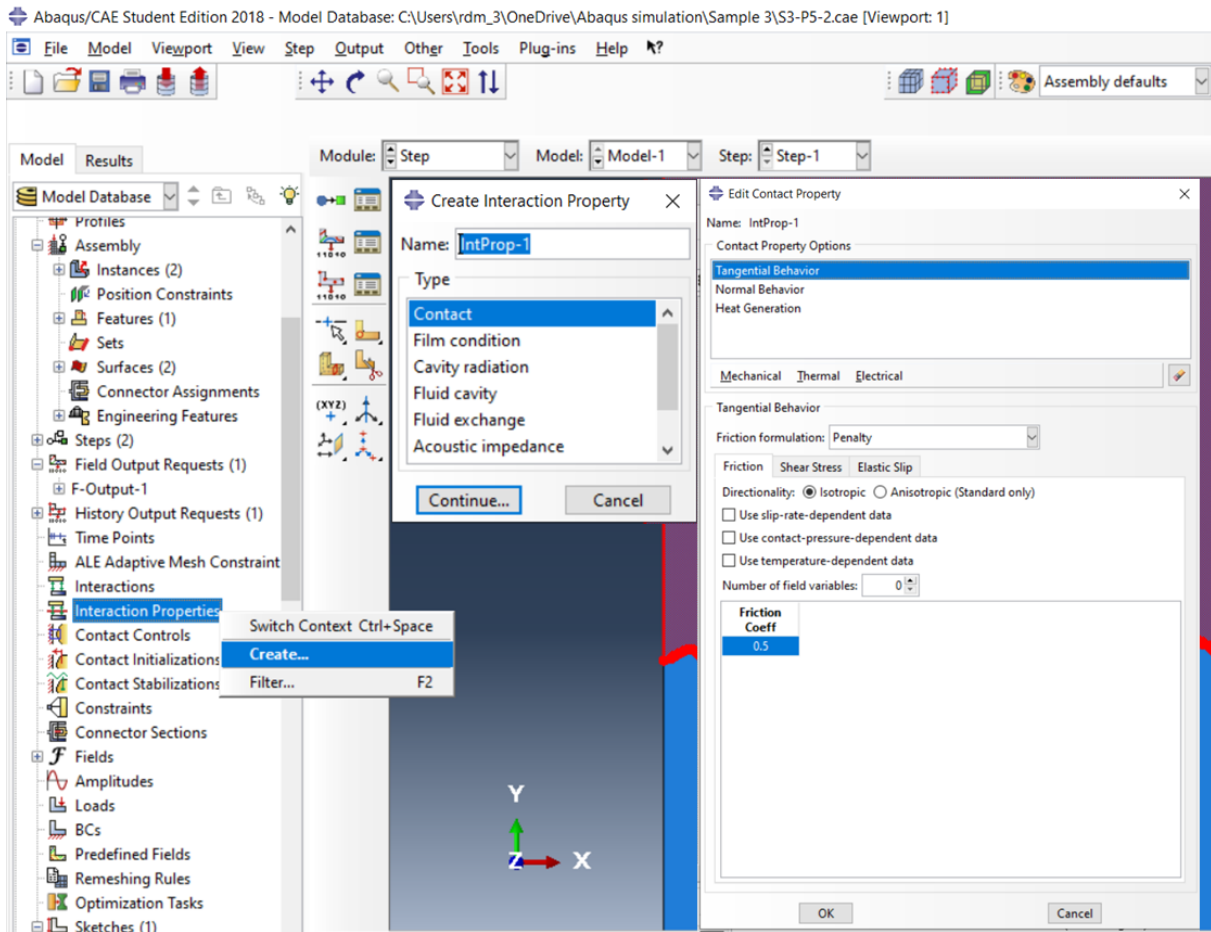


Figure C.26 Abaqus software: Interaction properties, contact type.

- 15) The subsequent step is to create the type of interaction that the step will use. **Figure C.27** shows the creation of the surface-to-surface contact interaction type. First, the contact interaction will be added to the Copper surface (created previously) and then to the Substrate surface.

