

**Enhancing Additive Manufacturing Applications through Fundamental
Studies and Advanced Post-Processing Techniques in Cold Spray
Technology**



uOttawa

by

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Abstract

Over the last decade, considerable effort has been dedicated to the application of cold spray copper coatings. Among those, the significance of the two applications stands out; corrosion protection of used fuel containers for the long-term management of used nuclear fuel and employing copper for its antimicrobial properties. A crucial step in implementing these advancements in specific applications is ensuring that the coatings have the necessary mechanical properties to meet demanding requirements, which depends on selecting the appropriate post-processing method.

The motivation behind this research lies in the expansion of the potential of cold spray copper by introducing techniques aimed at enhancing the coating quality to achieve the desired performance. It is essential to underscore that the quality and consistency of the feedstock powder play an important role in producing homogeneous and uniform coatings. Thus, it is imperative to store and handle this powder meticulously to preserve its quality.

Furthermore, it is of utmost importance to investigate whether the choice of powder characteristics or the storage conditions of the powder have an impact on the spraying process and the resulting coatings. In preparation for the study on the effects of storage, our objective is to establish precise material modeling parameters that will be used in the examination of the storage effect.

Preface

A statement regarding the contributions of myself and my co-authors to each of the articles presented in this thesis submission is provided below.

I am the primary author of the first paper entitled “***Material Model for Predicting Dynamic Response of Copper and Nickel at Very High Strain Rates under Cold Spray Conditions***” alongside Dr. Bertrand Jodoin. I have contributed directly to this article by planning and executing all work found within. Dr. Bertrand Jodoin, my PhD thesis supervisor, guided me through my experimental design and provided insights on my results and discussion. He was also integral in ensuring the quality of the manuscript through his careful review prior to submission.

I am the primary author (leading author) of the second paper entitled “***Bonding Mechanisms in Cold Spray: Influence of Surface Oxidation during Powder Storage***” alongside Dr. Saeed Rahmati, Dr. Alejandro Zúñiga, Dr. Denise Criado, and Dr. Bertrand Jodoin. I have played a direct role in this project by taking responsibility for the planning and execution of all tasks, except for the X-ray photoelectron spectroscopy and finite element model development related to impact and metallic bonding. Dr. Saeed Rahmati contributed by providing the physically based finite element model of impact enabling the prediction of bonding in cold spray coating process. Dr. Alejandro Zúñiga and Dr. Denise Criado contributed by characterizing samples using X-ray photoelectron spectroscopy and providing valuable feedback when interpreting the result. Dr. Bertrand Jodoin, my PhD thesis supervisor, played a crucial role in mentoring me throughout the process of designing my experiments and offered valuable insights during the analysis and discussion of my results. Furthermore, his meticulous review of the manuscript before submission significantly contributed to

its overall quality. It is worth noting that all co-authors of this paper unanimously acknowledge that I was the primary contributor responsible for producing this work, including all aspects of writing, submission, and revision.

I am the primary author of the third paper entitled “***Artificial neural networks approach for hardness prediction of copper cold spray laser heat treated coatings***” alongside Dr. Jean-Gabriel Legoux, Dr. Dominique Poirier, Dr. Bruno Guerreiro, Dr. Jason D Giallonardo, Dr. Bertrand Jodoin. I have made a direct contribution to this project by not only generating all the numerical data but also by designing and implementing the machine learning model. All the deposition and experimental works were performed under the supervision of Dr. Jean-Gabriel Legoux, Dr. Dominique Poirier, and Dr. Bruno Guerreiro at the National Research Council Canada Industrial Materials Institute-NRC Boucherville facility. As the fifth author, Dr. Jason D Giallonardo, along with other contributors, played an essential role in our deliberations on this subject matter. They offered valuable insights that significantly enhanced our comprehension and analysis of the topic, ensuring a high level of quality before our final submission. Dr Bertrand Jodoin, my PhD thesis supervisor, guided me through my experimental design and provided insights on my results and discussion. He was also integral in ensuring the quality of the manuscript through his careful review prior to submission. All co-authors of this paper have agreed that I have been the one to produce this work including all the writing, submission, and revision.

I am primary author of the forth paper entitled “***Biofilm Inhibition and Antiviral Response of Cold Sprayed and Shot Peened Copper Surfaces: Effect of Surface Morphology and Microstructure***” alongside Ms. Mayte Gonzalez, Mr.Naveen Singh, Dr. Cagla Eren Cimenci, Ms. Nicole Chu, Dr. Emilio I Alarcon, Dr. Julio Villafuerte, and Dr. Bertrand Jodoin. I played a direct role in the work

presented by supervising the production of all coatings, in addition to conducting all other experimental and characterization tasks. It's important to note that all the results presented in this work were derived from experiments that I personally carried out. Both the sample production and their subsequent characterization took place at the University of Ottawa's Cold Spray laboratory. Mr. Naveen Singh assisted in conducting the cold spray coating experiments, particularly because these tests necessitated the production of numerous and intricate samples. The biofilm inhibition and antiviral assessments of the created samples were carried out by Ms. Mayte Gonzalez, Dr. Cagla Eren Cimenci, and Ms. Nicole Chu all under the supervision of Dr. Emilio I Alarcon at the certified laboratory within the University of Ottawa Heart Institute. Dr. Julio Villafuerte, is credited as the sixth author among a group of contributors who participated in manuscript preparation and offered valuable insights into result interpretation.

Dr. Jodoin, my thesis supervisor, has guided me on the required tests to be performed. He also provided insights and reviewed the manuscript to ensure quality prior to submission. I am the first author of the paper as all co-authors agreed that I have been the one that has produced all the work and done all the writing, including production of figures, tables, typesetting, submission and review process, of the paper.

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In this acknowledgment section, I would like to express my heartfelt gratitude to Dr. Bertrand Jodoin, my dedicated supervisor, for their unwavering support, invaluable guidance, and unflagging commitment throughout my years of graduate studies. Dr. Bertrand Jodoin's mentorship and exemplary role modeling have not only enhanced my academic journey but also made each project an immensely enjoyable experience. I feel truly fortunate to have had Dr. Bertrand Jodoin as a mentor, and I am deeply thankful for everything they have done to help me succeed.

I also want to take this opportunity to extend my gratitude to my colleagues, whose presence has significantly contributed to the pleasantness of this experience. The spontaneous conversations, shared activities, countless dinners, and the humor we've shared have created cherished memories. Moreover, the invaluable discussions about each other's research projects have enriched the overall experience, making it all the more rewarding and enjoyable.

Acknowledgments are also owed to the skilled technicians from the Department of Mechanical Engineering's machine shop. Their invaluable contributions to the projects, coupled with their remarkable sense of humor, have transformed every visit into a truly worthwhile and enjoyable experience.

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1. INTRODUCTION

1.1 Background

The cold gas dynamic spraying (CGDS) technique, also referred to as cold spray additive manufacturing (CSAM) or simply cold spray (CS), is a solid-state thermal spray process that has traditionally been employed for coatings and dimensional restoration, as well as for repair purposes. Over two decades of fundamental studies [1], [2], [3], [4], [5], [6], [7], [8], [9] have established the theoretical principles of the process, which has led to the development of commercial equipment and applications [10], [11], [12], [13]. While no longer considered a novel thermal spray process for coatings and repairs [14], [15], [16], [17], it is still in its infancy as an additive manufacturing (AM) process [18], [19], [20], [21], [22], [23], [24], [25]. CS could be used for the production of metallic components, taking advantage of the low operating temperatures and large deposition rates possible with CS systems [26]. The CS process also results in high adhesion to the substrate [27], which could be used to fabricate extensions on existing parts. Another advantage of the CS process is components are not limited by tray size like in other AM processes.

High thermal and electrical conductivities of copper along with its corrosion resistance properties made it a material of interest for many applications. Copper has been extensively used for metallization of polymer surfaces for aerospace applications [28], in heat sinks for microelectronics [29], corrosion resistance in harsh urban, industrial, and marine environments [30], and for composites matrix material [31]. The ease of copper deposition through CS, the significant reduction in oxidation during the process because of the absence of high temperatures, and the distinctive microstructure and mechanical properties of the deposit render it particularly appealing for applications involving temperature-sensitive materials and a wide range of other uses [32].

Moreover, the high reflectivity of copper presents a challenge for laser-based additive manufacturing processes. Consequently, CS emerges as a promising alternative for copper AM [33].

On a related note, the resurgence of interest in copper coatings for antimicrobial, antibacterial, and antiviral applications have spurred numerous studies on CS as well [34]. Additionally, the method adopted by many countries for storing used nuclear fuel bundles involves placing them in copper cylinders machined from large ingots to the required size. In Canada, the plan for the long-term and safe management of used nuclear fuel in deep geological repositories is relying on copper-coated steel containers that incorporate a CS copper layer at the closure weld region of the used nuclear fuel containers [35]. This is likely to be one of the most intensive applications of CS technology for a few decades when the project officially starts its production phase.

To create copper coatings using the CS process, specific conditions must be met. In this CS procedure, particles are accelerated within a converging-diverging nozzle to attain a high velocity impact, which must be adequate to disrupt the thin native oxide layer present at the solid interfaces, bringing the two clean surfaces into close contact [36], [37]. The minimum particle velocity at which bonding occurs is known as the critical velocity and is an important parameter in CS [3], [38]. This velocity depends not only on the sprayed material and substrate properties, but also on powder size, morphology, composition, and impact temperature [39], [40]. Extensive experimental and numerical investigations have been undertaken to pinpoint the optimal powder and substrate characteristics required for generating high quality depositions. Given that cold spray impacts occur at very high impact velocities, especially for micron-sized particles, tracking deformation and process alterations using standard experimental equipment poses significant challenges. In cases where such observations are possible, it demands highly sophisticated and costly experimental and imaging procedures that are not readily accessible everywhere [41]. Numerical modeling was found to be a

practical alternative solution to track details of the particle impact and deformation process. It provides an informative insight into the deformation mechanisms and helps the process parameters optimization when the proper material models are used. However, most of the available and frequently used material models suffer from the fact that the tests used to provide the required empirical parameters were performed on bulk material at limited strain rates, much lower than those found in the cold spray process. Developing a proper material model suitable for high strain rate deformation in CS is essential. With the advent of advanced testing techniques such as laser-induced particle impact test, it is possible to study materials mechanics under extremely high deformation rates, i.e., above 10^6 s^{-1} .

As previously discussed, employing the appropriate material model is instrumental in the quest to identify the ideal combination of powder and surface morphologies for achieving a high-quality coating. Once the correct powder characteristics are determined, it becomes the responsibility of powder manufacturers to leverage the suitable process parameters to manufacture such a powder. These processing techniques and parameters exert a considerable influence on powder characteristics, encompassing aspects like morphology, microstructures, elemental composition, and the presence of impurities such as carbon, nitrogen, and oxygen. Among these factors, oxygen content stands out as the most critical element affecting the CS process.

In the context of the cold spray process conditions, it's worth emphasizing that the quality and consistency of feedstock powder are key in producing homogeneous and uniform coatings. This powder must be well-preserved and handled adequately to maintain its quality. It was shown that the properties of a coating are greatly affected by the chemistry of the raw materials [42]. Therefore, it is crucial to investigate the effect of naturally occurring oxides, formed on copper powder due to storage at ambient conditions, on the metallic bonding characteristics in CS.

Given these facts, the primary objectives of this research can be summarized as follows:

1. To address the issue of reduced ductility and increased hardness often observed in cold spray copper coatings. Since conventional oven heat treatments may not be practical for large parts, we aim to explore and develop a laser-based heat treatment method to restore ductility and hardness. This endeavor is challenging due to the lack of available data regarding laser heat treatment and its parameters. To overcome this challenge, we will employ Artificial Neural Networks (ANN) to minimize the need for extensive trials and identify optimal solutions.
2. Prior to applying copper coatings and testing laser heat treatments, it is imperative to determine whether the choice of powder characteristics or the storage conditions of the powder impact the spraying process and resulting coatings. Therefore, our first step involves investigating the storage effect and developing a model to comprehend the influence of storage duration on the metallic bonding process. This is essential to ensure that the laser treatments are applied to well-adhered coatings, thus preventing potential delamination caused by significant thermal gradients during laser treatment.
3. In preparation for the storage effect study, our aim is to establish accurate modeling parameters for the Peston-Tonks-Wallace (PTW) model, which will be applied during the investigation of the storage effect. This is essential since the current use of the JC model is considered suboptimal, and there is uncertainty regarding the adequacy of the existing PTW constants for copper at high strain rate deformation.
4. For the last objective, which has been prompted by the COVID-19 pandemic, we aim to evaluate the performance of copper when exposed to biofilms. Notably, the experimental approach for this objective deviate from conventional practices commonly

employed by other scientists. Instead of merely exposing the copper surface to bacteria and observing survival rates, our focus is on understanding the specific mechanisms through which copper responds to biofilm formation.

1.2 Motivation and Objectives

Over the last decade, considerable effort has been dedicated to the application of CS copper coatings. Among those, the significance of the two applications stands out; corrosion protection of used fuel containers (UFC) for the long-term management of used nuclear fuel and copper for antimicrobial applications. A crucial step into bringing these developments into the sought applications is to confirm the coating's ability to meet the required mechanical properties for this demanding application. The motivation of this work lays in expanding the potential of cold spray copper by introducing methods to improve the coating quality to target the desired performance. To succeed, it's equally important to consider grasping the fundamental facets of the process. This is done by introducing a new material model to predict particle deformation and bonding.

To attain this goal, we put forth the following four objectives.

Table 1: Research objectives and project descriptions.

Study	Title	Research methodology stages
Study I	Material model for copper under extreme impact condition	- Assessing the precision of widely employed copper material models in predicting high-velocity impact deformation. - Refining copper material models through real-time observation of particle impact. - Comprehending bonding and rebound mechanisms in cold spray deposition of copper powder.
Study II	The impact of powder	Exploring the influence of powder storage duration

	storage duration on powder surface chemistry and deposit characteristics	on powder characteristics. • Conducting a thorough analysis of naturally occurring oxides on the powder's outer shell. • Comparative deposition analysis for powders with varying shelf life. • Comparative study of the metallic bond quality for powders with differing surface oxide state. • Finite element model to understand oxide cleanup mechanism at the powder/substrate interface.
Study III	Integrating Laser Heat Treatment for Enhanced Mechanical Properties in Cold Spray Copper Coatings.	• Obtaining copper temperature profiles during the laser heat treatment process via numerical simulations. • Investigating the optimal heat treatment parameters to attain the desired ductility. • Creating an AI-based experimental configuration to establish correlations between ductility and temperature histories.
Study IV	Enhancing Biofilm Inhibition and Antiviral Properties through Surface Texturing of Copper	• Surface texturing of copper using cold spray coating and shot peening process. • Creating an experimental protocol to investigate the improved biofilm inhibition response of copper surfaces. • Gaining insight into the interplay between biofilm and copper ions within the studied samples.

These four objectives outlined are presented in the form of four published manuscripts, all with the same goal of progressing the science and engineering of copper cold spray process. While this study alone may not offer a comprehensive solution to all the complexities associated with cold spray deposition of copper coatings, it plays an essential role within the broader framework of comprehending the entirety of cold spray technology. Each of these objectives serves as a crucial piece in addressing gaps in existing literature.

1.3 Outline of the Thesis

The presented thesis has been formulated in six chapters. The current chapter (**Chapter 1**) provides essential background information for the study, outlines the research's motivation, and articulates its primary objectives."

Chapter 2 offers an extensive review of the CS process, providing insights into its current state of understanding and knowledge. This chapter provides an in-depth examination of current theories regarding adhesion and impact-induced deformation. It clearly delineates the anticipated influence of various parameters on the deposition process. Additionally, it offers a comprehensive review of material deformation mechanisms driven by applied strains, stresses, and strain rates.

In **Chapter 3**, a comprehensive exposition of the primary and specific objectives of this study is provided. It extends the discussion from the literature to elucidate the rationale behind each specific objective, articulating why achieving them contributes to the overarching goal of advancing the field of CS.

In **Chapter 4**, an intricate exploration of the experimental methodology and the research approach is offered. Each study is accompanied by a thorough presentation of essential details, including materials, process equipment, parameters, characterization techniques, and modeling specifics.

Chapter 5 unveils the outcomes and in-depth discussions stemming from each experiment. The chapter is organized into four distinct investigations, each independently tackling a core research objective, all of which have been peer-reviewed and published in reputable journals.

Lastly, in **Chapter 6**, the principal conclusions drawn from each investigation are summarized and interlinked, emphasizing their collective impact on advancing the adoption of cold spray. This chapter also offers insights into potential avenues for future research aimed at enhancing comprehension and advancing CS.

2. LITERATURE REVIEW

This section summarizes the relevant literature on the subject matter. It should provide context of why and how the objectives were chosen, as well as provide a comprehensive base knowledge to understand the approach and significance of each of the studies.

2.1 Cold Spray Process

2.1.1 Background

The cold spray process has been discovered in the 1980's at the Institute of Theoretical and Applied Mechanics in Novosibirsk Russia by A. Papyrin and colleagues [43], [44]. Its deposition and working principles have initially been found and revealed during the experimental and theoretical study of two-phase flow interactions [45]. During their experiments, they observed that as the flow velocity increased, the fine tracer particles in the supersonic flow would no longer erode the body but rather adhere upon impact to the immersed object, which resulted in the discovery of what they referred to as the “cold spray” phenomenon [46]. Following this discovery, work was performed to develop tools and devices capable of accelerating powder particles in a high-pressure gas flow at temperatures well below their melting point in order to form thick and dense coatings on a surface. They successfully deposited a wide range of pure metals, metal alloys, and composites onto a variety of substrate materials and demonstrated the feasibility of cold spray for various applications, which led to the formation of A U.S. patent on the cold spray technology in 1994 and a European one in 1995 [47].

After several years of research and development activities on the topic, many commercial systems have emerged and are now available from many equipment manufacturers in various forms, mainly categorized as low-pressure and high-pressure systems [46] while many in-house systems have been developed and used by various academic laboratories to pursue fundamental and explorative works on

the process [46].

2.1.2 Process Overview

CS process can be divided into two main systems based on the powder material injection location; high pressure cold spray (HPCS) and low pressure cold spray (LPCS). The former utilizes a powder injection located in the converging nozzle part, while the latter injects the powder material into the diverging nozzle section. In both systems, two gas streams enter the de-Laval nozzle. The first, referred to as the carrier gas, passes through a powder feeder after which it becomes loaded with the powder feedstock material. The second stream, referred to as the driving gas, passes at high pressure through a gas heater to reach high stagnation temperatures, then accelerates as it travels through the converging/diverging nozzle to supersonic velocities, by conversion of thermal energy to kinetic energy. Velocities up to 1300 m/s can be reached depending on the nature of the gas and set stagnation parameters.

The general features of the HPCS system are illustrated in Figure 1(a). Due to the axial injection location and to ensure proper flow of the particles, the powder feeder is operated at a pressure which can reach values above 4MPa. The HPCS process design allows for powder preheating in the pre-chamber section, as highlighted in Figure 1(a), prior to its acceleration. The preheating and particle temperature increase originate from heat transfer processes occurring at the hot stagnating gas and particle interface.

In Figure 1(b), illustrating the LPCS system, it is shown that the powder is propelled after the throat in the diverging portion of the nozzle. Generally, nozzle design in LPCS is restricted to a lower range of expansion Mach number, usually below 3 [48]. Since the injection is made inside the supersonic gas flow, the particles accelerate at high rates immediately after entering the nozzle but at the cost of remaining at very low in-flight temperatures. Generally, LPCS systems are more flexible, and the equipment is cheaper than HPCS.

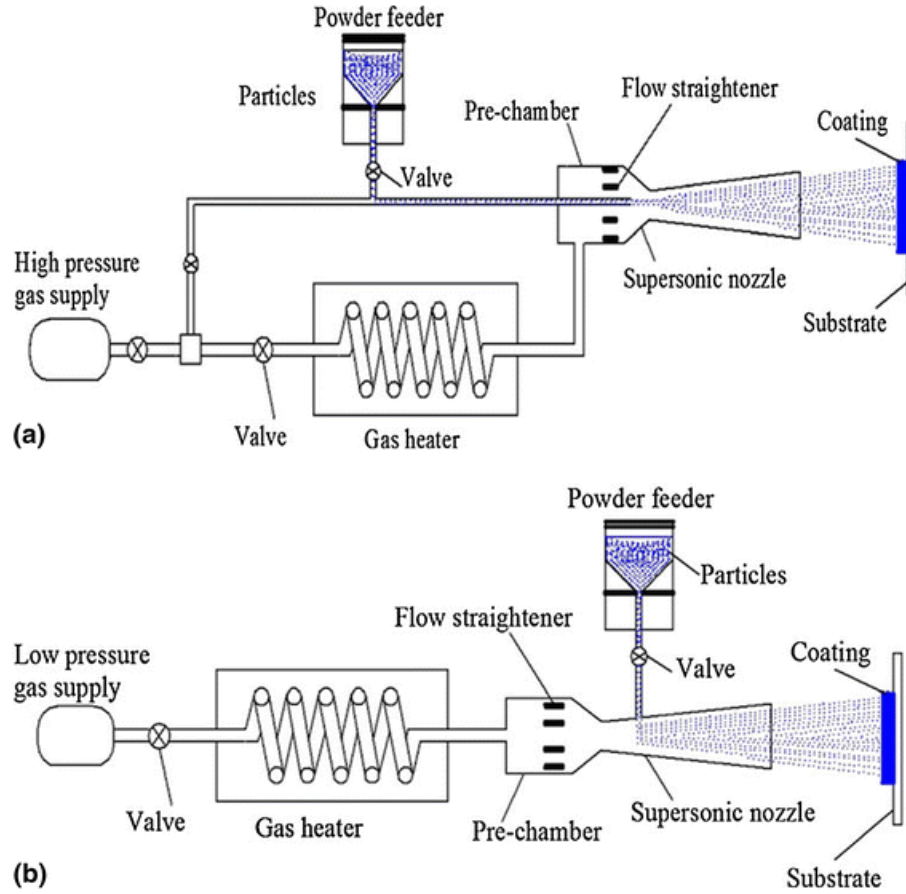


Figure 1: Schematic presentation of CS processes (a) High pressure CGDS system layout with powder injection occurring upstream in the stagnating gas of the converging nozzle section [2] (b) Low pressure CGDS system showing the downstream, in the supersonic flow, powder injection [49].

2.2 Particle Impact Process

2.2.1 Deposition Process

The bonding of particles in CS is known to be the result of extensive plastic deformation and related phenomena at the particle/substrate or particle/particle interfaces. When a particle impacts the substrate, the high kinetic energy of the particle generates extreme plastic deformation reaching strain rates up to 10^9s^{-1} [50], [51]. The plastic energy is almost fully converted into heat, i.e. 90% and more, while the remaining goes into viscoelastic deformation and elastic energy [52], [53]. Figure 2 shows a scanning

electron microscopy (SEM) image of a copper particle deposited onto a copper substrate [54]. As can be seen, severe plastic deformation occurred in both particle and substrate. The deformation process is assumed to be an adiabatic process because it occurs over a very short time in the order of nanoseconds [54]. Therefore, the generated heat during the plastic deformation increases the temperature of the deformed regions locally and results in thermal softening in those areas [50].

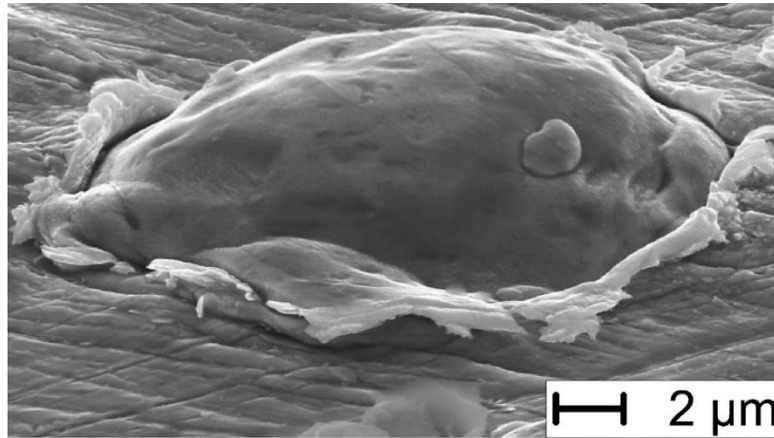


Figure 2: Cold spray impact induced particle microstructural features [55].

Some studies have shown that this temperature rise could even lead to melting in some zones of the particle appearing as ejecta or spheroidal particles as shown in Figure 3 [55], [56], [57]. On the other hand, other studies have reported that the deformation process stays below the melting point, and the deformation is completely a solid-state process [58], [59].

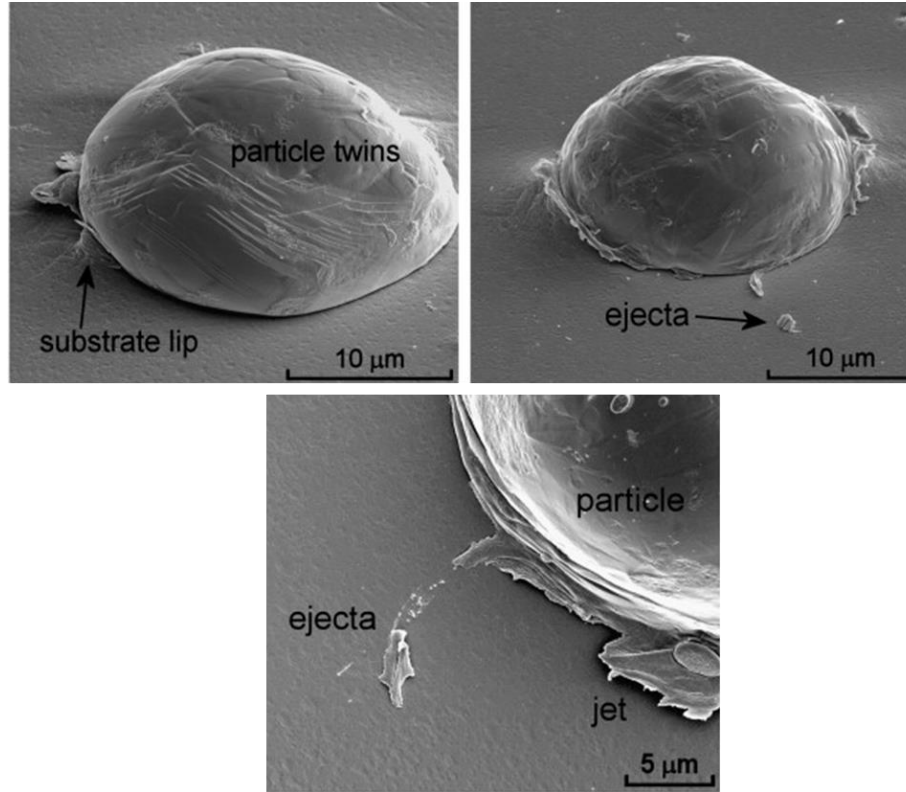


Figure 3: Cold spray impact induced particle microstructural features [55].

2.2.2 Bonding Processes

Material build-up in the CS process relies on the notion of impact-induced features that lead to particle bonding. While the precise deformation processes related to material bonding remain under investigation, several mechanisms have been proposed to elucidate the factors contributing to particle adhesion, including adiabatic shear instability [38], oxide layer breakup [36], localized melting, diffusion [57], interface amorphization and mechanical interlocking [60], [61]. In general, however, it is agreed that two type of adhesion processes lead to particle successful deposition: mechanical and metallic bonding [62]. Other adhesion mechanisms, such as Van der Waals and electrostatic forces, are considered to have limited influence. Analogously, solid diffusion processes are commonly hypothesized to be restricted due to the time frame at which bonding must occur in CS impacts.

Mechanical anchoring is a bonding mechanism in which mechanical interlocking promotes bonding materials at nano/micro scale level [63], [64]. The interlocking bonding can result from extreme impact induced deformations leading to vortex-like interfacial structures, from surface pre-treatments generating a target surface filled with hook-like features and from strong embedment into the substrate [65].

Metallurgical bonding is a chemical bonding and typically stronger than mechanical bonding. This type of bonding requires an intimate contact between oxide-free metallic surfaces at their atomic distances, which can be achieved by applying an appropriate localized pressure [66]. Most metals have an oxide layer on their surface, i.e. in exception of gold, which must be broken and properly ejected for atomic bonding to occur. Numerous studies have suggested that adiabatic shear instability is responsible for removing this oxide layer [51], [54], [67], [68], [69], [70], [71], [72], while some studies have shown that metallic bonding is not related to the occurrence of this phenomenon [73], [74]. In addition, studies have shown that partial melting in the contact region can cause the oxide removal and metallic bonding upon solidification [75], [76]. The direct observation of oxide break-up and surface cleaning process is not possible using current experimental techniques [41]. For this reason, numerical approaches have been largely used to investigate the particle deposition process [77], [78], [79], [80], [81], [82], [83], [84]. Despite all differences in the theories about the oxide layer removal during the deformation, studies agree that the particle requires a minimum impact velocity to adhere to the substrate, i.e. the critical velocity.

2.2.3 Critical Velocity

To ensure bonding, the particles need to reach a so-called critical velocity, upon which at impact the particle experiences all required material deformation and cleaning processes to generate metallurgical

bonding. It is dependent on the particle and substrate materials, particle size, materials temperature [51], [85]. Hassani-Gangaraj et al. [41] adapted the experimental technique proposed by Lee et al. and Veysset et al. [86], [87] to CS to assess precisely the critical velocity of different materials and particle sizes upon impact with polished substrates. Prior to that, several numerical works have been done to evaluate the critical velocity and/or simulate the particle deposition in CS [67], [68], [69], [88], [89], [90], [91], [92], [93], [94]. Assadi et al. [54] showed that metallic bonding can possibly be linked to adiabatic shear instability at the particle/substrate edges. They proposed a semi-empirical equation to predict the critical velocity for different materials. Kurochkin et al. [95] proposed a model based on the activation of the chemical bonds and recoil coefficient to estimate the relative bond strength between the particle and substrate. Wu et al. [96] developed this idea further and showed that the bond strength is related to the particle velocity. In this model, bonding can occur if the adhesion energy is higher than the rebound energy. However, their model lacks the role of the oxide layer and its effects on the metallic bonding, and also the adhesion energy in this model is set as a function of sublimation energy that is potentially different from the energy required to break the bonds between atoms in solid phase.

2.2.4 Microstructure of Cold Spray Coatings

The microstructure of the coating is dependent on the feedstock material, powders' shape, spray conditions, and many other parameters. One of the advantages of CS over other thermal spray processes is the fact that it is a solid-state process. This ensures that the main microstructural features of the sprayed powders remain after the deposition. Consequently, CS allows better control of the coating microstructure. Even though the main microstructure features persist in the coatings, there are still some microstructural evolutions in both particle and the substrate due to the severe plastic deformation that occurs at high strain rates. This rate of deformation causes a high dislocation density in crystalline

materials especially zones surrounding the particle/substrate interface [97].

In Figure 4, EBSD mapping of the cross-section of the as-sprayed nickel coating is presented [97]. This EBSD observations suggest that the formation of ultrafine grains, presented within the particle/particle boundary region is primarily due to dynamic recrystallization during the deformation process [97]. In addition, the average pattern quality value obtained for the center of ultrafine grains was observed to be notably lower than that of the central region of the particles. This discrepancy suggests a relatively higher defect density and/or lattice strain within the ultrafine grains at the bonding regions.

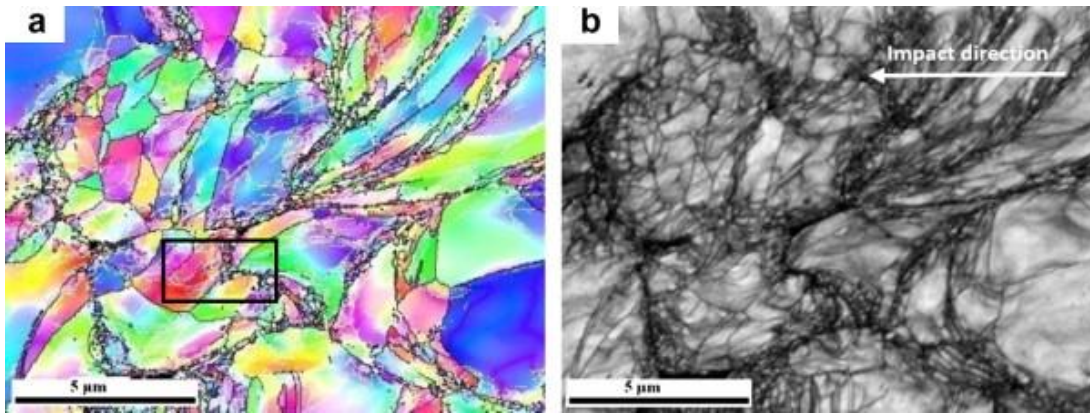


Figure 4: Electron backscattered diffraction (EBSD) characterization of the cross-section of the as-sprayed nickel coating: (a) Euler angle map and (b) pattern quality map of the same area as in (a) [97].

Material plastic behavior during high strain rate deformations and/or severe plastic deformations have been investigated for decades [98], [99], [100]. In high deformation rate processes, in-situ observation of microstructure evolution is a very difficult task to do. Molecular dynamics (MD) simulation is a common method used to investigate the material behavior at the atomic level, especially to model the deformation processes at strain rates higher than 10^6 s^{-1} [101], [102]. Several studies have been performed using MD to capture material behavior at high strain rates [103], [104], [105]. Yaghoobi and Voyiadjis [104] studied the temperature and strain rate effects in FCC and BCC metals and showed that

dislocation interactions is the dominant mechanism in the material hardening. They also indicated that the effects of thermally activated dislocation motion in FCC metals are negligible. In another study, Yaghoobi and Voyiadjis [103] showed that dislocation source length is independent of the system size during the extremely high strain rate deformation processes, and the related size effect mechanisms are not active in these regimes. Furthermore, Hasnaoui et al. [106] studied the interaction between dislocations and grain boundaries and indicated that grain boundaries not only act as a sink for dislocation nucleation, but they can also reflect and/or emit dislocations. Similarly, Zhang et al. [107] explored the grain boundaries migration under shear deformation. They elaborated that grain boundary sliding is caused by local atomic shuffling and dislocation nucleation from grain boundaries. They also found that migration of grain boundaries can be regarded as sliding of grain boundary dislocations and their combination with the boundary plane.

3. RESEARCH OBJECTIVES

3.1 Material Model for Copper under Extreme Impact Condition

In CS, materials experience very high strain rates (10^6 - 10^9 1/s) while their temperature prior to impact is kept below their melting point [108]. Given that the complete deformation process occurs in less than 100 nanoseconds and involves exceptionally tiny particles, monitoring and studying the in-situ evolution of particle deformation becomes exceedingly challenging. Numerical modeling was found to be a practical alternative solution to track details of the impact and deformation process. It provides an informative insight into the deformation mechanisms and helps for process parameters optimization. Many modeling efforts have been conducted over the last decades using finite element method [109], [38], [110], [111], [112], smoothed particle hydrodynamics (SPH) [113], [114], molecular dynamics [115], [116], as well as computational fluid dynamics [117], [118] to study physics of single-particle impact. These studies have led to enhanced understanding of the process fundamentals such as the effect of feedstock and substrate material nature, particle size and morphology [40], driving gas nature and parameters [118], nozzle standoff distance and impact angle [114], [117]. Numerical modeling is also a useful tool to design CGDS nozzles and study particle and flow/nozzle interaction considering different particle injection locations, particle size, and nozzle material [119], [120], [121], [122].

The Johnson-Cook (JC) empirical constitutive model [123] is the most frequently used material model in CS [38], [110], [113], [124], [125]. Nevertheless, the model parameters are typically valid only for the low strain rate regime (up to 10^3 1/s), which means it is not proficient in accurately predicting the stress-strain behavior at high strain rates [111]. The Zerilli and Armstrong (ZA) model, on the other hand, is a physical-based material model based on the dislocation mechanism in FCC and BCC materials [126]. The stress results obtained from this model are in good agreement with the experimental values for strain rates up to 10^3 1/s and low-temperature range [111], [127]. Nevertheless, the

dependence of flow stress on the strain is decoupled from temperature and strain rate for BCC materials, which demonstrate inconsistencies when applied to elevated temperature regime [128], [129], [127]. A modified ZA (MZA) model was proposed for which the coupling effect of strain, strain rate, and temperature of flow stress was integrated [129], [130], [131]. Although this MZA model demonstrates better results particularly at high temperatures, these results are only valid for the relatively low strain rates, up to 10^3 for copper [129]. The Preston–Tonks–Wallace (PTW) model has also been used in CS modeling. It is also a physical-based constitutive model suitable for the inelastic response of the material at very high strain rates, similar to hypervelocity impact [132]. This model accounts for both mechanisms of thermally activated dislocation motion at lower strain rates ($\leq 10^4$ 1/s) [133] and nonlinear drag dominated dislocation motion, predominant in strong shock wave regime (up to 10^{12} 1/s). So far, this material model is known to be one of the best models to predict material plastic behavior at high strain rates [111]. There have been many other empirical and physical-based models developed in the past years [128], [134]. Nevertheless, all these models suffer from the fact that the tests used to provide the ‘parameters’ required for each model were performed on bulk material at strain rates much lower than what is found in CS [135], [136], [137], [138], [139], [140], [141]. Johnson and Cook, for example, used the torsion test and dynamic Hopkinson bar tensile test [135] over a range of strain rates (up to 400 1/s) and temperature to extract the JC model parameters for oxygen-free high conductivity (OFHC) copper, Armco iron and 4340 steel, nickel and eight other materials [123]. The Hopkinson bar technique was also used to evaluate the validity of the mechanical threshold stress model (MTS). The model capability in predicting the material stress state at annealed and pre-strained conditions at low-temperature and strain rates from 0.001 1/s to 5000 1/s was investigated [142]. Lee et al. studied the plastic behavior of Ti–6Al–4V alloy subjected to strain rates from 500 1/s to 3000 1/s under various temperature conditions (room temperature up to 1100°C) using split-Hopkinson bar technique [143].

The test was performed on a 10 mm diameter hot-rolled bar and the results were used to identify the JC material model parameters [143]. The Taylor impact test [144] was conducted on the cylinder shape OFHC copper (99.99%) and Armco iron to derive the ZA material model parameters [126]. PTW parameters [132] were calculated for OFHC annealed (0.9999 Cu) copper with an average grain diameter of 40 μm . A uniaxial compression test was performed to measure the dynamic response of copper under the strain rate spanning from 10^{-4} to 10^4 [137]. To add to the inadequate strain rates tested by these experiments, powder materials used in CS are likely to behave differently than bulk material, and thus even the most suitable plasticity model for high strain rates potentially suffer from improper data taken from bulk material. Furthermore, the strain rate behavior of material at ultra-high impact velocity is reported to be size-dependent [145].

Real-time observation of single-particle impact using laser-induced projectile impact test (LIPIT) [146], [147], [148], [149], [150], [151], [152] has shown potential to extract the high strain rate data required to determine the material models 'parameters' for micron-size particles. These would allow sufficiently precise modeling of impact, rebound, and adhesion phenomena in CS. LIPIT data are more reliable than the data obtained for bulk materials since it represents the real-time response of CS materials under extreme dynamic load and thus yields more accurate data for CS simulation. In the recent work by Wang et al., LIPIT results were used to successfully modify the strain rate-related parameters in JC and ZA titanium strength models to improve their ability to predict particle deformation [153].

This work aims at developing new PTW parameters suitable for high strain rate deformation in CS using LIPIT results for copper and nickel [149], [152]. Accordingly, a series of FEM simulations of single-particle impacts are conducted, and an optimized procedure is applied to develop new PTW parameters for copper and nickel that can reproduce the LIPIT results. The comparison is made based on the coefficient of restitution (CoR); a normalized parameter defined as the ratio of the particle rebound

velocity to the particle impact velocity. It is also shown that the PTW model with improved parameters is also capable of predicting the crater diameter left by rebounded particles. Additionally, experiments and modeling are conducted to explore the bonding mechanism and rebound phenomena of copper powder cold sprayed on low carbon steel substrate.

3.2 The Impact of Powder Storage Duration on Powder Surface Chemistry and Deposit Characteristics

Achieving the proper particle impact velocity in CS is important, as it must be sufficient to disrupt the thin native oxide layer present at the solid interfaces and bring the two clean surfaces in contact [36], [37], [154], [155]. If the deformation level is not sufficient, some debris will remain at the interface and hinder local intimate contact [156], [157], [158]. Comprehensive studies have been conducted aiming to identify ideal powder and substrate properties to produce high-quality depositions. Powder manufacturers use different processing methods and parameters that affect powder characteristics such as morphology, microstructures, element content, and impurities such as carbon, nitrogen, and oxygen, the latter of which is most significant for this study. The quality and consistency of feedstock powder are key in producing homogeneous and uniform coatings in CS. This powder must be well preserved and handled adequately to maintain its quality. It was shown that the properties of a coating are greatly affected by the chemistry of the raw materials [42]. Powder surface oxygen content influences the powder critical velocity and thus the required spray parameters. Studies have shown that as the feedstock powder oxygen content is increased, the critical velocity also increases [156], [159], [160], [161]. In general, oxidation has two deleterious effects on feedstock powder. Firstly, the presence of oxygen in the form of solid solution can cause a loss of ductility due to oxide dispersion and interstitial hardening, reducing the deformation level upon impact [108]. Secondly, the oxide scale at the particle/substrate

interface hinders the formation of particle/substrate bonding during impact [157], [159]. Oxygen in the form of solid solution and oxide film is unfavorable.

The effect of oxidation on the critical velocity for copper, 316L stainless steel, and Monel alloy has already been investigated and the results indicated an increase in critical velocity with an increase in oxygen content [161]. The dependency of the critical velocity on material properties was more dominant at lower oxygen contents. The critical velocity of all the powders reached almost the same value beyond a certain oxidation level [161]. The influence of oxidation on the deposition efficiency (DE) and adhesion strength of CS coatings has also been analyzed. Copper powder was isothermally oxidized at 200°C. The deposition results indicated a drop in the coating adhesion strength and DE when the oxide content increased [156].

All the previous studies demonstrated the important role of oxygen content in the overall CS coating formation at the macroscale. However, the detailed effect of the surface oxidation condition on the quality of interfacial bonding at the individual particle level has not yet been studied thoroughly. Understanding the bonding behavior of individual particles is important for the development of CS technology and the enhancement of particle adhesion strength.

The purpose of this part of the thesis is to investigate the effect of naturally occurring oxides (formed on copper powder due to storage at ambient conditions) on the metallic bonding characteristics in CS. Low carbon steel is selected as the substrate and the bonding characteristics are studied at the individual splat level. Detailed qualitative and quantitative composition analyses of the powder surface before and after room condition oxidation are performed using X-ray photoelectron spectroscopy (XPS). This study provides a comprehensive elemental analysis of the oxide at the powder outer shell and precise measurement of oxide film thickness for micron size particles. This approach provides information used to explain the different deposition behavior of individual copper particles with different shelf time (oxide

layer thickness and composition). Particle interface characterization is conducted using local adhesion test experiments [162]. A physically based finite element modeling method is implemented in the commercially available Finite Element software ABAQUS/Explicit to predict metallic bonding. It is used to explain the bonding requirements as the powder oxide scale increases. This model also further reveals the oxide cleanup mechanism when the soft powder impacts hard substrate at high strain rates.

3.3 Integrating Laser Heat Treatment for Enhanced Mechanical Properties in Cold Spray Copper Coatings

Deposit ductility is a crucial property for most CS applications. In general, as-sprayed CS coatings or parts are brittle as a result of the intense cold working experienced by the feedstock materials during the process. Consequently, they often need to go through post-spray annealing heat treatments to regain ductility [163], [164], [165], [166], [167], [168], [169]. For example, Vo et al. [168] showed that the ductility increased from $0.5 \pm 0.2\%$ in the as-sprayed condition to $34 \pm 3\%$ when CS copper coatings were heat-treated at 600°C for 1 hour. However, such a furnace annealing treatment is unsuitable in several circumstances. For instance, heat treatment of an added CS feature without affecting the remaining component state (heat-treated condition, tightly machined dimensions and/or surface exempt of oxidation) is often desirable but not easy to achieve, while furnace heat treatment of large parts or parts made of dissimilar materials is impractical. To fully benefit from CS advantages as an AM technique, localized heat treatments, such as laser heat treatment, have gained a lot of attention [168], [170], [171], [172]. A conventional furnace annealing treatment is typically a relatively prolonged process: the part is slowly heated up and cooled down to avoid thermal stresses and the hold time at the annealing temperature is long enough to ensure uniform temperature through the part. The exact annealing conditions will depend on the material, desired degree of softening, component shape, furnace load, etc.

For copper, typical annealing temperatures range between 250 to 750°C, while an annealing time of about 1 hour is common [173].

In contrast to conventional furnace heat treatments, lasers provide rapid heating rates and the ability to generate highly specific temperature profiles. Given the need to scan across the entire surface, it is crucial to minimize the dwell time at each area to maintain process efficiency. The local thermal history of the treated part is influenced by various process parameters, including laser spot size, impact angle, energy density, and raster speed. As a result, it becomes challenging to extrapolate suitable laser heat treatment conditions based on conventional furnace heat treatment procedures. Furthermore, the rapid and localized nature of laser heat treatment is likely to yield diverse temperature profiles at distinct locations within the part. These varying temperature histories add complexity to the task of establishing correlations or predicting hardness reductions at each specific location.

Over the last decade, extensive work has been performed for the use of CS copper coatings for corrosion protection of used fuel containers (UFC) for the long-term management of used nuclear fuel [174], [35], [175], [168], [176]. A crucial step to bring these developments into the sought application is to confirm the coating ability to meet the required mechanical properties for this demanding application [177], [178]. Mechanical modelling studies have shown that a coating ductility allowing at least 10% elongation is required [175], [178], [169]. Preliminary trials have shown that a reduction in coating hardness to 66 HV or lower is indicative of restored coating ductility [173].

Laser heat treatment demonstrated promising results to tailor material microstructures and achieve the desired material hardness [179], [180], [181], [182]. By controlling the laser parameters and depending on the nature of the material being heat-treated and its microstructure, the laser heat treatment can be used to increase or decrease the material hardness. For instance, enhanced formability with a minimum strength loss was achieved by local laser heat treatment of steel sheet [179]. Park et al. also showed that

an increased hardness of mild steel can be achieved by high-power laser surface heat treatment [182]. In another work, notable enhancement in wear resistance of titanium alloys was achieved through laser hardening. This improvement was attributed to the reduction in grain size that laser hardening induced [180]. The specimens subjected to laser treatment exhibited significantly higher hardness, as determined by SEM analysis of the fretting surface, in comparison to both untreated and laser-treated specimens. Consequently, their capacity to withstand abrasion, adhesion, oxidation, and plastic deformation was substantially improved [180].

This work aims at developing a tool that allows determining the laser heat treatment conditions that result in desired hardness profile. The physical driving force of hardness reduction in the material is the local thermal history. Laser heat treatment is a complex process in terms of local temperature history and the measurement of temperature profile experimentally is not possible. Thermal modeling of the laser heat treatment process provides the temperature histories at any point inside the coating.

The artificial neural networks model (ANN) is proposed to find the complex correlation between the temperature history and the hardness reduction. This is done by obtaining the local temperature history of a laser-treated CS part through thermal modeling (input in ANN model) and correlating the local hardness profiles measured experimentally (output in ANN model) to the local temperature profile histories.

The ANN, therefore, allows prescribing the proper laser process parameters for the desired hardness reduction.

3.4 Enhancing Biofilm Inhibition and Antiviral Properties through Surface Texturing of Copper

The antimicrobial properties of copper surfaces have been extensively studied [183], [184], [185], [186].

It was shown that exposure to metallic copper can rapidly kill bacteria according to several potential mechanisms [187]. Many studies suggested that copper ions released from the copper surfaces cause a decline in the cell membrane integrity leading to leakage of cell nutrients causing loss of function of proteins [188]. Other studies related the antibacterial activity of copper to its capacity to release ions which function as catalysts in reactions generating reactive oxygen species [189]. DNA damage is also known as a secondary reason causing cell death [190]. The inherent contact killing effectiveness of copper can be further improved by surface modification processes such as cold spray or shot peening. CS generally induces localized grain refinement and dynamic recrystallization of the sprayed material [97], as a result of the accumulation of dislocations during severe plastic deformation. These accumulated dislocations restructure and form sub-grains that eventually turn into ultrafine grains [97], [191]. The improved antibacterial properties of CS copper coating over bulk copper, at the planktonic state, have been explained by the presence of many favorable ion diffusion paths which enhance the surface copper ionic release [34], [192], [193], [194].

The antiviral effectiveness of cold sprayed copper can be improved by using nano-crystalline copper powder [194]. This was attributed to the increased grain boundaries and dislocation densities in the nano-crystalline copper coatings leading to higher ion diffusivity [194]. Surface modification techniques, such as surface nano-crystallization (SNC), can be used to enhance surface ion diffusion by increasing surface dislocation densities and grain refinement. Shot peened surfaces present enhanced antibacterial properties over bulk copper [195].

Several studies have investigated the effects of surface roughness on cell attachment. It has been suggested that surface topography affects the ability of bacteria to adhere to the surface and to develop colonies. In one study, surfaces with similar surface chemistry but different surface roughness exhibited different bacteria retention abilities depending on the size of bacteria used [196]. It was also reported

that high surface roughness improves the antibacterial property of copper by improving its hydrophobicity [197]. As opposed to many studies reporting hydrophobicity in favour of antibacterial effectiveness, others demonstrated higher bacterial adhesion on hydrophobic surfaces compared to hydrophilic surfaces [198], [199], with the mechanism still not understood. A different contact killing mechanism is considered when dealing with nanoscale surface roughness. It was proposed that the contact killing mechanism of nano-textured surfaces was mechanical rupture of cell membrane induced upon contact with the sharp nano-features [200], [201].

Many uncertainties are involved in identifying methodically and separately the effect and mechanisms of surface roughness on the bacterial attachment and inactivation. This makes the problem even more complicated when surface modification/treatment processes involving surface topography modifications also involve grain size modification at surfaces, creating a convoluted situation [202]. Furthermore, examination of the literature [183], [184], [197], [203], [204], [205], [206], [207] on anti-pathogenic properties of copper surfaces reveals that almost all of these studies were focused on antibacterial properties in a planktonic state [183], [184], [197], [203], [204], [205], [206], [207], not as a biofilm [208], [209], [210].

Undesired biofilm represents a significant economic burden regardless of the industry or economic area and is a major threat to public health [211], [212]. The development of biofilms occurs in five stages: Cell attachment, micro-colony formation, biofilm formation, biofilm growth and maturation, and eventually dispersal stage where the bacterial cells depart biofilms and can return to planktonic state [213], [214]. The antibacterial properties of copper are commonly associated with the released copper ions that will cause cell damage [183], [184], [205]. However, the copper interaction with biofilm is significantly different and the action of copper surfaces and copper ions will not only focus on cell interaction but will also interfere with extracellular polymeric secretions (EPS) [215]. It was reported

that exposure to CuO nanoparticles increased the production of loosely bound EPS on wastewater biofilms. These CuO nanoparticles altered the EPS structure and its chemical composition, affecting significantly the functional groups of proteins and polysaccharides of loosely bound EPS [208]. CuO nanoparticles have been found attached to and embedded in an EPS matrix in wastewater biofilm [208]. Developing antimicrobial surfaces with improved anti-biofilm and self-sanitizing performances is a critical task. This can be tailored by first understanding the mechanisms affecting the anti-biofilm response of the surfaces. Further, limited studies also reported the antiviral properties of metallic copper and copper ions [216], [217], [218], [219].

This work aims at understanding the differences in biofilm resistance of bulk copper, cold-sprayed, and shot-peened copper surfaces and identifying the major biofilm control mechanisms. The growth behavior of *P. aeruginosa* biofilm on modified surfaces was compared using stainless steel as a control, due to its prevalent use for touch surfaces. First, biofilm inhibition tests are performed on copper and two types of stainless-steel samples. Then the effect of surface microstructure is presented by a comparison between polished as-received and cold sprayed copper surfaces. Last, the effect of surface roughness on the biofilm inhibition performance of copper is presented using three shot peened samples as a comparison. The role of surface roughness and the grain size is illustrated and mechanisms affecting the biofilm inhibition properties of the surfaces are studied by performing complementary ion measurement tests using inductively coupled plasma optical emission spectroscopy (ICP-OES) [220]. Also, the antiviral performance of the copper cold sprayed and the shot peened samples was also investigated. Using the best biofilm inhibition performance materials, the antiviral performance of these copper samples was compared with bulk copper and control samples using a lentivirus surrogate model of SARS CoV-2.

4. METHODOLOGY and RESEARCH APPROACH

In this chapter, we outline the research approach crafted to achieve the four objectives outlined earlier. Each objective is accompanied by detailed information regarding the materials, experimental configurations, modeling details, and characterization techniques employed.

4.1 Material Model for High Strain Rate Impact in CS Process

4.1.1 Background

The recent development of a new high-speed imaging technique for visualizing CS particle impact allows investigating the particle kinetics in real-time. The laser-induced particle impact test (LIPIT) has been employed to study high-speed impact micro-particle adhesion process [146], [149], [152]. This technique enables the direct analysis of particles individually before impact and provides a precise detail on particle impact/rebound velocities with a precision of $\pm 2\%$ [149]. More details on the experimental procedure are provided in an early study conducted by Veyssset et al. [146], and Hassani et al. [149].

Experimental data obtained from the literature using LIPIT is used for verification/validation of the material strength model. The impact/rebound velocities of copper particles with an average diameter of $12.5 \pm 1.0 \mu\text{m}$ impacting the copper substrate are used for this purpose [152]. The validity of the CoR-fitted PTW model in predicting the substrate crater diameter will also be confirmed using scanning electron microscope (SEM) images of craters reported by Sun et al. [152]. Similar modification steps are carried out for nickel. The LIPIT data reported by Hassani et al. [149] is used for the case of nickel. These LIPIT results contain the CoRs of nickel powder with the average particle size of 10 ± 2 impacting the nickel substrate at various impact velocities. The data are extracted from the referred papers using GetData Graph Digitizer software. Experiments will also be conducted to understand the rebound phenomena in CS of dissimilar materials.

4.1.2 Materials

As-received gas atomized copper powder (Plasma Giken Co. Ltd., Japan) with the native oxide film of 6 nm is selected as feedstock material. This powders with the initial size distribution of 5-53 μm is sieved to a narrower size distribution between 20 μm and 32 μm . SEM (EVO MA-10, Carl Zeiss AG, Oberkochen, Germany) images of loose powder and Zeiss SmartTiffV3 software are used to determine powder size distribution and analyze the powder surface morphology. All powders are mounted and polished for microstructural examination using SEM.

Low carbon steel (ASTM SA516 grade70- 25 mm x 35 mm x 75 mm) is used as substrates to study the powder adhesion/rebound characteristics. The substrates surface is polished mechanically with a 1 μm diamond suspensions to create a mirror finish surface before spraying.

4.1.3 Cold Spray Process

The powder is deposited using a commercially available EP Series SST Cold Spray system (Centerline (Windsor) Ltd. Windsor, Ontario, Canada). Nitrogen is used as propellant gas with the stagnation pressure and temperature of 3.4 MPa and 500°C, respectively. To examine the deformation characteristics of individual impacting particles, the spray conditions are adjusted to achieve a limited number of deposited particles on the substrate. For this purpose, a low feeding rate and a high gun traverse speed (200 mm/s) are used. The nozzle stand-off distance is set as 10 mm.

4.1.4 Particle Impact Velocity Measurement

The powder in-flight velocity is measured using a Cold Spray Meter (CSM) eVOLUTION (Tecnar Automation Ltd, St-Bruno, Canada). CSM is an optical sensing device commonly used in the field of CS to perform an in-flight diagnostic on individual particles that provides complete velocity and size

distribution data. This system uses a continuous 3.3 W laser (CW, Class IV) with an optical two-slit photomask to detect traveling particles. In this study, the velocity measurements were performed at a location 10 mm downstream from the center of the cold spray nozzle exit. Measurements are taken for several minutes to ensure the collection of a robust data set. The data is collected for over 5000 collected data points.

4.1.5 Sample Characterization

The deformation behavior of deposited particles is studied using SEM. Particle interface characterization is conducted using local adhesion test experiments. This method enables the observation of fractured contact surfaces of multiple particles at the same time [162]. To perform the test, a metallic pin is partially adhered to the as-sprayed sample using a thermally cured elastomeric adhesive (FM-1000, Cytec Engineering Materials, with an adhesive strength of 70 MPa). The metallic pin is then pulled off using Pull-off Adhesion Tester (DeFelsko ATA PosiTest Automatic Pull-Off Adhesion Tester), locally removing the adhered particles. The details on the procedure are available elsewhere [162]. Non-adhered particles are collected by locating an adhesive carbon tape in the vicinity of the substrate during deposition and SEM analysis was performed to analyze their deformation. These particles impacted the substrate and bounced-off as their velocity is lower than the critical velocity. These particles are referred to as ‘recovered non-adhered’.

4.1.6 Finite Element Analysis

4.1.6.1 Material Constitutive Model

The plastic response of the material is evaluated using the PTW material constitutive model [132]. This physically-based model has been demonstrated as an ideal model to predict the material yield strength

at both conventional strain rates and overdriven shock regime [111], [112], [221], [222]. The model strain-rate dependence is divided into two distinct regions. In both regions, plastic deformation is governed by the dislocation generation rate and dislocation kinetics.

In the first region i.e. quasi-static regime, material strengthening is controlled by the impediment of dislocation motion (solid solution strengthening, precipitation hardening, and grain boundary strengthening) and creation of additional dislocations by Frank-Read source [223]. In the second region, i.e. shock loading regime, the plastic deformation is dominated by the dislocation generation mechanisms at high strain rates. Dislocations simultaneously nucleate at the shock front and heterogeneously propagate throughout the materials. Dislocation loops are formed and expand into the lattice and can lead to the formation of a cellular structure after multiple cross slip and annihilation mechanisms. However, as strain rate increases, the microstructure changes from cells to stacking faults and eventually to deformation twins [224], [225]. Additionally, dynamic lattice compression is also observed during shock loading [224]. In both regions, material response to the dynamic load is highly influenced by the initial microstructure of the material tested.

The equations defining the PTW model are presented here. These equations are implemented into ABAQUS/Explicit using the VUHARD subroutine [111]. The PTW flow stress is given by a linear Voce hardening law as:

$$\sigma_y(\varepsilon_p, \dot{\varepsilon}_p, T) = \begin{cases} 2 \left[\tau_s + \alpha \ln \left[1 - \varphi \exp \left(-\beta - \frac{\theta \varepsilon_p}{\alpha \varphi} \right) \right] \right] \mu(p, T) & \text{Thermal regime} \\ 2 \tau_s \mu(p, T) & \text{Shock regime} \end{cases} \quad \text{Eq 1}$$

with

$$\alpha = \frac{s_0 - \tau_y}{d} \quad \text{Eq 2}$$

$$\beta = \frac{\tau_s - \tau_y}{\alpha} \quad \text{Eq 3}$$

$$\varphi = \exp(\beta) - 1 \quad \text{Eq 4}$$

where ε_p is the plastic strain, $\dot{\varepsilon}_p$ is the plastic strain rate, T is the temperature, τ_s is a normalized work hardening saturation stress, θ is the hardening constant, d is a dimensionless material parameter, τ_y is normalized yield stress, and s_0 is the value of τ_s at 0 K.

Moreover, $\mu(p, T)$, denotes the shear modulus and is a function of temperature and density of the material. It has been shown that the mechanical threshold stress (MTS) model [137], [226], which is a physically-based model, is capable of predicting the shear modulus for the range of the temperature and strain rates that exist in CS [222]. The MTS shear modulus has the form as:

$$\mu(T) = \mu_0 - \frac{D}{\exp(T_0/T) - 1} \quad \text{Eq 5}$$

Where T is the material temperature, μ_0 is the shear modulus at 0 K, and D and T_0 , are material constants.

τ_s , and τ_y , are defined as:

$$\tau_s = \max \left\{ s_0 - (s_0 - s_\infty) \operatorname{erf} \left[\kappa \hat{T} \ln \left(\frac{\gamma \dot{\xi}}{\dot{\varepsilon}_p} \right) \right], s_0 \left(\frac{\dot{\varepsilon}_p}{\gamma \dot{\xi}} \right)^{s_1} \right\} \quad \text{Eq 6}$$

$$\tau_y = \max \left\{ y_0 - (y_0 - y_\infty) \operatorname{erf} \left[\kappa \hat{T} \ln \left(\frac{\gamma \dot{\xi}}{\dot{\varepsilon}_p} \right) \right], \min \left\{ y_1 \left(\frac{\dot{\varepsilon}_p}{\gamma \dot{\xi}} \right)^{y_2}, s_0 \left(\frac{\dot{\varepsilon}_p}{\gamma \dot{\xi}} \right)^{s_1} \right\} \right\} \quad \text{Eq 7}$$

where $\hat{T} = T/T_m$, T is the temperature and T_m , is the material melting point, s_∞ , is the value of τ_s near the melting point, y_0 , and y_∞ , the value of τ_y at zero and very high temperatures, respectively. Other parameters i.e. $\gamma, \kappa, s_1, y_1, y_2$ are all material constants. Furthermore, $\dot{\xi}$, the reciprocal of the time for a transverse sound wave to cross an atom, is given as

$$\dot{\xi} = \frac{1}{2} \left(\frac{4\pi\rho}{3M} \right)^{\frac{1}{3}} \left(\frac{\mu(\rho, T)}{\rho} \right)^{1/2} \quad \text{Eq 8}$$

where ρ , is the density and M , denotes the atomic mass of the material.

The PTW parameters to be re-calibrated in this work are listed in Table 2. These parameters control the material mechanical behaviors at the strain rates dominant in CS.

Table 2: PTW Parameters to be re-calibrated based on LIPIT data.

Strain rate dependence (γ)
Strain hardening rate (θ)
Medium strain rate (y_1)
Medium strain rate exponent (y_2)
Saturation stress at 0 K (s_0)
Temperature dependence (κ)

Parameters y_1, y_2 determine the stress flow at the intermediate strain rates (approximately 10^3 - 10^7 1/s). In this regime, the mechanism controlling the dislocation motion gradually changes from thermally activated to drag dominated mechanism. At very high strain rates, above 10^8 1/s for example, the plastic flow in metals is controlled by the overdriven shocks. An abrupt increase in stress flow is observed in this regime. The strain rate dependence parameter, γ , defines the dependency of stress to strain rates at high strain rates. The material constant κ describes the dependency of the flow stress to the temperature. The two other parameters, θ, s_0 control the level of work hardening in the material.

Grain sizes in CS powders, as opposed to the bulk materials commonly tested, are small (order of a few microns). For materials with characteristic dimensions of a few microns, the deformation behavior is characterized by the deformation of only a few grains. This leads to the difference in deformation mechanisms compared to bulk counterparts, displaying significantly enhanced strengthening effect [227], [228], [229]. The strength of micron-size polycrystals depends on many factors such as the grain size range, distribution pattern, grain shape, and orientation. It has been known that refining the metals grain size can significantly increase the material yield stress [229], [230] which is estimated using the Hall-Petch equation [231]. Hence, the scale-dependent yield stress and grain size strengthening effect must be assigned to the PTW model parameters to accurately predict the plastic deformation of CS particles. This consideration is included by re-calibrating the θ , and s_0 parameters so that the scale dependency of mechanical properties is integrated into the original PTW model. Besides, grain size can

also affect the strain rate sensitivity of materials under dynamic loading [232]. This is considered by modifying the y_1 , and y_2 values.

4.1.6.2 Details of Modeling Steps

First, the ability of the commonly used material models in CS i.e. JC [123] and original PTW [132] in reproducing the laser-induced projectile impact test (LIPIT) results is evaluated. FEM is used for this purpose and the comparison is made between modeled and experimental CoRs (the ratio of the particle rebound velocity to the particle impact velocity, V_r/V_i). Upon impact, the initial particle kinetic energy is mostly dissipated into heat and plastic work of the particle and substrate, and the remaining is temporarily stored in the form of elastic energy. This recoverable elastic energy is released at the end of the deformation process and causes a reversing of direction of the particle velocity, called rebound velocity. The particle rebound velocity is calculated from simulated rebound kinetic energy knowing the particle mass. The particle impacts the substrate at different initial velocities and the corresponding rebound kinetic energies (and thus rebound velocities) are obtained from the FEM model. This rebound kinetic energy is evaluated when it remains unchanged after particle rebounds, which is nearly 20 ns after the particle detaches from the substrate.

LIPIT experimental CoR are available for copper particles impacting copper substrate with the particle average diameter of $12.5 \pm 1.0 \mu\text{m}$ [152] and nickel particles on nickel substrate, with nickel average particle size of $10 \pm 2 \mu\text{m}$ [149]. Hence, the FEM analysis is conducted for the impact pairs of identical material (Cu-Cu and Ni-Ni) with $12 \mu\text{m}$ powder diameter to be able to validate the model with LIPIT results from the literature.

The PTW parameters for bulk materials available in the literature are summarized in Table 3. The PTW calibration process is conducted by modifying and optimizing the $\gamma, \theta, y_1, y_2, s_0, \kappa$ parameters for

copper and nickel so that the CoR matches the LIPIT results.

Table 3: Original PTW strength model parameters.

PTW parameters	Copper [132]	Nickel [221]	SS 304 [132]
Strain rate dependence constant (γ)	1e-5	1e-5	0.001
Strain hardening rate (θ)	0.025	0.01	0.020
Strain hardening constant (d)	2	2	10
Yield stress constant at 0 K (y_0)	0.0001	0.0001	0.0069
Yield stress constant at melting (y_∞)	0.0001	0.0001	0.0015
Medium strain rate constant (y_1)	0.094	0.094	0.050
Medium strain rate exponent (y_2)	0.575	0.575	0.46
High strain rate exponent (s_1)	0.25	0.25	0.25
Saturation stress at 0 K (s_0)	0.0085	0.0045	0.050
Saturation stress at melting (s_∞)	0.00055	0.00055	0.0075
Temperature dependence constant (κ)	0.11	0.11	0.300
Atomic mass (M), kg	1.055×10^{-25}	9.74627×10^{-26}	9.27×10^{-26}
Shear modulus at 0 K (G_0), GPa	51.8	85.1	85.0
Material constant (D), GPa	3	9.13	10.00
Temperature material constant (T_0), K	165	269	298

The first step in modifying the original PTW model is conducted by calibrating the PTW parameters ($\gamma, \theta, y_1, y_2, s_0, \kappa$) in order for the stress-strain rate curve to better fit the stress-strain rate (SSR) data obtained from bulk material testing. This set of parameters is referred to as the “SSR-fitted PTW model”.

The capability of this set in replicating the CoRs from LIPIT tests will then be investigated.

Next, the PTW parameters are calibrated so that the simulated CoR best fits the LIPIT results (CoRs) and this modified PTW model is called the “CoR-fitted PTW model”. The calibration process aims to include both the effects of characteristic length scale and grain size on the material yield strength and simultaneously satisfy the LIPIT experimental results.

To understand how each of the six selected parameters ($\gamma, \theta, y_1, y_2, s_0, \kappa$) controls the prediction of

flow stress and CoRs (at different particle impact velocities), it is necessary to conduct the sensitivity analysis. For this purpose, each of these parameters is evaluated at different values higher and lower than the original amount reported in Table 3. Then the upper and lower range of each parameter is determined based on the ability in predicting CoR and whether the SSR values are physically reasonable. In order to fulfill the experimental results for all the impact velocities, a combination of parameter values, from the predetermined ranges, are simulated.

The ability of each trial set parameters in predicting the experimental results (CoRs) is evaluated using the mean square error (MSE). The parameter set exhibiting the lowest Mean Squared Error (MSE) value is the one that is chosen as the optimized configuration. MSE is defined as:

$$\text{Mean Square Error (MSE)} = \frac{1}{n} \sum_{i=1}^n (Y_i - \hat{Y}_i)^2 \quad \text{Eq 9}$$

where n is the total number of data points that is the number of initial particle impact velocity simulated. For each data point, Y_i is the CoR value predicted by the simulation. The least-square method is a widely used regression analysis when dealing with statistical data. Herein, we use this method to find the line best fits the LIPIT experimental data (CoRs). $\hat{Y}_i$ is the value of CoR calculated compared with this line.

4.1.6.3 Simulation Setup

To simulate the high-velocity impact of a single particle, an axisymmetric model using the commercially available FEM software ABAQUS/Explicit [233] is implemented. A schematic of the geometry and the mesh contours are provided in Figure 5. The particle diameter is 12 μm and the substrate is modeled as a cylinder with the radius and height five-time larger than particle diameter. The bottom of the substrate is assumed to be constrained in all directions and the axisymmetric boundary condition is considered for the substrate left wall. Both the particle and the substrate initial temperature is set to 298 K. Surface to surface interaction using a penalty contact algorithm with the coefficient of friction of 0.5 is

introduced at the particle/substrate contact surface [234].

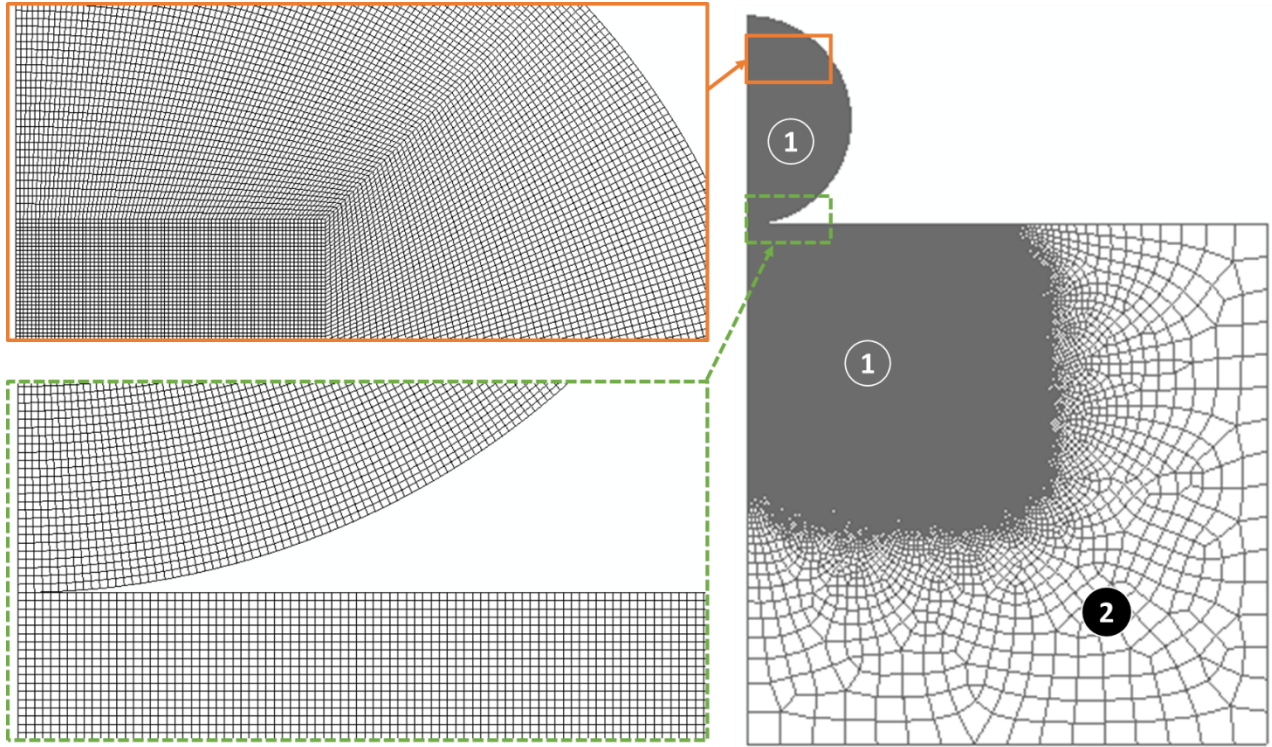


Figure 5: Schematic of the 2D axisymmetric FEM model for the impact simulation. Region 1 is structurally meshed with the element size of $1/100$ of particle diameter and region 2 is free meshed with quadrilateral elements using the advancing front algorithm.

To reduce the severe element distortion due to the large plastic deformation found in CS [234], an Arbitrary Lagrangian-Eulerian (ALE) adaptive mesh method with the 5 re-meshing sweeps per each increment is implemented.

Particle and substrate are meshed with a 4-node bi-linear axisymmetric quadrilateral with reduced integration and hourglass control. The impact region illustrated as region 1 in Figure 5 is structurally meshed with the element size of $1/100$ the radius of the particle. The mesh size of the substrate away from the impact region, region 2, is increased gradually to reduce the computational cost. In this region, free meshing with quadrilateral elements using advancing front algorithm is selected. Mesh study will

also be conducted [112].

The material response in the elastic domain is modeled using a linear Mie-Gruneisen equation of state (EOS) that is frequently used in CS and able to express material pressure accurately at high strain rates [38].

In this work, three different materials, i.e. copper, nickel, and SS 304 is modeled. The calibration process is conducted for identical particle and substrate materials, Cu-Cu, and Ni-Ni. Then, an additional modeling is performed to enhance understanding the bonding/rebound phenomena for dissimilar materials. The copper powder is simulated using CoR-fitted PTW model, impacting on the low carbon steel substrate. In this modeling, the low carbon steel substrate is approximated by the SS 304 PTW parameters, the most similar available material model. The material general properties are listed in Table 4.

Table 4: Material general and elastic properties.

Properties	Copper [111]	Nickel [110], [221]	SS 304 [221]
Density (ρ), kg/m ³	8960	8890	7920
Young's modulus (E), GPa	124	207	200
Poison's ratio (ν)	0.34	0.31	0.3
Thermal conductivity (κ), W/mK	401	91	15
Specific heat (C_p), J/kgK	383	456	450
Shear modulus (G), GPa	45	76	86
Melting temperature (T_m), K	1356	1728	1673
EOS parameters, C_0 (m/s), s , Γ_0	3952, 1.49, 2.01	4650, 1.45, 1.93	4570, 1.49, 1.93

At a very high strain rate, close to 100% of the plastic work is converted to heat [235]. Despite the in-situ temperature change during dynamic loading, the deformation process is assumed to be adiabatic with no heat being transferred [38]. This assumption is also supported by many other experiments performed at very high strain rates [236], [237].

To examine the accuracy of the proposed material model parameters in reproducing the CoRs, a set of

different initial impact velocities is simulated (50-650 m/s for copper and 200-650 m/s for nickel) and the rebound particle velocities are calculated using the rebound kinetic energy of the particle. To ensure the particle is not in contact with the substrate at the end of the simulation, the total impact time is set as 45 ns.

4.2 Understanding the Effect of Particle Native Oxide Scale on CS Process

4.2.1 Materials

As-received gas atomized copper powder (Plasma Giken Co. Ltd., Japan) is used as feedstock material to investigate the effect of powder shelf time on the deposit characteristics. This powder has a purity level of 99.9%, and a diameter size range from 5 μm to 53 μm . The as-received powder is sieved to a narrower size distribution between 20 μm and 32 μm . Part of this powder is kept in vacuum-sealed conditions, labeled as powder type 1. Some of this powder is left at room conditions in a plastic bag (pressure of 1 atm, the relative humidity of 50%, and temperature of 30°C) for a duration of 30 days (labeled powder type 2), and 60 days (labeled powder type 3) respectively.

The exposure of copper to room conditions is expected to lead to the formation of copper oxide layers of different thicknesses and compositions depending on the exposure time. Copper reacting with oxygen forms cuprous oxide (Cu_2O). Higher exposure time results in the formation of cupric oxide (CuO) by further reaction of Cu_2O with oxygen. The oxidation of copper powder is usually limited to a superficial film of a few nanometers in thickness. This native oxide layer acts as a diffusion barrier for oxygen and copper, therefore, the growth rate drops as the oxide layer thickness grows [238].

Low carbon steel (ASTM SA516 grade70- 25 mm x 35 mm x 75 mm) is used as substrates to examine the effect of the powder oxide scale on the deposition characteristics and the interfacial bonding characteristics. The substrates surface is polished mechanically with a 1 μm solution to create a mirror

finish surface before spraying.

4.2.2 Cold Spray Process

The copper powder is deposited using a commercially available EP Series SST Cold Spray system (Centerline (Windsor) Ltd. Windsor, Ontario, Canada). A De-Laval tungsten carbide nozzle having a throat and exit diameters of 2 mm and 6.6 mm respectively along with a diverging section length of 120 mm is used. The spray parameters that are used for the copper deposition are presented in Table 5. To examine the deformation characteristics of individual impacting particles, the spray conditions are adjusted to achieve a limited number of deposited particles on the substrate. For this purpose, a low feeding rate and a high gun traverse speed is used [239], [240].

Table 5: Cold spray processing parameter.

Parameter	Value
Propellant Gas	Nitrogen
Gas Pressure	3.4 MPa
Gas Temperature	500°C
Traverse Speed	200 mm/s
Standoff Distance	10 mm

4.2.3 Powder Characterization

4.2.3.1 Powder Size Distribution and Characteristics

Scanning electron microscopy (SEM) (EVO MA-10, Carl Zeiss AG, Oberkochen, Germany) images of loose powder and Zeiss SmartTiffV3 software is used to determine powder size distribution. A portion of powders will be mounted, polished, and then etched (etchant: 100 ml ethanol, 25 ml hydrochloric acid, and 5 grams ferric chloride) for microstructural examination using SEM.

4.2.3.2 XPS Analysis of Powder Surface

Detailed qualitative and quantitative composition analyses of the powder surface before and after room condition oxidation are performed using X-ray photoelectron spectroscopy (XPS). This analysis provides a comprehensive elemental analysis of the oxide at the powder outer shell and precise measurement of oxide film thickness for micron size particles [241], [242]. The powder samples are analyzed in a ThermoFisher Scientific K-alpha spectrometer (monochromated Al K α X-ray source), using an X-ray beam of 400 μm in size, and charge compensation. Different spectra per powder is analyzed to ensure the consistency of the results. All spectra are charged corrected to fit the adventitious C 1s spectral component to the binding energy of 284.8 eV [241] and is analyzed using a standard Shirley background. See references [241], [242], [243], [244] for calculation details and further in depth explanation. The XPS method provides a proper and direct estimation of the copper oxide film thickness on the powder surface whereas other studies indirectly attribute the entire powder oxygen content to the oxide film. Hassani-Gangaraj et al, for example, used the weight percentage of copper powder and estimated a relative oxide thickness by assuming that the entire oxygen content of the feedstock powder was present at the film layer [150]. This assumption may result in an overestimation of the oxide film thickness. Additionally, the XPS analysis provides extra information that allows studying powder oxide growth as a function of ambient exposure time. For this purpose, the powder oxide shell elemental compositions, as well as oxide film thicknesses, are compared at two different stages: after 30 days of ambient exposure (first stage) and after 30 days following the first stage (second stage).

4.2.3.3 Powders Nano-hardness Measurement

In order to ensure that the presence of oxygen is restricted to the particle outer shell, the nanoindentation hardness measurements are performed on powder cross-sections at room temperature (ASTM E2546).

Powders is mounted in resin and is mechanically polished using a 0.05 μm -diameter diamond solution. An NHT³ Nanoindentation Tester (Anton Paar) equipped with a Berkovich– diamond indenter tip is used. Five different indentations are made for each case. To avoid stress field interference, each indentation is performed on a different particle. The indenter load applied is 15 mN at a loading rate of 30 mN/min.

4.2.3.4 Particle Velocity Measurement

The powders inflight velocity is measured using a ColdSprayMeter (CSM) eVOLUTION (Tecnar Automation Ltd, St-Bruno, Canada). CSM is an optical sensing device used in the field of cold spray to perform an in-flight diagnostic on individual particles which allows complete velocity and size distribution analysis. This system uses a continuous 3.3 W laser (CW, Class IV) with an optical two-slit photomask to detect passing particles. In this study, the velocity measurements is performed at a location 10 mm downstream from the center of the cold spray nozzle exit. Measurements are taken for several minutes to ensure the collection of a robust data set. The data are represented through box and whisker plots for over 5000 collected data points for each type of powder.

4.2.4 Sample Characterization

Deformation behavior of deposited particles is studied using an optical microscope (VHX –1000, Keyence Corporation, Osaka, Japan) and a scanning electron microscope equipped with secondary (SE) and back-scattering electron (BSE) detectors as well as X-ray energy dispersive spectroscopy (EDS).

4.2.4.1 Deposition Efficiency Measurement

To characterize the effect of oxide shell thickness on the powder deposition behavior, DE is measured

as the ratio of adhered particles to the total number of observed impacts (craters and adhered particles). For this purpose, the number of adhered particles and the total number of craters are counted using the Image J processing software. The analysis is conducted for ten separate images per deposit.

4.2.4.2 Metallic Bonding Quantification

To evaluate the interfacial bonding at the particle/substrate interface, a new approach is used to allow observation of fractured contact surfaces [162]. This method provides the feasibility of analyzing multiple individual particles at the same time, without using complex techniques such as focused ion beam, transmission electron microscopes [245], [246], [247], [248], [249], [250], [251] or modified cavitation tests [252].

The experimental setup is illustrated in Figure 6. A thermally cured elastomeric adhesive (FM-1000, Cytec Engineering Materials, with an adhesive strength of 70 MPa) is used. Figure 6 (a) illustrates a metallic pin, which is adhered to the as-sprayed sample. The metallic pin is then pulled off using Pull-off Adhesion Tester (DeFelsko ATA PosiTest Automatic Pull-Off Adhesion Tester), locally removing the particles. Detached particles and the craters left on the substrate are illustrated in Figure 6 (b). Analysis of fractured surfaces at the particle/substrate interfaces enables understanding the effect of oxide films on the quality of metallic bonding. A schematic of a single detached particle is shown in Figure 6 (c).

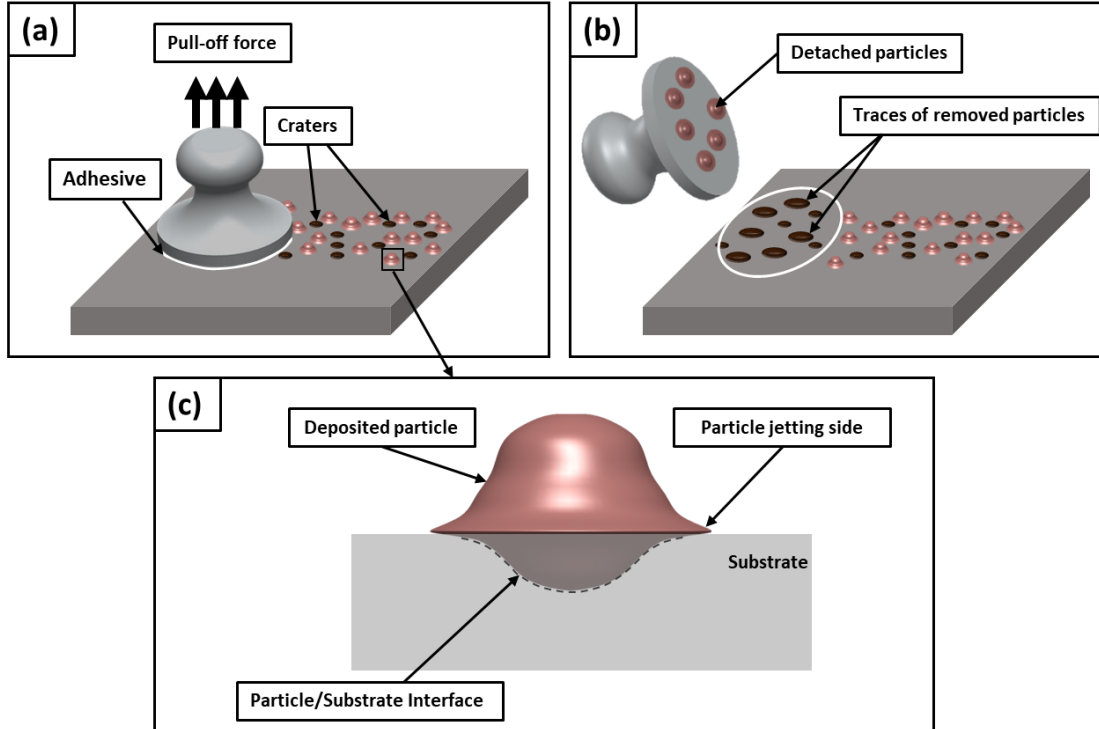


Figure 6: Schematic of the local pull-off test setup, (a) metallic pin glued on the as-sprayed sample, (b) metallic pin was pulled-off and detached particles, as well as the traces of removed particles, are observed (c) Side view of a deposited particle.

4.2.4.3 Numerical Model

To improve the understanding of the role of powder surface oxides on the adhesion mechanism, a numerical model to simulate and predict the adhesion in dissimilar materials when the oxide film thickness increases. For this purpose, the metallic bonding prediction model proposed by Rahmati et al [112] is implemented in the commercially available Finite Element (FE) software ABAQUS/Explicit. In this model, the Preston–Tonks–Wallace (PTW) constitutive model is used, which is also integrated into ABAQUS through a user subroutine (VUHARD). The PTW constitutive model has been shown to be the model providing the most accurate particle deformation prediction at high strain rates (larger than 10^7 s^{-1}) found in cold spray [111], [221].

An axisymmetric geometry is used in the simulation. Particles are assumed to be perfectly spherical with 26 μm diameter, and the substrate geometry is modeled as a cylinder with a radius and height each 5 times larger than the particle diameter.

The particle and substrate materials used for the simulation are copper and stainless steel, respectively. Stainless steel 304 is used due to the lack of available data for 316L for the PTW model. The mechanical and thermal properties of both materials are available [112], [253]. The modeling framework and simulation parameters for this study were described in detail elsewhere [112].

Metallic bonding in CS is modeled based on the bonding theory of the cold-welding process. Based on this theory, bonds at metal surfaces are formed when oxide-free surfaces come into contact. Figure 7 illustrates the joining mechanism of the cold-welding process. Naturally, metallic surfaces are covered by a native oxide film (Figure 7 (a)). This oxide film must be stretched and broken first (Figure 7 (b)). Then enough pressure must remain to extrude the materials into cracks and allow intimate contact, leading to metallic bonding (Figure 7 (c)). In this theory, the bond strength between the two welded surfaces is obtained as follows:

$$\sigma_B = P \cdot \Psi \quad \text{Eq 10}$$

where P is the contact pressure at the interface, and Ψ is the surface expansion factor. The surface expansion factor represents the material deformation extent and surface cleanliness [254], [255]. Ψ is defined as follows:

$$\Psi = \frac{A_1 - A_0}{A_1} \quad \text{Eq 11}$$

where A_0 and A_1 are the initial and the final deformed surface area, respectively (Figure 7).