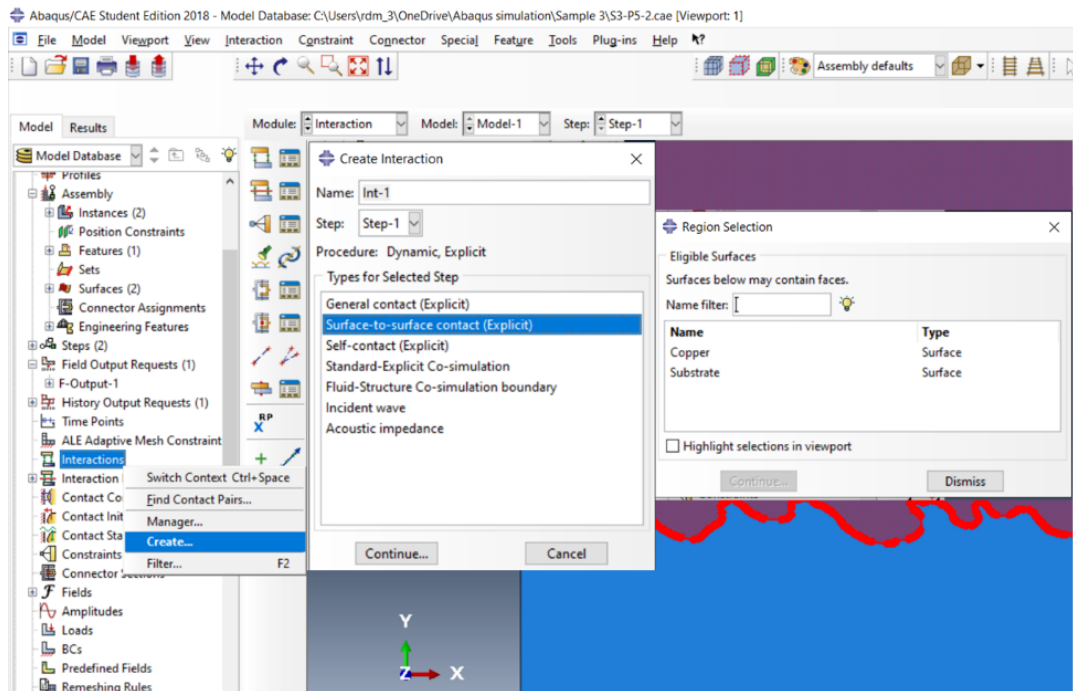


Figure C.27 Abaqus software: interaction surface-to-surface contact (explicit).

Finally, when creating the interaction it is important to select the contact interaction property created in the previous step, this is circled in **Figure C.28**.

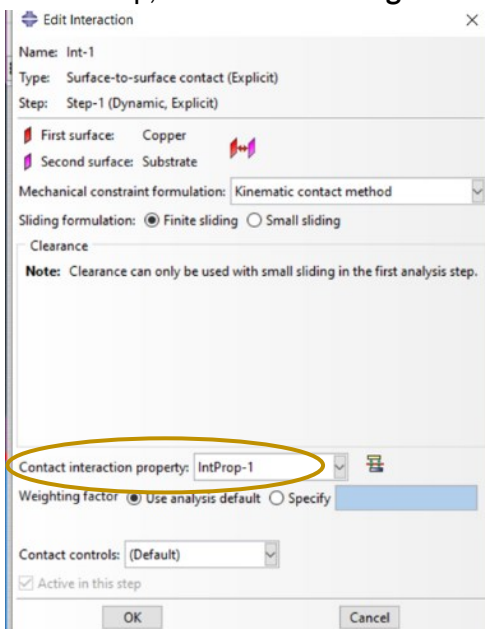


Figure C.28 Abaqus software: edit interaction.