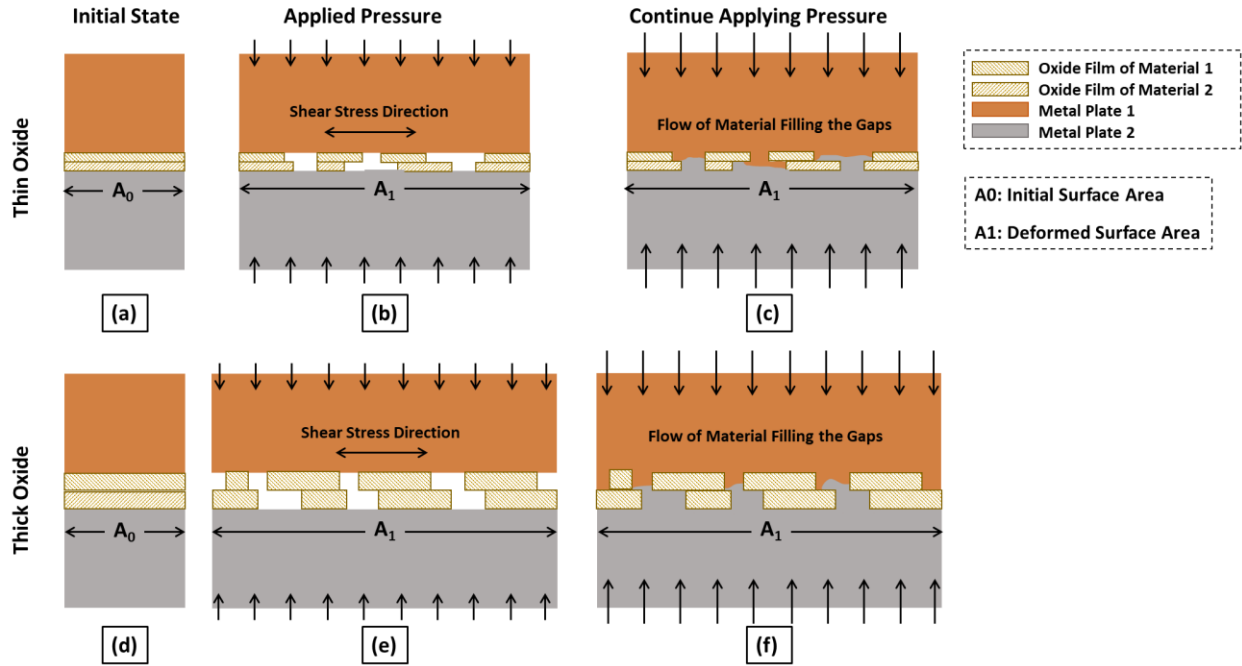


Figure 7: Schematic of joining mechanism in cold welding process proposed by Bay et al. [56, 57], (a) initial state of a plate covered by oxide film, (b) surface expansion and oxide break up due to applied pressure, (c) metallic bonding formation as a result of applied pressure, (d-f) are similar to (a-c) respectively, for the case of a thicker oxide film.

It was experimentally shown that bonding is not achieved unless Ψ reaches a critical surface expansion value, $\Psi_{\min}$ [254], [256]. $\Psi_{\min}$ is the minimum surface expansion required to cause the fracture of the oxide film and create a sufficient gap along the oxide layer. This threshold value, which is dependent on the metal combination and oxide film thickness, ensures a proper surface cleanup [254], [256]. Bay et al. reported $\Psi_{\min}$ values for successful bonding in the cold-welding process for different metallic surfaces [254], [256].

The schematic presented in Figure 7 also compares the key steps for the adhesion mechanism in the surfaces covered by thin (Figure 7 (a-c)) and thick (Figure 7 (d-f)) oxide films. According to Khaledi et al., the minimum surface expansion increases as the oxide layer grows [257], shown in Figure 7 (d-f). The minimum surface expansion values $\Psi_{\min}$ for relevant materials are presented in Table 6. Particles and the substrate are made of copper and stainless steel, respectively. The threshold surface expansion

of 0.44 is used for particle 1, and $\Psi_{\min}$ of 0.6 is approximated for the substrate [254].

Table 6: Minimum surface expansion ($\Psi_{\min}$) values of solid surfaces studied in the modeling.

	PARTICLE 1	PARTICLE 2	SUBSTRATE
MINIMUM SURFACE EXPANSION, $\Psi_{\min}$	0.44	0.6	0.6

Based on Bay et al., the surface expansion value for iron is $\Psi_{\min}=0.6$. Since the literature lacks $\Psi_{\min}$ data for stainless steel, 0.6 is used in this modeling due to the similar nature of these two materials. Also, the oxide film thickness for particle 2 is slightly larger than for particle 1. Although the correlation between $\Psi_{\min}$ and film thickness is not known for particle 2, the data for particle 1 is used to provide an estimation. Therefore, the $\Psi_{\min}$ value for particle 2 is taken as 0.6, slightly higher than that for particle 1.

To implement the proposed bonding mechanism in the FEM modeling, the surface expansion is defined by measuring the strain applied on the contact surfaces. As mentioned previously, an axisymmetric geometry is chosen for this study. In an axisymmetric geometry, the contact surface is modeled by only one edge. The surface expansion at the contact surface is defined by measuring the strain applied on the contact edge. Therefore, Ψ is expressed as [112]:

$$\Psi = 1 - \frac{1}{e^{\varepsilon_r} e^{\varepsilon_\theta}} \quad \text{Eq 12}$$

where ε_r is the logarithmic plastic strain along the element direction obtained by using transformation equations for plane strain (or radial strain), and ε_θ is the logarithmic hoop (or circumferential) plastic strain.

A series of numerical modeling at different impact velocities is conducted to predict the numerically based critical velocity for both particle 1 and 2. For this purpose, the simulation is started at 550 m/s initial impact velocity, and this value is increased by an increment of 20 m/s until evidence of metallic bonding was observed in the model results. The deformation and adhesion mechanism of the particles 1 and 2 will then be studied under the predicted numerically based critical velocity impact velocities.

4.3 Integrating Laser Heat Treatment for Enhanced Mechanical Properties in Cold Spray Copper Coatings

4.3.1 Material

The feedstock material is high purity spherical powder from 5N Plus (Ville St. Laurent, Quebec, Canada). The powder is kept under inert conditions prior to spraying in order to avoid oxidation during storage [258]. Two different powder batches are used (EFF071 and EGK022), with similar particle size distribution, purity and oxygen levels provided in Table 7.

Table 7: Characteristics of the feedstock powder used in the cold spray trials.

	EFF071	EGK022
Particle size distribution (D10, D50, D90) (μm)	17, 31, 52	26, 37, 54
Purity (%)	99.99	99.9
Oxygen (ppm)	140	120

CS copper coatings are deposited on three types of steel substrates: mild steel plates (76.2 mm $\times$ 76.2 mm $\times$ 3.2 mm), ASTM A516 Gr. 70 large plates (152.4 mm $\times$ 152.4 mm $\times$ 38.1 mm) and ASTM A106 Gr. C short cylinders (~610 mm long, ~559 mm outer diameter and ~457 mm inner diameter). The short cylinders are of similar dimensions as the used fuel container prototype developed by the Nuclear Waste Management Organization (NWMO) in Canada, but with a shorter length [176]. This short cylinder

serves as a testing benchmark to assess the potential of an artificial neural network model as a predictive tool for estimating hardness reduction in the component after undergoing laser heat treatment conditions. Depending on the substrate type, different preparation methods are used, either grit blasting (Canablast Model M101P unit with grit 24 alumina) or laser ablation (DRL, Qantel Laser). The former method is used on the plates (small and large size), and the latter is used on the short cylinder. Grit blasting is a standard and easy-to-use method for surface cleaning in CS; however, for the specific application, non-contact cleaning techniques are required. Therefore, the laser ablation technique (DRL laser) is used.

4.3.2 Cold Spray Coating Process

Coatings are sprayed using a PCS-800 CS system (Plasma Giken Co., Yorii-machi, Saitama, Japan). The spray conditions employed in this study were previously fine-tuned to guarantee the formation of dense coatings [169], [171]. These parameters remain consistent throughout the current study: nitrogen is used as the carrier gas at 800°C and 4.9 MPa with a 30 mm standoff distance.

For laser heat treatments, stationary and moving laser configurations are investigated. In the case of the stationary laser test, mild steel is used as a substrate. Gun traverse speed and powder feed rate are 300 mm/s and 85 g/min, respectively. The coatings with a final thickness of around 4 mm are detached from the substrate. These standalone coatings are used for stationary heat treatment tests since the amount of heat input from the laser for these cases is low and heat distribution is local and not influenced by the substrate.

Due to the challenges associated with handling large cylindrical substrates and the cost and time constraints of coating production, smaller coupons are employed during the development of the moving laser cases. These flat coupons are made of steel of grade ASTM A516 Gr. 70. Coating build-up is performed in two sequential steps. The initial step involves enhancing the adhesion of the copper coating

to the steel substrate by applying a bond layer through laser-assisted Cold Spray. This process utilizes a 4kW, 1064 nm wavelength fiber laser sourced from IPG Photonics (Oxford, MA, USA) and operates at a gun traverse speed of 100 mm/s. The powder feed rate is set at ~15 g/min for this first layer [259]. Next, the coating build-up is performed using regular CS to produce 3-4 mm coating thickness. For the second step, the gun traverse speed is set at 300 mm/s, while the powder feed rate is approximately 85 g/min. (Table 8).

Table 8: Substrate type, preparation, roughness, powder lot for the samples prepared for different studied cases.

Case	Substrate type and preparation	Surface roughness prior to spray	Powder lot	Comments
Stationary	Mild steel substrate; grit blasted (grit 24); no laser-assisted adhesion layer	3-6 μm	EFF071	Standalone coating used in laser HT
Moving	ASTM A516 Gr. 70 steel plates; grit blasted (grit 24); laser-assisted adhesion layer	3-6 μm	EFF071	Coating with substrate used in laser HT

The short cylinder plays a crucial role in the prediction and validation study for laser heat treatment. Its surface, composed of ASTM A106 Gr. C. steel grade, is prepared using laser ablation. Subsequently, a laser-assisted CS adhesion layer is applied to facilitate the bond between copper and steel. The copper coating, approximately 4 mm thick, is applied using powder lot EGK022. To simplify the process, the temperature history of a flat plate is used for the cylinder, given that its curvature radius allows for this approximation. Boundary conditions and the number of laser paths are adjusted accordingly to suit the cylinder's geometry.

4.3.3 Coating Characterization

Coatings are sectioned perpendicularly to the spray direction using a coolant-assisted cutting wheel, and subsequently cold-vacuum mounted in an epoxy resin. Afterwards, the resin-mounted samples are

ground and polished using standard techniques. Cross-sections of the coatings are observed using a field emission gun scanning electron microscope Hitachi S-4700 (FEG-SEM).

Micro-hardness measurements are performed on as-polished samples using Clemex MMT-X7B s/n MM6095X micro-hardness tester with a Vickers indenter. All tests are performed using 300 gf loads with 10 s dwell time.

The depth profile of the micro-hardness for the standalone sample for the case of stationary laser heat treatment is measured from the top surface (where laser pulse hits the surface) to the bottom in 300 μm intervals. In addition, lateral micro-hardness measurements are conducted at the average depth of 400 μm with an average interval of 500 μm on both sides of the laser spot.

Similarly, for the moving laser cases, the hardness measurement spots are located at quarter-length and half-length of the laser path at depth intervals of 300 μm from the surface to the coating-substrate interface. Additional measurements are also conducted at lateral locations on both sides of the laser path in some of the moving laser cases to enhance the training data set for the ANN models. The lateral measurements are located at depths of 400 μm , 1500 μm , and 3500 μm from the top surface. The distance between lateral points is approximately 500 μm .

The hardness reduction resulting from the heat treatment is calculated using the following equation:

$$X\% = \frac{HV_0 - HV_i}{HV_0} \times 100 \quad \text{Eq13}$$

where HV_0 is the as-sprayed hardness value (124 HV) and HV_i is the hardness value after laser heat treatment.

4.3.4 Laser Heat Treatment Procedure

Laser heat treatments are performed with a 4kW, 1064 nm wavelength fibre laser from IPG Photonics (Oxford, MA, USA). To enhance copper absorptivity at this wavelength, the coatings are painted black

with high heat enamel (TREMCLAD) aerosol spray. Three different laser heat treatments is performed: stationary laser (used to validate the thermal model), moving laser in an XY fashion (the laser is set on a robot) and moving the laser while rotating the cylinder samples (the laser is set on a robot and the movement of the sample is provided by a rotating table). Further details are given in Table 9.

Table 9: Experimental details for the laser heat treatments.

Case	Laser parameters				
	Robot Speed	Angle	Power	Pulse time	Spot size
Stationary	0 mm/s	45°	1-4 kW	20 – 400 ms	1.8 mm
Moving	18 mm/s; 0 or 2 mm laser step size	10°	4 kW	2.82 s	1.8, 2.5 mm

The standalone coatings used for stationary heat treatment tests are thermally insulated at the back. Sample sides and top are cooled down by natural air convection.

The coupons used in moving laser cases are protected by two L-shape aluminum plates on the side walls to prevent the side walls from being heated by the laser beam. The other sample surfaces are cooled down by natural air convection. Lastly, short cylinders are cooled down by natural convection at the inner and outer surfaces and the side walls.

4.3.5 Thermal Modeling

The coating local temperature history during the laser heat treatment determines the final local microstructural characteristics and mechanical behaviour of the work piece. Once the temperature history is obtained, it can be used to correlate the material hardness to the temperature history.

In the current work, a thermal transient model is used to predict the temperature profile within the copper coating. Commercially available Ansys software (ANSYS , Inc. Product 2020 R2) is used. The

governing equation is derived from the 1st law of thermodynamics, and with the absence of flow in the calculation domain it simply becomes the heat diffusion equation (HDE) [260]:

$$\frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + \dot{q} = \rho c \frac{\partial T}{\partial t} \quad \text{Eq14}$$

where ρ is the material density (kg/m³), c is the specific heat (J/kg.K) and k is the thermal conductivity (W/m.K). In this equation, $\dot{q}$ denotes the rate of internal energy generation per unit volume (W/m³). T is the temperature (K), which is a function of location and time (x,y,z,t).

It is assumed that the material is homogeneous and isotropic and the material physical properties such as thermal conductivity and specific heat are independent of temperature [261]. In addition, there is no source of internal heat generation. Therefore, the HDE for the cases studied here is reduced to:

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad \text{Eq15}$$

where $\alpha = k/\rho c$, is the thermal diffusivity (m²/s).

Initial and boundary conditions must be applied to the equation system in order to get the sought specific solutions. The initial condition assumes a uniform temperature distribution throughout the sample:

$$T(x, y, z, 0) = T_0 \quad \text{Eq16}$$

where T_0 is room temperature taken as 22°C.

The boundary condition at the coating top surface is given by the local energy balance between conduction into the coating, convection to the surrounding air and heat flux from the incoming laser spot as illustrated in Figure 8.

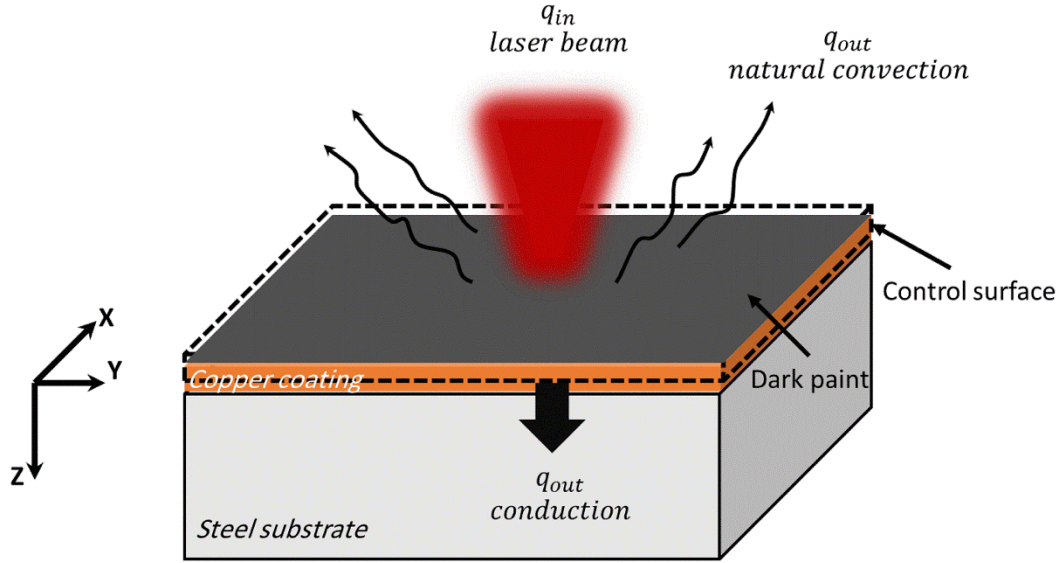


Figure 8: Boundary condition at the coating top surface.

This boundary condition is mathematically expressed as:

$$Q_{laser} = -k \frac{dT}{dz} + h(T - T_0) \quad \text{Eq17}$$

where Q is the laser heat flux (w/m^2), h , is the air natural heat convection coefficient selected as $5 \text{ w/m}^2\text{K}$ [262]. It is assumed that the laser heat treatment will not result in local melting. The boundary conditions on the other surfaces are free convection or insulated depending on the experimental setup used.

4.3.5.1 Gaussian Heat Source

A Gaussian heat distribution is assumed to model the actual heat distribution from the incoming laser beam [263]. This Gaussian heat source model for a laser beam normal to the surface with constant incident power is described by:

$$Q(x, y, z) = \frac{\alpha q}{2\pi\sigma^2} e^{-[\frac{x^2+y^2}{2\sigma^2}]} \quad \text{Eq18}$$

where Q is the laser heat flux (w/m^2), q is the amount of heat introduced by the source (w), and σ is the

Gaussian beam radius. In this equation, α is the beam absorption coefficient, which is a property of the base material. The emissivity of the black paint will be determined experimentally using a controlled heat plate, calibrated infrared camera and thermocouple. X and Y are the position coordinates. The laser beam heat flux distribution is uniform in the x and y directions in a normal laser, and it forms a circular profile.

Due to the potential lens damage caused by beam reflection, the application of normal beam is limited. Accordingly, in this study, a combination of tilted beam angles, one close to normal (10 degree) and the other 45 degree is studied. Therefore, it is necessary to find a transformed Gaussian distribution for the tilted cases.

The schematic in Figure 9(a) shows the Gaussian heat distribution transformation from a normal beam to a tilted beam. Normal beam forms a circular heat distributed profile with the uniform Gaussian distribution in all directions within the circular region in x-y plane. In contrast, heat distribution in tilted beams is not uniform. As seen in Figure 9(a), it forms an ellipse with the heat-affected zone larger in laser front, i.e., y-direction.

For a tilted power source, the Gaussian distribution is expressed as:

$$Q(x, y, z) = \frac{\alpha q \cos(\theta)}{2\pi\sigma^2} e^{-[\frac{x^2 + y^2 \cos^2(\theta)}{2\sigma^2}]} \quad \text{Eq19}$$

where θ is the laser angle with respect to the surface normal.

Figure 9(b) compares the Gaussian heat distribution of a normal beam and a tilted (45 degrees) beam, in x and y-direction. The laser power and step size are 4 kW and 1.8 mm, respectively. As seen, the heat flux distribution is identical in the x and y direction for a normal beam shown with dash line in Figure 9(b). For the tilted beam, the heat flux distribution is different in the x and y direction, with y direction having a larger heat distributed area. Also, the maximum laser heat flux reduces by a factor of $\cos(\theta)$ in tilted laser beam.

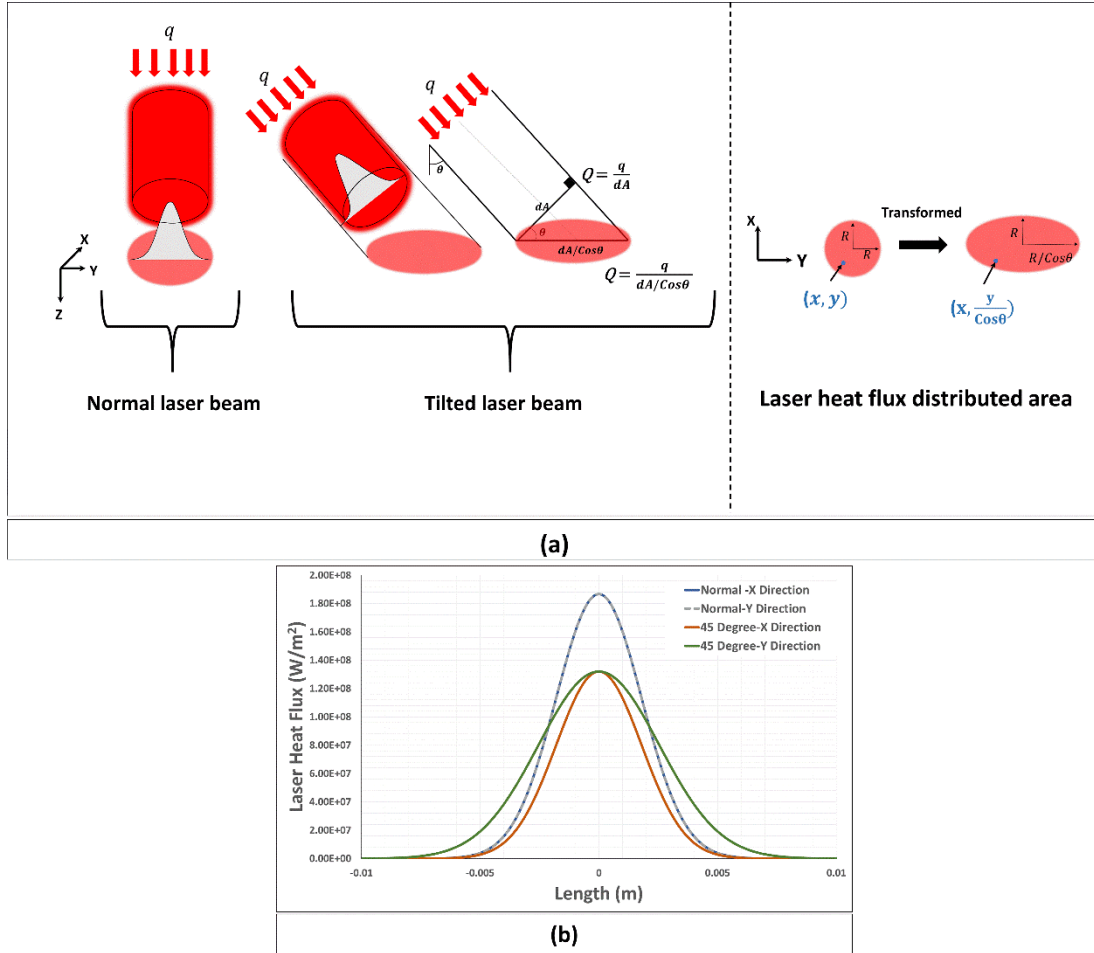


Figure 9: Gaussian heat distribution model (a) schematic showing the Gaussian heat distribution transformation from normal beam to a tilt beam, (b) Gaussian distribution comparison for normal and 45 degree tilted laser with the laser power of 4 kW, and a beam spot size of 1.8 mm.

4.3.5.2 Problem Geometry and Boundary Conditions

Figure 10 illustrates the geometry and boundary conditions for stationary and moving laser cases. The depth and lateral measurement locations are also shown.

As seen in Figure 10, the lateral measurement points are positioned symmetrically with respect to the laser beam location. Therefore, hardness values measured for any two corresponding locations should be equal. For consistency, the hardness measurements are performed for all the lateral points located on

both sides of the laser beam and the average values were used.

Figure 10(a) shows the experimental conditions for the stationary laser tests. The two top images illustrate the experimental setup for the stationary case with the laser beam shown in red and traces left after heat treatment shown with arrows. The 3D schematic illustrates the sample dimensions and boundary conditions. For the stationary tests, the laser beam is tilted at 45 degree. The top and side surfaces are cooled by free convection and the back of the sample is insulated. The 2D schematic is a cross-section at the heat-treated spot with the depth and lateral measurement points presented.

For the moving laser case illustrated in Figure 10(b), the laser was tilted at 10 degrees with respect to the surface normal, as used in the experimental conditions. Free convection is applied on all surfaces. The laser power of 4 kW is used for all the moving cases. A perfect bonding is considered at the copper/steel interface. As illustrated in Figure 10 (b), for the actual experimental setup, L-shape aluminum plates were placed on the sample side walls to ensure the laser beam won't touch the side walls. For the numerical analysis, in order to decrease the computational time, the aluminum plates are not modelled. Our study shows that replacing the effect of heat transfer through aluminum plates with free convection boundary conditions can accurately estimate the actual experimental conditions.

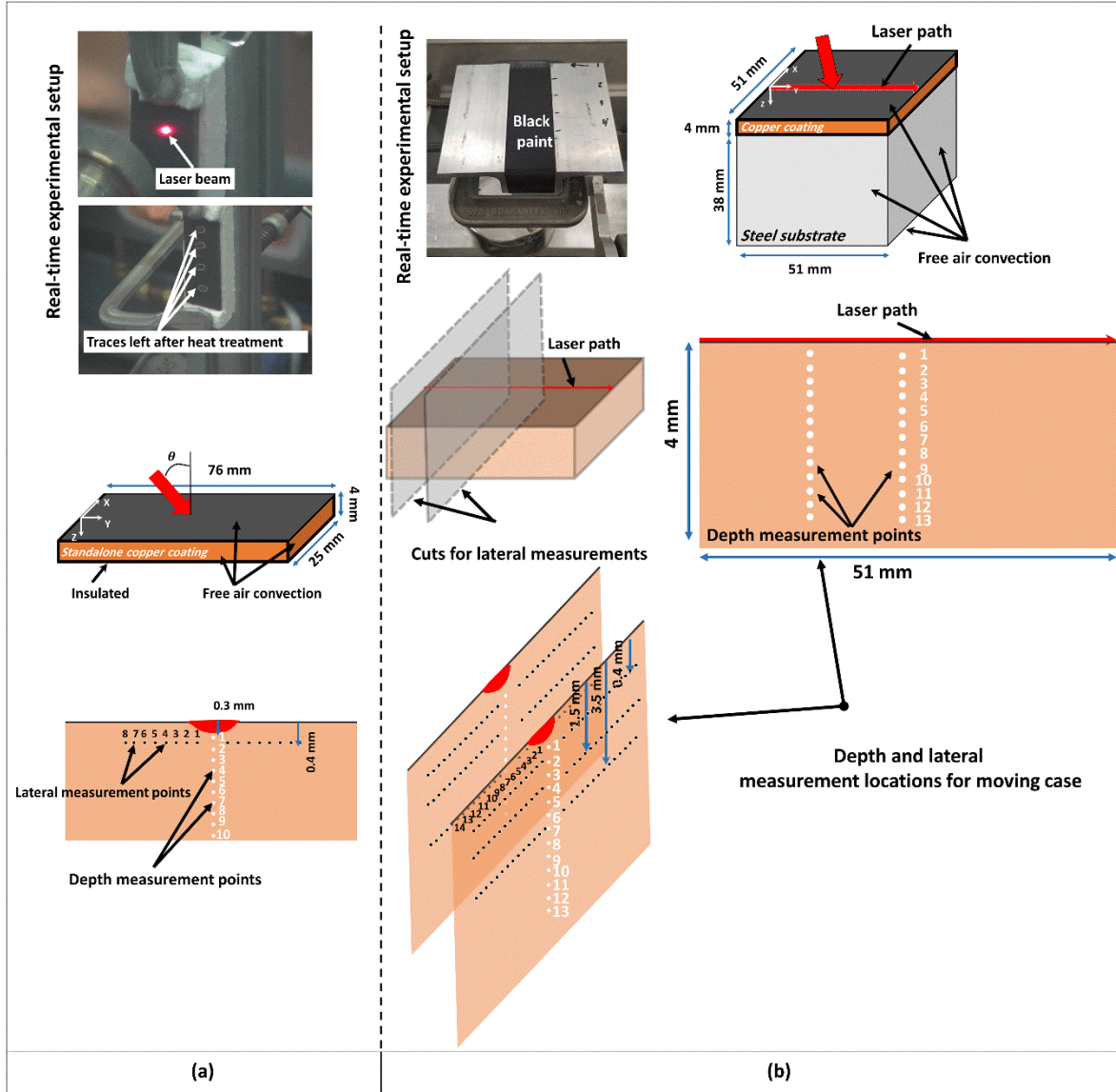


Figure 10: Geometry, dimensions, and measurement locations used for the thermal modelling (a) standalone coating used for stationary laser heat treatment, beam angle 45°, (b) small coupon of copper coating with steel substrate used for moving laser heat treatment, laser beam angle 10°. For moving cases, the laser beam scans the surface one or two times with a step size of 2 mm. Depth points are located 300 μm from the top surface with 300 μm intervals. Lateral points are located at 400 μm from the surface with a 500 μm distance from each other.

For each case, the plate is left to cool down to a temperature below 150°C. This cooling temperature selection is based on the typical minimum annealing temperature in copper [173].

The thermal properties of copper and steel used in this study are provided in Table 10 :

Table 10: Thermal properties for copper and steel used in the simulation [264], [265].

Material	ρ (kg/m ³)	k (W/m.K)	C (J/kg.K)
Copper	8933	400	385
Steel	7800	52	470

The thermal property values provided in the table are the properties of pure copper. The thermal properties of the as-sprayed copper may differ from the pure copper depending on the spray condition used [266]. It has been shown that porosity is the main factor influencing the thermal conductivity of copper coating [267]. In this study, the use of high-pressure cold spray system with high spray parameters results in dense coatings and hence a closer value to the thermal conductivity of bulk copper. Mesh size analysis and time step study is performed to ensure grid and time-step independence of the solution.

4.3.6 Artificial Neural Networks

Artificial neural network (ANN) is an established field in computer science inspired by functional aspects of neurons in the biological brain [268], [269]. This mathematical approach mimics the way the human brain operates. ANNs is used as data mining techniques for regression, clustering, and classification purposes. In general, they bring new insights into the study of complex problems by recognizing underlying patterns from extensive and complicated data. This powerful tool has been successfully utilized in solving a wide range of problems in fields as diverse as engineering, medicine, economics, environment, and finance [270], [268], [271].

4.3.6.1 Foundation of ANN

ANNs consist of independent processors, the neurons. These neurons form a network that is organized

in layers. Neurons in the network are interconnected by several connections called links. The most popular ANN algorithm is the multilayer perceptron (MLP). The architecture structure of an MLP is illustrated in Figure 11(a). In the MLP, the neurons are organized into three layers: one input layer, one or multiple hidden layers, and one output layer. The number of neurons in the input layer represents the number of input variables whereas the output-layer neurons denote the output variables. The neurons in the hidden layer are responsible for recognizing the pattern and storing the data during the training process. Figure 11(b) shows the main elements of a neural network: inputs ($x_1, x_2, \dots, x_n$), outputs ($y_1, y_2, \dots, y_m$), neurons in hidden layer ($h_1, h_2, \dots, h_k$), transfer function (Σ), bias vector (b), and activation function (f). w_{ji} and w_{lj} are weights that are responsible to connect neurons in an ANN model. w_{ji} is the weight connecting the input x_i to j th neuron in the hidden layer (h_j); w_{lj} is the weight connecting the j th neurons in the hidden layer (h_j) to the output y_l .

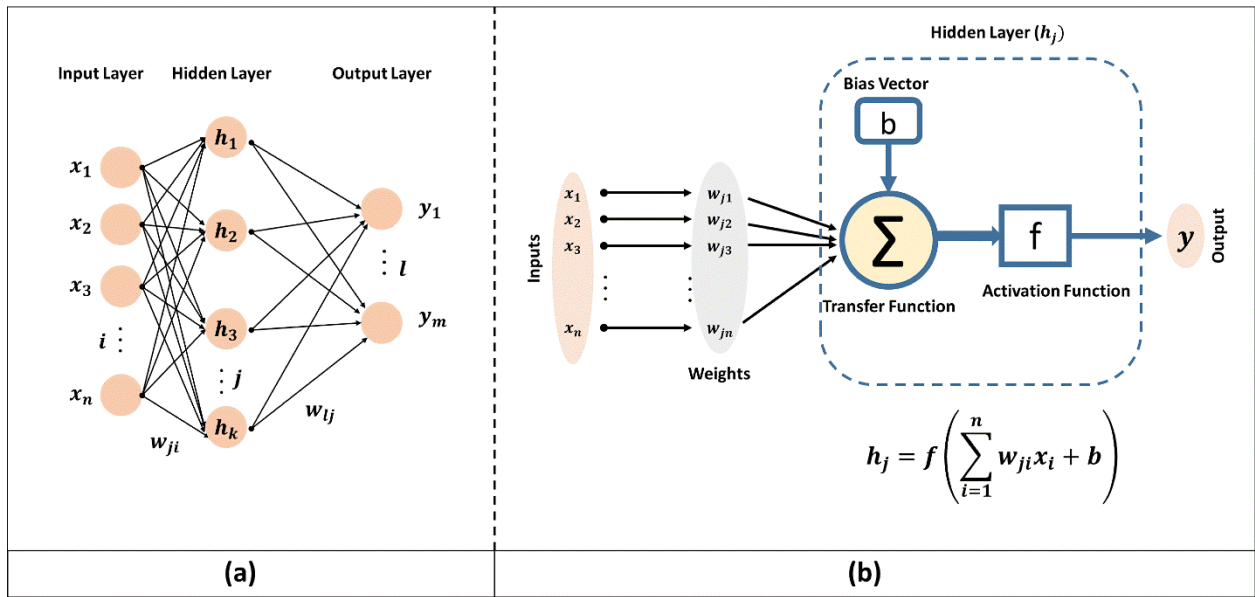


Figure 11: Schematic diagram demonstrates an artificial neural network (ANN) (a) a multilayer perceptron (MLP) with one hidden layer and (b) structure of an ANN for single neurons in hidden layer with one output. In this figure, $x_1, x_2, \dots, x_n$ represent the inputs in the input layer, $y_1, y_2, \dots, y_m$ are outputs in output layer, and $h_1, h_2, \dots, h_k$ are the neurons in hidden layer. n, k , and m are the number of neurons in input layer, hidden layer and output layer, respectively. w_{ji} is the weight connecting the input x_i to j th neuron in the hidden layer (h_j); w_{lj} is the weight connecting the j th neurons in hidden layer (h_j) to the output y_l . In the hidden layer in an ANN model, b is bias vector, Σ denotes for transfer function, and f is activation function.

The mathematical representation of the connection in these elements is described as follows [272]:

$$h_j = f(\sum_{i=1}^n w_{ji}x_i + b_j) \quad \text{Eq20}$$

$$y_l = f(\sum_{j=1}^n w_{lj}h_j + b_l) \quad \text{Eq21}$$

The activation function, f , is fixed for each neuron and it can be either a nonlinear or linear function of its activation value [273]. Three common activation functions that are usually used are the sigmoid function, hyperbolic tangent functions, and rectified linear activation function (or ReLU) functions. These functions are described as:

$$f = \text{sigmoid}(x) = \frac{1}{1+e^{-x}} \quad \text{Eq22}$$

$$f = \text{tanh}(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}} \quad \text{Eq23}$$

$$\text{ReLU} = \begin{cases} 0 & x \leq 0 \\ x & x > 0 \end{cases} \quad \text{Eq24}$$

Data pre-processing is an important step in the training procedure, and it is critical for model convergence. It involves using feature-scaling techniques such as normalization, standardization, and log transformation to re-scale input and output variables prior to training the neural network model. These techniques help maintain the general distribution and ratios in the source data while reducing redundancy and complexity. This improves the performance and training stability of the model.

Training the neural network involves using an optimization algorithm to best map the inputs to outputs with a set of parameters (model weights). The most frequently used algorithm is the back-propagation method. In this method, the difference between the expected output value and the observed value (loss) is calculated. Then, the loss is distributed back to the network by calculating partial derivatives of the loss with respect to weights and biases and updating each weight and bias. The purpose of this step is to adjust the parameters to minimize the loss or error. This process is repeated for all cases, called an epoch. After several epochs, the error converges to a minimum level and the training stage ends.

Overfitting and underfitting are the two common problems in the neural network approach. Overfitting happens when a very complex model is used, and the model fits the training data too well but it performs poorly on the testing set [274]. Underfitting occurs when the algorithm cannot capture the underlying trend of the data. Both underfitting and overfitting lead to poor performance of prediction [272]. Underfitting can be prevented by increasing the training data and the model complexity by increasing the number of neurons or adding hidden layers [269]. To avoid overfitting, it is necessary to split the data into validation dataset in addition to the training and test datasets. The training dataset is the sample of input data used to fit the model. In other words, the model learns from this training data. A validation dataset is the sample of data used to provide an unbiased evaluation of a model fit on the training dataset while tuning model parameters. This validation dataset is used to evaluate the performance of the training model while developing the model. And lastly, the test dataset is the sample of data used to provide an unbiased evaluation of a final model fit on the training dataset. The dataset split ratio into training, validation and test depends on the total training samples and on the type of model that is used [275].

The performance of the model is evaluated using the root mean square error (RMSE).

$$\text{Performance} = (1 - \text{RMSE}) \%, \text{ with } \text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (y_i^t - y_i^p)^2}{n}} \quad \text{Eq25}$$

where y_i^t , and y_i^p are the target and predicted values, respectively.

4.3.6.2 ANN Approach in Current Work

In this work, a *regression* artificial neural network is used. The first step into training the ANN model is to determine the input and output variables. Figure 12 shows the input and output for each measurement point.

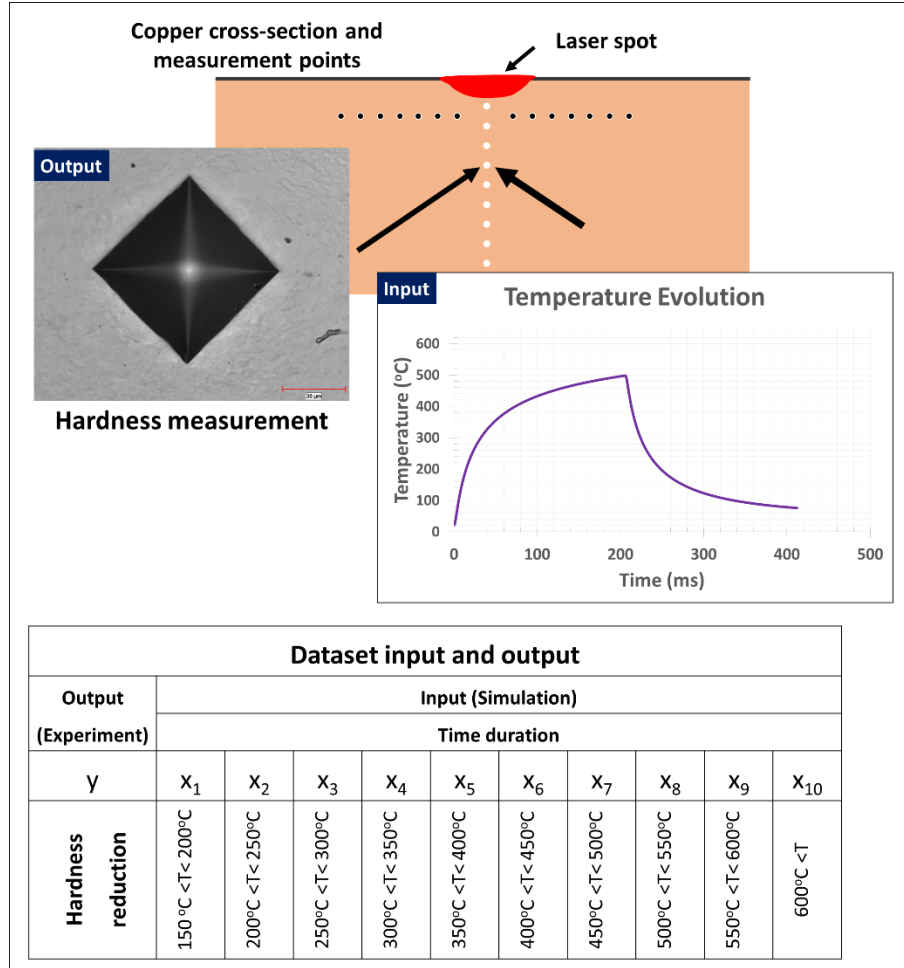


Figure 12: The framework for the ANN prediction modelling demonstrating the input and output for each sample in the dataset and the temperature discretized configuration.

As presented, the input is the temperature history obtained from the simulation i.e., the time duration the sample was in a certain temperature range. The output is the hardness reduction values measured experimentally. As such, combined hardness reduction and corresponding temperature history at a point structure one sample for the ANN dataset. As shown in Figure 12, the simulated temperature histories are a continuous function of time. To be able to feed them for the ANN training, these data are discretized into the temperature families from 150°C to above +600°C with an increment of 50°C. The

time durations within each temperature range become the inputs.

Several laser treatment cases are performed to collect a big enough dataset for the training of ANN model. This dataset is sufficiently large to represent the unknown underlying mapping function from inputs to outputs. The number of neurons for the hidden layers is determined by trial and error. Several networks with different numbers of hidden neurons are evaluated. Also, different combinations of data split ratios for training, test and validation are examined and the different activation functions are tested. Once the best model is defined, it is used for the hardness reduction prediction of a new set of data on the cylinder that has never been used in the ANN model (unseen data).

4.4 Development of Copper Surface with Enhanced Biofilm Inhibition Properties using CS process

4.4.1 Material

In this study, copper and stainless steel are used. Discs of 10 mm diameter and 4 mm thickness are machined from as-received copper round bars (grade C101) as well as as-received stainless steel round bars (grade 316). The stainless-steel discs are used only as control substrates for the biofilm inhibition response tests. The shot peening and cold spray processes are performed on copper discs. In order to remove any machining imperfections and to standardize the substrate surface properties, all discs surfaces are ground using a 220 grit (~63 μm) diamond-grinding disc prior to each experiment.

The coating process is performed using copper powder with an irregular shape and with a purity of 99.7%, as specified by the powder manufacturer. The powder size distribution ranges from 5 μm to 45 μm , as specified by the powder manufacturer. The glass beads are spherical with an average particle size distribution of 88-149 μm and Mohs hardness of 4-5, as reported by the glass bead manufacturer.

4.4.2 Cold Spray Process

Coating and shot peening procedures are conducted using a commercially available EP Series SST cold spray system (CenterLine (Windsor) Limited, Windsor, Ontario, Canada). De-Laval tungsten carbide and steel nozzles are used for coating and shot peening processes, respectively. These nozzles have throat and exit diameters of 2 mm and 6.6 mm, respectively, along with a diverging section length of 120 mm.

The process parameters used to perform the cold spray and shot peening treatments are listed in Table 11. Three different peening parameters are used, i.e., SP1, SP2, and SP3. Samples prepared using SP1 parameters, undergo the largest peening intensity and coverage. SP2 and SP3 samples experience similar peening conditions except for the peening scan speed. These peening parameters are selected to produce refined grain sizes with different surface roughness values.

Table 11: Coating and shot peening process parameters with the sample ID for each surface treatment listed.

Surface Treatments		Gas Condition		Gun Traverse Speed (mm/s)	Powder Feed Rate (gr/min)	No. of Surface Scans	Surface Coverage	Particle Velocity (m/s)
		Pressure (MPa)	Temperature (°C)					
Copper Coating	CS	3.4	500	40	9.1	5	-	539±66
Shot Peening	SP1	0.7	25	20	34.8	5	10000%	208±32
	SP2	0.7	25	40	16.7	1	500%	
	SP3	0.7	25	200	16.7	1	97%	

4.4.3 Biofilm inhibition and Antiviral Test Protocol

4.4.3.1 Biofilm Inhibition Test Methodology

The biofilm inhibition response of the various copper samples is evaluated using *Pseudomonas aeruginosa* bacteria (PA14). *P. aeruginosa* is a gram-negative rod-shaped pathogen with an average

size of 0.5-3 μm [276]. This pathogen uses several attachment organelles to adhere to surfaces and form biofilm [212], [214], [277]. The schematic in Figure 13 illustrates the biofilm inhibition response test. All experiments are carried out in a biosafety level 2 (BSL2 laboratory). Experiments are divided into three stages; biofilm formation, biofilm disruption, and quantification of colonies.

PA14 bacteria are allowed to grow in Lysogeny Broth in an orbital shaker, at 37°C and aerobic conditions. The absorbance characterization is performed on the bacteria suspension using spectrometer (SpectraMax M2). Bacteria suspension are adjusted to 0.7 optical density (OD) and then diluted by a factor of 10 using an LB broth (Figure 13, Biofilm formation step a). From this solution, 500 μL of bacteria solution with initial concentration of $\sim 10^8$ colony forming unit/mL (CFU/mL) is used for each disc. The 5 discs from each group are placed in a sterile plate and 500 μL of the bacteria stock solution are spread over each sample. Unused wells are covered with 750 μL of sterile H_2O to preserve the humidity (Figure 13, Biofilm formation step b and c). Then, the plate is placed in a humidity incubator at 37°C at an inclination of 45° (Figure 13, Biofilm formation step d). The discs are incubated for 1 hr, 6 hr, and 18 hr to allow the bacteria colonization and biofilm formation. Next, the biofilm is removed, see Figure 13, and resuspended in M63 media, plated and survival colonies is counted (18 hr incubation, 10-100 μL sample plated at 37°C).

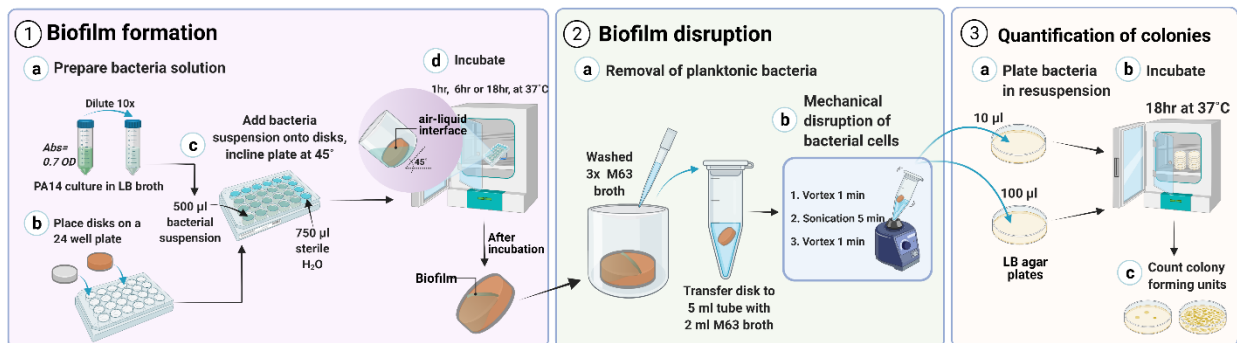


Figure 13: Schematic of the biofilm inhibition test methodology conducted for the samples in this study. This figure was generated using BioRender.

4.4.3.2 Anti-Viral Test Methodology

To evaluate the contact killing ability of copper samples when exposed to viral pathogens, a viral photoinactivation experiment is performed using a lentivirus surrogate model of SARS-CoV-2. The schematic of the antiviral test methodology is illustrated in Figure 14. The test procedure is divided into four steps; cell preparation, virus preparation, cell/virus combination, and qRT_PCR analysis.

Cell Preparation: L929 fibroblasts is used. These cells are cultured in cell culture media DMEM/MEM supplemented with 1% Penicillin Streptomycin (PS), and 10% Fetal Bovine Serum (FBS). Cells are trypsinated, counted, and cell density is adjusted to 15,000 cells/mL in 10 mL using DMEM. 100 μ L of this cell solution is seeded into 96 wells and incubated for 24 hr at 37°C.

Virus Preparation: The lentivirus (pLL-CMV-rFLuc-T2A-GFP-Puro Lenti-Labeler™ Lentivector, LL310VA-1, SBI System Biology) is diluted in saline solution and used at a viral dosage of 10^8 International units per milliliter (IU/mL), shown in Figure 14. Discs (two discs from each copper group) are placed in a 24 well-plate. A 5 μ L drop of viral solution is placed on top of each disc (Figure 14) and incubated for 10 min at room temperature (Figure 14, Lentivirus Preparation, step c). After 10 min, 100 μ L of Hank's Balanced Salt Solution (HBSS) is added on top of each disc, which is mixed with the viral solution. HBSS is a buffer used for maintaining the physiological pH range and osmotic balance of the solution. This plate is incubated for 2 hr at room temperature (Figure 14, Lentivirus Preparation, step e).

Cell/Virus Combination: First the culture media from the 96-well plate (Figure 14, red well plate from L929 Cell Preparation part step d) are replaced with 100 μ L of fresh DMEM/MEM cell culture media to provide enough nutrients to feed cells. Then 105 μ L solution from each treatment well (Figure 14, blue well plate from Lentivirus Preparation part step e) is added to the L929 cells plate. Positive control (100 μ L of DMEM/MEM culture media + 100 μ L of Hank's solution with 5 μ L viral solution) and additional negative control (100 μ L of DMEM/MEM culture media + 100 μ L of Hank's solution)

groups will be introduced to the L929 cells in the 96-well plate (Figure 14, part 3). This 96-well plate is then incubated at 37°C for 48 hr. Then, viral RNA is extracted and quantification analysis is performed.

Quantification Analysis: Quantitative RT-PCR (qRT-PCR), shown in Figure 5 part 4, is performed for the qPCR Lentivirus Complete Titration Kit Cat#LV900 (Applied Biological Materials Inc, Canada). Samples from the 96-well plate are collected into 0.5 mL Eppendorf tubes individually and centrifuged at 2000 g for 5 minutes to remove cells/debris. 10 µl of viral supernatant and control samples will then be mixed with 10 µl of Viral Lysis Buffer and incubated at room temperature for 3 minutes. The qPCR reaction is prepared by mixing 12.5 µl fluorescent dyes (2X SYBR Green qPCR Mastermix), viral lysate or standards (2.5 µl), reagent mix (10 µl) for a total volume of 25 µl per reaction. Real-time qPCR instrument (LightCycler 480, Roche) is programmed with reverse transcription at 42°C for 20 minutes, enzyme activation at 95°C for 10 minutes, denaturation at 95°C for 15 seconds and annealing/extension at 60°C for 1 min - repeating the last two steps for 40 cycles. Melting / Dissociation Curve Analysis will then be performed at the end of the last annealing cycle by melting the product at 95°C. The titer of the samples is calculated using the Ct values obtained from the LightCycler® 480 Software and the Lentiviral titer calculator tool at ABM's corresponding website as suggested by the manufacturer.

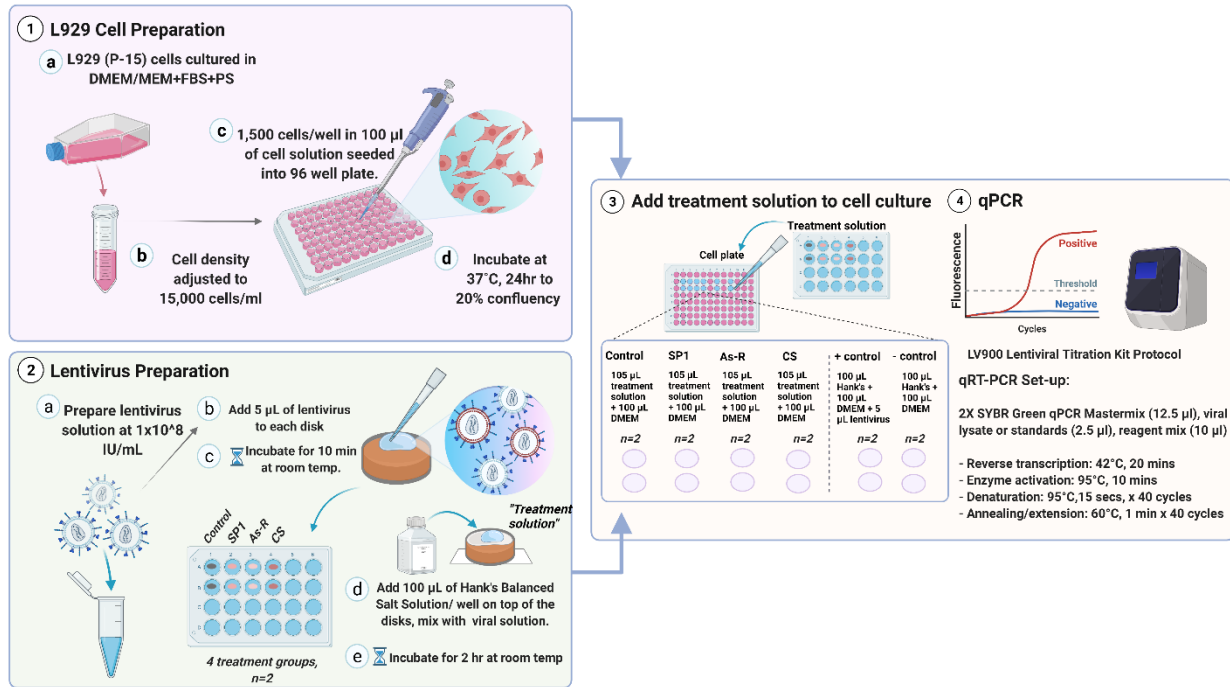


Figure 14: Graphical protocol illustrating the viral test procedure. The “+control” is the virus-only group and the “-control” is the no virus (media only) group. This figure was generated using BioRender.

4.4.4 Surface Characterization

Microscope observation of sample cross-section is performed to study the samples microstructure after surface treatments. The cross-sections of the samples (As-R, CS, SP1, SP2, SP3) is ground with a 220 grit ($\sim 63 \mu\text{m}$) diamond grinding disc and diamond paste solution down to $0.05 \mu\text{m}$ and etched for 5 s in a solution of $5\text{g FeCl}_3 + 25 \text{ ml HCl} + 100 \text{ ml ethanol}$ to reveal the grain boundaries. Optical microscopy observations is performed using an optical microscope (VHX—1000, Keyence Corporation, Osaka, Japan). The surface topography of the samples is also analysed with the optical microscope. Ten 3D images per sample is taken to calculate sample surface roughness (Ra). This is done by extracting the surface topography using VHX-2000 3D Shape Measurement Software. A Matlab code (R2018b) is developed to measure the surface roughness from the exported data points.

Detailed observation of near surface grain structure is done using scanning electron microscope (SEM)

(EVO MA-10, Carl Zeiss AG, Oberkochen, Germany) equipped with secondary (SE) and back-scattering electron (BSE) detectors. Image J software is used to perform the grain size measurements of shot peened and cold sprayed surfaces down to 20 microns deep. Prior to the analysis, all samples are cleaned ultrasonically with ethanol and dried with air to remove any surface contamination.

4.4.5 Copper Ion Measurement

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is used to measure and compare the copper ion release from the studied samples (SP1, SP2, SP3, As-R, CS). Prior to the experiment, the side wall and base of all the discs are painted to prevent copper diffusion from these surfaces to allow comparing the copper ion diffusion of the modified surfaces only.

Copper discs from each studied groups are placed in a 24-well sterile plate and covered with 500 μ L of LB broth. This plate is then placed in a humidity incubator at an inclined angle of 45° and a constant temperature of 37°C. These sample groups are incubated for 1 hr, 6 hr or 18 hr. Next, discs are removed and the solution containing copper ions is transferred to vials for quantification analysis.

The copper concentrations are determined for each sample using ICP-OES (Agilent Technologies Inc. 5110 ICP-OES) with the detection limit below 0.0006 ng/g or parts per billion (PPB). The weight of 0.1 ml of the solution is measured. This solution is then be diluted in 1% HNO₃ solution with the dilution factor of 1:100. This diluted sample is used for the ion concentration measurement. Before each measurement the calibration is done using the plasma calibration standard (Cu 1001 $\pm$ 5 μ g/ml 4 % HNO₃). The concentration of copper in the solution is reported in μ g/g

5. Results and Discussion

This chapter is presented in four sections, each containing a research paper addressing one of the main objectives outlined in Chapter 3. All these papers were peer reviewed and published in an international journal relevant in the subject of CS, the Journal of Thermal Spray Technology.

5.1 Research Project 1: Material Model for Copper under Extreme Impact Condition

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This work aims at establishing the first step into full coating build-up modeling by developing new PTW parameters suitable for high strain rate deformation in CS using LIPIT results for copper and nickel. Accordingly, a series of FEM simulations of single-particle impacts are conducted, and an optimized procedure is applied to develop new PTW parameters for copper and nickel that can reproduce the LIPIT results. The comparison is made based on the coefficient of restitution (CoR), a normalized parameter defined as the ratio of the particle rebound velocity to the particle impact velocity. It is also shown that the PTW model with improved parameters is also capable of predicting the crater diameter left by rebounded particles. Additionally, experiments and modeling are conducted to explore the bonding mechanism and rebound phenomena of copper powder cold sprayed on low carbon steel substrate.

This peer-reviewed paper addresses the objectives presented in section 3.1.



Material Model for Predicting Dynamic Response of Copper and Nickel at Very High Strain Rates Under Cold Spray Conditions

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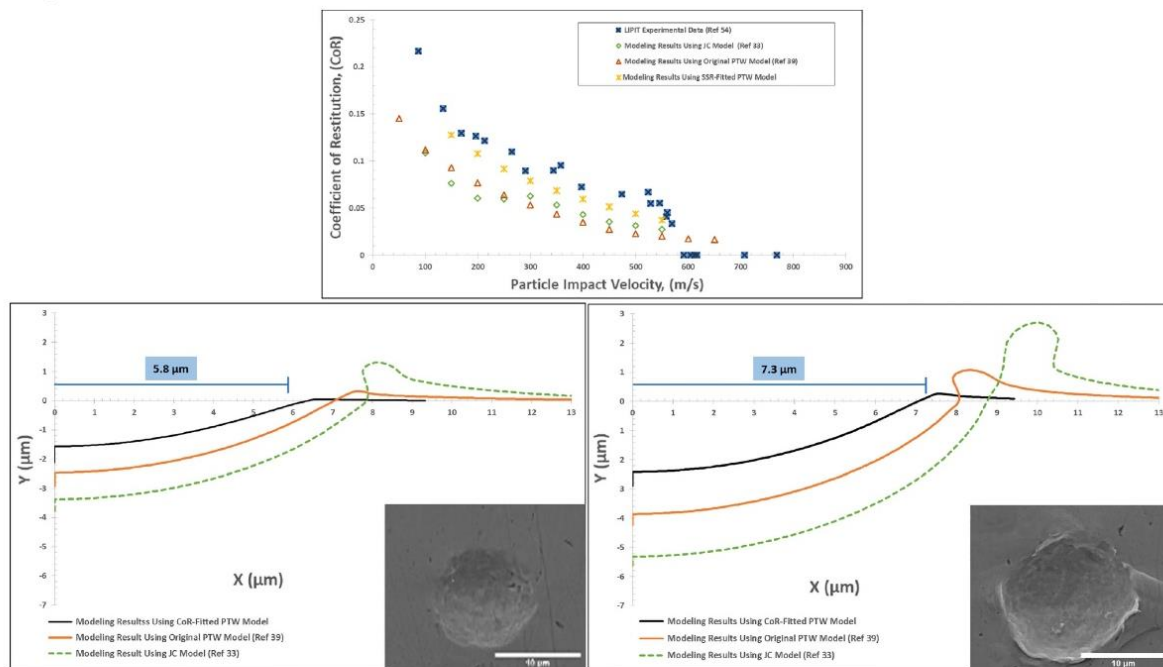
Abstract Numerous material models have been proposed to describe material properties under impact-induced extreme conditions. All these models suffer from the fact that the tests used to provide the required empirical parameters were performed on bulk material at limited strain rates, much lower than those found in the cold spray process. In this work, recent published results available in the literature that were obtained using advanced imaging techniques are used to modify material plasticity models to accurately predict the material plastic flow stress under cold spray conditions. The capability of two frequently used material models, Johnson–Cook and Preston–Tonks–Wallace models, to predict real-time experimental data for

copper and nickel particles is evaluated. A series of finite element simulations are conducted and the comparison is made with the coefficient of restitution from laser-induced projectile impact test data. The original empirical parameters in Preston–Tonks–Wallace model are re-calibrated so that the coefficient of restitution matches the laser-induced projectile impact test data, providing an enhanced quality in the particle impact behavior predictions. Additionally, experiments and modeling are conducted to explore the bonding mechanism and rebound phenomena of copper powder cold sprayed on low carbon steel substrate.

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Graphic Abstract



Keywords cold spray process · finite element simulation · high strain rates · high-velocity impact · material strength model · Preston–Tonks–Wallace · rebound phenomena

Introduction

Cold gas dynamic spraying (CGDS), or cold spray (CS), is a solid-state joining process. In CS, micron-size powders are accelerated using a propellant gas (usually nitrogen, helium, or air) traveling through a converging–diverging (De Laval) nozzle and adhere to a substrate following severe plastic deformation upon impact with a substrate. In CS, materials experience very high strain rates (10^6 – 10^9 1/s) while their temperature prior to impact is kept below their melting point (Ref 1). Since the entire deformation process lasts less than 100 ns and involves such small particles, it is hardly possible to monitor and study the in situ particle deformation evolution.

Numerical modeling was found to be a practical alternative solution to track details of the impact and deformation process. It provides an informative insight into the deformation mechanisms and helps for process parameters optimization. Many modeling efforts have been conducted over the last decades using finite element method (FEM) (Ref 2–6), smoothed particle hydrodynamics (SPH) (Ref 7, 8), molecular dynamics (MD) (Ref 9), as well as computational fluid dynamics (CFD) (Ref 10, 11) to study

physics of single-particle impact. These studies have led to enhanced understanding of the process fundamentals such as the effect of feedstock and substrate material nature, particle size and morphology (Ref 12), driving gas nature and parameters (Ref 11), nozzle stand-off distance and impact angle (Ref 8, 10). Numerical modeling is also a useful tool to design CGDS nozzles and study particle and flow/nozzle interaction considering different particle injection locations, particle size, and nozzle material (Ref 13–15).

In CS, particles adhere to the substrate provided that they reach or exceed a certain impact velocity known as the critical velocity (Ref 16). This velocity is a function of many factors such as feedstock and substrate materials nature, particle size, particle impact temperature, and surface oxidation level (Ref 17, 18). Different approaches have been proposed to theoretically assess the critical velocity. Pioneering work by Assadi et al. suggested that adiabatic shear instability (ASI) is the main mechanism for successful bonding (Ref 3). Observation of ASI in single-particle impact modeling was characterized by a localized abrupt increase in temperature and plastic strain (Ref 19, 20). The formation of peripheral particle jetting and ejection of material at the outermost particle edge is commonly interpreted as ASI in single-particle impact simulations (Ref 20, 21). Li et al., on the other hand, demonstrated that appropriate simulation settings such as element type, mesh size, Arbitrary Lagrangian–Eulerian

(ALE) adaptive meshing, and contact interaction can significantly affect the resulting output (Ref 22) and onset of ASI. Careful attention is required when dealing with these simulation parameters to achieve a reliable outcome. It has also been reported that material jetting at the particle interface can enhance oxide film cleanup (Ref 23), which is a key process in the bonding mechanism (Ref 24, 25). According to the most accepted theory in CS, bonding is achieved when two oxide-free surfaces are brought into close contact at the interatomic distance, thus requiring both a critical amount of surface cleanup and sufficient contact pressure be present to achieve bonding (Ref 6, 26). Many other bonding criteria such as partial melting (Ref 27), recrystallization (Ref 28), interface amorphization (Ref 29), and diffusion (Ref 30) can be linked to the oxide cleanup process.

Although the single-particle impact process has been thoroughly investigated with numerous models, the actual bonding mechanism of CS particles has not been included in most of these simulations. A cohesive stress model based on Dugdale–Barenblatt (Ref 31) along with adhesion energy similar to the Griffith model in crack behavior (Ref 31) was implemented at the particle/substrate contact interface using in-house SPH code to include bonding. In this model, a constant interfacial force was considered to prevent bodies from separation when the inter-SPH particle distance at the interface reaches a critical value. Both these studies failed to predict the localized bonding correctly and are unable to model the rebounding phenomena often observed in CS. A combination of conventional and tie-break contact algorithm was implemented by Yildirim et al. (Ref 32) to simulate particle bonding as well as rebounding. In this model, the interfacial cohesive strength parameter available in surface-based cohesive tools in the commercially available FEM software ABAQUS/Explicit was modified to predict the critical velocity. Despite some improvements by this model, the condition affecting the bonding such as surface oxide film was not considered and the model was unable to predict the actual bonded surfaces. In recent work by Rahmati and Jodoin (Ref 6), the adhesion mechanism based on the cold welding bonding theory was included through FEM. This physical-based method enables demonstrating the localized metallic bonding at the particle/substrate interface and supports/consolidates the findings of the bonding mechanism theories. Unfortunately, like all other FEM approaches, the quality of the modeling results is highly dependent on the material plasticity model used.

The Johnson–Cook (JC) empirical constitutive model (Ref 33) is the most frequently used material model in CS (Ref 3, 4, 7, 34, 35). However, the model parameters are typically valid only for the low strain rate regime (up to 10^3 1/s), thus its inability to properly predict the stress–strain

behavior at high strain rates (Ref 5). The Zerilli and Armstrong (ZA) model, on the other hand, is a physical-based material model based on the dislocation mechanism in FCC and BCC materials (Ref 36). The stress results obtained from this model are in good agreement with the experimental values for strain rates up to 10^3 1/s and low-temperature range (Ref 5). Nevertheless, the dependence of flow stress on the strain is decoupled from temperature and strain rate for BCC materials, which demonstrate inconsistencies when applied to elevated temperature regime (Ref 37, 38). A modified ZA (MZA) model was proposed for which the coupling effect of strain, strain rate, and temperature of flow stress was integrated (Ref 38). Although this MZA model demonstrates better results particularly at high temperatures, these results are only valid for the relatively low strain rates, up to 10^3 for copper (Ref 38). The Preston–Tonks–Wallace (PTW) model has also been used in CS modeling. It is also a physical-based constitutive model suitable for the inelastic response of the material at very high strain rates, similar to hypervelocity impact (Ref 39). This model accounts for both mechanisms of thermally activation dislocation motion at lower strain rates ($\leq 10^4$ 1/s) (Ref 40) and nonlinear drag-dominated dislocation motion, predominant in strong shock wave regime (up to 10^{12} 1/s). So far, this material model is known to be one of the best models to predict material plastic behavior at high strain rates (Ref 5). There have been many other empirical and physical-based models developed in the past years. Nevertheless, all these models suffer from the fact that the tests used to provide the ‘parameters’ required for each model were performed on bulk material at strain rates much lower than what is found in CS (Ref 41–47). Johnson and Cook, for example, used the torsion test and dynamic Hopkinson bar tensile test (Ref 41) over a range of strain rates (up to 400 1/s) and temperature to extract the JC model parameters for oxygen-free high conductivity (OFHC) copper, Armco iron and 4340 steel, nickel and 8 other materials (Ref 33). The Hopkinson bar technique was also used to evaluate the validity of the mechanical threshold stress model (MTS). The model capability in predicting the material stress state at annealed and pre-strained conditions at low-temperature and strain rates from 0.001 1/s to 5000 1/s was investigated (Ref 48). Lee et al. studied the plastic behavior of Ti-6Al-4V alloy subjected to strain rates from 500 1/s to 3000 1/s under various temperature conditions (room temperature up to 1100 °C) using split-Hopkinson bar technique. The test was performed on a 10-mm-diameter hot-rolled bar, and the results were used to identify the JC material model parameters (Ref 49). The Taylor impact test (Ref 50) was conducted on the cylinder shape OFHC copper (99.99%) and Armco iron to derive the ZA material model parameters (Ref 36). PTW parameters (Ref 39) were calculated for

OFHC annealed (0.9999 Cu) copper with an average grain diameter of 40 μm . A uniaxial compression test was performed to measure the dynamic response of copper under the strain rate spanning from 10^{-4} to 10^4 (Ref 43). To add to the inadequate strain rates tested by these experiments, powder materials used in CS are likely to behave differently than bulk material, and thus even the most suitable plasticity model for high strain rates potentially suffer from improper data taken from bulk material. Furthermore, the strain rate behavior of material at ultra-high impact velocity is reported to be size-dependent (Ref 51).

Real-time observation of single-particle impact using laser-induced projectile impact test (LIPIT) (Ref 52–54) has shown potential to extract the high strain rate data required to determine the material models ‘parameters’ for micron-size particles. These would allow sufficiently precise modeling of impact, rebound, and adhesion phenomena in CS. LIPIT data are more reliable than the data obtained for bulk materials since it represents the real-time response of CS materials under extreme dynamic load and thus yields more accurate data for CS simulation. In the recent work by Wang et al., LIPIT results were used to successfully modify the strain rate-related parameters in JC and ZA titanium strength models to improve their ability to predict particle deformation (Ref 55).

Despite the numerous single-particle impact simulations found in the literature and cited previously, only a few efforts have been made to model complete coating build-ups. SPH was used to simulate multiple impacts and to study the particle interaction (Ref 56). In another study, Trinichi et al. (Ref 57) developed a phenomenological model, based on empirical data. This model focused on predicting the coating porosity for spherical feedstock powders. A promising coating build-up model was developed by Delloro et al. (Ref 58). In this model, the data from a two-dimensional FEM simulation of spherical powders, with different sizes and initial impact velocities, were combined into a data library. The build-up procedure was conducted using the deformation field from the data library and using an interpolation technique (Ref 58). The ability of the coating build-up model in producing accurate results is highly dependent on the reliability of the ‘data library’ it uses. A combination of different factors such as proper numerical modeling setups, accurate bonding mechanisms, and more importantly an effective material strength model are required to be fulfilled to build a powerful ‘data library’ of single-particle impact.

As such, this work aims at establishing the first step into full coating build-up modeling by developing new PTW parameters suitable for high strain rate deformation in CS using LIPIT results for copper and nickel (Ref 53, 54).

Accordingly, a series of FEM simulations of single-particle impacts are conducted, and an optimized procedure is applied to develop new PTW parameters for copper and nickel that can reproduce the LIPIT results. The comparison is made based on the coefficient of restitution (CoR), a normalized parameter defined as the ratio of the particle rebound velocity to the particle impact velocity. It is also shown that the PTW model with improved parameters is also capable of predicting the crater diameter left by rebounded particles. Additionally, experiments and modeling are conducted to explore the bonding mechanism and rebound phenomena of copper powder cold sprayed on low carbon steel substrate.

Finite Element Simulation

Material Constitutive Model

The plastic response of the material is evaluated using the PTW material constitutive model (Ref 39). This physically-based model has been demonstrated as an ideal model to predict the material yield strength at both conventional strain rates and overdriven shock regime (Ref 5, 6, 59). The model strain rate dependence is divided into two distinct regions. In both regions, plastic deformation is governed by the dislocation generation rate and kinetics.

In the first region, i.e., quasi-static regime, material strengthening is controlled by the impediment of dislocation motion (solid solution strengthening, precipitation hardening, and grain boundary strengthening) and creation of additional dislocations by Frank–Read source (Ref 60). In the second region, i.e., shock loading regime, the plastic deformation is dominated by the dislocation generation mechanisms at high strain rates. Dislocations simultaneously nucleate at the shock front and heterogeneously propagate throughout the materials. Dislocation loops are formed and expand into the lattice and can lead to the formation of a cellular structure after multiple cross-slip and annihilation mechanisms. However, as strain rate increases, the microstructure changes from cells to stacking faults and eventually to deformation twins (Ref 61). Additionally, dynamic lattice compression is also observed during shock loading (Ref 61). In both regions, material response to the dynamic load is highly influenced by the initial microstructure of the material tested.

The equations defining the PTW model are presented here. These equations are implemented into ABAQUS/Explicit using the VUHARD subroutine (Ref 5).

The PTW flow stress is given by a linear Voce hardening law as:

$$\sigma_y(\epsilon_p, \dot{\epsilon}_p, T) = \begin{cases} 2 \left[\tau_s + \alpha \ln \left[1 - \varphi \exp \left(-\beta - \frac{\theta \epsilon_p}{\alpha \varphi} \right) \right] \right] \mu(p, T) & \text{Thermal regime} \\ 2 \tau_s \mu(p, T) & \text{Shock regime} \end{cases} \quad (\text{Eq 1})$$

with

$$\alpha = \frac{s_0 - \tau_y}{d} \quad (\text{Eq 2})$$

$$\beta = \frac{\tau_s - \tau_y}{\alpha} \quad (\text{Eq 3})$$

$$\varphi = \exp(\beta) - 1 \quad (\text{Eq 4})$$

where ϵ_p is the plastic strain, $\dot{\epsilon}_p$ is the plastic strain rate, T is the temperature, τ_s is a normalized work-hardening saturation stress, θ is the hardening constant, d is a dimensionless material parameter, τ_y is normalized yield stress, and s_0 is the value of τ_s at 0 K.

Moreover, $\mu(p, T)$ denotes the shear modulus and is a function of temperature and density of the material. It has been shown that the mechanical threshold stress (MTS) model (Ref 43), which is a physically-based model, is capable of predicting the shear modulus for the range of the temperature and strain rates that exist in CS (Ref 62). The MTS shear modulus has the form as:

$$\mu(T) = \mu_0 - \frac{D}{\exp(T_0/T) - 1} \quad (\text{Eq 5})$$

where T is the material temperature, μ_0 is the shear modulus at 0 K, and D and T_0 are material constants.

τ_s and τ_y are defined as:

$$\tau_s = \max \left\{ s_0 - (s_0 - s_\infty) \operatorname{erf} \left[\kappa \hat{T} \ln \left(\frac{\gamma \dot{\epsilon}}{\dot{\epsilon}_p} \right) \right], s_0 \left(\frac{\dot{\epsilon}_p}{\gamma \dot{\epsilon}} \right)^{s_1} \right\} \quad (\text{Eq 6})$$

$$\tau_y = \max \left\{ y_0 - (y_0 - y_\infty) \operatorname{erf} \left[\kappa \hat{T} \ln \left(\frac{\gamma \dot{\epsilon}}{\dot{\epsilon}_p} \right) \right], \min \left\{ y_1 \left(\frac{\dot{\epsilon}_p}{\gamma \dot{\epsilon}} \right)^{y_2}, s_0 \left(\frac{\dot{\epsilon}_p}{\gamma \dot{\epsilon}} \right)^{s_1} \right\} \right\} \quad (\text{Eq 7})$$

where $\hat{T} = T/T_m$, T is the temperature and T_m is the material melting point, s_∞ is the value of τ_s near the melting point, y_0 , and y_∞ , the value of τ_y at zero and very high temperatures, respectively. Other parameters, i.e., $\gamma, \kappa, s_1, y_1, y_2$ are all material constants. Furthermore, $\dot{\epsilon}$, the reciprocal of the time for a transverse sound wave to cross an atom is given as

$$\dot{\epsilon} = \frac{1}{2} \left(\frac{4\pi\rho}{3M} \right)^{\frac{1}{3}} \left(\frac{\mu(\rho, T)}{\rho} \right)^{\frac{1}{2}} \quad (\text{Eq 8})$$

where ρ is the density and M denotes the atomic mass of the material.

The PTW parameters to be re-calibrated in this work are listed in Table 1. These parameters control the material mechanical behaviors at the strain rates dominant in CS.

Parameters y_1, y_2 determine the stress flow at the intermediate strain rates (approximately 10^3 – 10^7 1/s). In this regime, the mechanism controlling the dislocation motion gradually changes from thermally activated to drag-dominated mechanism. At very high strain rates, above 10^8 1/s for example, the plastic flow in metals is controlled by the overdriven shocks. An abrupt increase in stress flow is observed in this regime. The strain rate dependence parameter, γ , defines the dependency of stress to strain rates at high strain rates. The material constant κ describes the dependency of the flow stress to the temperature. The two other parameters, θ, s_0 control the level of work hardening in the material.

Grain sizes in CS powders, as opposed to the bulk materials commonly tested, are small (order of a few microns). For materials with characteristic dimensions of a few microns, the deformation behavior is characterized by the deformation of only a few grains. This leads to the difference in deformation mechanisms compared to bulk counterparts, displaying significantly enhanced strengthening effect (Ref 63, 64). The strength of micron-size polycrystals depends on many factors such as the grain size range, distribution pattern, grain shape, and orientation. It has been known that refining the metals grain size can significantly increase the material yield stress which is estimated using the Hall–Petch equation (Ref 64). Hence, the scale-dependent of yield stress and grain size strengthening effect must be assigned to the PTW model parameters to accurately predict the plastic deformation of CS particles. This consideration is included by re-calibrating the θ , and s_0 parameters so that the scale dependency of mechanical properties is integrated into the

Table 1 PTW parameters to be re-calibrated based on LIPIT data

Strain rate dependence (γ)
Strain hardening rate (θ)
Medium strain rate (y_1)
Medium strain rate exponent (y_2)
Saturation stress at 0 K (s_0)
Temperature dependence (κ)

original PTW model. Besides, grain size can also affect the strain rate sensitivity of materials under dynamic loading (Ref 65). This is considered by modifying the y_1 and y_2 values.

Details of Modeling Steps

First, the ability of the commonly used material models in CS, i.e., JC (Ref 33) and original PTW (Ref 39) in reproducing the laser-induced projectile impact test (LIPIT) results is evaluated. FEM is used for this purpose and the comparison is made between modeled and experimental CoRs (the ratio of the particle rebound velocity to the particle impact velocity, V_r/V_i). Upon impact, the initial particle kinetic energy is mostly dissipated into heat and plastic work of the particle and substrate, and the remaining is temporarily stored in the form of elastic energy. This recoverable elastic energy is released at the end of the deformation process and causes a reversing of direction of the particle velocity, called rebound velocity. The particle rebound velocity is calculated from simulated rebound kinetic energy knowing the particle mass. The particle impacts the substrate at different initial velocities and the corresponding rebound kinetic energies (and thus rebound velocities) are obtained from the FEM model. This rebound kinetic energy is evaluated when it remains unchanged after particle rebounds, which is nearly 20 ns after the particle detaches from the substrate.

LIPIT experimental CoR are available for copper particles impacting copper substrate with the particle average diameter of $12.5 \pm 1.0 \mu\text{m}$ (Ref 54) and nickel particles on nickel substrate, with nickel average particle size of $10 \pm 2 \mu\text{m}$ (Ref 53). Hence, the FEM analysis is conducted for the impact pairs of identical material (Cu-Cu

and Ni-Ni) with $12 \mu\text{m}$ powder diameter to be able to validate the model with LIPIT results from the literature.

The PTW parameters for bulk materials available in the literature are summarized in Table 2. The PTW calibration process is conducted by modifying and optimizing the $\gamma, \theta, y_1, y_2, s_0, \kappa$ parameters for copper and nickel so that the CoR matches the LIPIT results.

The first step in modifying the original PTW model is conducted by calibrating the PTW parameters ($\gamma, \theta, y_1, y_2, s_0, \kappa$) in order for the stress–strain rate curve to better fit the stress–strain rate (SSR) data obtained from bulk material testing. This set of parameters is referred to as the “SSR-fitted PTW model”. The capability of this set in replicating the CoRs from LIPIT tests is then investigated.

Next, the PTW parameters are calibrated so that the simulated CoR best fits the LIPIT results (CoRs) and this modified PTW model is called the “CoR-fitted PTW model”. The calibration process aims to include both the effects of characteristic length scale and grain size on the material yield strength and simultaneously satisfy the LIPIT experimental results.

To understand how each of the six selected parameters ($\gamma, \theta, y_1, y_2, s_0, \kappa$) controls the prediction of flow stress and CoRs (at different particle impact velocities), it is necessary to conduct the sensitivity analysis. For this purpose, each of these parameters was evaluated at different values higher and lower than the original amount reported in Table 2. Then the upper and lower range of each parameter is determined based on the ability in predicting CoR and whether the SSR values are physically reasonable. In order to fulfill the experimental results for all the impact velocities, a combination of parameter values, from the predetermined ranges, are simulated. A total of 60 different

Table 2 Original PTW strength model parameters

PTW parameters	Copper (Ref 39)	Nickel (Ref 59)	SS 304 (Ref 39)
Strain rate dependence constant (γ)	1e–5	1e–5	0.001
Strain hardening rate (θ)	0.025	0.01	0.020
Strain hardening constant (d)	2	2	10
Yield stress constant at 0 K (y_0)	0.0001	0.0001	0.0069
Yield stress constant at melting (y_∞)	0.0001	0.0001	0.0015
Medium strain rate constant (y_1)	0.094	0.094	0.050
Medium strain rate exponent (y_2)	0.575	0.575	0.46
High strain rate exponent (s_1)	0.25	0.25	0.25
Saturation stress at 0 K (s_0)	0.0085	0.0045	0.050
Saturation stress at melting (s_∞)	0.00055	0.00055	0.0075
Temperature dependence constant (κ)	0.11	0.11	0.300
Atomic mass (M), kg	1.055×10^{-25}	9.74627×10^{-26}	9.27×10^{-26}
Shear modulus at 0 K (G_0), GPa	51.8	85.1	85.0
Material constant (D), GPa	3	9.13	10.00
Temperature material constant (T_0), K	165	269	298

combination sets of PTW parameters and for each set 10 different particle impact velocities were simulated resulting in a total of 600 FEM simulations.

The ability of each trial set parameters in predicting the experimental results (CoRs) is evaluated using the mean square error (MSE). The parameter set with the least MSE value is the optimized set chosen. MSE is defined as:

$$\text{Mean Square Error (MSE)} = \frac{1}{n} \sum_{i=1}^n (Y_i - \hat{Y}_i)^2 \quad (\text{Eq 9})$$

where n is the total number of data points that is the number of initial particle impact velocity simulated. For each data point, Y_i is the CoR value predicted by the simulation. The least-square method is a widely used regression analysis when dealing with statistical data. Herein, we use this method to find the line best fits the LIPIT experimental data (CoRs). $\hat{Y}_i$ is the value of CoR calculated compared with this line.

Simulation Setup

To simulate the high-velocity impact of a single particle, an axisymmetric model using the commercially available FEM software ABAQUS/Explicit (Ref 66) is implemented. A schematic of the geometry and the mesh contours are provided in Fig. 1. The particle diameter is 12 μm and the substrate is modeled as a cylinder with the radius and height five-time larger than particle diameter. The bottom of the substrate is assumed to be constrained in all direction, and the axisymmetric boundary condition is considered for the substrate left wall. Both the particle and the substrate initial temperature are set to 298 K. Surface-to-surface interaction using a penalty contact algorithm with

the coefficient of friction of 0.5 is introduced at the particle/substrate contact surface (Ref 22).

To reduce the severe element distortion due to the large plastic deformation found in CS (Ref 22), an ALE adaptive mesh method with the 5 re-meshing sweeps per each increment is implemented.

Particle and substrate are meshed with a 4-node bilinear axisymmetric quadrilateral with reduced integration and hourglass control. The impact region illustrated as region 1 in Fig. 1 is structurally meshed with the element size of 1/100 the radius of the particle. The mesh size of the substrate away from the impact region, region 2, is increased gradually to reduce the computational cost. In this region, free meshing with quadrilateral elements using advancing front algorithm is selected. Mesh study analysis has shown that the convergence is achieved using a mesh size as 1/100 of particle radius (Ref 6).

The material response in the elastic domain is modeled using a linear Mie–Gruneisen equation of state (EOS) that is frequently used in CS and able to express material pressure accurately at high strain rates (Ref 3).

In this work, three different materials, i.e., copper, nickel, and SS 304 are modeled. The calibration process is conducted for identical particle and substrate materials, Cu–Cu, and Ni–Ni. Then, an additional modeling is performed to enhance understanding the bonding/rebound phenomena for dissimilar materials. The copper powder is simulated using CoR-fitted PTW model, impacting on the low carbon steel substrate. In this modeling, the low carbon steel substrate is approximated by the SS 304 PTW parameters, the most similar available material model. The material general properties are listed in Table 3.

At a very high strain rate, close to 100% of the plastic work is converted to heat (Ref 67). Despite the in situ

Fig. 1 Schematic of the 2D axisymmetric FEM model for the impact simulation. Region 1 is structurally meshed with the element size of 1/100 of particle diameter and region 2 is free meshed with quadrilateral elements using the advancing front algorithm

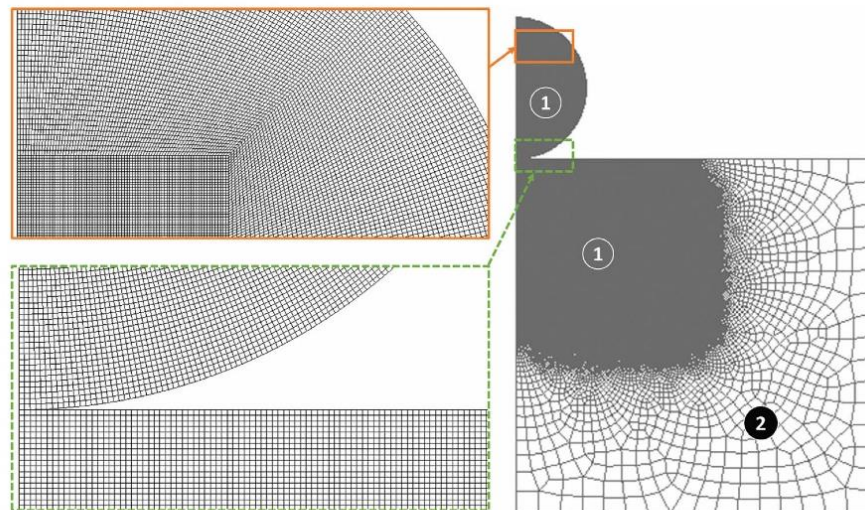


Table 3 Material general and elastic properties

Properties	Copper (Ref 5)	Nickel (Ref 4, 59)	SS 304 (Ref 59)
Density (ρ), kg/m ³	8960	8890	7920
Young's modulus (E), GPa	124	207	200
Poisson's ratio (ν)	0.34	0.31	0.3
Thermal conductivity (κ), W/mK	401	91	15
Specific heat (C_p), J/kgK	383	456	450
Shear modulus (G), GPa	45	76	86
Melting temperature (T_m), K	1356	1728	1673
EOS parameters, C_0 (m/s), s , F_0	3952, 1.49, 2.01	4650, 1.45, 1.93	4570, 1.49, 1.93

temperature change during dynamic loading, the deformation process is assumed to be adiabatic with no heat being transferred (Ref 3). This assumption is also supported by many other experiments performed at very high strain rates (Ref 68).

To examine the accuracy of the proposed material model parameters in reproducing the CoRs, a set of different initial impact velocities are simulated (50–650 m/s for copper and 200–650 m/s for nickel) and the rebound particle velocities are calculated using the rebound kinetic energy of the particle. To ensure the particle is not in contact with the substrate at the end of the simulation, the total impact time is set as 45 ns.

Materials and Experimental Procedures

The recent development of a new high-speed imaging technique for visualizing CGDS particle impact allows investigating the particle kinetics in real-time. The laser-induced particle impact test (LIPIT) has been employed to study high-speed impact micro-particle adhesion process (Ref 52–54). This technique enables the direct analysis of particles individually before impact and provides a precise detail on particle impact/rebound velocities with a precision of $\pm 2\%$ (Ref 53). More details on the experimental procedure are provided in an early study conducted by Veyssset et al. (Ref 52, 53).

Experimental data obtained from the literature using LIPIT was used for verification/validation of the material strength model. The impact/rebound velocities of copper particles with an average diameter of $12.5 \pm 1.0 \mu\text{m}$ impacting the copper substrate were used for this purpose (Ref 54). The validity of the CoR-fitted PTW model in predicting the substrate crater diameter was also confirmed using scanning electron microscope (SEM) images of craters reported by Sun et al. (Ref 54). Similar modification steps were carried out for nickel. The LIPIT data reported by Hassani et al. (Ref 53) were used for the case of nickel. These LIPIT results contain the CoRs of nickel powder with the average particle size of $10 \pm 2 \mu\text{m}$ impacting the

nickel substrate at various impact velocities. The data were extracted from the referred papers using GetData Graph Digitizer software.

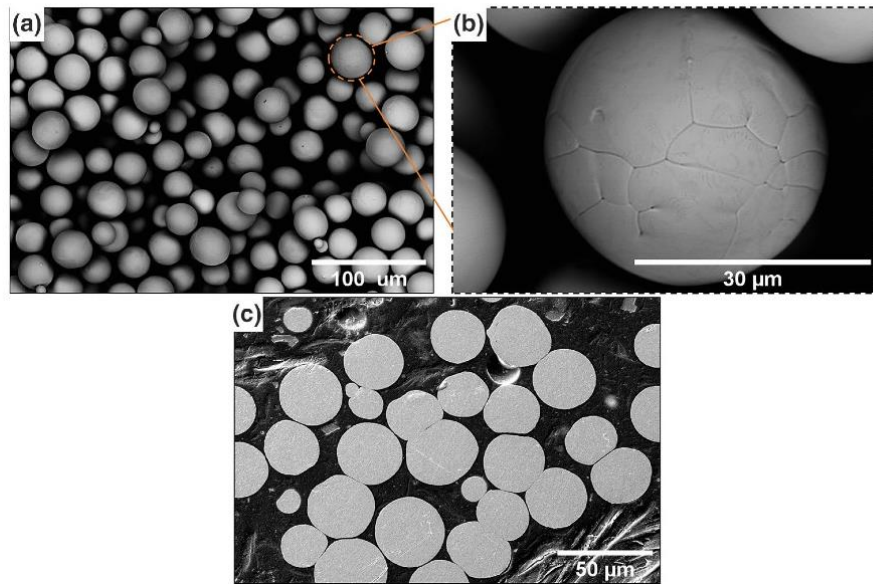
Experiments were also conducted to understand the rebound phenomena in CS of dissimilar materials. As-received gas-atomized copper powder (Plasma Giken Co. Ltd., Japan) with the native oxide film of 6 nm was selected as feedstock material. These powders with the initial size distribution of 5–53 μm were sieved to a narrower size distribution between 20 and 32 μm . SEM (EVO MA-10, Carl Zeiss AG, Oberkochen, Germany) images of loose powder and Zeiss SmartTiffV3 software were used to determine powder size distribution and analyze the powder surface morphology. All powders were mounted and polished for microstructural examination using SEM. Powder size distribution and geometry are illustrated in Fig. 2. All the powders are spherical, and a smooth surface is observed. Powders appear to have a combination of fine and coarse equiaxed grains. The cross-section images of these powders show dense microstructure as no internal pores or other defects is observed.