16) Now the boundary conditions are created and are to be generated for the step created previously. All the boundary conditions employed in this simulation are mechanical. The first one is shown in **Figure C.29**, this is a velocity/angular velocity boundary condition for the top of the coating that is moving vertical (y direction) at a speed of 0.02 mm/s as dictated by the ASTM 633-C. The next boundary condition has a type of symmetry/antisymmetric/encastre, this condition will fix the base at the bottom of the substrate using the encastre boundary condition option. And the last boundary condition aims to achieve the objective that the walls of the coating and substrate were constrained only to allow only vertical movement. The type of the last boundary condition is symmetry/antisymmetric/encastre with the option XSYMM ($U_1=U_2=U_3=0$)

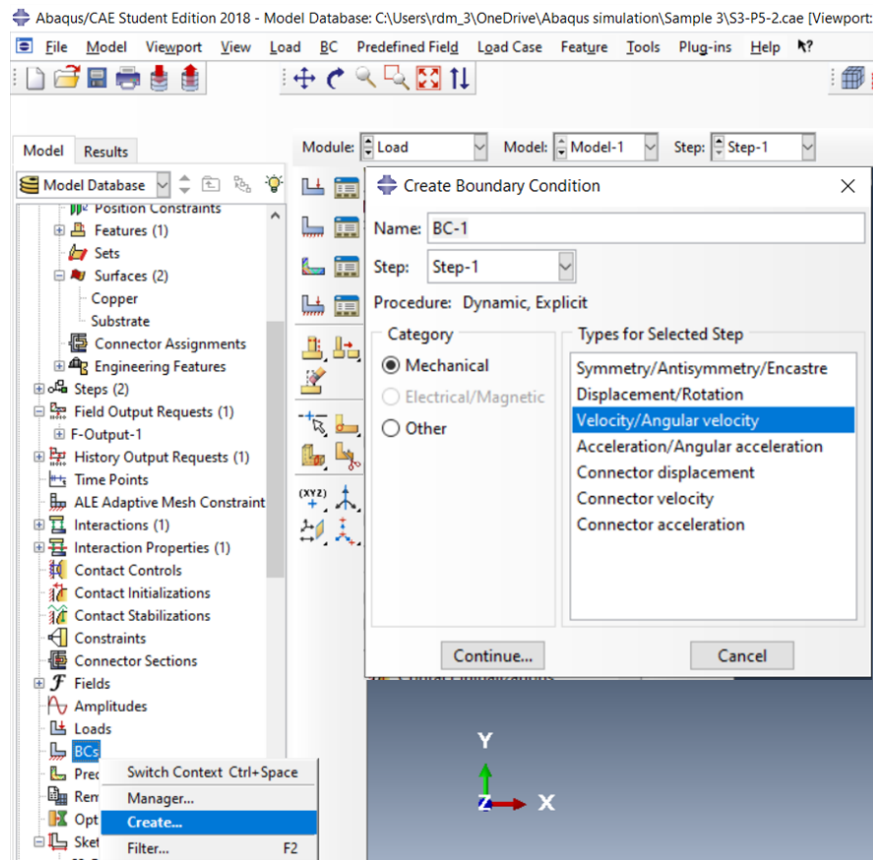


Figure C.29 Abaqus software: mechanical boundaries conditions.

17) The last step of developing the part for the simulation is the creation of predefined fields (show in **Figure C.30**). The first field indicates that the coatings and substrates are assumed to be at room temperature during the simulation.