Low carbon steel (ASTM SA516 grade70- 25 mm $\times$ 35 mm $\times$ 75 mm) was used as substrates to study the powder adhesion/rebound characteristics. The substrates surface was polished mechanically with a 1 μm solution to create a mirror finish surface before spraying.

The powders were deposited using a commercially available EP series SST cold spray system (Centerline (Windsor) Ltd. Windsor, Ontario, Canada). Nitrogen was used as propellant gas with the stagnation pressure and temperature of 3.4 MPa and 500 $^{\circ}\text{C}$, respectively. To examine the deformation characteristics of individual impacting particles, the spray conditions were adjusted to achieve a limited number of deposited particles on the substrate. For this purpose, a low feeding rate and a high gun traverse speed (200 mm/s) were used. The nozzle stand-off distance was set as 10 mm.

The powders in-flight velocity were measured using a cold spray meter (CSM) eVOLUTION (Tecnar Automation Ltd, St-Bruno, Canada). CSM is an optical sensing device commonly used in the field of CS to perform an in-

Fig. 2 SEM images showing the (a) powder size distribution and morphology, (b) high magnification image of an individual powder showing the equiaxed grain shape, (c) powder cross section



flight diagnostic on individual particles that provides complete velocity and size distribution data. This system uses a continuous 3.3 W laser (CW, Class IV) with an optical two-slit photomask to detect traveling particles. In this study, the velocity measurements were performed at a location 10 mm downstream from the center of the cold spray nozzle exit. Measurements were taken for several minutes to ensure the collection of a robust data set. The data were collected for over 5000 collected data points.

The deformation behavior of deposited particles was studied using SEM. Particle interface characterization is conducted using local adhesion test experiments. This method enables the observation of fractured contact surfaces of multiple particles at the same time (Ref 69). To perform the test, a metallic pin is partially adhered to the as-sprayed sample using a thermally cured elastomeric adhesive (FM-1000, Cytec Engineering Materials, with an adhesive strength of 70 MPa). The metallic pin is then pulled-off using Pull-off Adhesion Tester (DeFelsko ATA PosiTest Automatic Pull-Off Adhesion Tester), locally removing the adhered particles. The details on the procedure are available elsewhere (Ref 69). Non-adhered particles were collected by locating an adhesive carbon tape in the vicinity of the substrate during deposition and SEM analysis was performed to analyze their deformation. These particles impacted the substrate and bounced-off as their velocity was lower than the critical velocity. These particles are referred to as ‘recovered non-adhered’.

Results and Discussion

Experimentally-Based Material Strength Model

The first step is to evaluate the accuracy of the two commonly used models, that is JC and original PTW model (Ref 33, 39), for copper. Figure 3(a) and (b) compares the ability of both material strength models in predicting the stress flow at various strain rates with that of the experiment on bulk copper material (Ref 43, 44, 46, 47, 70).

It can be observed that the JC model fails to follow the bulk stress–strain rate results even at lower strain rates. The original PTW parameters, by Preston (Ref 39), are seen to be unable to perfectly follow the bulk experimental values starting at medium strain rates, i.e., between 10^5 1/s and 10^7 1/s. The model parameters were refined to obtain a more accurate match to the bulk experimental data, called the SSR-fitted PTW model, and results are also shown in Fig. 3(a) and (b), indicating a better fit at high strain rates.

Figure 3(c) displays the ability of these three models in reproducing the CoRs obtained from LIPIT experiments found in the literature (Ref 54). Although all the material strength models studied in this work are able to predict the gradual decrease in CoR as impact velocity increases, none of these material constitutive models is capable of replicating the CoRs. Despite some improvements observed for the SSR-fitted PTW model, the CoR is still underestimated at all impact velocities. Furthermore, some inconsistencies are observed for the JC model at impact velocities between 200 and 300 m/s.

It is hypothesized that the inability of the models to generate accurate CoRs, even for the SSR-fitted model, is

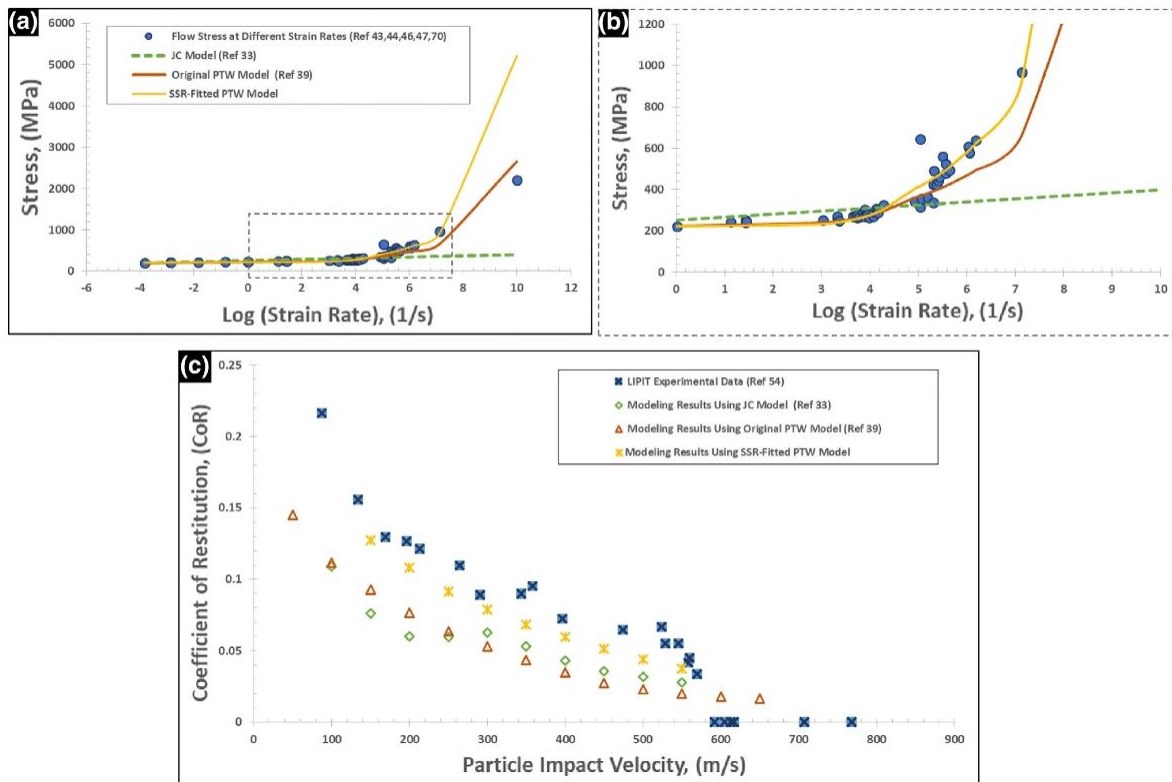


Fig. 3 (a) Flow stress of copper at various strain rates, from (Ref 43, 44, 46, 47, 70), stress flow predicted using JC model (Ref 33), original PTW model (Ref 39), and SSR-fitted PTW parameter, (b) zoom of (a) at the location where shown by the dashed rectangle,

(c) comparative study between LIPIT experimental data (cu, $12.5 \pm 1.0 \mu\text{m}$) (Ref 54) and modeling results (cu $12 \mu\text{m}$) using JC (Ref 33), original PTW (Ref 39), and SSR-fitted PTW models

explained by the fact that the experimental tests were conducted with bulk materials that present different microstructures and mechanical properties compared to the micron-size powders used for the LIPIT tests. For example, the high strain rate experiments were conducted on copper samples fully annealed, highly pure (> 0.9999), OFHC, and mono-crystalline or polycrystalline solids. However, in CS, feedstock materials are different in terms of microstructure and purity. They are generally polycrystalline with the grain size of a few microns, not annealed, and with different levels of impurity depending on the powder manufacturing process. In a crystal, imperfections interact with the dislocation glide and hinder their motion. However, at high strain rates, the dislocation kinematic is affected by resistance occurring from obstacles as well as viscous drag produced by the interaction of dislocation with the photons and electrons on the crystals (Ref 71). It has been shown that metals microstructure features such as grain size, impurity content, or initial heat treatment can significantly affect the material strength by affecting dislocation motions (Ref 60). These obstacles can also

interfere with the shock motion and lead to higher dislocation nucleation and hence larger material strength (Ref 72). Polycrystallinity, for example, creates irregularities at shock front which results in a greater dislocation generation at high strain rates (Ref 61). Thus, the microstructural differences of CS particles with regard to the bulk materials result in different stress–strain rate behaviors than what observed in Fig. 3(a). Furthermore, as displayed in Fig. 3, the experimental data points used to develop the models are mostly concentrated at strain rates below 10^6 1/s whereas in CS the initial strain rate upon impact is much larger.

Figure 4(a) compares the CoRs predicted by single-particle modeling using the CoR-fitted PTW model with experimental results from LIPIT tests. Reasonably good agreement is achieved using this new set of PTW parameters. The stress flow predicted by this set is compared with the stress–strain rate experiment results for bulk material, in Fig. 4(b) and (c). Interestingly, despite the ability in replicating the CoRs, the stress predicted by the model does not follow the data point for bulk materials.

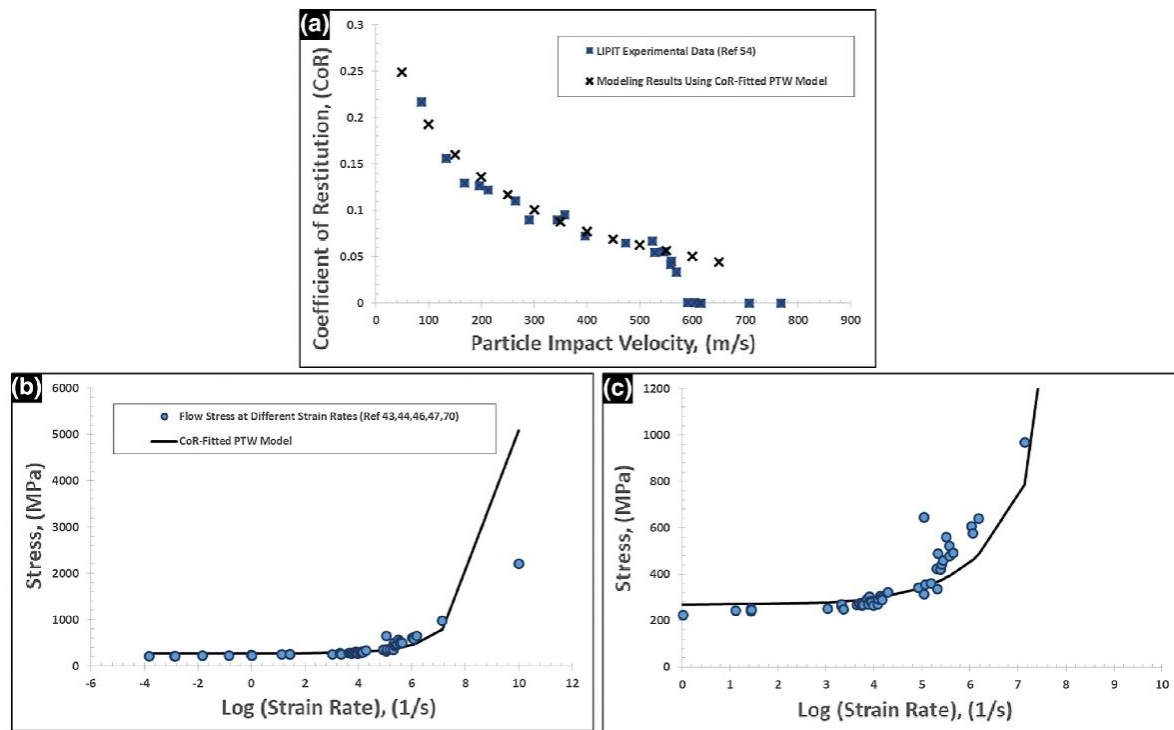


Fig. 4 (a) Comparison between the predicted CoRs using CoR-fitted PTW model and the LIPIT experimental data (Ref 54), (b) stress flow predicted by the CoR-fitted PTW model vs. the bulk material

experimental data (Ref 43, 44, 46, 47, 70), (c) zoom of figure (b) at strain rates where experimental data are scattered the most

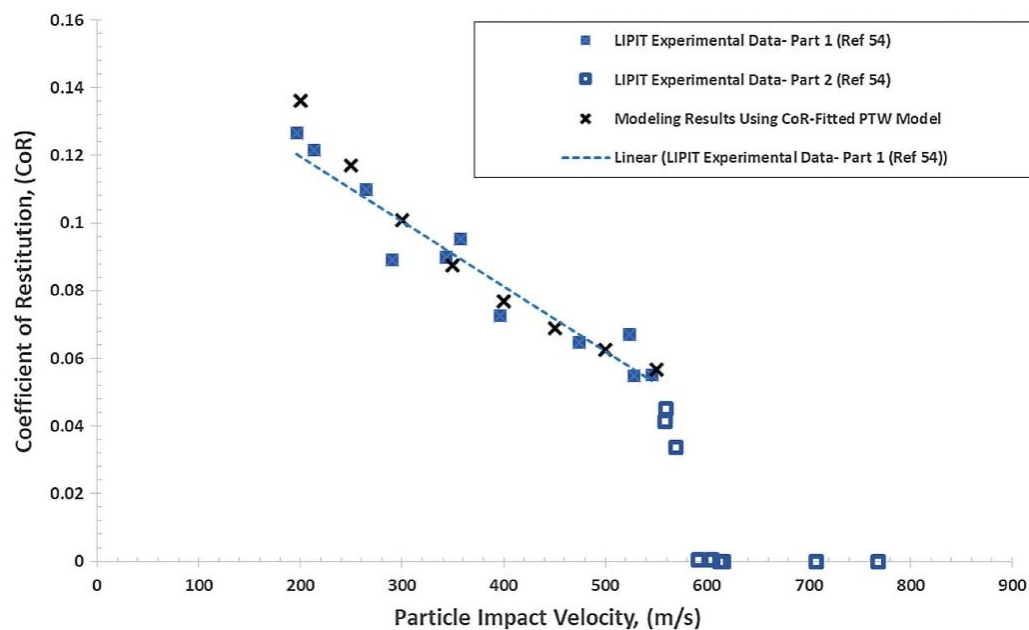


Fig. 5 Evaluation of the accuracy of the PTW parameter sets in predicting the LIPIT experimental CoRs (Ref 54). The line best fits the experimental data points using the least-square method

The accuracy of each set of material models in reproducing the CoRs was evaluated using the MSE technique. Figure 5 presents the distribution of the experimental and modeling CoRs compared with the experimental CoRs linear fit. The least-square method was used to find this best line fit. The line was fitted to the data points right before the velocity where CoR starts to drop. This velocity is 550 m/s for copper–copper materials. As seen in Fig. 5, the solid squares show the data point included in the evaluation process, while empty squares are not considered as bonding or partial bonding has occurred.

The MSE for the CoRs computed for different material models are reported in Table 4. As seen, the best accuracy is achieved using the CoR-fitted PTW model by the least MSE value of $5.2\text{e}-5$. The MSE for SSR-Fitted PTW Model is an order of magnitude larger than the CoR-fitted PTW model as for the experimental data. These results show the improved ability of the CoR-fitted PTW model in predicting the material rebound velocities (CoRs).

The macroscopic accuracy of the CoR-fitted PTW model is investigated by comparing the measured and modeled substrate crater diameter left after impact. Figure 6 illustrates a comparison between the crater sizes from JC, original PTW, and CoR-fitted PTW models with the one from LIPIT experiments for the initial impact velocities of 400 m/s and 550 m/s. It should be noted that the results from the modeling in Fig. 6(a) and (c) display half of the substrate crater. The LIPIT crater size was measured and the dimensions are 5.8 and 7.3 μm for particle impact of 400 s and 550 m/s, respectively (displayed in blue box in Fig. 6a and c).

As observed, the CoR-fitted PTW model is also capable of predicting the substrate craters with reasonable accuracy. Both the other models overestimated the crater sizes for particle impact velocities of 400 and 550 m/s. As shown in Fig. 6(b), no visible peripheral jetting is detected for the LIPIT crater at 400 m/s, which is also predicted accurately by the CoR-fitted PTW model (black solid line in Fig. 6a). Both the JC and original PTW model exaggerated the plastic deformation at the crater outermost edges.

When comparing the experiments and modeling results of rebound velocities at various particle impact velocities, it is revealed that rebound velocities reach a plateau at the impact velocity around 500 m/s and starts to drop when

approaching the powder critical velocity (580 ± 12 m/s) (Ref 54). This feature is presented in Fig. 7(a). The drop in rebound velocity observed in the experiments at 550 m/s was explained as extra energy spent for the particle/substrate deformation and to break the partial metallic bond at the particle/substrate interface (Ref 54). This feature was also reported using a physically-based bonding model (Ref 6). Molinari and Ortiz (Ref 73) explained the kinetic energy loss of steel particles at high-velocity impacts by the shear localization instability mechanism that results in material softening and hence larger plastic deformation.

Since the computed rebound velocities using the CoR-fitted PTW model do not account for the energy loss for breaking potential partial bonding, it was expected that the rebound velocities would keep rising as the initial impact velocity increases. However, a different trend is observed by further increasing the impact velocity beyond 550 m/s (Fig. 7a). This finding is explained by comparing the deformation level and deformation mechanism in the particle and the substrate for impact velocities of 550, 600, 650, 700, and 750 m/s, presented in Fig. 7(b) and (c) for the substrate and particle separately.

As the particle impact velocity increases, the elastic energy stored in the material also increases, theoretically providing a larger energy source for rebounding. However, the rebound velocity comes from the release of stored elastic energy parallel to the impact direction. Starting at 550 m/s, as visually observed in Fig. 7(b), material flows laterally into the outermost substrate edge. Meaning that a higher amount of initial kinetic energy is converted to deform elastically and plastically the substrate in a radial direction, parallel to the substrate surface. As such, from the increased impact velocity proportionally less elastic energy is released in the impact direction. Therefore, the rebound velocity increases.

To investigate the accuracy of existing nickel material models in replicating LIPIT results and modifying the PTW model if necessary, a similar procedure as the one used for copper was performed for nickel with results presented in Fig. 8. As seen in Fig. 8(a), the modeling results from the original PTW (Ref 59) and JC (Ref 33) models significantly deviate from the LIPIT results (Ref 53). Both these models underestimate the CoRs. The CoR-fitted PTW model, on the other hand, is capable of accurately reproducing the experimentally measured CoRs.

Table 4 Mean square error calculated for different material models vs. linear best-fit line

Data	Experiment (Ref 54)	PTW (Ref 39)	JC (Ref 33)	SSR-fitted PTW model	CoR-fitted PTW model
Mean square error (MSE)	4.95e−5	1.66e−3	1.45e−3	2.48e−4	5.2e−5

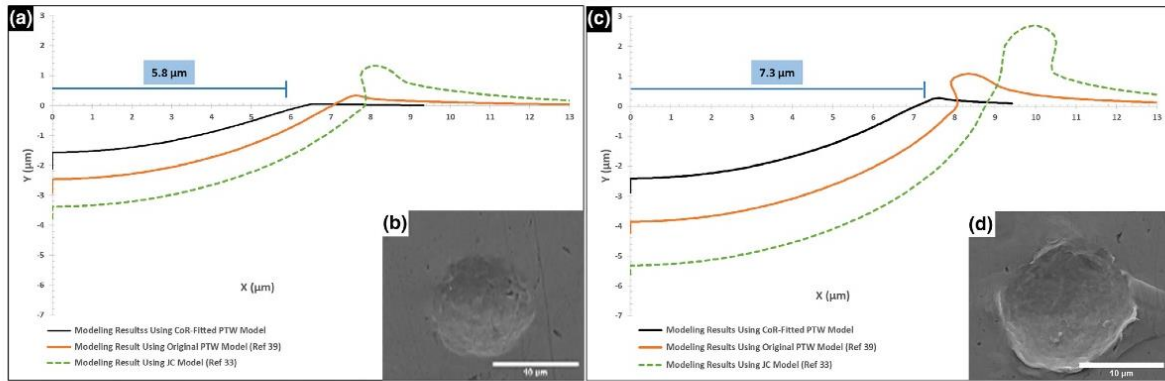


Fig. 6 Comparison between substrate crater size predicted by different models and the LIPIT experiment (Ref 54). (a), (c) The half substrate crater modeled using CoR-fitted PTW, original PTW (Ref 39), and JC (Ref 33) models for 12 μm powder and impact velocities of 400 m/s and 550 m/s, respectively. (b), (d) LIPIT

substrate crater left after the impact velocities of 400 m/s and 550 m/s, respectively, copper powder with the average particle diameter of $12.5 \pm 1.0 \mu\text{m}$ and a copper substrate. Values in the blue boxes are the LIPIT substrate crater radius

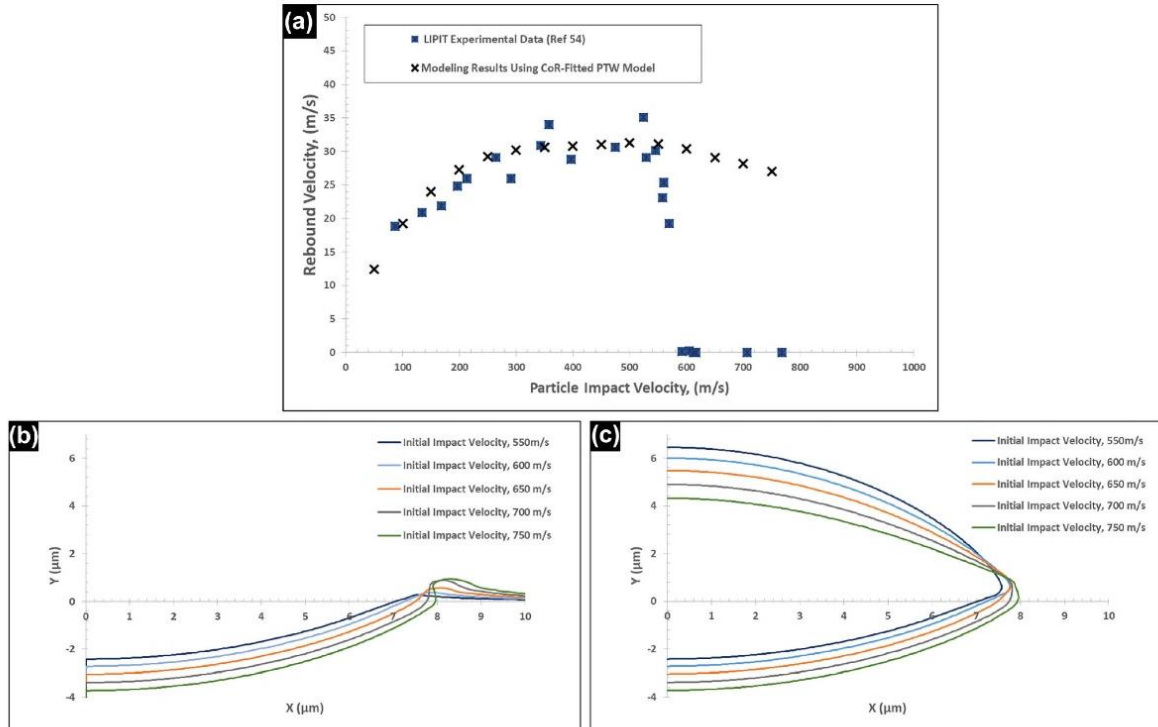


Fig. 7 (a) Comparison between rebound velocities obtained from LIPIT experiments (Ref 54) and simulation using the CoR-fitted PTW model for copper. (b) Simulated substrate craters using the CoR-fitted

PTW model for initial impact velocities of 550, 600, 650, 700, 750 m/s. (c) Simulated particle deformation using the CoR-fitted PTW model for initial impact velocities of 550, 600, 650, 700, 750 m/s

A huge gap observed in Fig. 8(a) between the results computed using the original PTW model parameters and the LIPIT results. This gap was narrower for copper (shown in Fig. 3c). This is due to the fact that the original PTW parameters for nickel were calculated using data

extracted from a limited number of relatively low strain rate experiments and MD simulations (Ref 74, 75), compounding the departure with microns-size CS particle impacts.

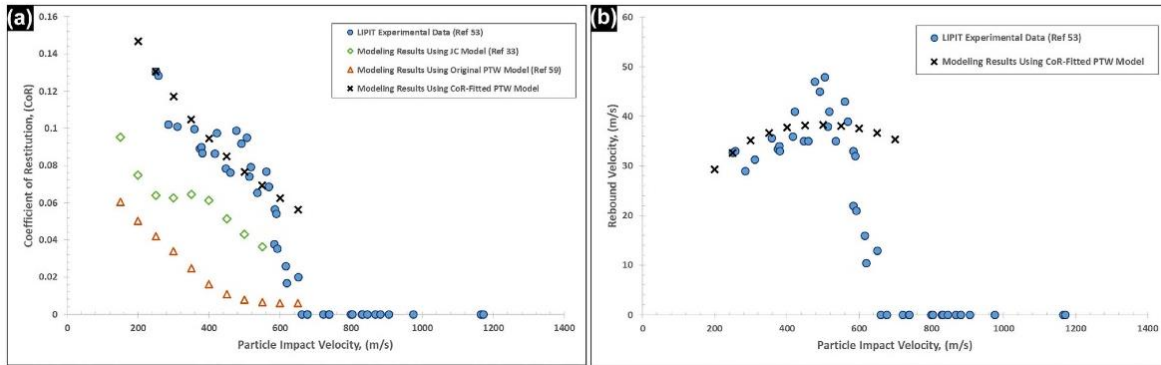


Fig. 8 (a) Comparative study between LIPIT data, Ni powder, $10 \pm 2 \mu\text{m}$, on nickel substrate (Ref 53) and modeling results, Ni powder $12 \mu\text{m}$ using JC (Ref 33), original PTW (Ref 59), and CoR-

fitted PTW models. (b) Rebound velocity as a function of impact velocity for LIPIT and modeling results using the CoR-fitted PTW

Table 5 CoR-fitted PTW model for copper and nickel

CoR-fitted PTW parameters	Copper	Nickel
Strain rate dependence constant (γ)	$1\text{e-}5$ [5.5e-6]	$1\text{e-}5$ [5.5e-5]
Strain hardening rate (θ)	0.025	0.01 [0.0095]
Strain hardening constant (d)	2	2
Yield stress constant at 0 K (y_0)	0.0001	0.0001
Yield stress constant at melting (y_∞)	0.0001	0.0001
Medium strain rate constant (y_1)	0.094 [0.0094]	0.094 [0.28]
Medium strain rate exponent (y_2)	0.575 [0.4]	0.575
High strain rate exponent (s_1)	0.25	0.25
Saturation stress at 0 K (s_0)	0.0085 [0.014]	0.0045 [0.0245]
Saturation stress at melting (s_∞)	0.00055	0.00055
Temperature dependence constant (κ)	0.11 [0.08]	0.11
Atomic mass (M), kg	1.055×10^{-25}	9.74627×10^{-26}
Shear modulus at 0 K (G_0), GPa	51.8	85.1
Material constant (D), GPa	3	9.13
Temperature material constant (T_0), K	165	269

The rebound velocity as a function of particle impact velocity for LIPIT and computed results using the CoR-fitted PTW model is plotted in Fig. 8(b). Interestingly, a similar behavior as illustrated in Fig. 7(a) for copper is also observed for nickel. An abrupt decrease in particle rebound velocity is evident for LIPIT experiments at the impact velocity close to critical velocity ($655 \pm 5 \text{ m/s}$). This drop can be attributed to the energy loss to break partial bonding, directional elastic loading/unloading, and extra energy dissipation due to the thermal softening mechanism.

Even though the CoR-fitted PTW model does not account for the kinetic energy loss of breaking partial bonding, computed particle rebound velocity shows a gradual drop for the impact velocity beyond 600 m/s. This drop is explained by the amount of elastic loading/unloading in the impact direction perpendicular to the

substrate surface. As the particle impact velocity increases, the strain energy stored/released parallel to the substrate surface increases, result in decreasing the normal kinetic rebound energy.

Table 5 provides the CoR-fitted PTW model for copper and nickel, with re-calibrated parameters reported in square brackets.

These new PTW parameters result in an improved prediction of the LIPIT experimental data and they are also physically reasonable. Higher material strength was expected for micro-polycrystalline powders that was included by increasing the s_0 value for copper. The grain size dependence of the strain rate sensitivity is also considered by increasing the slope of the SSR curve at high strain rates by calibrating γ . Similarly, a sharper transition from low strain rate thermally activated dislocation motion

to shock driven regime is also expected for medium strain rates which is included by decreasing both the values of y_1 and y_2 .

Transition from Rebounding to Bonding

To study the impact/rebound phenomena in CS of dissimilar materials and study the deformation mechanism associated with it, the computed rebound velocities using the CoR-fitted PTW parameters for copper impacting low carbon steel substrate are presented, and experimental results are provided.

The modeled rebound velocities of spherical copper powder with the initial diameter of $32\ \mu\text{m}$ impacting with initial velocities from 50 to 900 m/s the low carbon steel substrate are presented in Fig. 9(a). One can clearly observe two peaks: one at 350 m/s and one at 850 m/s.

For particle impact velocities below 350 m/s, the material elastic loading is concentrated in the impact

direction. This stored elastic energy increases as impact velocity increases and results in a faster rebound velocity upon elastic energy unloading. However, between 350 and 500 m/s, a different trend is observed. As the particle impact velocity increases, the particle rebound velocity gradually decreases (Fig. 9a). As illustrated in Fig. 9(b) and (c), at 350 m/s the particle starts to deform more in the radial direction parallel to the substrate surface as opposed to the impact direction. Thus, part of elastic energy is stored in a direction that does not contribute to speed up the particle rebounding (Fig. 9b). This feature is visualized by the flow of the particle radially at the particle periphery. Starting at 500 m/s, the rebound velocity increases again as the particle impact velocity increases. As seen in Fig. 9(d) and (e), although there is still an extent of radial deformation in the particle (Fig. 9d), substrate deformation along the impact direction becomes more pronounced (Fig. 9e). Therefore, the increase in impact velocity results in more elastic energy stored in the impact

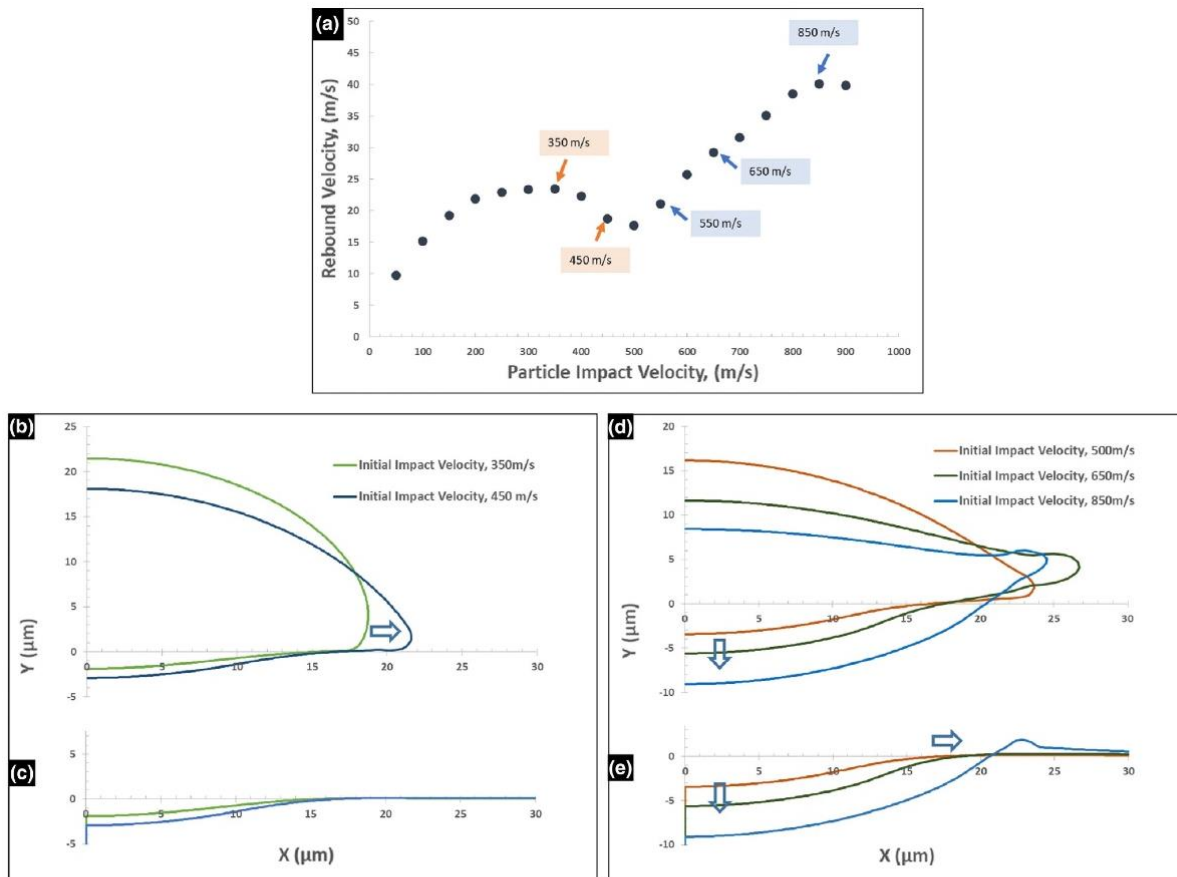


Fig. 9 Modeling results (a) particle rebound velocity of $32\ \mu\text{m}$ copper powder on steel substrate at various impact velocities (b), (c) particle and substrate deformation at velocities of 350, 450 m/s,

respectively (d), (e) particle and substrate deformation at impact velocities of 550, 650, 850 m/s, respectively

direction. This leads to an increase in rebound velocity. At 850 m/s, the rebound velocity starts to drop again. The second drop is due to the radial elastic loading/unloading in the substrate that means less elastic energy is available in the impact direction (Fig. 9d and e).

To complement the model results for the understanding of the rebound phenomena, an experimental study was conducted. Copper powders were deposited on a low carbon steel substrate. The particle velocity analysis results show an average in-flight velocity of 515 ± 61 m/s. The impact velocities vary from 200 to 600 m/s depending on the particle size and its location in the flow inside the nozzle (Ref 76).

Figure 10(a) shows the top view SEM image of the substrate after deposition. Higher magnification images of the selected deposited particles are displayed in Fig. 10(b) and (c). An example of recovered non-adhered particles collected and analyzed under SEM is presented in Fig. 10(d). Top view of a recovered particle on the left and the bottom view of a particle on the right are marked in Fig. 10(d).

As displayed in Fig. 10, particle peripheral jetting is observed for both the deposited and recovered non-adhered particles suggesting that the presence of particle peripheral jetting at the particle is not solely a sign of bonding in CS.

The left particle in Fig. 10(d) was severely deformed and flattened.

Further investigations were performed to examine the condition for bonding. This was achieved by comparing the substrate crater diameter for both the deposited particles and recovered non-adhered particles. Substrate crater diameter and particle splat diameter are shown schematically in Fig. 11(a). An example of a recovered non-adhered and a removed particle is shown in Fig. 11(b) and (c), respectively. Substrate crater diameter is measured from the crater imprinted by the particle where the dome shape ends that is also demonstrated by arrows in Fig. 11(b). The particle splat diameter is the average diameter of a circle that encloses the particle-inner and -outer deformed edges indicated by the green and orange arrows in Fig. 11(b), respectively. The results of the crater and splat diameters of non-adhered and adhered particles are provided in Fig. 11(d).

As illustrated, the substrate crater for the deposited particles is above a distinct value (approximately $25 \mu\text{m}$). As also presented in Fig. 10, material jetting is a common feature of all the deposited particle and most non-adhered particles. This emphasizes that observation of jetting is not a complete sign of bonding; it suggests that a critical substrate deformation is also necessary to allow bonding.

Fig. 10 SEM images of (a) deposited particles, (b), (c) close-up view of single particles, (d) recovered non-adhered particles, top view on the left, and bottom view on the right are shown

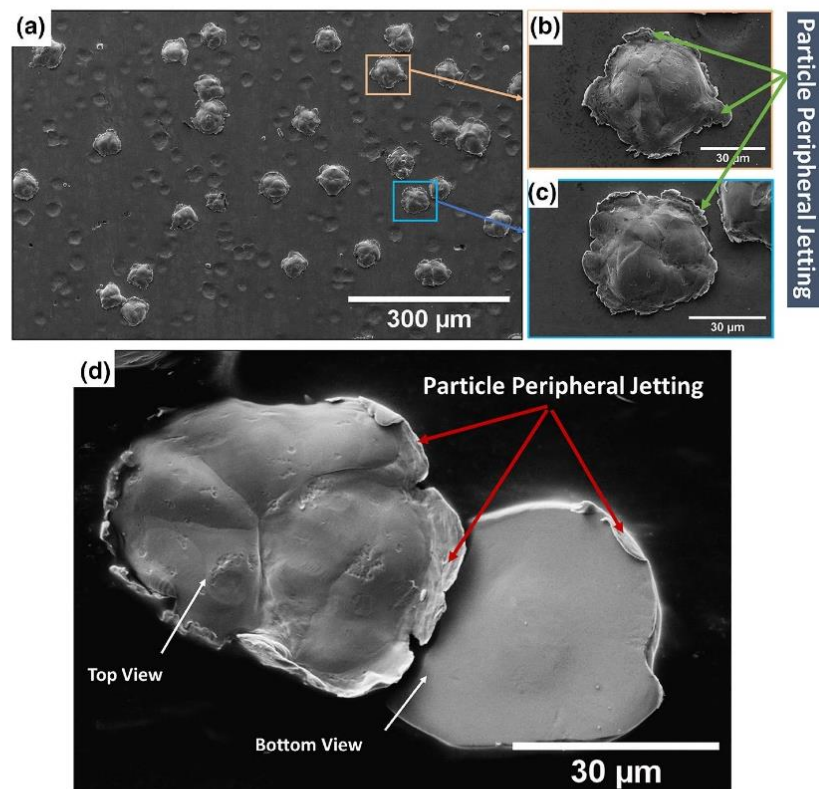


Fig. 11 Comparison between the substrate crater and particle splot diameter for bonded particle and recovered non-adhered particles. (a) Schematic illustration of substrate crater and particle splot diameter. (b) Impact interface of a recovered non-adhered particle. (c) Contact interface of a pulled-off particle. (d) Results of the substrate crater and particle splot diameter measurements

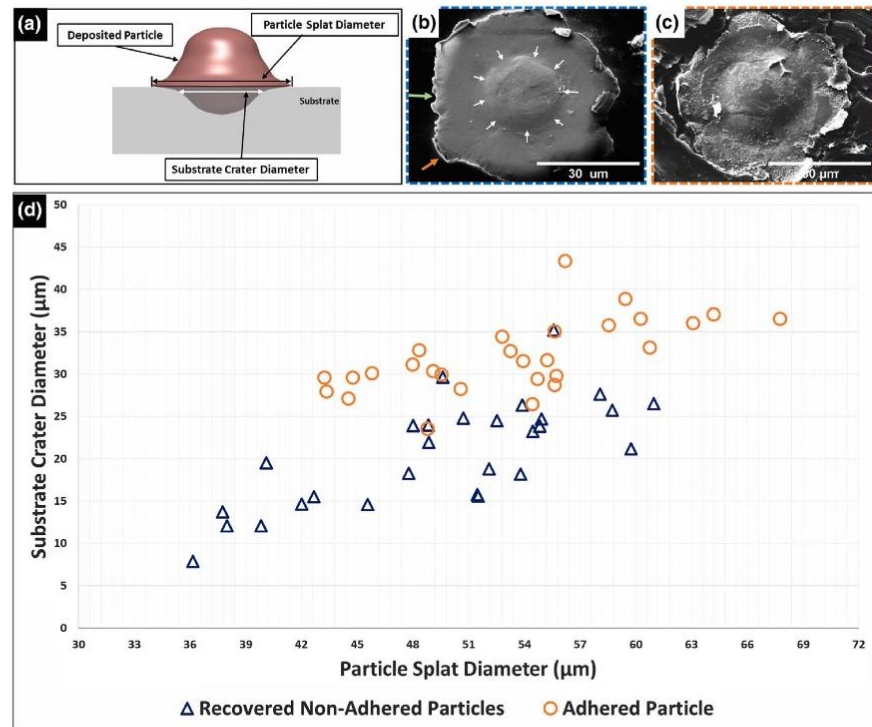
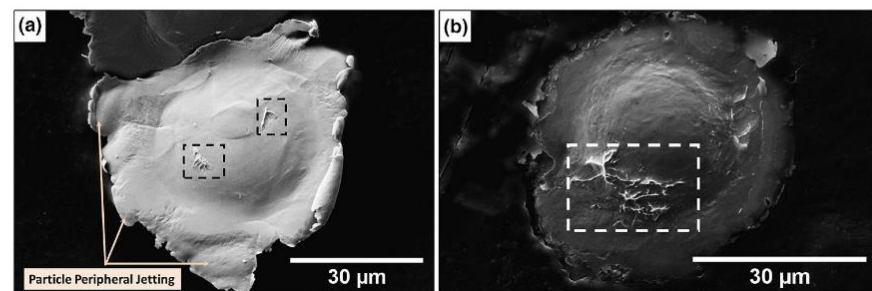


Fig. 12 SEM image of (a) recovered non-adhered copper particle, (b) pulled-off copper particle that was bonded to the substrate. The fractured interfaces are marked by dashed boxes



This finding is also in agreement with the bonding theory that enough impact pressure and threshold oxide cleaning is essential for both the contact surfaces.

The investigation also revealed visible evidence of ductile fracture for some of the recovered non-adhered particles. To confirm the presence of ductile fracture at these particles, the fractured surfaces were analyzed using the EDS analysis. The residual material was identified as copper. One example is shown in Fig. 12(a). In this case, the particle is partially bonded to the substrate during the impact. However, the localized bonding was not enough to overcome the rebound elastic energy, and thus the particle detached from the substrate. This phenomenon is expected to happen in the particle velocity range 500–850 m/s in Fig. 9, where the particle is excessively deformed and the substrate also experiences a noticeable deformation level.

One example of a permanently bonded particle is illustrated in Fig. 12(b). As shown, the sign of ductile fracture is significantly larger than the particle in Fig. 12(a). Thus, the adhesion strength was enough to overcome the elastic unloading, and the particle remained attached. For both the particles in Fig. 12, the particle crater size is larger than 25 µm. However, it is expected that the initial impact velocity of the bonded particle (Fig. 12b) was larger (after the second peak in Fig. 9). It should be reminded that the substrate material model parameters were estimated by the stainless Steel 304. This can result in an overestimation in the impact velocity where the peaks in Fig. 9 appear.

Conclusion

The capability of two commonly used material strength models in CS (JC and PTW models) in predicting experimental CoR results for copper and nickel was evaluated. It was shown that these material models failed to predict the CoR data accurately. JC model showing some inconsistencies as the particle impact velocity increases. The PTW model parameters were optimized and re-calibrated. An improved prediction of CoRs was achieved for both copper and nickel using the new model parameters. The PTW model with improved parameters was also able to predict crater diameter measured experimentally. The particle rebound velocity as a function of particle impact velocity was also studied. A sharp drop in particle rebound velocity was observed experimentally when reaching the critical value. This explained by the material deformation mechanism and the energy loss of breaking the partial bonding during rebounding.

A gradual drop in simulated particle rebound velocity, using the CoR-fitted PTW model, was observed for both nickel and copper. This drop was explained by the directional elastic loading and unloading during the deformation process. It was experimentally demonstrated that for the impact of copper powder on low carbon steel substrate, the presence of particle peripheral jetting is not a complete sign of bonding. A threshold substrate deformation is suggested to ensure the permanent particle adhesion. In addition, the presence of ductile fracture for the recovered non-adhered particle proves the theory of energy loss to break the partial bonding during the particle rebounding.

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5.2 Research Project 2: The Impact of Powder Storage Duration on Powder Surface Chemistry and Deposit Characteristics

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The current work aims to investigate the effect of naturally occurring oxides (formed on copper powder due to storage at ambient conditions) on the metallic bonding characteristics in CS. Low-carbon steel is selected as the substrate and the bonding characteristics are studied at the individual splat level. Detailed qualitative and quantitative composition analyses of the powder surface before and after room condition oxidation are performed using x-ray photoelectron spectroscopy (XPS). This study provides a comprehensive elemental analysis of the oxide at the powder outer shell and precise measurement of oxide film thickness for micron size particles. This approach provides information used to explain the different deposition behavior of individual copper particles with different shelf time (oxide layer thickness and composition). Particle interface characterization is conducted using local adhesion test experiments. A physically based finite element modeling method is implemented in the commercially available finite element software ABAQUS/Explicit to predict metallic bonding. It is used to explain the bonding requirements as the powder oxide scale increases. This model also further reveals the oxide cleanup mechanism when the soft powder impacts hard substrate at high strain rates.

This peer-reviewed paper addresses the objectives presented in section 3.2.



Bonding Mechanisms in Cold Spray: Influence of Surface Oxidation During Powder Storage

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Abstract Cold spray is a solid-state process in which solid particles are subjected to severe plastic deformation to form a coating. The effect of naturally occurring oxides on bonding in the cold spray was investigated in this work. Deposition characteristics of copper powder with different surface oxide thicknesses on steel substrate were examined using a local pull-off test. This enables the investigation of individual particle/substrate interfaces. X-ray photoelectron spectroscopy was used to study thoroughly the powder surface chemistry and the oxide thickness as a function of exposure time. This study revealed that the oxide film thickness grew from 6 nm for the as-received powder to 11.6 nm after 2 months of exposure to atmospheric conditions. Scanning electron microscopy and x-ray energy dispersive spectroscopy were used to characterize the particle/substrate interfacial bonding. Adhesion test results show that the bond strength is highly influenced by the surface oxide thickness. Different bonding behaviors and a drop in coating deposition efficiency were observed as the oxide thickness increased. Finite element simulations supplemented our understanding of the particle adhesion dynamics as the oxide film thickness increases. They were also used to study the surface oxide cleanup and bonding mechanism for particles with different oxide film thicknesses.

Keywords cold spray process · finite element simulation (FEM) · interfacial bonding · local pull-off test · oxide thickness · scanning electron microscopy (SEM) · X-ray photoelectron spectroscopy (XPS)

Introduction

Cold spray (CS) is a solid-state manufacturing process by which feedstock powder is deposited on a substrate following intensive plastic deformation due to high-velocity impact (Ref 1–4). This enables the formation of highly dense coatings with low oxide content since the feedstock powder is kept well below their melting temperature during their flight in an inert environment (Ref 1, 5).

According to the prevailing bonding theories in solid-state joining processes such as cold welding (Ref 6, 7), all metals and alloys are capable of forming bonds when their clean surfaces are brought together within the range of interatomic forces (Ref 8). However, different metals exhibit different abilities to form bonds, which has been attributed to differences in their oxide films (Ref 8). Depending on their chemical composition and thickness, these oxide films may have different mechanical properties that affect the bonding mechanism.

Achieving the proper particle impact velocity in CS is important, as it must be sufficient to disrupt the thin native oxide layer present at the solid interfaces and bring the two clean surfaces in contact (Ref 9–19). If the deformation level is not sufficient, some debris will remain at the interface and hinder local intimate contact (Ref 15–17, 19–22). The minimum particle velocity at which bonding occurs is known as the critical velocity and is an important parameter in CS (Ref 23–25). This velocity depends not only on the sprayed material and substrate properties, but

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also on powder size, morphology, composition, and impact temperature (Ref 24–30).

Comprehensive studies have been conducted aiming to identify ideal powder and substrate properties to produce high-quality depositions. Powder manufacturers use different processing methods and parameters that affect various powder characteristics such as morphology, microstructures, element content, and impurities such as carbon, nitrogen, and oxygen, the latter of which is most significant for this study. The quality and consistency of feedstock powder are key in producing homogeneous and uniform coatings in CS. This powder must be well-preserved and handled adequately to maintain its quality. It was shown that the properties of a coating are greatly affected by the chemistry of the raw materials (Ref 31). Powder surface oxygen content influences the powder critical velocity and thus the required spray parameters. Studies have shown that as the feedstock powder oxygen content is increased, the critical velocity also increases (Ref 15, 20, 32, 33). In general, oxidation has two deleterious effects on feedstock powder. Firstly, the presence of oxygen in the form of solid solution can cause a loss of ductility due to oxide dispersion and interstitial hardening, reducing the deformation level upon impact (Ref 34). Secondly, the oxide scale at the particle/substrate interface hinders the formation of particle/substrate bonding during impact (Ref 16, 20). Oxygen in the form of solid solution and oxide film is unfavorable. However, if the oxygen forms a second phase precipitate, it could improve the acceleration of grain refinement during recrystallization (Ref 35).

The effect of oxidation on the critical velocity for copper, 316L stainless steel, and Monel alloy has already been investigated and the results indicated an increase in critical velocity with an increase in oxygen content (Ref 33). The dependency of the critical velocity on material properties was more dominant at lower oxygen contents. The critical velocity of all the powders reached almost the same value beyond a certain oxidation level (Ref 33). The influence of oxidation on the deposition efficiency (DE) and adhesion strength of CS coatings has also been analyzed. The copper powder was isothermally oxidized at 200 °C. The deposition results indicated a drop in the coating adhesion strength and DE when the oxide content increased (Ref 15).

All of the previous studies demonstrated the important role of oxygen content in the overall CS coating formation at the macroscale. However, the detailed effect of the surface oxidation condition on the quality of interfacial bonding at the individual particle level has not yet been studied thoroughly. Understanding the bonding behavior of individual particles is important for the development of CS technology and the enhancement of particle adhesion strength.

Copper is widely used in CS and its potential use for antibacterial and antiviral applications is a current subject of study (Ref 36–38).

The current work aims to investigate the effect of naturally occurring oxides (formed on copper powder due to storage at ambient conditions) on the metallic bonding characteristics in CS. Low-carbon steel is selected as the substrate and the bonding characteristics are studied at the individual splat level. Detailed qualitative and quantitative composition analyses of the powder surface before and after room condition oxidation are performed using x-ray photoelectron spectroscopy (XPS). This study provides a comprehensive elemental analysis of the oxide at the powder outer shell and precise measurement of oxide film thickness for micron size particles. This approach provides information used to explain the different deposition behavior of individual copper particles with different shelf time (oxide layer thickness and composition). Particle interface characterization is conducted using local adhesion test experiments (Ref 39). A physically based finite element modeling method is implemented in the commercially available finite element software ABAQUS/Explicit to predict metallic bonding. It is used to explain the bonding requirements as the powder oxide scale increases. This model also further reveals the oxide cleanup mechanism when the soft powder impacts hard substrate at high strain rates.

Materials and Experimental Procedures

Materials

As-received gas atomized copper powder (Plasma Giken Co. Ltd., Japan) was selected as feedstock material. This powder has a purity level of 99.9%, and a diameter size range from 5 μm to 53 μm . The as-received powder was sieved to a narrower size distribution between 20 μm and 32 μm . Part of this powder was kept in vacuum-sealed conditions, labeled as powder type 1. Some of this powder was left at room conditions in a plastic bag (pressure of 1 atm, the relative humidity of 50%, and temperature of 30°C) for 30 days (labeled powder type 2), and 60 days (labeled powder type 3).

The exposure of copper to room conditions leads to the formation of copper oxide layers of different thicknesses and compositions depending on the exposure time. Copper reacts with oxygen and forms cuprous oxide (Cu_2O). Higher exposure time results in the formation of cupric oxide (CuO) by further reaction of Cu_2O with oxygen. The oxidation of copper powder is usually limited to a superficial film on the order of a few nanometers. This native oxide layer acts as a diffusion barrier for oxygen and

copper; therefore, the growth rate drops as the oxide layer thickness grows (Ref 40).

The size of the substrates used for the depositions was 25 mm × 35 mm × 75 mm. The substrate material, used to examine the effect of the powder oxide thickness on the deposition characteristics and the interfacial bonding characteristics, was low-carbon steel (ASTM SA516 grade70). The substrate surface was polished mechanically with a 1-μm solution to create a mirror finish surface before spraying.

Cold Spray Parameters

The copper powders were deposited using a commercially available EP Series SST Cold Spray system (Centerline Ltd. Windsor, Ontario, Canada). A De-Laval tungsten carbide nozzle having throat and exit diameters of 2 mm and 6.6 mm, respectively, along with a diverging section length of 120 mm was used. The spray parameters used for the copper deposition are given in Table 1. To examine the deformation characteristics of individual impacting particles, the spray conditions were adjusted to achieve a limited number of deposited particles on the substrate. For this purpose, a low feeding rate and a high gun traverse speed were used (Ref 25, 41, 42).

Sample Characterization

Scanning electron microscopy (SEM) (EVO MA-10, Carl Zeiss AG, Oberkochen, Germany) was used for image analysis of free powder. Zeiss SmartTiffV3 software was used to determine powder size distribution. All powders were mounted, polished, and then etched (etchant: 100 ml ethanol, 25 ml hydrochloric acid, and 5 grams ferric chloride) for microstructural examination using SEM. XPS was used to study the surface chemistry of the copper powder and for the quantitative analysis of the surface oxide film thickness. The free powder was analyzed in a ThermoFisher Scientific K-alpha spectrometer (monochromated Al K α x-ray source), using an x-ray beam of 400 μm, and charge compensation. Two spectra per powder type were analyzed, and the results were consistent with each other. All spectra were charge corrected to fit the adventitious C 1 s spectral component to the binding

energy of 284.8 eV (Ref 43) and analyzed using a standard Shirley background.

The oxide thickness can be estimated by relating the XPS intensities to the inelastic mean free path of the appropriate photoelectrons within the material. In other words, the oxide thickness can be related to the attenuation of the XPS signal, which in turn can be related to the ratio of the intensities of the photoelectrons from the oxide and the metal. This method provides a proper and direct estimation of the copper oxide film thicknesses on the powder surface, whereas other studies indirectly attributed the entire powder oxygen content to the oxide film. Hassani-Gangaraj et al. (Ref 44), for example, used the weight percentage of copper powder and estimated a relative oxide thickness by assuming that the entire oxygen content of the feedstock powder was present at the film layer. This assumption may result in an overestimation of the oxide film thickness. Additionally, the XPS analysis provides extra information that allows studying powder oxide growth as a function of ambient exposure time. For this purpose, the powder oxide shell elemental compositions, as well as oxide film thicknesses, are compared at two different stages: after 30 days of ambient exposure (first stage) and after 60 days of ambient exposure (second stage).

Nano-hardness indentation measurements were performed on powder cross sections at room temperature. Powders were mounted in resin and mechanically polished using a 0.05-μm-diameter diamond solution. An NHT³ Nanoindentation Tester (Anton Paar) equipped with a Berkovich diamond indenter tip was used. Five different indentations were made for each case. To avoid stress field interference, each indentation was performed on a different particle. The indenter load applied was 15 mN at a loading rate of 30 mN/min. An average penetration depth of approximately 800 nm was measured for all the powder samples.

The powder in-flight velocity was measured using a ColdSprayMeter (CSM) eVOLUTION (Tecnar Automation Ltd, St-Bruno, Canada). CSM is an optical sensing device used in the field of cold spray to perform an in-flight diagnostic on individual particles which allows complete velocity and size distribution analysis. This system uses a continuous 3.3 W laser (CW, Class IV) with an optical two-slit photomask to detect passing particles. In this study, the velocity measurements were performed at a location 10 mm downstream from the center of the cold spray nozzle exit. Measurements were taken over several minutes to ensure the collection of a robust data set. The data are represented through box and whisker plots for over 5000 collected data points for each type of powder.

Deformation behavior of deposited particles was studied using an optical microscope (VHX –1000, Keyence

Table 1 Cold spray processing parameter

Parameter	Value
Propellant gas	Nitrogen
Gas pressure	3.4 MPa
Gas temperature	500 °C
Traverse speed	200 mm/s
Standoff distance	10 mm

Corporation, Osaka, Japan) and a scanning electron microscope equipped with secondary (SE) and back-scattering electron (BSE) detectors as well as x-ray energy dispersive spectroscopy (EDS).

To characterize the effect of oxide shell thickness on the powder deposition behavior, DE was measured as the ratio of adhered particles to the total number of observed impacts (craters and adhered particles). For this purpose, the number of adhered particles and the total number of craters were counted using the ImageJ processing software. The analysis was conducted for ten separate images per deposit. Each image covers a 5.2 mm x 6.4 mm area, and approximately 2500 impacts for powder type 1, 2500 impacts for powder type 2, and 3000 impacts for type 3 were counted.

To evaluate the interfacial bonding at the particle/substrate interface, a new approach was used to allow observation of fractured contact surfaces (Ref 39). This method provides the ability to analyze multiple individual particles simultaneously, without using complex techniques such as focused ion beam, transmission electron microscopes (Ref 42, 45–51), or modified cavitation tests (Ref 42). The experimental setup is illustrated in Fig. 1. A thermally cured elastomeric adhesive (FM-1000, Cytec Engineering Materials, with an adhesive strength of 70 MPa) was used. Figure 1(a) illustrates a metallic pin, which is adhered to

the as-sprayed sample. The metallic pin is then pulled off using Pull-off Adhesion Tester (DeFelsko ATA PosiTest Automatic Pull-Off Adhesion Tester), locally removing the particles. Detached particles and the craters left on the substrate are illustrated in Fig. 1(b). Analysis of fractured surfaces at the particle/substrate interfaces enables the understanding of the effect of oxide films on the quality of metallic bonding. A schematic of a single detached particle is shown in Fig. 1(c).

Numerical Model

To improve our understanding of the role of powder surface oxides on the adhesion mechanism, a numerical model was used to simulate and predict the adhesion in dissimilar materials when the oxide film thickness increases. For this purpose, the metallic bonding prediction model proposed by Rahmati et al. (Ref 52) was implemented in the commercially available finite element (FE) software ABAQUS/Explicit.

In this model, the Preston–Tonks–Wallace (PTW) constitutive model was used, which was also integrated into ABAQUS through a user subroutine (VUHARD). The PTW constitutive model has shown to be the model providing the most accurate particle deformation prediction at

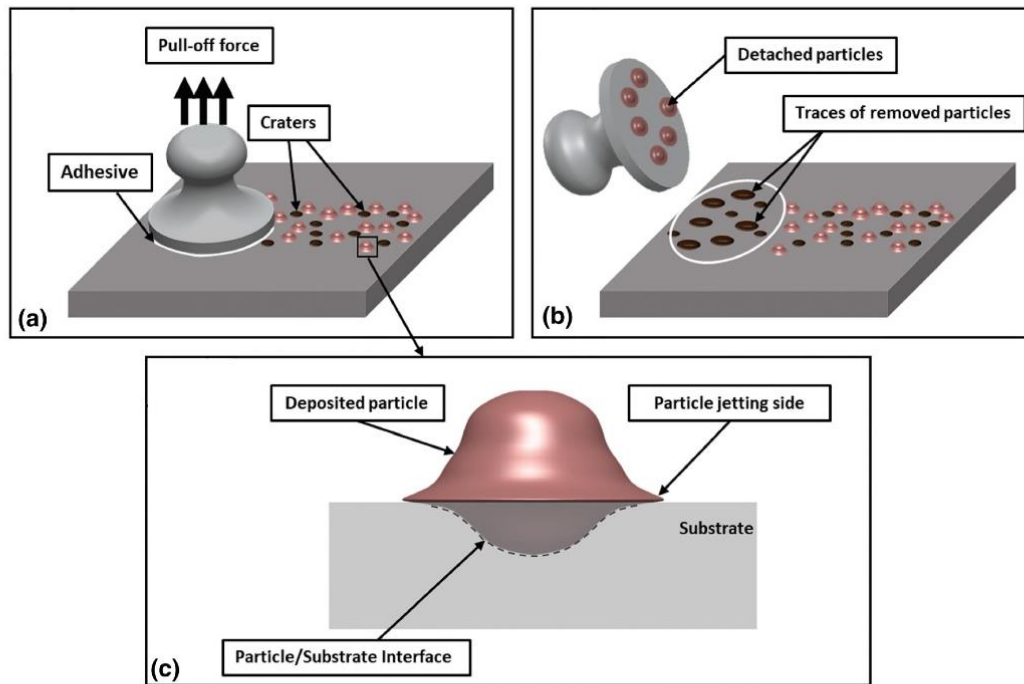


Fig. 1 Schematic of the local pull-off test setup. (a) metallic pin glued on the as-sprayed sample, (b) metallic pin was pulled off and detached particles, as well as the traces of removed particles, are observed (c) side view of a deposited particle

high strain rates (larger than 10^7 s^{-1}) found in cold spray (Ref 53, 54).

An axisymmetric geometry was used in the simulation. Particles were assumed to be perfectly spherical with $26 \mu\text{m}$ diameter, and the substrate geometry was modeled as a cylinder with a radius and height each 5 times larger than the particle diameter.

The particle and substrate materials used for the simulation were copper and stainless steel, respectively. Stainless steel 304 was used due to the lack of available data for 316L for the PTW model. The mechanical and thermal properties of both materials are available (Ref 52, 55). The modeling framework and simulation parameters used in this study were described in detail elsewhere (Ref 52).

Metallic bonding in CS is modeled based on the bonding theory of the cold welding process. Based on this theory, bonds at metal surfaces are formed when oxide-free surfaces come into contact. Figure 2 illustrates the joining mechanism of the cold welding process. Naturally, metallic surfaces are covered by a native oxide film (Fig. 2(a)). This oxide film must be stretched and broken first (Fig. 2(b)). Then, enough pressure must remain to extrude the materials into cracks and allow intimate contact, leading to metallic bonding (Fig. 2(c)).

In this theory, the bond strength between the two welded surfaces is obtained as follows:

$$\sigma_B = P \cdot \Psi$$

where P is the contact pressure at the interface, and Ψ is the surface expansion factor. The surface expansion factor represents the material deformation extent and surface cleanliness (Ref 7, 56). Ψ is defined as follows:

$$\Psi = \frac{A_1 - A_0}{A_1}$$

where A_0 and A_1 are the initial and the final deformed surface area, respectively (Fig. 2).

It was experimentally shown that bonding is not achieved unless Ψ reaches a critical surface expansion value, $\Psi_{\min}$ (Ref 56, 57). $\Psi_{\min}$ is the minimum surface expansion required to cause the fracture of the oxide film and create a sufficient gap along the oxide layer. This threshold value, which is dependent on the metal combination and oxide film thickness, ensures a proper surface cleanup (Ref 56, 57). Bay et al. reported $\Psi_{\min}$ values for successful bonding in the cold welding process for different metallic surfaces (Ref 56, 57).

The schematic shown in Fig. 2 also compares the key steps for the adhesion mechanism in the surfaces covered

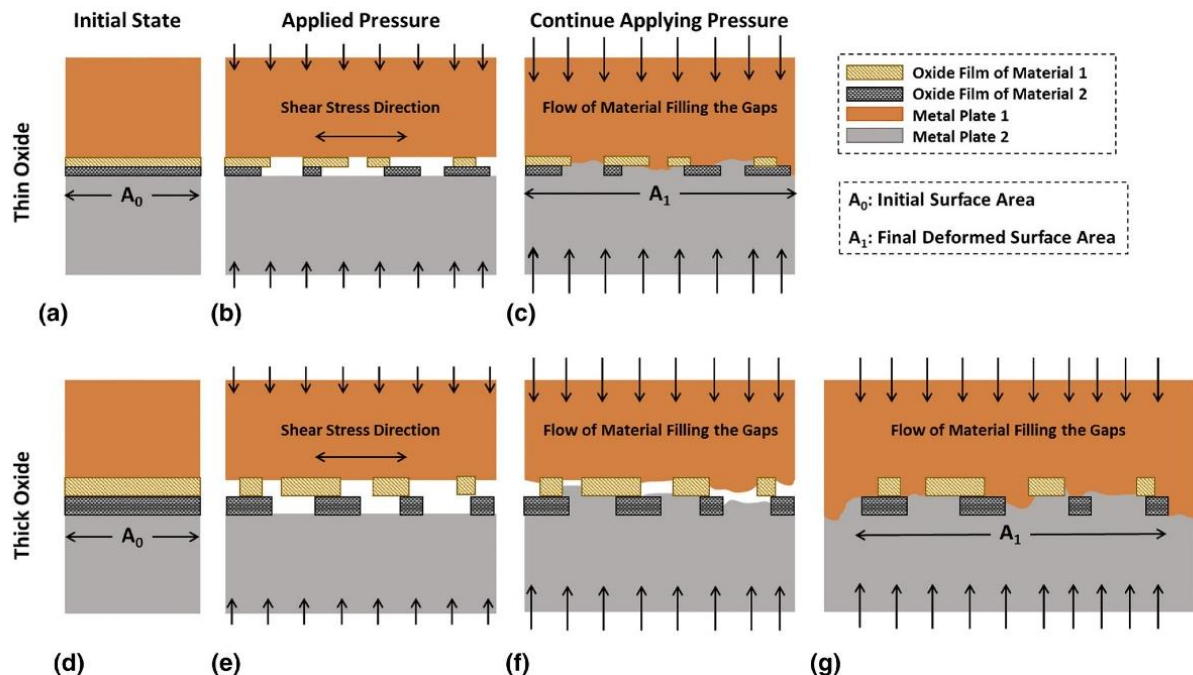


Fig. 2 Schematic of joining mechanism in cold welding process proposed by Bay et al. (Ref 56, 57), (a) initial state of a plate covered by thin oxide film, (b) surface expansion and oxide layer break up due to applied pressure, (c) metallic bond formation of two fresh surfaces in contact, (d) initial state of a plate covered by a thicker oxide film,

(e) surface expansion and oxide break up due to applied pressure, (f) absence of bond as pressure is insufficient to induce complete material extrusion (surface area in (c), and (f) are equal), (g) metallic bond formation when the required surface expansion is achieved, allowing complete material extrusion

by thin (Fig. 2(a)–(c)) and thick (Fig. 2(d)–(g)) oxide films. According to Khaledi et al., the minimum surface expansion increases as the oxide layer grows (Ref 58), shown by Fig. 2(d)–(g).

The minimum surface expansion values $\Psi_{\min}$ for relevant materials are presented in Table 2. Particles and the substrate are made of copper and stainless steel, respectively. The threshold surface expansion of 0.44 is used for particle 1, and $\Psi_{\min} = 0.6$ is approximated for the substrate (Ref 56).

Based on Bay et al., the surface expansion value for iron is $\Psi_{\min} = 0.6$. Since the literature lacks $\Psi_{\min}$ data for stainless steel, 0.6 was used in this modeling due to the similar nature of these two materials. Also, the oxide film thickness for particle 2 is slightly larger than for particle 1. Although the correlation between $\Psi_{\min}$ and film thickness is not known for particle 2, the data for particle 1 is used to provide an estimation. Therefore, the $\Psi_{\min}$ value for particle 2 was taken as 0.6, slightly higher than that for particle 1.

To implement the proposed bonding mechanism in the FEM modeling, the surface expansion was defined by measuring the strain applied on the contact surfaces. As mentioned previously, an axisymmetric geometry was chosen for this study. In an axisymmetric geometry, the contact surface is modeled by only one edge. The surface expansion at the contact surface is defined by measuring the strain applied on the contact edge. Therefore, Ψ is expressed as (Ref 52):

$$\Psi = 1 - \frac{1}{e^{\varepsilon_r} e^{\varepsilon_\theta}}$$

where ε_r is the logarithmic plastic strain along the element direction obtained by using transformation equations for plane strain (or radial strain), and ε_θ is the logarithmic hoop (or circumferential) plastic strain.

To predict the critical velocity, a series of numerical modeling simulations at different impact velocities were conducted. For this purpose, the simulation was initialized with an impact velocity of 550 m/s, increased by an increment of 20 m/s until evidence of metallic bonding was observed. This procedure resulted in critical velocities of 680 m/s and 700 m/s as numerically predicted critical velocities for particles 1 and 2, respectively. The deformation and adhesion mechanism of particles 1 and 2 were

then studied under impact velocities of 680 m/s and 700 m/s. These results are reported in the result section.

Results and Discussions

Powders Morphology and Microstructure

The morphology and size distribution of the feedstock powder were examined using SEM. As shown in Fig. 3, all the powder particles are spherical. Some satellites are attached to the larger particles, which is a common feature in gas atomized particles (Ref 59). Images at higher magnifications of powders type 1, 2, and 3 are provided in Fig. 3(d), (e), and (f), respectively. These images depict a smooth surface for all particles. Powders appear to have a combination of fine and coarse equiaxed grains.

The particle cross-section images of the as-received powder are shown in Fig. 4. The powders show dense microstructure since no internal pores or other defects are observed (Fig. 4(a)). The cross-section image of etched powder is shown in Fig. 4(b). Particle grain boundaries are observed showing the equiaxed grain structure with grain dimensions varying from 6 to 20 μm .

The powder surface chemistry was studied using XPS. Using this technique, the thickness of the analyzed layer was found to be approximately 10–20 nm. The corresponding XPS survey analyses are shown in Fig. 5, which indicate the presence of Cu, O, and C only (with the latter being associated with surface contamination).

The calculated chemical compositions (excluding carbon) provided in Table 3 indicate that the near-surface oxygen content of powders type 2 and type 3 are higher (58.9 and 59.3%, respectively) than that of powder type 1 (42.8%).

To elucidate the chemical state in which copper is found at the surface of the powders, Cu(0) (metal Cu), Cu(I) (Cu_2O), or Cu(II) (CuO), high-resolution Cu 2p XPS spectra were collected (Fig. 6). These exhibited the main Cu 2p_{3/2} emission line at 932–933 eV, and shake-up peaks of variable intensities at 940–945 eV. Shake-up peaks are present in the spectra of d^9 Cu(II) containing samples but are absent in d^{10} Cu(0) or Cu(I) spectra (Ref 60). Consequently, the main Cu 2p_{3/2} emission line contains Cu(0), Cu(I), and Cu(II) contributions, whereas the shake-up

Table 2 Minimum surface expansion ($\Psi_{\min}$) values of solid surfaces studied in the modeling

	Particle 1 (Ref 56)	Particle 2 (approximated)	Substrate (Ref 56)
Minimum surface expansion ($\Psi_{\min}$)	0.44	0.6	0.6

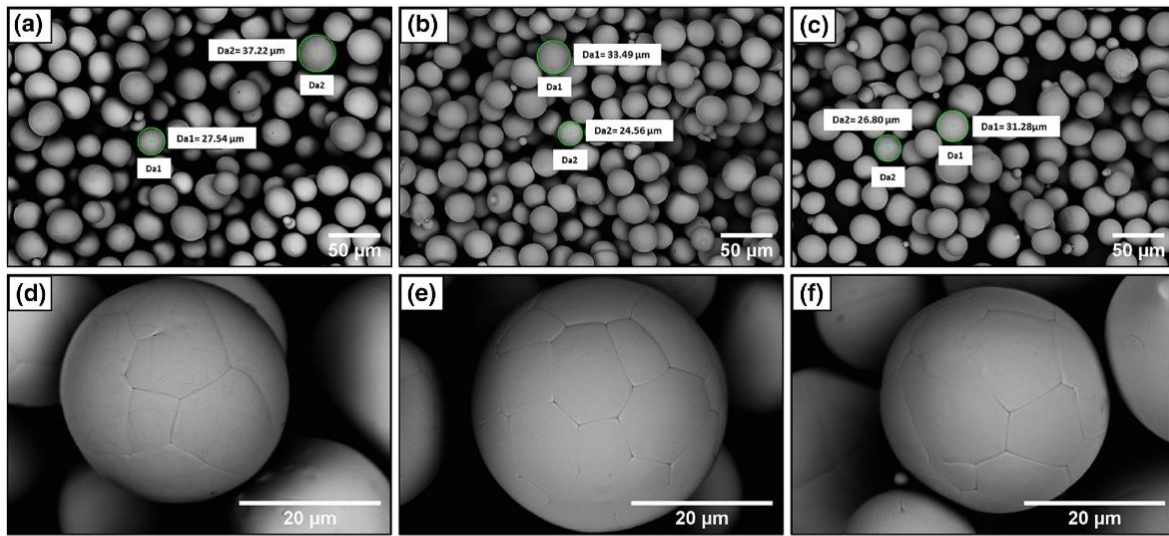


Fig. 3 SEM morphology and size distribution of (a) copper powder type 1, (b) copper powder type 2, (c) copper powder type 3, high magnification images of one individual particle from (a), (b), and (c) are shown in (d), (e), and (f), respectively

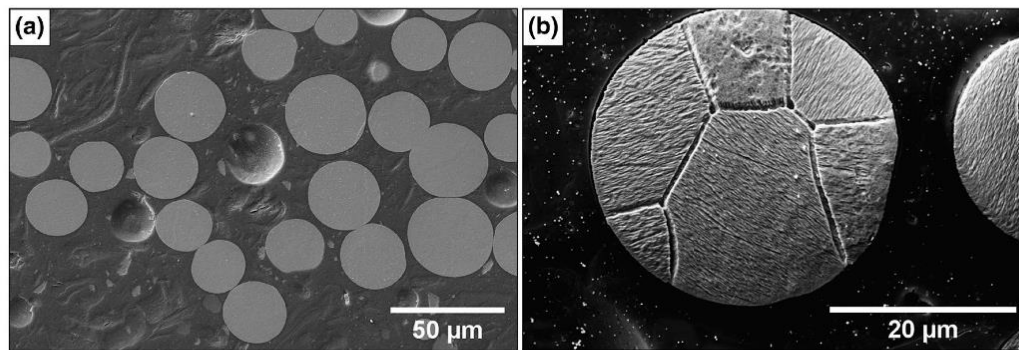


Fig. 4 Cross-section SEM images of as-received copper powder (a) before etching and (b) after etching

satellite intensity is entirely attributed to the Cu(II) state. In this experiment, powder type 1 exhibits a weak shake-up peak, while type 2 and type 3 powders both exhibit strong shake-up peaks. Therefore, qualitatively, type 2, and type 3 powders both contain more CuO than type 1 powder.

To quantify the atomic percentage associated with the [Cu(0) + Cu(I)] and Cu(II) chemical states, the Cu 2p spectra were analyzed using the following equations (Ref 43, 61):

$$\%[\text{Cu}(0) + \text{Cu}(\text{I})] = \frac{A - (A_{1s}/B_s)B}{A + B} \times 100$$

$$\%\text{Cu}(\text{II}) = \frac{B(1 + (A_{1s}/B_s))}{A + B} \times 100$$

where A is the peak area associated with the main Cu 2p_{3/2} emission line, B is the peak area associated with the shake-up satellite (Fig. 6), and A_{1s}/B_s is the ratio of the main-

peak/shake-up peak areas for a 100% pure Cu(II) sample (~ 1.89 for CuO (Ref 43)).

The results of this quantification are presented in Table 4, which confirms that powders type 2 and type 3 contain more CuO than the powder type 1 at the outermost layer ($\sim 78\%$ versus $\sim 16\%$, respectively).

For improved differentiation of the Cu(0), Cu(I), and Cu(II) states at the surface of the powders, high-resolution Cu L₃M_{4,5}M_{4,5} Auger spectra were collected (Fig. 6). Previous works have shown that a clearer differentiation among copper species can be made using the Cu L₃M_{4,5}M_{4,5} Auger spectral line as compared with the use of Cu 2p line (Ref 62, 63).

Biesinger recently published (Ref 43) a complete list of Cu L₃M_{4,5}M_{4,5} Auger fitting parameters for several high-quality copper-containing species. In particular, the analysis includes spectral lines for Cu, Cu₂O, and CuO using

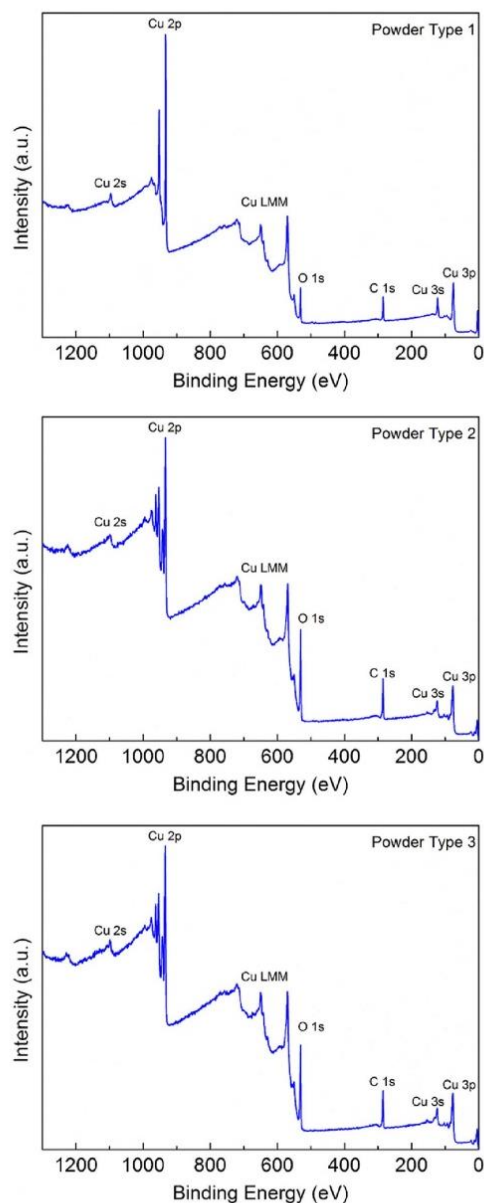


Fig. 5 XPS survey spectra

Table 3 Near-surface chemical composition of the powders (XPS survey analyses)

Element	Powder type 1	Powder type 2	Powder type 3
Copper, %	57.2	41.1	40.7
Oxygen, %	42.8	58.9	59.3

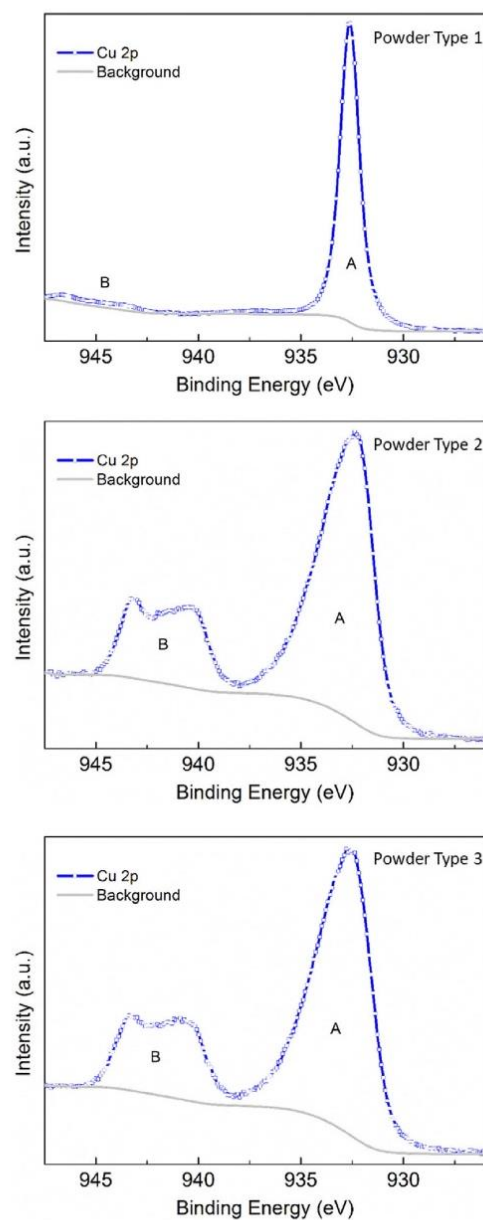
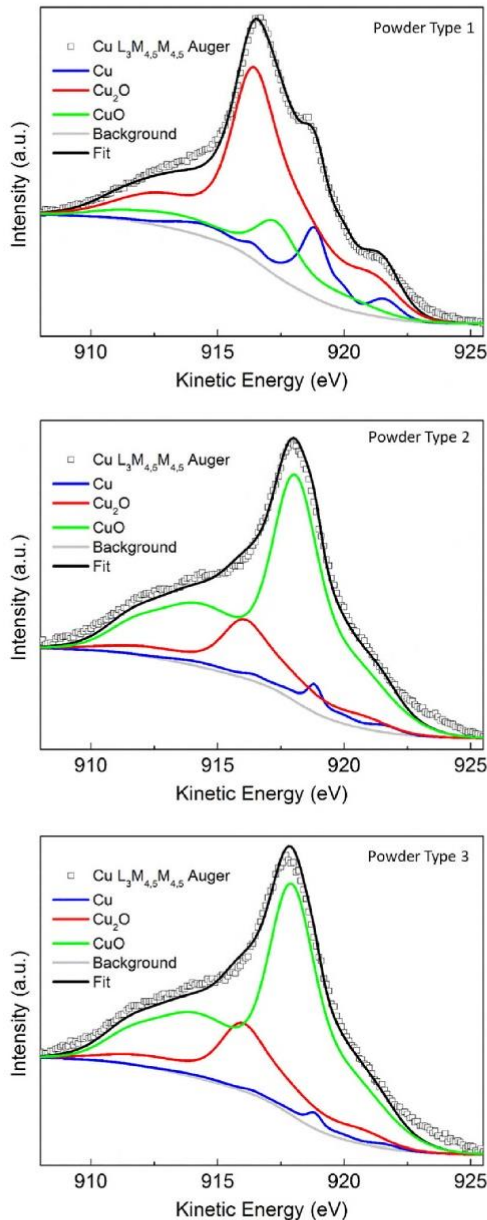


Fig. 6 High-resolution Cu 2p_{3/2} spectra

seven, four, and four peaks, respectively. His report also contains all corresponding peak positions, Full Width at Half Maximum (FWHM) values, and peak areas.) Biesinger's fitting parameters were used to fit our Cu L₃M_{4,5}M_{4,5} Auger data points by considering the simultaneous contributions of Cu, Cu₂O, and CuO. The peak positions in the fitting process were constrained to the values reported by Biesinger within ± 0.8 eV to account for the charging effects and inaccuracies of the method.

Table 4 Atomic Percentage of [Cu(0) + Cu(I)] and Cu(II), estimated using the Cu 2p spectral line

	Powder type 1	Powder type 2	Powder type 3
[Cu(0) + Cu(I)], %	83.6	21.4	21.7
Cu(II), %	16.4	78.6	78.3

**Fig. 7** High-resolution Cu $L_{3}M_{4.5}M_{4.5}$ Auger spectra

The results of the Cu $L_{3}M_{4.5}M_{4.5}$ Auger fitting process are shown in Fig. 7 and the corresponding phase quantification (using the peak areas) are reported in Table 5.

Table 5 Atomic percentage of Cu, Cu_2O , and CuO estimated using the Cu $L_{3}M_{4.5}M_{4.5}$ auger spectral line

	Powder type 1	Powder type 2	Powder type 3
Cu, %	15.7	5.6	3.1
Cu_2O , %	66.1	19	21.4
CuO, %	18.2	75.4	75.5

It can be observed that powder type 1 contains more Cu and Cu_2O whereas powder type 2 and powder type 3 contains more CuO. Table 5 shows that the amounts of CuO and [Cu + Cu_2O] are in agreement with the values obtained using the Cu 2p spectral line (Table 4).

The copper oxide layer thickness in the powder samples (t_{ox}) can be estimated from the ratio of Cu_2O and CuO oxides to Cu peaks intensity (I_{ox}/I_m) in the Cu $L_{3}M_{4.5}M_{4.5}$ Auger spectral line using the Strohmeier equation (Ref 64):

$$t_{ox} = \lambda_{ox} \sin \theta \ln \left(\frac{N_m \lambda_m I_{ox}}{N_{ox} \lambda_{ox} I_m} + 1 \right)$$

where N_m and N_{ox} are the volume densities of the metal atoms in the metal and oxide, respectively ($N_m/N_{Cu_2O} = 1.68$, and $N_m/N_{CuO} = 1.78$ (Ref 43), λ is the inelastic mean free path of the photoelectrons, and θ is the photoelectron take-off angle (90° for our spectrometer). The values of λ for Cu $L_{3}M_{4.5}M_{4.5}$ Auger electrons are $\lambda_m(Cu) = 1.54$ nm, $\lambda_{ox}(Cu_2O) = 1.77$ nm, and $\lambda_{ox}(CuO) = 1.76$ nm (Ref 43).

The estimated powder oxide thicknesses are shown in Table 6. The total oxide thickness varied from 6 nm (powder type 1) to 11.6 nm (powder type 3).

The elemental analysis of the powder outer shell presented in Table 5, as well as the estimated oxide thicknesses, shown in Table 6, provide a framework for the oxide growth as a function of ambient exposure time for copper powder. Oxide growth occurs within the first thirty days of exposure. Analysis of the data provided in Table 5 reveals that a high portion of Cu_2O and Cu from the as-received powder is transformed into CuO at the end of the first stage (powder type 2). Although the oxide growth continued after the first stage, this change occurred at a slower rate. The oxide layer thickness (as presented in Table 6) increases by approximately 3.5 nm during the first oxidation stage and approximately 2.1 nm during the second stage.

Table 6 Thickness of the oxide layer, estimated using the Cu $L_{3M_{4,5}}$ auger spectral line

	Powder type 1	Powder type 2	Powder type 3
Cu ₂ O film thickness, nm	3.9	3.6	4.7
CuO film thickness, nm	2.1	5.9	6.9
Total oxide film thickness, nm	6.0	9.5	11.6

Table 7 Nano-hardness Indentation at Interior Copper Powder Cross-section

	Powder type 1	Powder type 2	Powder type 3
Nano-hardness, MPa	1111.9 ± 213.5	1011.5 ± 114.2	1128.9 ± 122.7

Nano-hardness analyses of the powder cross sections are presented in Table 7. The results suggest that the powders have nearly the same hardness. This finding along with the XPS analysis results confirm that the presence of oxygen is mostly restricted to the particle outer shell. The large standard deviation of the measured hardness may be attributed to experimental uncertainties such as powder/epoxy separation during loading.

Powder Deposition Characterization

The particle velocity analysis results are shown in Fig. 8. The average impact velocities and particle velocity distributions appear to be roughly identical for all powder types. This result suggests that as one would expect, particle in-flight velocity is independent of particle surface oxidation for the powder oxide film thicknesses presented in this study. The particle in-flight velocity distribution is a result of the non-uniform flow path inside the nozzle as well as the distribution of particle size. The observed velocity distribution is typical of CS (Ref 29, 65).

Top-view images of as-sprayed samples were investigated to measure deposition efficiency (DE). The results are presented in Table 8. A drop in DE is observed as the surface oxide thickness increases. This result is in agreement with the observed increase in critical velocity and with the trends from the literature (Ref 15, 20, 33).

Deposition efficiency links the number of successful impacts with the total impacts. Particles which deposit on the substrate are, in general, those with impact velocities equal to or larger than the critical velocity. The results from particle velocimetry along with the DE measurements are used to estimate the critical velocities of each powder type (Ref 66). First, DE results are used to find the percentage of successfully bonded particles. Next, the Cold Spray Meter (CSM) results are investigated. As shown in Fig. 9, the deposited particles are those which are in the top portion of particles with respect to velocity. As such, the lowest velocity in this range represents the critical velocity. Approximately, 760 particles out of total 5225 impacts (to match as best as possible the measured DE) had an impact velocity on average more than 560 m/s (553–565 m/s bin).