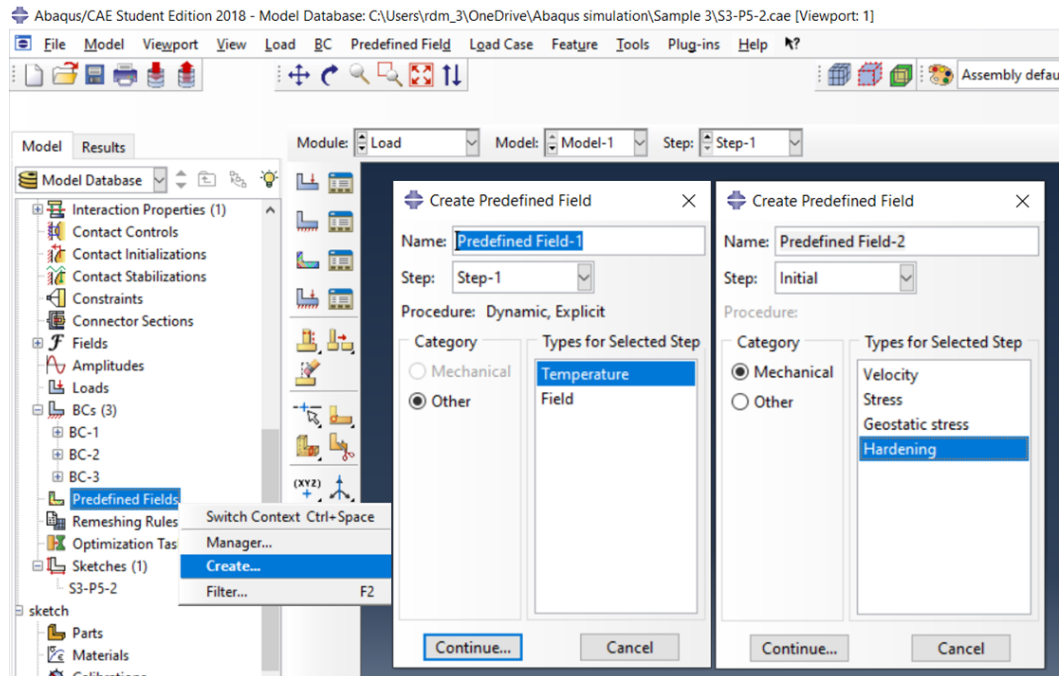


Figure C.30 Abaqus software: predefined fields.

Mesh Procedure

1. The mesh employed in this simulation is a dense mesh for the interface area and a coarser mesh for the rest of the substrate and coating. A quad-dominated mesh (as shown in **Figure C.31**) was used with a four-point strain element type (CPE4R). The element type is explicit with a family of plane strain.

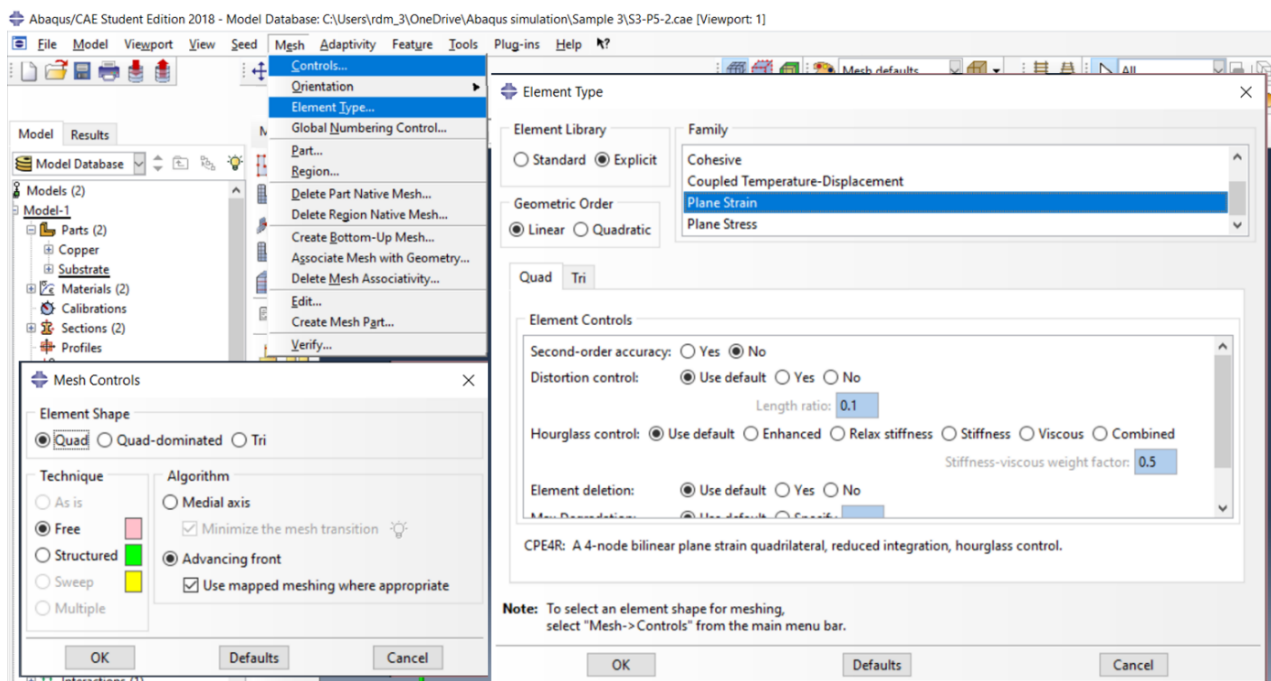


Figure C.31 Abaqus software: Mesh properties.