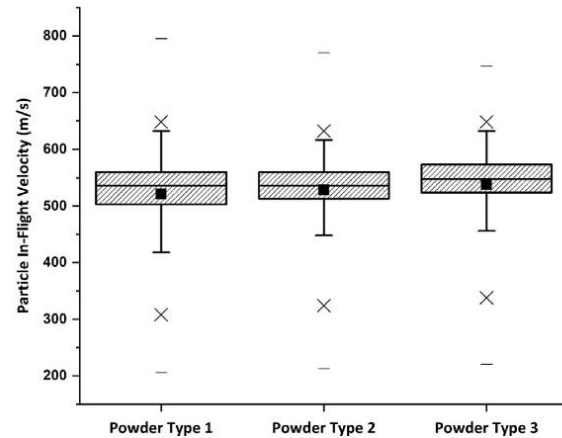


Fig. 8 Particle in-flight velocities of copper powder type 1, type 2, and type 3 (box and whisker plot with filled square representing the mean, X representing the 1st–99th percentile, —representing the minimum and maximum value, the box representing first, second, and third quartile (25th–50th–75th percentile, respectively), the whisker representing 1.5 times the interquartile range (IQR) below the first quartile, and above the third quartile. IQR is the first quartile subtracted from the third quartile

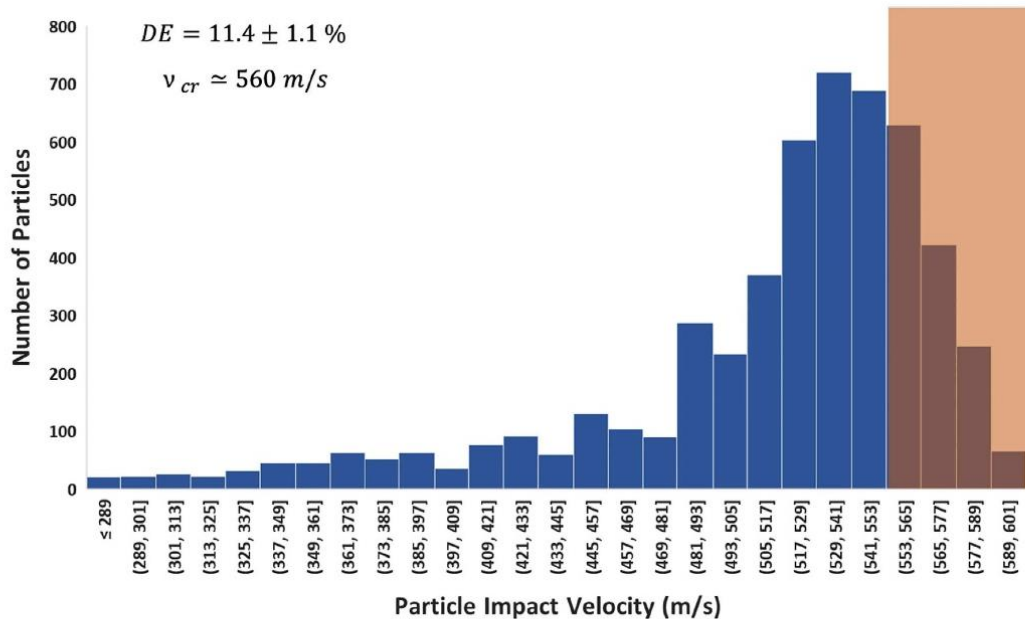
This critical velocity for powder type 1 is in agreement with what has been reported for copper on steel (Ref 12). The results for each powders type are given in Table 9.

Next, the deposited particles as well as the particle/substrate interfaces are analyzed. Figure 10 illustrates an example of the analysis procedure for deposited particles. Figure 10(a) shows a schematic cross-section view of a deposited particle that was used to identify the analysis spots. The top view of each adhered particle (such as Fig. 10(b)) is studied and the splat deformation behavior of different feedstock powders is compared. Then, the deposited particles are removed and evidence of ductile fracture (caused by the presence of metallic bonding) on substrate and powder are investigated in detail (Fig. 10(c), (d) respectively). The surface area of the particles covered by ductile fracture dimples is measured and the collected data is compared for powders type 1, type 2, and type 3.

Figure 11 illustrates the top-view SEM images of deposited particles of type 1, type 2, and type 3. A

Table 8 Deposition efficiency for powder type 1, type 2, and type 3

Feedstock powder	Powder type 1	Powder type 2	Powder type 3
Deposition efficiency, %	11.4 ± 1.1	7.3 ± 0.4	6.4 ± 0.2

**Fig. 9** Determination of critical velocity based on the DE and CSM results for powder type 1, the colored box indicates the total deposited particles and the range of their impact velocities**Table 9** Critical velocity-based DE calculated using the CSM results

Feedstock powder	Powder type 1	Powder type 2	Powder type 3
Critical velocity range, m/s	[553–565]	[561–575]	[584–598]

comparison between these images indicates that there are no noticeable differences in the particle deformation behavior. This confirms that the particle surface oxidation state plays a minor role in the degree of plastic deformation. The extent of material jetting is also similar for each particle type. However, their deposition efficiencies are different. This finding is in agreement with what was observed by Ichikawa and Ogawa (Ref 50).

SEM images of detached particles (over thirty particles for each type) were studied and their adhesion features investigated. Detached particles were classified into two categories: particles showing evidence of ductile fracture (category 1) and particles with no signs of ductile fracture (category 2). The SEM images of the detached particles are presented in Fig. 12(a) with cohesive rupture zones highlighted by yellow dashed lines. Figure 12(b) displays the craters left after removing the particles in category 2 from Fig. 12(a).

No sign of bonding was observed in the top view of the category 2 particles. However, the corresponding craters contained signs of ductile fracture. This suggests that bonding is present in Category 2 particles but too small to be observed in the images. Therefore, SEM is an inconclusive tool when investigating ductile fracture zones at this scale.

To support our understanding of this phenomenon, EDS analysis was conducted on the craters. The residual material was identified as copper, indicating that the particle/substrate interfacial bond strength was higher than the cohesive strength of copper. This proves that bonding occurs in category 2 particles, despite the lack of detection by SEM.

It is observed that ductile fracture zones are not uniformly distributed at the particle/substrate interface. Heterogeneous distribution of impact pressure, lack of proper surface cleaning, and non-uniform oxide scale

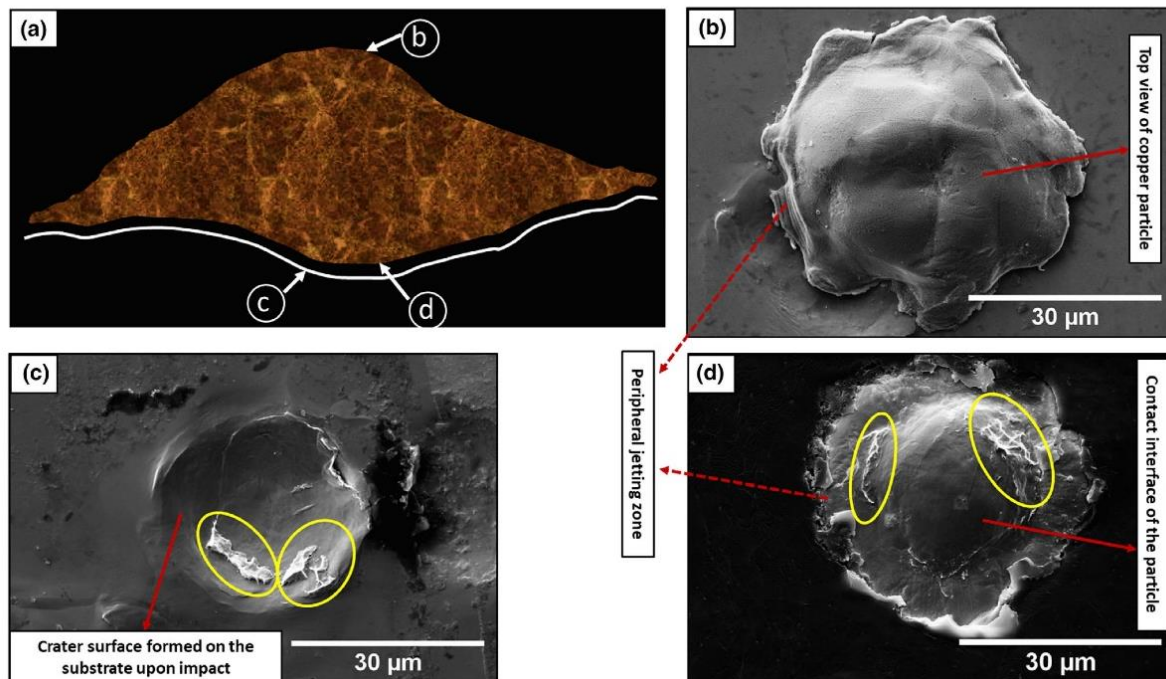


Fig. 10 Example of the analysis spots for deposited particles (a) schematic cross-section view of a deposited particle, (b) top-view splatted particle, (c) fractured surface at the substrate (d) fractured surface on the detached particle

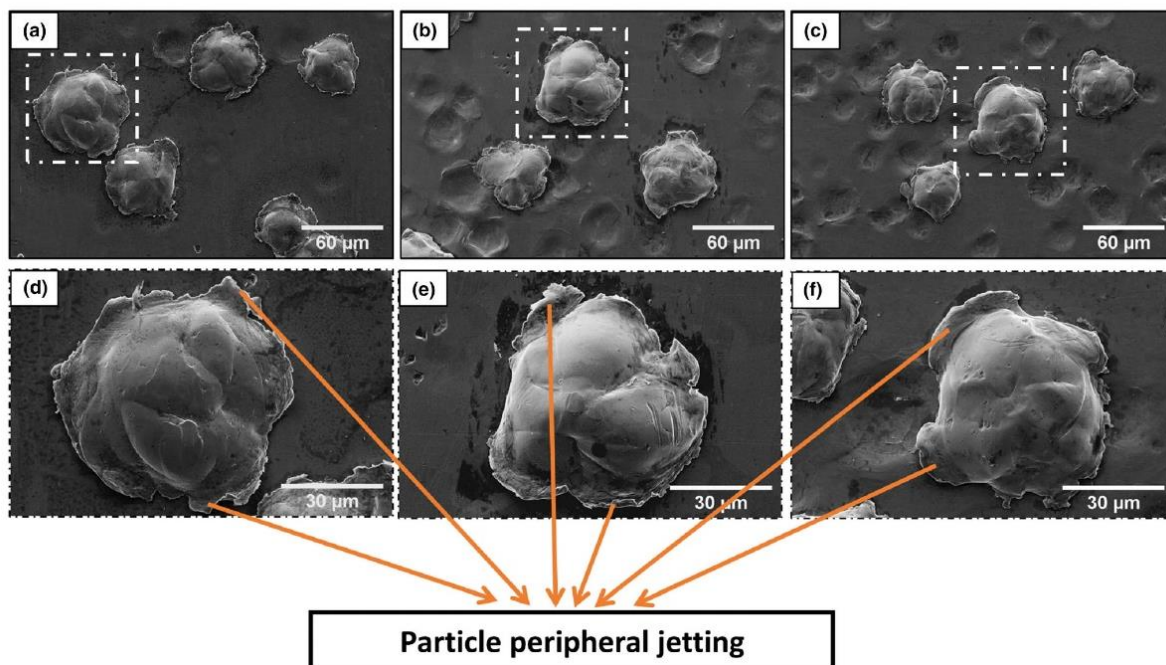


Fig. 11 Morphology of deposited particles, image (a), (b), and (c) are SEM images of powder type 1, powder type 2, and powder type 3, respectively, and (d), (e), and (f), are the close-up view of the selected single particles, the peripheral jetting zone of the particles are shown

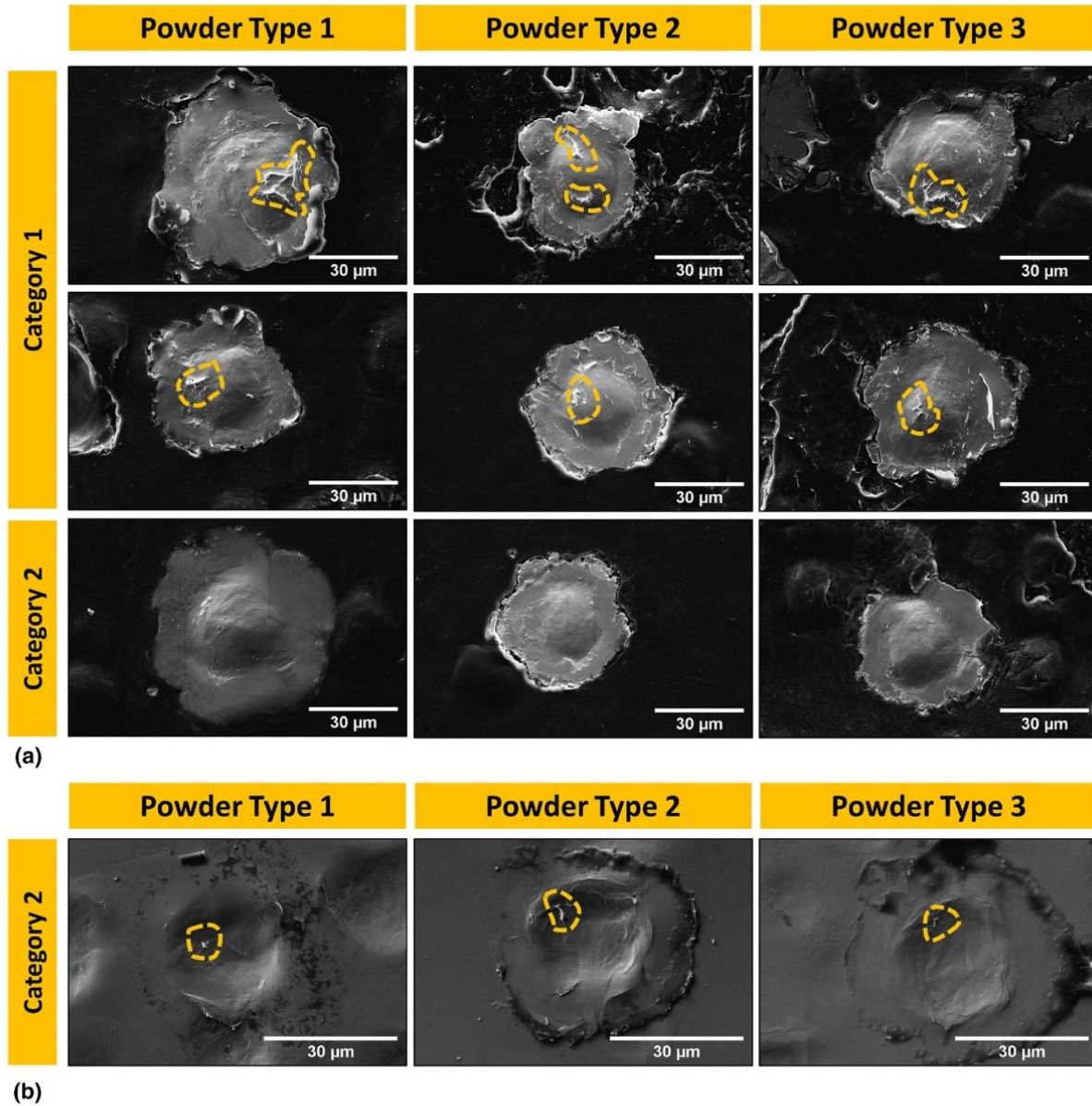


Fig. 12 Analysis of the fracture surfaces on (a) detached particles, (b) substrates. Yellow dashed lines present the ductile fractured zone

distribution at the particle surfaces can all have contributed to this behavior.

It is also observed that none of the detached particles has any signs of ductile fracture at the splat center. This finding reveals that the conditions to form bonds are unlikely to be satisfied at the splat center. Generally, the oxide scale rupture occurs upon impact. These oxide fragments must then be removed, otherwise, the intimate contact between the substrate and the particle may be obstructed. Material flow at the shearing zone catalyzes this cleaning process.

However, material flow is limited at the splat center (where shearing is less intense) and oxide debris are locked up, impeding fresh metallic contact (Ref 9, 13, 42, 51, 67, 68).

Figure 13 displays evidence of ductile fracture at the jetting zone, which is not a common feature of single-particle deposition. Further investigation showed that this occurs when a deposited particle is subjected to a second impact with an incoming particle. This subsequent impact enhances the adhesion by improving the surface cleanups

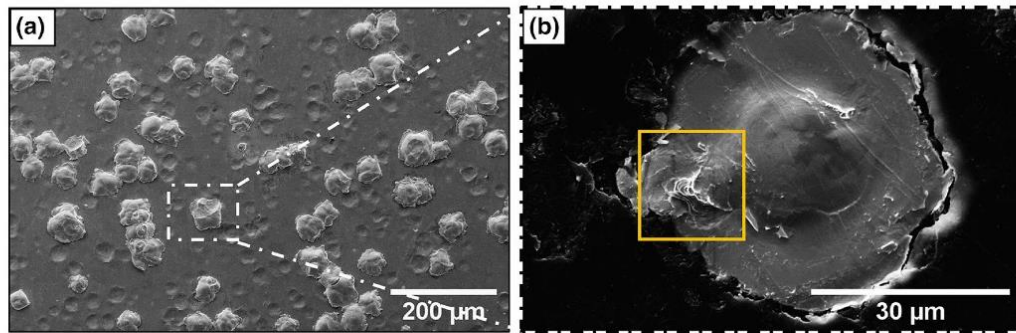


Fig. 13 SEM images of (a) deposited particles, the particle with the history of multiple impacts highlighted in the dashed box, (b) fractured surface of the detached particle with the history of multiple impacts,

evidence of cohesive rupture on the jetting side highlighted in the yellow box

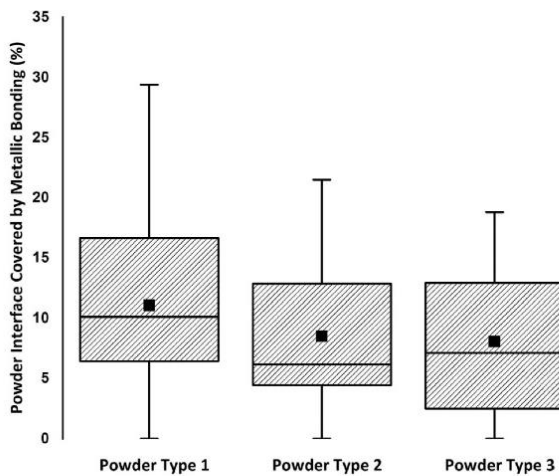


Fig. 14 Percentage of particle surface covered by cohesive rupture signs, (box and whisker plot with filled square representing the mean, the box representing first, second, and third quartile (25th–50th–75th percentile, respectively), the whisker representing the lowest and highest value

and providing sufficient impact pressure, resulting in bonding.

To quantify the results obtained from detached particle analysis, the percentage of the particle interface covered by cohesive rupture was measured and the results are plotted in Fig. 14.

The results show that the average area showing signs of cohesive rupture for powder type 1 is 11%. This value drops to 8.5 and 8.1% for powder type 2 and type 3, respectively. These data suggest that the adhesion mechanisms are influenced by the powder oxidation conditions, although the observation is limited to the SEM examination. No considerable differences in the average area for powder type 2 and powder type 3 are observed. The results also show that maximum visible signs of ductile rupture

zones are achieved for powder type 1 (maximum bond area of 29.4%), with this value dropping as the surface oxidation level increases until reaching the lowest maximum value of 18.8%. It is then concluded that not only the deposition efficiency but also the quality of adhesion are reduced with increased surface oxidation.

However, it was observed that the detrimental effect of surface oxide film thicknesses on DE and particle adhesion is more pronounced when comparing types 2 and 3 to type 1, but less pronounced between types 2 and 3.

Impact Modeling Results

Impact modeling provides additional insight into bonding mechanisms as the oxide layer thickness increases. The focus of the current numerical model is to study particle bonding, with different values of $\Psi_{\min}$ (oxide scale thickness). Figure 15 illustrates the contact impact pressure for an impact velocity of 680 m/s at 27 ns after impact. It is maximum at the initial impact point, and this value decreases toward the particle edge.

The contour of surface expansion (Ψ) and equivalent plastic strain (PEEQ) at the particle interface are shown in Fig. 16. As illustrated, the location where Ψ is maximum differs from the region where maximum PEEQ is reached. The differences are explained by the way Ψ and PEEQ are calculated. Surface expansion is only a function of the hoop (or circumferential) and the radial strains of each element at the contact surface, while the PEEQ is calculated from all plastic strain components.

PEEQ has been used frequently in CS as bonding criteria and for critical velocity prediction (Ref 32, 69). However, as seen here, PEEQ distribution differs from the Ψ distribution and thus may not be a proper indication for bonding. The maximum surface expansion is located where the pressure is nearly maximum, while PEEQ is maximum at the particle jetting zone where contact pressure is near

Fig. 15 Simulated contact pressure at 680 m/s impact velocity and 27 ns after impact (a) contact pressure variation at particle interface with trendline shown in the orange color, (b) visual illustration of the contact pressure contour

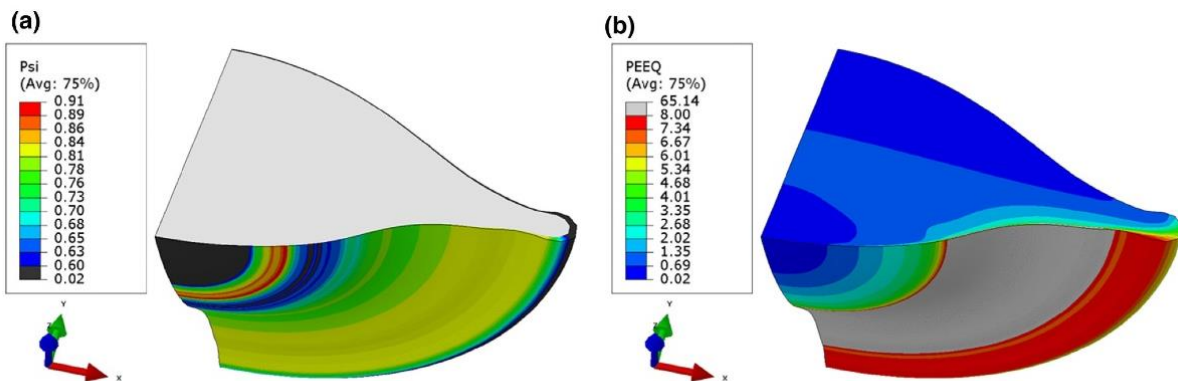
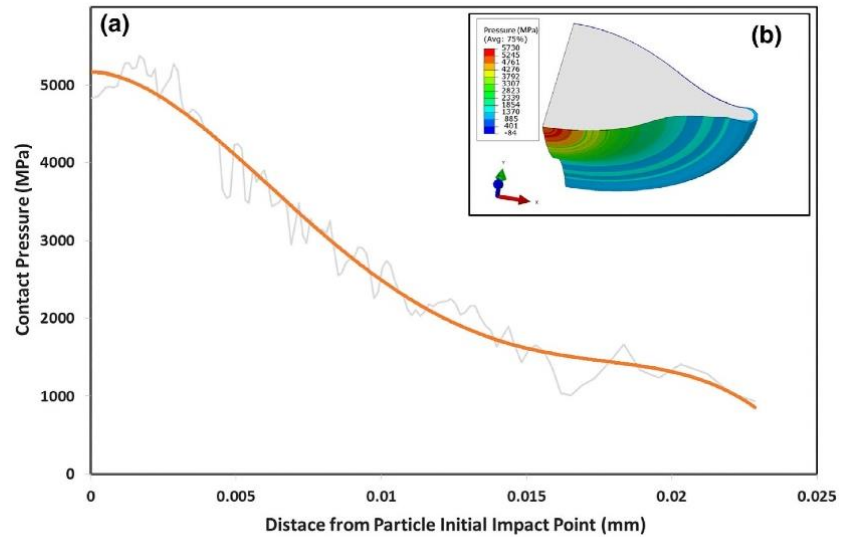


Fig. 16 Simulated contour pattern of (a) surface expansion (Ψ), and (b) equivalent plastic strain (PEEQ), for 26 μm copper powder deforming under 680 m/s impact velocity, 27 ns after impact

the lowest, as observed in Fig. 15. Besides, as shown in Fig. 12, the bonded region is away from the jetting zone of the particle. This is explained by the role of contact pressure in the bonding mechanism. Enough pressure is required to extrude the fresh material through the oxide-free gaps and create intimate contact between surfaces. There is not enough contact pressure at the jetting zone to press materials against each other and create bonding. The stress at the jetting zone is almost pure shear.

As mentioned previously, both Ψ and pressure play a role in the adhesion mechanism. As such, a zone with proper Ψ and pressure for bonding is not necessarily a region demonstrating the highest PEEQ.

The surface expansion values for the substrate and particles with different oxide film thicknesses (different $\Psi_{\min}$) as a function of the radial position are illustrated in Fig. 17. The particles are deformed under a fixed impact

velocity of 680 m/s. The orange and green curves depict the surface expansion distribution in particles and the substrate, respectively. Both particles 1 and 2 are deformed identically under equivalent impact velocity since the model does not include the effect of the oxide layer in the deformation. The only difference is in the $\Psi_{\min}$ they must reach to bond. Horizontal dotted lines mark the Ψ threshold limits which is 0.44 for particle 1 and 0.6 for both particle 2 and the substrate.

As shown in Fig. 17, by increasing the powder oxide thickness (thus the required $\Psi_{\min}$), a slightly smaller surface area reaches $\Psi_{\min}$ for particle 2. As a result, a slightly smaller surface area is available for bonding. The substrate interface, on the other hand, exhibits a much smaller zone reaching $\Psi_{\min}$ of 0.6 and thus is the limiting material in the bonding process. As shown in Fig. 17(a), it is concluded that adhesion is dominated by the extent of substrate oxide

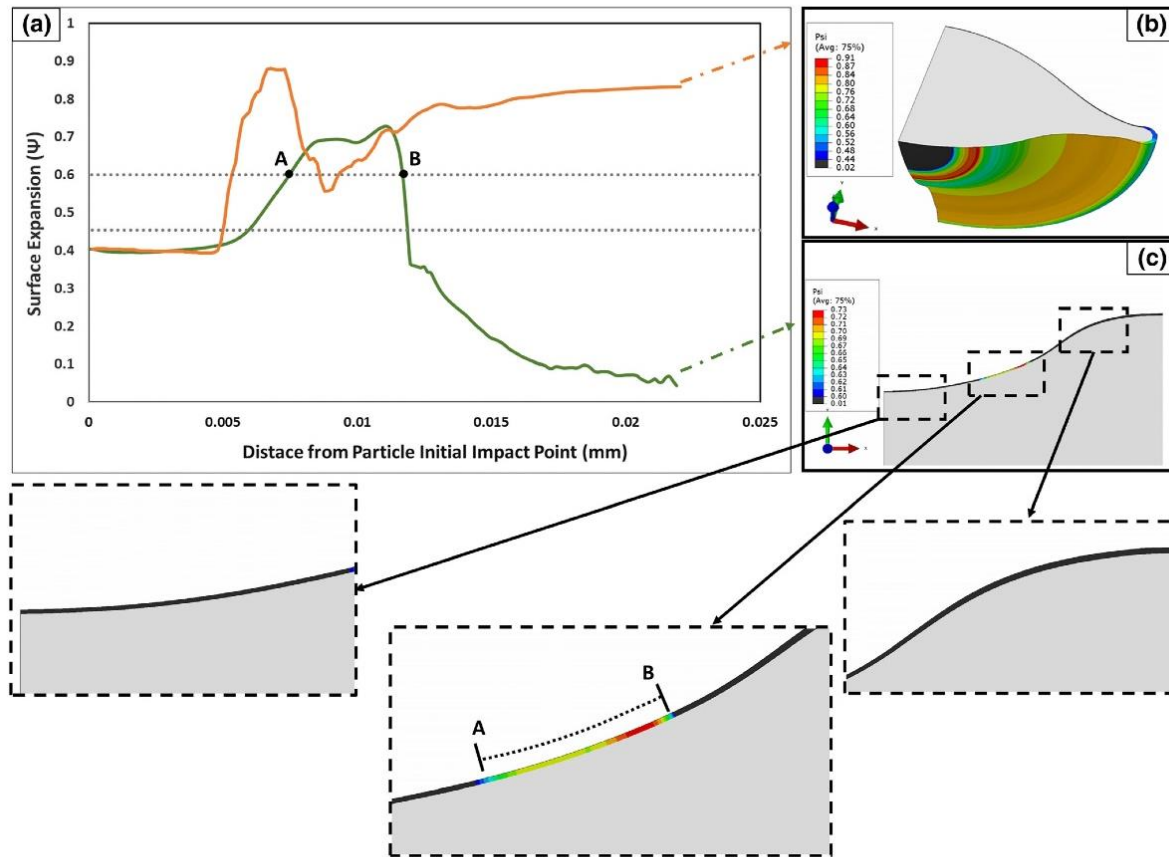


Fig. 17 Simulated surface expansion (a) for particle 1 and 2 (in orange), and substrate (in green), 680 m/s impact velocity. The dotted lines indicate the critical surface expansion of 0.44 for particle 1 and

0.6 for both particle 2 and the substrate. (b) and (c) contour of Ψ distribution at the particle, and the substrate, respectively

cleanup. Only a small portion of the substrate is free of oxides (Fig. 17, point A to B on the curve) and therefore available for bonding, while the particle surface is mostly clean.

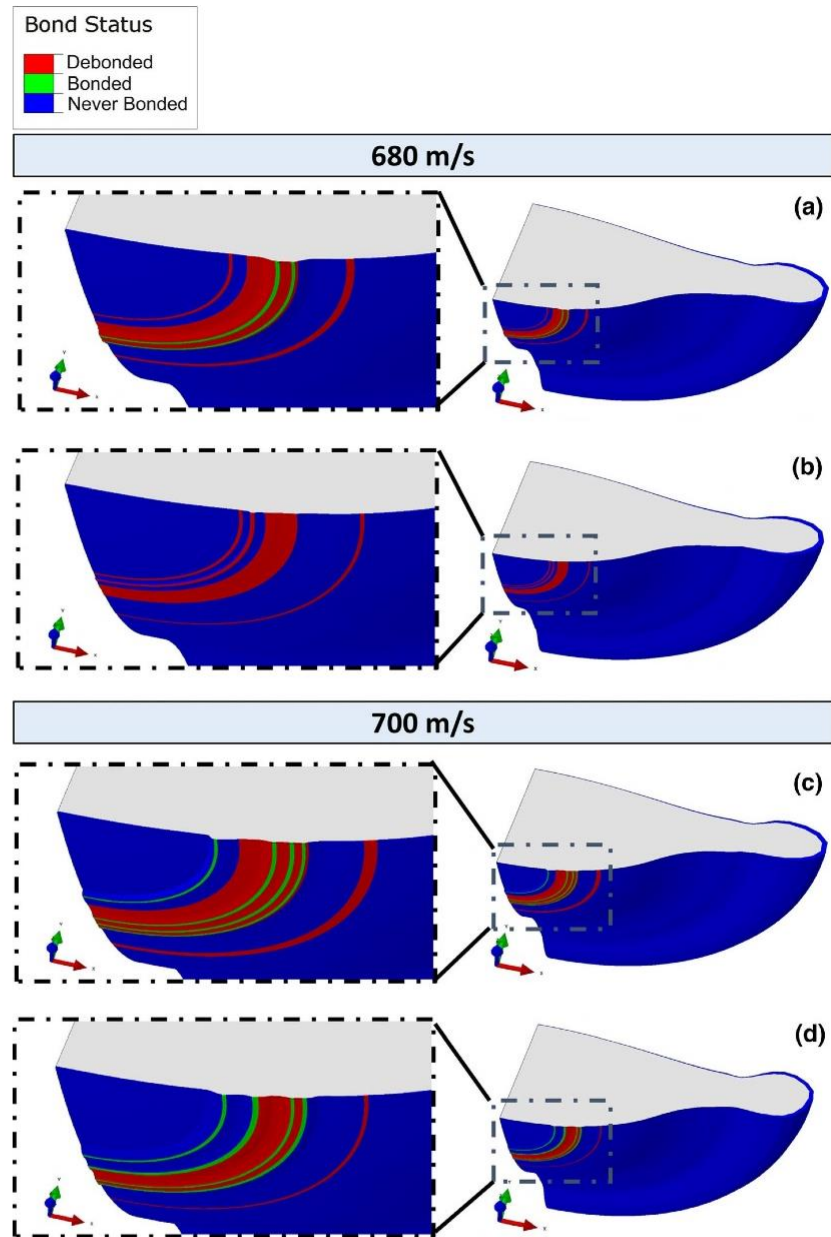
Careful observation reveals that while $\Psi_{\min}$ is achieved in the particle jetting zone, it is not the case for the substrate located beneath that jetting zone. This result serves to explain the lack of metallic bonding detected at the edges of detached particles, as shown in Fig. 12. Also, it is observed that the initial impact point and its vicinity suffer the least deformation in both the particles and the substrate. Neither the particle nor the substrate deformed sufficiently to reach their corresponding $\Psi_{\min}$. This supports the results obtained from Fig. 12 in which all detached particles demonstrated a smooth surface free of bonding at the particle impact center.

It is also valuable to study the adhesion mechanism as the impact velocity increases. Figure 18 shows the bond status of particle 1 ($\Psi_{\min} = 0.44$) and particle 2 ($\Psi_{\min} = 0.6$) deformed under impact velocities of 680 m/s

and 700 m/s. These velocities are the critical velocities predicted by numerical modeling for particle 1 and particle 2, respectively. These velocities are higher than the critical velocity-based DE reported in Table 9. The differences are mainly due to the material model approximation, and in particular, the lack of adequate data for the PTW model for the substrate material as specified in the modeling section. It is worth mentioning that although there is a discrepancy between the numerical and experimental results, the gap in critical velocities of particles 1 and 2 is nearly identical (approximately 20 m/s) for both experimental and numerical approaches.

Three different colors are identified at the particle interfaces displayed in Fig. 18. The green regions are locations where metallic bonding is predicted. Red regions, named as “debonded”, are locations where the bonding criteria were satisfied upon particle impact but particle debonded due to elastic particle rebounding (Ref 70–72). Lastly, “never bonded” regions (blue regions) are locations where the bond criteria were not met during the impact.

Fig. 18 Bond status of (a) particle 1 under 680 m/s, (b) particle 2 under 680 m/s, (c) particle 1 under 700 m/s, (d) particle 2 under 700 m/s impact velocity. Particle diameter 26 μm



Close observation of the particle bond status for an impact velocity of 680 m/s, shown in Fig. 18(a), (b) reveals that the bond minimum requirement was only satisfied by particle 1 (Fig. 18(a)). No metallic bonding is predicted for particle 2 (Fig. 18(b)). For this particle, although the surface expansion threshold is partially reached (Fig. 17), the corresponding impact pressure is not enough to form bonding.

Though no metallic bond is achieved between particle 2 and the substrate (Fig. 18(b)), a part of the contact area is

covered by the debonded region. This is also the case for particle 1 shown in Fig. 18(a), in which a relatively large debonded region compared to the bonded region is observed. The recoverable elastic energy stored in the material is responsible for this large debonded area displayed in Fig. 18 (Ref 52, 73). Although recoverable elastic strain energy is relatively small compared to the dissipated energy, it can result in particle detachment from the substrate. In addition, the amount of strain energy stored in the substrate is much larger than it is in the

particle and so the particle bounce-off phenomenon is mainly due to the substrate elastic energy (Ref 52). It is also reported that this recoverable elastic energy is higher when a soft particle hits a hard substrate (Ref 74) which is the case for the current work.

The particle bonding evolution at an impact velocity of 700 m/s is presented in Fig. 18(c), (d). Both particles demonstrate nearly identical bond status. The same results were also reported for DE (Table 8) and bonded area measurements (Fig. 14) where the powder type 2 and type 3 had nearly the same measurements. This observation is explained by the extent of particle deformation and the fact that the substrate oxide cleanup plays a major role in bond formation. Upon high-velocity impact, the soft particle experiences an excessive amount of plastic deformation. At a high enough impact velocity, the deformation is such that the particle oxide cleaning reaches its maximum limit. Under this condition, it is mainly the substrate oxide cleanup, contact pressure, and the recoverable elastic energy that determine the adhesion.

Conclusion

The effects of naturally occurring oxidation (a function of powder storage time) of copper feedstock powders on deposition efficiency and bonding were investigated at the individual particle level. The extensive analysis revealed that as the powder exposure time to ambient condition increases, the particle oxide thickness increases, reducing the deposition efficiency and visible particle bonding areas. However, the rate of this oxide growth is more pronounced within the first thirty days of exposure and limited effects on the deposition process are observed for particles exposed to ambient conditions for an additional thirty days. It was also shown that the nature of the oxide layer evolves from Cu_2O in the as-received state to CuO after the first thirty days of exposure time. FEM results revealed that as the particle oxide thickness increases, the extent of particle surface cleanup slightly decreases. Therefore, a slightly higher impact velocity is required to ensure proper oxide cleanup to allow bonding, thus increasing the critical velocity. It was shown that the substrate deformation level is the limiting factor in the bonding process, as the soft particles deform more extensively than the hard substrate. It was observed that the location where the maximum surface oxide cleanup and pressure (and hence bonding) is achieved is different from where the PEEQ is maximum, suggesting that PEEQ may not be an appropriate variable for bonding prediction. The modeling results also provided insight into the lack of metallic bond at the initial particle impact point as well as the particle jetting area.

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5.3 Research Project 3: Integrating Laser Heat Treatment for Enhanced Mechanical Properties in Cold Spray Copper Coatings.

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This work aims at developing a tool that permits determining the laser heat treatment conditions that result in the desired hardness profile. The physical driving force of hardness reduction in the material is the local thermal history. Laser heat treatment is a complex process in terms of local temperature history and the measurement of temperature profile experimentally is not possible. Thermal modeling of the laser heat treatment process provides the temperature histories at any point inside the coating.

The artificial neural network approach is proposed to find the complex correlation between the temperature history and the hardness reduction. This is done by obtaining the local temperature history of a laser-treated CS part through thermal modeling (input in ANN model) and correlating the local hardness profiles measured experimentally (output in ANN model) to the local temperature profile histories. The ANN, therefore, allowed prescribing the proper laser process parameters for the desired hardness reduction. It is also shown that the neural network model can be effectively used to detect possible interfacial modifications that can interfere with the heating/hardness reduction of the part. This peer-reviewed paper addresses the objectives presented in section 3.3.



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July 12, 2022

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SUBJECT: 2022 HTS/Bodycote Best Paper in Heat Treating Award

Dear Maryam:

I am pleased to inform you, on behalf of the Heat Treating Society Board, that you have been selected to receive the 2022 HTS/Bodycote Best Paper Award for your paper entitled:

“Data-Driven Design Framework for Laser Heat Treatment Process of Cold Spray Coating”

This award, established in 1997 by the ASM Heat Treating Society, recognizes a paper represents advancement in heat treating technology, or promotes heat treating in some substantial way or represents a clear advancement in managing the business of heat treating. We will announce you as the recipient of this year's award in an upcoming issue of *HTPro*.

The award is sponsored by Bodycote Thermal Process-North America and consists of a recognition plaque and a check for \$2,500.

The award presentation will be made at the 2022 IMAT ASM's Annual Meeting, The Circular Materials Economy to be held in New Orleans, LA, September 12-15, 2022. You will be recognized at the ASM annual luncheon held on

ASM Leadership Award Luncheon

Monday, September 12, 2022

11:30 am – 1:30 pm

Ernest N. Morial Convention Center

Room TBD

New Orleans, LA

Co-located with IMAT 2022 and Thermal Spray and Surface Engineering Forum & Expo

We hope you will attend ASM IMAT 2022 Conference and Exposition to accept the award and look forward to a favorable response.

In the meantime, please send your photo and biography as soon as possible to Mary Anne Jerson at maryanne.jerson@asminternational.org. Mary Anne can answer any questions you might have.

Once again on behalf of the HTS Board, congratulations!

Sincerely,



Lesley D. Frame
President, HTS

cc: Mr. Eric Hutton, HTS Awards & Nominations Committee Chair
Mr. Benjamin Bernard, HTS Vice President
Mrs. Nicole Hale, Director of Membership & Affiliates, ASM International
Prof. Bertrand Jodoin, FASM, Professor, University of Ottawa



Artificial Neural Networks Approach for Hardness Prediction of Copper Cold Spray Laser Heat Treated Coatings

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Abstract Laser heat treatment offers localized heating zone, high processing speed, and feasibility to treat complex large parts, making it a technology of choice to tailor the hardness and fatigue properties of parts. Determining laser heat treatment process parameters is important to achieve the sought material performance; however, the technique's high speed makes it difficult to record the thermal history of the part via standard measurement techniques. Furthermore conducting experiments to explore the effect of process parameters is costly. This work aimed at designing a laser heat treatment to be applied to as-deposited copper cold spray coating to meet a 30% through-thickness hardness reduction. An artificial

neural network model was developed and used to find laser heat treatment conditions allowing meeting the sought hardness reduction. The thermal histories were obtained through thermal modeling of the laser heating process and the resulting hardness reductions obtained experimentally. This allowed the neural network to correlate the local hardness reduction (model output) to local thermal history (model input). The model was capable of predicting the local hardness reduction of the part according to the local thermal history resulting from various laser heat treatment conditions and thus, may eventually be used to assist in process parameters selection and optimization.

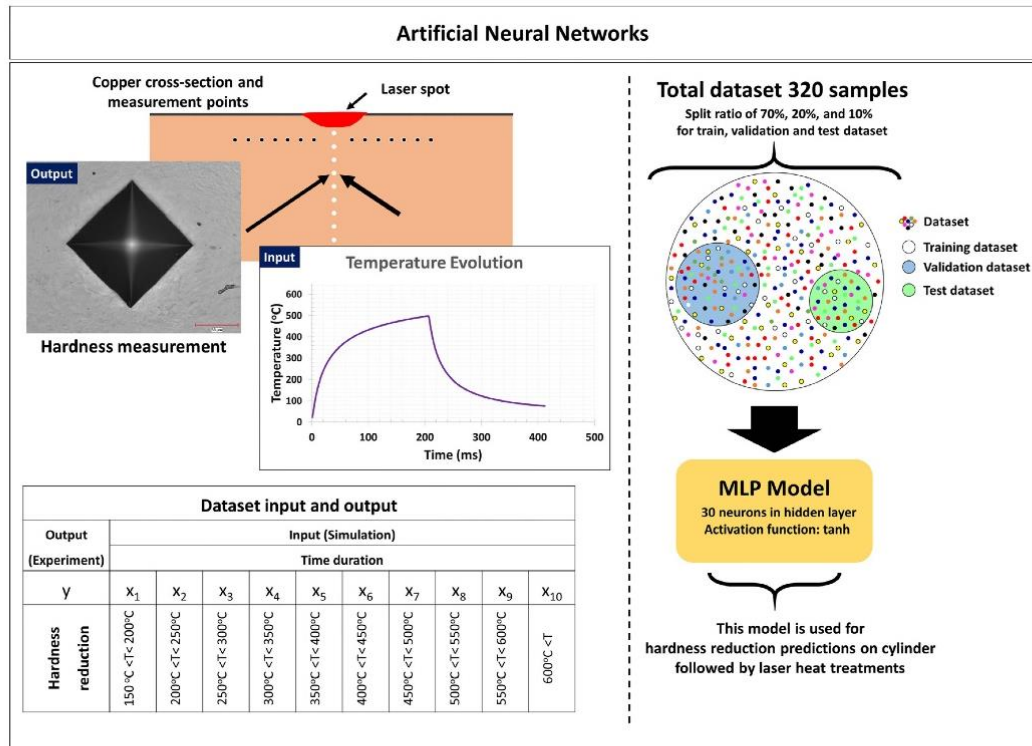
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Graphical Abstract Demonstrating ANN model input and output and the methods they were collected $140 \times 101\text{mm}$ (600×600 DPI)



Keywords artificial neural networks · cold spray additive manufacturing · hardness reduction · laser heat treatment · numerical modeling

Introduction

Cold spray (CS) is a solid-state coating process and an emerging additive manufacturing (AM) process (Ref 1-3). CS tool path can be programmed either to fabricate coatings, freestanding parts or to build additional features on existing components with very good mechanical integrity (Ref 4-6). In comparison to other AM techniques, cold spray additive manufacturing (CSAM) presents several advantages such as fast buildup rates while having virtually no limit in terms of final part size as it does not involve a build tray (Ref 4, 7). The absence of melting of the feedstock materials during CS makes it an interesting technique for processing temperature-sensitive materials, for the deposition of materials with very different melting points, and the manufacturing of graded structures and metal-

matrix composites (Ref 8, 9). Furthermore, CS allows achieving very good adhesion (Ref 8).