2. The mesh near to the interface is finer with an approximate size of 0.00075 mm at the interface and coarser as the going to the farther from the interface until 0.01 mm and the second part with a mesh uniform of 0.01 mm size (as shown in Figure C.32).

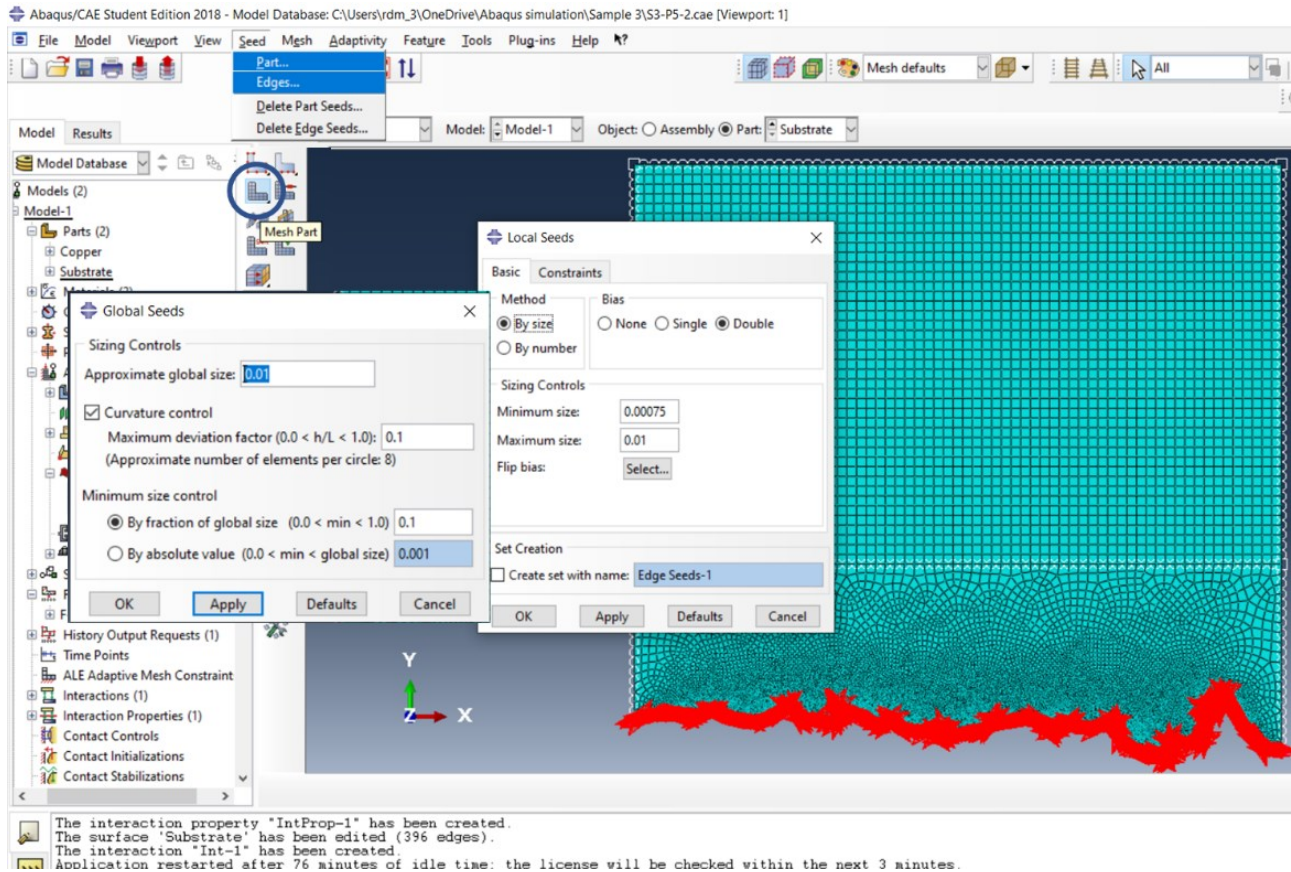


Figure C.32 Abaqus software: mesh part and edges.