Deposit ductility is a crucial property for most CSAM applications. In general, as-sprayed CS coatings or parts are brittle as a result of the intense cold working experienced by the feedstock materials during the process. Consequently, they often need to go through post-spray annealing heat treatments to regain ductility (Ref 10-16). For example, Phuong et al. (Ref 15) showed that the ductility increased from $0.5 \pm 0.2\%$ in the as-sprayed condition to $34 \pm 3\%$ when CS copper coatings were heat-treated at 600°C for 1 hour; however, a standard furnace annealing treatment is unsuitable in several circumstances. For instance, heat treatment of an added CS feature without affecting the remaining component state (heat-treated condition, tightly machined dimensions, and/or surface exempt of oxidation) is often desirable but not easy to achieve, while furnace heat treatment of very large parts or parts made of dissimilar materials is impractical. To fully benefit from CS advantages as an AM technique, localized

heat treatments, such as laser heat treatment, have gained a lot of attention (Ref 15, 17–19).

A conventional furnace annealing treatment is typically a relatively long process: the part is slowly heated up and cooled down to avoid thermal stresses and the hold time at the annealing temperature is long enough to ensure uniform temperature through the part. The exact annealing conditions will depend on the material, desired degree of softening, component shape, furnace load, etc. For copper, typical annealing temperatures range between 250 and 750 °C, while an annealing time of about 1 hour is common (Ref 20).

As opposed to furnace heat treatments, lasers can provide very fast heating rates and extreme temperature profiles. Since the laser spot needs to be rastered to cover a whole surface, the holding time at each area needs to be as short as possible to ensure an efficient process. Several process parameters, such as laser spot size, impact angle, energy density, and raster speed, will affect the local thermal history of the treated part. Consequently, it is hardly possible to extrapolate appropriate laser heat treatment conditions from standard furnace heat treatment procedures. In addition, the fast and localized laser heat treatment is likely to result in various temperature histories at the different part locations. These temperature histories complicate the task of correlating or predicting the hardness reductions at each location.

Over the last decade, extensive work has been performed for the use of CS copper coatings for corrosion protection of Used Fuel Containers (UFC) for the long-term management of used nuclear fuel (Ref 15, 21–24). A crucial step to bring these developments into the sought application is to confirm the coating's ability to meet the required mechanical properties for this demanding application (Ref 25, 26). Mechanical modeling studies have shown that a coating ductility allowing at least 10% elongation is required (Ref 16, 23, 26). Preliminary trials have shown that a reduction in coating hardness to 66 HV or lower is indicative of restored coating ductility (Ref 20).

Laser heat treatment demonstrated promising results to tailor material microstructures and achieve the desired material hardness (Ref 27–30). By controlling the laser parameters and depending on the nature of the material being heat-treated and its microstructure, the laser heat treatment can be used to increase or decrease the material hardness. For instance, enhanced formability with a minimum strength loss was achieved by local laser heat treatment of steel sheet (Ref 27). Park et al. also showed that an increased hardness of mild steel can be achieved by high-power laser surface heat treatment (Ref 30). In another work, laser surface hardening improved the wear resistance of titanium alloys (Ref 28). A significant improvement in abrasion, adhesion, and oxidation resistance was observed

in the laser heat-treated sample (Ref 28). In the case of pure copper, the heat treatment leads to hardness reduction (Ref 31).

This work aims at developing a tool that permits determining the laser heat treatment conditions that result in the desired hardness profile. The physical driving force of hardness reduction in the material is the local thermal history. Laser heat treatment is a complex process in terms of local temperature history and the measurement of temperature profile experimentally is not possible. Thermal modeling of the laser heat treatment process provides the temperature histories at any point inside the coating.

The artificial neural network (ANN) approach is proposed to find the complex correlation between the temperature history and the hardness reduction. This is done by obtaining the local temperature history of a laser-treated CS part through thermal modeling (input in ANN model) and correlating the local hardness profiles measured experimentally (output in ANN model) to the local temperature profile histories.

The ANN, therefore, allowed prescribing the proper laser process parameters for the desired hardness reduction. It is also shown that the neural network model can be effectively used to detect possible interfacial modifications that can interfere with the heating/hardness reduction of the part.

Experimental Procedures

Coating Preparation

Feedstock Powder

The feedstock material was high purity spherical powder from 5N Plus (Ville St. Laurent, Quebec, Canada). The powder was kept under inert conditions prior to spraying in order to avoid oxidation during storage (Ref 32). Two different powder batches were used (EFF071 and EGK022), with similar particle size distribution, purity, and oxygen levels provided in Table 1.

Substrate Type and Preparation

CS copper coatings were deposited on three types of steel substrates: mild steel plates (76.2 mm × 76.2 mm × 3.2 mm), ASTM A516 Gr. 70 large plates (152.4 mm × 152.4 mm × 38.1 mm), and ASTM A106 Gr. C short cylinders (~610 mm long, ~559 mm outer diameter and ~457 mm inner diameter). The short cylinders are of similar dimensions as the used fuel container prototype developed by the Nuclear Waste Management Organization (NWMO) in Canada, but with a shorter length (Ref 24). This short

Table 1 Characteristics of the feedstock powder used in the cold spray trials

	EFF071	EGK022
Particle size distribution (D10, D50, D90) (μm)	17, 31, 52	26, 37, 54
Purity (%)	99.99	99.9
Oxygen (ppm)	140	120

Table 2 Substrate type, preparation, roughness, powder lot for the samples prepared for different studied cases

Case	Substrate type and preparation	Surface roughness prior to spray	Powder lot	Comments
Stationary	Mild steel substrate; grit-blasted (grit 24); no laser-assisted adhesion layer	3–6 μm	EFF071	Standalone coating used in laser HT
Moving	ASTM A516 Gr. 70 steel plates; grit-blasted (grit 24); laser-assisted adhesion layer	3–6 μm	EFF071	Coating with substrate used in laser HT

cylinder was used to evaluate the ability of an artificial neural network model to be used as a design tool for predicting the hardness reduction of the part following the laser heat treatment conditions.

Depending on the substrate type, different preparation methods were used, either grit blasting (Canablast Model M101P unit with grit 24 alumina) or laser ablation (DRL, Quantel Laser). The former method was used on the plates (small and large size), and the latter was used on the short cylinder. Grit blasting is a standard and easy-to-use method for surface cleaning in CS; however, for the specific application, non-contact cleaning techniques are required. Therefore, the laser ablation technique (DRL laser) was used.

Cold Spray

Coatings were sprayed using a PCS-800 CS system (Plasma Giken Co., Yorii-machi, Saitama, Japan). Spray conditions used in this work were previously developed to ensure dense coatings (Ref 16, 18) and were kept constant: nitrogen was used as the carrier gas at 800 °C and 4.9 MPa with a 30 mm standoff distance.

For the laser heat treatment tests, stationary and moving laser configurations were studied. For the stationary laser test case, mild steel was used as a substrate. Gun traverse speed and powder feed rate were 300 mm/s and 85 g/min, respectively. The coatings with a final thickness of around 4 mm were detached from the substrate. These standalone coatings were used for stationary heat treatment tests since the amount of heat input from the laser for these cases is low and heat distribution is local and not influenced by the substrate.

Since handling the large cylindrical substrates is challenging and the coating production is expensive and time-consuming, smaller coupons were used during development for the moving laser cases. These flat coupons are made of steel of grade ASTM A516 Gr. 70. Coating build-up was performed in two sequential steps. In the first step, to promote adhesion of the copper coating to the steel substrate, a bond layer was sprayed with laser-assisted CS, using a 4kW, 1064 nm wavelength fiber laser from IPG Photonics (Oxford, MA, USA), and with 100 mm/s gun traverse speed. The powder feed rate was ~ 15 g/min for this first layer (Ref 33). Next, the coating build-up was performed using regular CS to produce 3–4 mm coating thickness. The gun traverse speed and powder feed rate, for this second step, were 300 mm/s and ~ 85 g/min, respectively (Table 2).

The short cylinder was used for the laser heat treatment prediction/validation study. The cylinder surface (steel grade ASTM A106 Gr. C.) was prepared prior to coating buildup using laser ablation and a laser-assisted CS adhesion layer was applied for the copper/steel bond layer. A copper coating thickness of ~ 4 mm was applied to this cylinder. The copper coating was produced using powder lot EGK022. The temperature history of a flat plate was used for the cylinder case. The curvature radius of the cylinder is large enough that it allows this simplification. The boundary conditions and the number of laser paths were adjusted accordingly for the cylinder geometry.

Coating Characterization

Coatings were sectioned perpendicularly to the spray direction using a coolant-assisted cutting wheel, and subsequently, cold-vacuum mounted in an epoxy resin.

Afterward, the resin-mounted samples were ground and polished using standard techniques. Cross-sections of the coatings were observed using a field emission gun scanning electron microscope Hitachi S-4700 (FEG-SEM).

Microhardness measurements were performed on as-polished samples using Clemex MMT-X7B s/n MM6095X microhardness tester with a Vickers indenter. All tests were performed using 300 gf loads with 10 s dwell time.

The depth profile of the microhardness for the standalone sample for the case of stationary laser heat treatment was measured from the top surface (where laser pulse hits the surface) to the bottom in 300 μm intervals. In addition, lateral microhardness measurements were conducted at the average depth of 400 μm with an average interval of 500 μm on both sides of the laser spot.

Similarly, for the moving laser cases, the hardness measurement spots were located at quarter-length and half-length of the laser path at depth intervals of 300 μm from the surface to the coating-substrate interface. Additional measurements were also conducted at lateral locations on both sides of the laser path in some of the moving laser cases to enhance the training data set for the ANN models. The lateral measurements were located at depths of 400, 1500 and 3500 μm from the top surface. The distance between lateral points is approximately 500 μm .

The hardness reduction resulting from the heat treatment is calculated using the following equation:

$$X\% = \frac{HV_0 - HV_i}{HV_0} \times 100 \quad (\text{Eq 1})$$

where HV_0 is the as-sprayed hardness value (124 HV) and HV_i is the hardness value after laser heat treatment.

Laser Heat Treatment Procedure

Laser heat treatments were performed with a 4kW, 1064 nm wavelength fiber laser from IPG Photonics (Oxford, MA, USA). To enhance copper absorptivity at this wavelength, the coatings were painted black with high heat enamel (TREMCLAD) aerosol spray. Three different laser heat treatments were performed: stationary laser (used to validate the thermal model), moving the laser in an XY fashion (the laser is set on a robot), and moving the laser while rotating the cylinder samples (the laser is set on a robot and the movement of the sample is provided by a rotating table). Further details are given in Table 3.

The standalone coatings used for stationary heat treatment tests were thermally insulated at the back. Sample sides and top were cooled down by natural air convection.

No hardness reduction was observed for stationary heat treatment tests with laser power below 3 kW and laser pulse duration below 100 ms. Therefore, these measurements are not reported in this work.

The coupons used in moving laser cases were protected by two L-shape aluminum plates on the side walls to prevent the sidewalls from being heated by the laser beam. The other sample surfaces were cooled down by natural air convection. Lastly, short cylinders were cooled down by natural convection at the inner and outer surfaces and the side walls.

Thermal Modeling

The coating local temperature history during the laser heat treatment determines the final local microstructural characteristics and mechanical behavior of the workpiece. Once the temperature history is obtained, it can be used to correlate the material hardness to the temperature history.

Problem Description

In the current work, a thermal transient model is used to predict the temperature profile within the copper coating. The solver used is the commercially available Ansys software (ANSYS, Inc. Product 2020 R2). The governing equation is derived from the 1st law of thermodynamics, and with the absence of flow in the calculation domain it simply becomes the heat diffusion equation (HDE) (Ref 34):

$$\frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + \dot{q} = \rho c \frac{\partial T}{\partial t} \quad (\text{Eq 2})$$

where ρ is the material density (kg/m^3), c is the specific heat ($\text{J/kg}\cdot\text{K}$) and k is the thermal conductivity ($\text{W/m}\cdot\text{K}$). In this equation, $\dot{q}$ denotes the rate of internal energy generation per unit volume (W/m^3). T is the temperature (K), which is a function of location and time (x, y, z, t).

It is assumed that the material is homogeneous and isotropic and the material physical properties such as thermal conductivity and specific heat are independent of

Table 3 Experimental details for the laser heat treatments

Case	Laser parameters				
	Robot Speed	Angle	Power	Pulse time	Spot size
Stationary	0 mm/s	45°	1–4 kW	20–400 ms	1.8 mm
Moving	18 mm/s; 0 or 2 mm laser step size	10°	4 kW	2.82 s	1.8, 2.5 mm

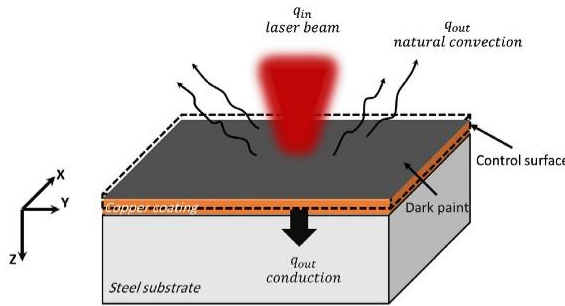


Fig. 1 Boundary condition at the coating top surface

temperature (Ref 35). In addition, there is no source of internal heat generation. Therefore, the HDE for the cases studied here is reduced to:

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad (\text{Eq 3})$$

where $\alpha = k/\rho c$, is the thermal diffusivity (m^2/s).

Initial and boundary conditions must be applied to the equation system in order to get the sought specific solutions. The initial condition used assumes a uniform temperature distribution throughout the sample:

$$T(x, y, z, 0) = T_0 \quad (\text{Eq 4})$$

where T_0 is room temperature taken as 22 °C.

The boundary condition at the coating top surface is given by the local energy balance between conduction into the coating, convection to the surrounding air and heat flux from the incoming laser spot as illustrated in Fig. 1.

This boundary condition is mathematically expressed as:

$$Q_{\text{laser}} = -k \frac{dT}{dz} + h(T - T_0) \quad (\text{Eq 5})$$

where Q is the laser heat flux (W/m^2), h , is the air natural heat convection coefficient selected as $5 \text{ W}/\text{m}^2\cdot\text{K}$ (Ref 36). In this study, the natural air convection coefficient values of $5 \text{ W}/\text{m}^2\cdot\text{K}$ and $50 \text{ W}/\text{m}^2\cdot\text{K}$ were examined and no distinct differences in generated temperature histories were observed. Therefore, the value of $5 \text{ W}/\text{m}^2\cdot\text{K}$ was used in all the cases.

It is assumed that the laser heat treatment will not result in local melting.

The boundary conditions on the other surfaces are free convection or insulated depending on the experimental setup used.

Gaussian Heat Source

Gaussian heat distribution is assumed to model the actual heat distribution from the incoming laser beam (Ref 37).

This Gaussian heat source model for a laser beam normal to the surface with constant incident power is described by:

$$Q(x, y, z) = \frac{\alpha q}{2\pi\sigma^2} e^{-\left[\frac{x^2+y^2}{2\sigma^2}\right]} \quad (\text{Eq 6})$$

where Q is the laser heat flux (W/m^2), q is the amount of heat introduced by the source (W), and σ is the Gaussian beam radius. In this equation, α is the beam absorption coefficient, which is a property of the base material. Here this coefficient is estimated as 0.95 for the black painted copper surface. The emissivity of the black paint was determined experimentally using a controlled heat plate, calibrated infrared camera, and thermocouple.

Letters x , y , and z denote the position coordinates. The laser beam heat flux distribution is uniform in x and y direction in a normal laser and it forms a circular profile.

Due to the potential lens damage caused by beam reflection, the application of a normal beam is limited. Accordingly, in this study, a combination of tilted beam angles, one close to normal (10°) and the other 45° is studied. Therefore, it is necessary to find a transformed Gaussian distribution for the tilted cases.

The schematic in Fig. 2(a) shows the Gaussian heat distribution transformation from a normal beam to a tilted beam. Normal beam forms a circular heat distributed profile with the uniform Gaussian distribution in all directions within the circular region in x - y plane. In contrast, heat distribution in tilted beams is not uniform. As seen in Fig. 2(a), it forms an ellipse with the heat-affected zone larger in laser front, i.e., y -direction.

For a tilted power source, the Gaussian distribution is expressed as:

$$Q(x, y, z) = \frac{\alpha q \cos(\theta)}{2\pi\sigma^2} e^{-\left[\frac{x^2+y^2 \cos^2(\theta)}{2\sigma^2}\right]} \quad (\text{Eq 7})$$

where θ is the laser angle with respect to the surface normal.

Figure 2(b) compares the Gaussian heat distribution of a normal beam and a tilted (45°) beam, in x and y -direction. The laser power and step size are 4 kW and 1.8 mm, respectively. As seen, the heat flux distribution is identical in x and y direction for a normal beam shown with dash line in Fig. 2(b). For the tilted beam, the heat flux distribution is different in x and y direction, with y -direction having a larger heat distributed area. Also, the maximum laser heat flux reduces by a factor of $\cos(\theta)$ in the tilted laser beam.

Problem Geometry and Boundary Conditions

Figure 3 illustrates the geometry and boundary conditions for stationary and moving laser cases. The depth and lateral measurement locations are also shown.

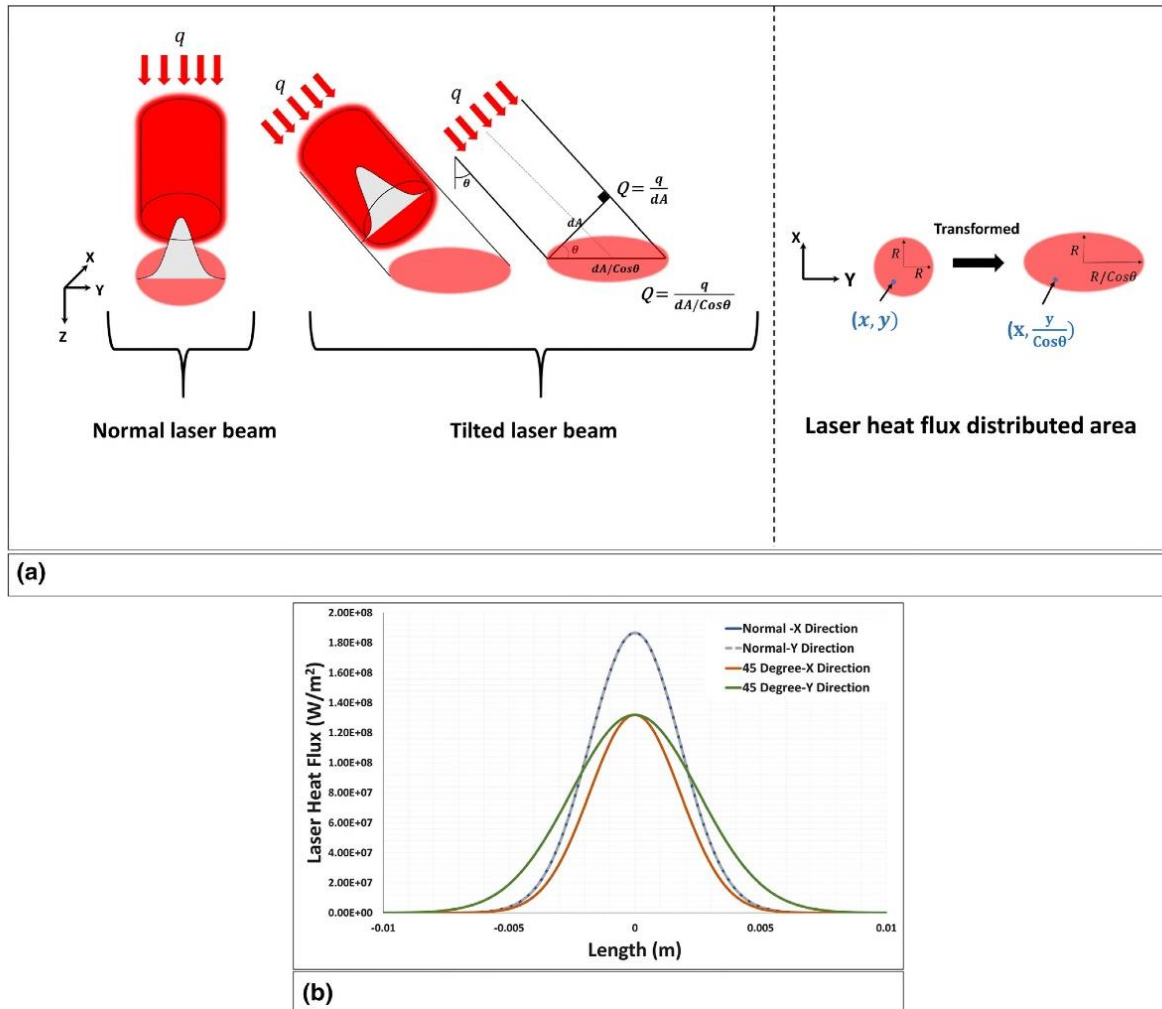


Fig. 2 Gaussian heat distribution model (a) schematic showing the Gaussian heat distribution transformation from normal beam to a tilt beam, (b) Gaussian distribution comparison for normal and 45° tilted laser with the laser power of 4 kW, and a beam spot size of 1.8 mm

As seen in Fig. 3, the lateral measurement points are positioned symmetrically with respect to the laser beam location. Therefore, hardness values measured for any two corresponding locations should be equal. For consistency, the hardness measurements were performed for all the lateral points located on both sides of the laser beam and the average values were used.

Figure 3(a) shows the experimental conditions for the stationary laser tests. The two top images illustrate the experimental setup for the stationary case with the laser beam shown in red and traces left after heat treatment shown with arrows. The 3D schematic illustrates the sample dimensions and boundary conditions. For the stationary tests, the laser beam is tilted at 45°. The top and side surfaces are cooled by free convection and the back of

the sample is insulated. The 2D schematic is a cross-section at the heat-treated spot with the depth and lateral measurement points presented.

For the moving laser case illustrated in Fig. 3(b), the laser was tilted at 10° with respect to the surface normal, as used in the experimental conditions. Free convection is applied on all surfaces. The laser power of 4 kW is used for all the moving cases. A perfect bonding is considered at the copper/steel interface. As illustrated in Fig. 3(b), for the actual experimental setup, L-shape aluminum plates were placed on the sample side walls to ensure the laser beam won't touch the side walls. For the numerical analysis, in order to decrease the computational time, the aluminum plates are not modeled. Our study shows that replacing the effect of heat transfer through aluminum plates with free

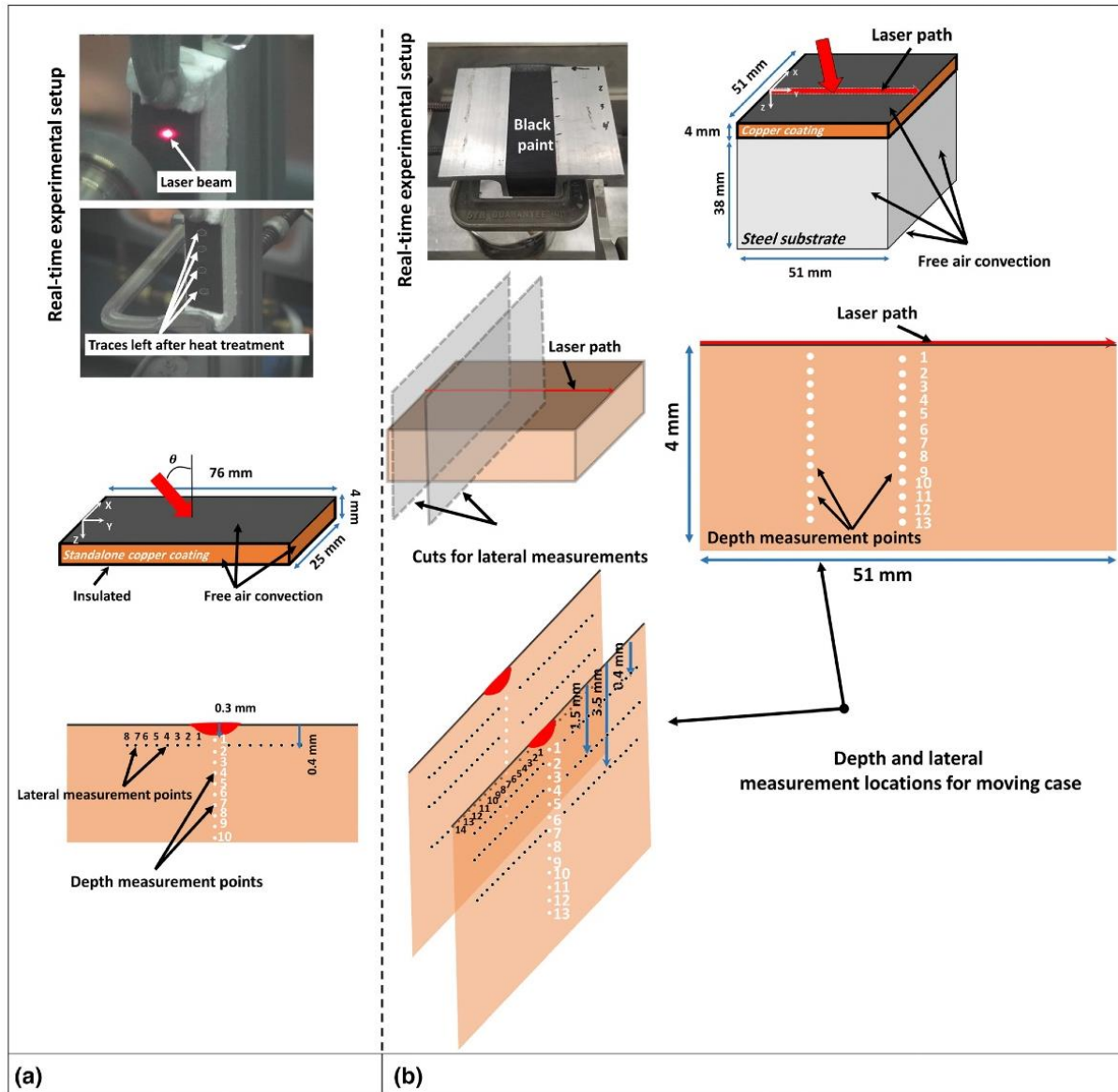


Fig. 3 Geometry, dimensions, and measurement locations used for the thermal modeling (a) standalone coating used for stationary laser heat treatment, beam angle 45° , (b) small coupon of copper coating with steel substrate used for moving laser heat treatment, laser beam

angle 10° . For moving cases, the laser beam scans the surface one or two times with a step size of 2 mm. Depth points are located $300\ \mu\text{m}$ from the top surface with $300\ \mu\text{m}$ intervals. Lateral points are located at $400\ \mu\text{m}$ from the surface with a $500\ \mu\text{m}$ distance from each other

convection boundary conditions can accurately estimate the actual experimental conditions.

For each case, the plate was left to cool down to a temperature below 150°C . This cooling temperature selection is based on the typical minimum annealing temperature in copper (Ref 20).

Locations of the depth and lateral measurement points for both the stationary and moving laser cases are shown in Table 4.

The thermal properties of copper and steel used in this study are provided in Table 5:

The thermal property values provided in the table are the properties of pure copper. The thermal properties of the as-sprayed copper may differ from the pure copper depending on the spray condition used (Ref 40). It has been shown that porosity is the main factor influencing the thermal conductivity of copper coating (Ref 41). In this study, the use of a high-pressure cold spray system with high spray

Table 4 Depth and lateral measurement locations for stationary and moving laser cases

Points	Stationary Laser													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Depth (μm)	300	600	900	1200	1500	1800	2100	2400	2700	3000				
Lateral (μm)	500	1000	1500	2000	2500	3000	3500	4000						
Points	Moving Laser													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Depth (μm)	300	600	900	1200	1500	1800	2100	2400	2700	3000	3300	3600	3900	
Lateral (μm)	500	1000	1500	2000	2500	3000	3500	4000	4500	5000	5500	6000	6500	7000

Table 5 Thermal properties for copper and steel used in the simulation (Ref 38, 39)

Material	ρ (kg/m ³)	k (W/m·K)	C (J/kg·K)
Copper	8933	400	385
Steel	7800	52	470

parameters results in dense coatings and hence a closer value to the thermal conductivity of bulk copper. In this study, the coating thermal conductivity was not measured and the thermal conductivity of bulk copper was assumed for all studied cases.

Mesh size analysis and time step study were performed to ensure grid and time-step independence of the solution. Results showed that using a mesh size of $7e-4$ m and a time step of $3e-4$ s are sufficient to achieve solution convergence independence.

For each case, the corresponding temperature profile of all the experimental points is exported, pre-processed, and then used by the neural network model as inputs to train the network.

Artificial Neural Network

Artificial neural network (ANN) is an established field in computer science inspired by functional aspects of neurons in the biological brain (Ref 42, 43). This mathematical approach mimics the way the human brain operates. ANNs are used as data mining techniques for regression, clustering, and classification purposes. In general, they bring new insights into the study of complex problems by recognizing underlying patterns from extensive and complicated data. This powerful tool has been successfully utilized in solving a wide range of problems in fields as diverse as engineering, medicine, economics, environment, and finance (Ref 42, 44, 45).

Foundation of ANN

ANNs consist of independent processors, the neurons. These neurons form a network that is organized in layers. Neurons in the network are interconnected by several connections called links. The most popular ANN algorithm is the multilayer perceptron (MLP). The architecture structure of an MLP is illustrated in Fig. 4(a). In the MLP, the neurons are organized into three layers: one input layer, one or multiple hidden layers, and one output layer. The number of neurons in the input layer represents the number of input variables whereas the output-layer neurons denote the output variables. The neurons in the hidden layer are responsible for recognizing the pattern and storing the data during the training process. Figure 4(b) shows the main elements of a neural network: inputs ($x_1, x_2, \dots, x_n$), outputs ($y_1, y_2, \dots, y_m$), neurons in the hidden layer ($h_1, h_2, \dots, h_k$), transfer function (Σ), bias vector (b), and activation function (f). w_{ji} and w_{lj} are weights that are responsible to connect neurons in an ANN model. w_{ji} is the weight connecting the input x_i to j th neuron in the hidden layer (h_j); w_{lj} is the weight connecting the j th neurons in the hidden layer (h_j) to the output y_l .

The mathematical representation of the connection in these elements is described as follows (Ref 46):

$$h_j = f \left(\sum_{i=1}^n w_{ji} x_i + b_j \right) \quad (\text{Eq 8})$$

$$y_l = f \left(\sum_{j=1}^n w_{lj} h_j + b_l \right) \quad (\text{Eq 9})$$

The activation function, f , is fixed for each neuron and it can be either a nonlinear or linear function of its activation value (Ref 47). Three common activation functions that are usually used are the sigmoid function, hyperbolic tangent functions, and rectified linear activation function (or ReLU) functions. These functions are described as:

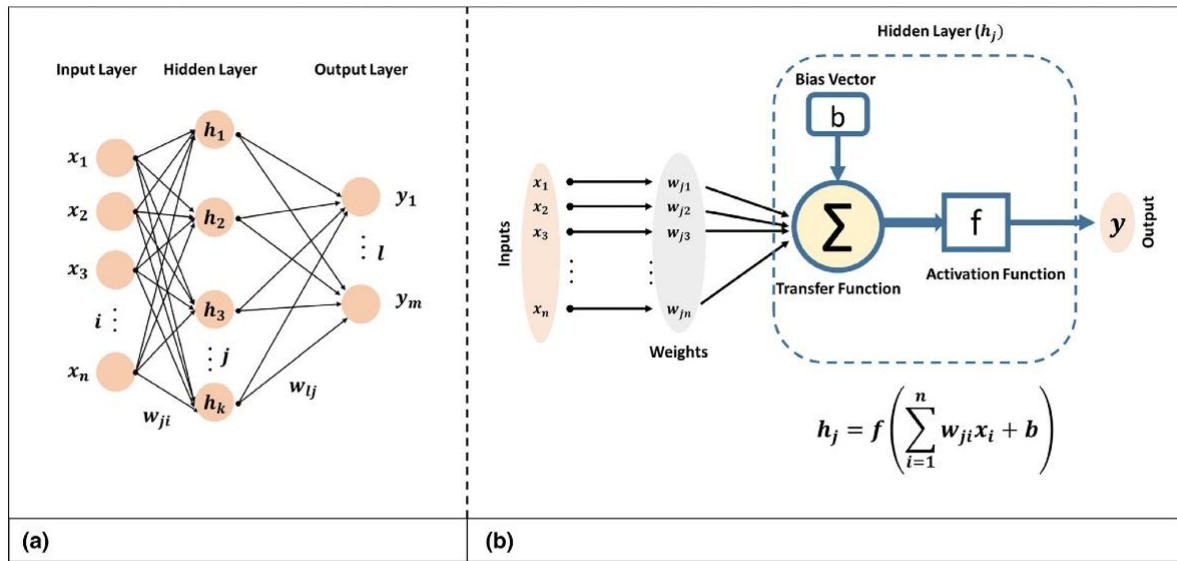


Fig. 4 Schematic diagram demonstrates an artificial neural network (ANN) (a) a multilayer perceptron (MLP) with one hidden layer and (b) structure of an ANN for single neurons in hidden layer with one output. In this figure, $x_1, x_2, \dots, x_n$ represent the inputs in the input layer, $y_1, y_2, \dots, y_m$ are outputs in output layer, and $h_1, h_2, \dots, h_k$ are the neurons in hidden layer. n, k , and m are the number of neurons in

input layer, hidden layer and output layer, respectively. w_{ji} is the weight connecting the input x_i to j th neuron in the hidden layer (h_j); w_{lj} is the weight connecting the j th neurons in hidden layer (h_j) to the output y_l . In the hidden layer in an ANN model, b is bias vector, Σ denotes for transfer function, and f is activation function

$$f = \text{sigmoid}(x) = \frac{1}{1 + e^{-x}} \quad (\text{Eq 10})$$

$$f = \tanh(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}} \quad (\text{Eq 11})$$

$$f = \text{ReLU} = \begin{cases} 0 & x \leq 0 \\ x & x > 0 \end{cases} \quad (\text{Eq 12})$$

Data pre-processing is an important step in the training procedure and it is critical for model convergence. It involves using feature-scaling techniques such as normalization, standardization, and log transformation to re-scale input and output variables prior to training the neural network model. These techniques help maintain the general distribution and ratios in the source data while reducing redundancy and complexity. This improves the performance and training stability of the model.

Training the neural network involves using an optimization algorithm to best map the inputs to outputs with a set of parameters (model weights). The most frequently used algorithm is the back-propagation method. In this method, the difference between the expected output value and the observed value (loss) is calculated. Then, the loss is distributed back to the network by calculating partial derivatives of the loss with respect to weights and biases and updating each weight and bias. The purpose of this step is to adjust the parameters to minimize the loss or error. This process is repeated for all cases, called an epoch. After

several epochs, the error converges to a minimum level and the training stage ends.

Overfitting and underfitting are the two common problems in the neural network approach. Overfitting happens when a very complex model is used and the model fits the training data too well but it performs poorly on the testing set (Ref 48). Underfitting occurs when the algorithm cannot capture the underlying trend of the data. Both underfitting and overfitting lead to poor performance of prediction (Ref 46). Underfitting can be prevented by increasing the training data and the model complexity by increasing the number of neurons or adding hidden layers (Ref 43). To avoid overfitting, it is necessary to split the data into validation dataset in addition to the training and test datasets. The training dataset is the sample of input data used to fit the model. In other words, the model learns from this training data. A validation dataset is the sample of data used to provide an unbiased evaluation of a model fit on the training dataset while tuning model parameters. This validation dataset is used to evaluate the performance of the training model while developing the model. And lastly, the test dataset is the sample of data used to provide an unbiased evaluation of a final model fit on the training dataset. The dataset split ratio into training, validation, and test depends on the total training samples and on the type of model that is used (Ref 49).

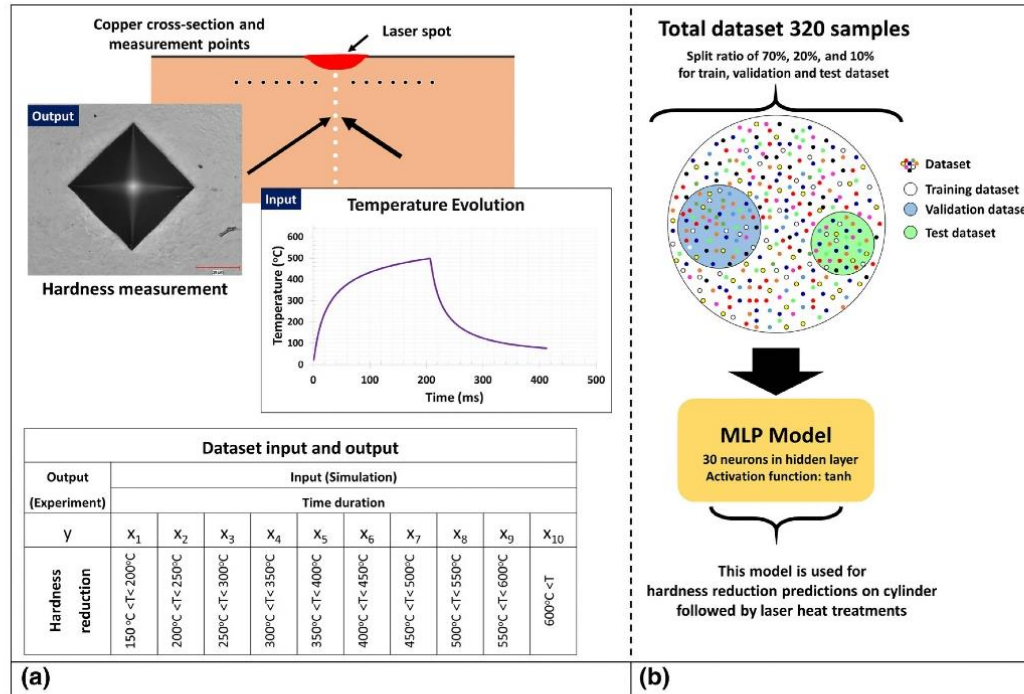


Fig. 5 The framework for the ANN prediction modeling, (a) input and output for each sample in the dataset and the temperature discretized configuration, (b) the schematic of all datasets, 320

samples, used for ANN training, validation, and test to build the multilayer perceptron (MLP) model. The final ANN model information is presented

The performance of the model is evaluated using the root mean square error (RMSE).

Performance = $(1 - \text{RMSE})\%$, with RMSE

$$= \sqrt{\frac{\sum_{i=1}^n (y_i^t - y_i^p)^2}{n}} \quad (\text{Eq 13})$$

where y_i^t , and y_i^p are the target and predicted values, respectively.

ANN Approach in the Current Work

In this work, a regression artificial neural was used. The first step into training the ANN model is to determine the input and output variables. Figure 5(a) shows the input and output for each measurement point. As presented, the input is the temperature history obtained from the simulation i.e., the time duration the sample was in a certain temperature range. The output is the hardness reduction values measured experimentally. As such, combined hardness reduction and corresponding temperature history at a point structure one sample for the ANN dataset. As shown in Fig. 5(a), the simulated temperature histories are a continuous function of time. To be able to feed them for the ANN training, these data are discretized into the temperature families from 150 °C to above +600 °C with an

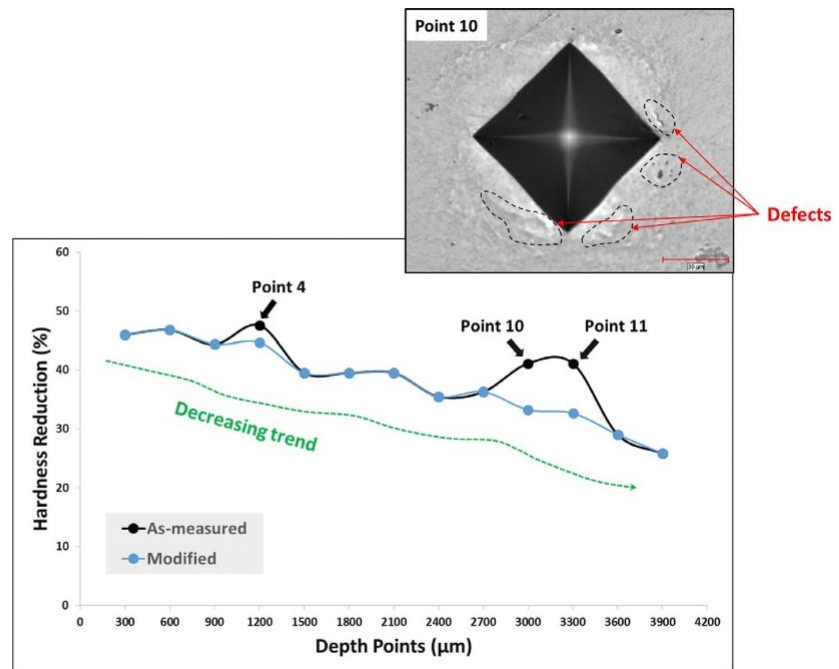
increment of 50 °C. The time durations within each temperature range become the inputs.

In total 320 samples were collected from many laser treatment cases performed for this work. This dataset is big enough to represent the unknown underlying mapping function from inputs to outputs.

In this study, an MLP system with three layers (one hidden layer) is used. The number of neurons in the hidden layer is often determined by trial and error. Several networks with different numbers of hidden neurons (from 4 to 35) have been evaluated. Also, different combinations of data split ratios for training, test and validation were examined and the different activation functions provided in part 4.1 were tested. The best model accuracy was achieved using the split ratio of 70, 20, and 10%, for the training, validation and, test dataset, with the number of 30 neurons in the hidden layer and using “hyperbolic tangent” as the activation function, shown in Fig. 5(b). This model is used for the hardness reduction prediction of a new set of data on the cylinder that has never been used in the ANN model (unseen data)

As mentioned, data pre-processing is of paramount importance to ensure the reliability of datasets (Ref 50). Log transformation and anomaly (or outlier)

Fig. 6 As-measured and modified microhardness reduction values for a moving laser case. The laser with the power of 4 kW, and a spot size of 2.5 mm scans the width of the sample with the traverse speed of 18 mm/s. SEM image shows the presence of cracks and defects in the vicinity of the indenter



detection/modification are the two main pre-processing steps performed in the current work.

The heat treatment process is longer in the moving laser cases compared with the stationary ones. For instance, the time duration in which the temperature stays between 150 and 200 °C varies from 20 ms in a stationary case to 5100 ms in the moving one. This results in a broad variation range in input variables. To reduce the range of input variables, and help to improve the ANN model performance and speed up the training process a log transformation was employed, which is applied by replacing the original data with the logarithm of that data as follows:

$$\hat{x} = \log(x) \quad (\text{Eq 14})$$

Anomaly detection was another data pre-processing used, which is the process of identifying and modifying the outliers in the output dataset. Outliers skew data distribution resulting in a misleading representation of the underlying relationships. Anomaly detection is done by re-evaluating the experimentally measured microhardness values and modifying the inconsistent data. Figure 6 demonstrates an example of the hardness reduction measured for a moving laser case. In this heat treatment case, laser power is 4 kW, with a spot size of 2.5 mm. The laser beam scans the width of the sample with a traverse velocity of 18 mm/s. It is expected that for the copper sample with the heat treatment condition applied, i.e., the laser beam impacting only the top surface, the microhardness reduction should decrease as the distance from the heat source

(laser beam) increases. Points further from the heat source experience less thermal energy than those closer to the surface and hence their corresponding hardness reduction values should be lower than those above; however, as seen in Fig. 6, inconsistencies are observed for points shown with arrows (points 4, 10, 11 at depths of 1200, 3000 and 3300 μm, respectively). Examination of hardness indentation traces shows the presence of local defects that artificially reduces the hardness at these points. One example of the indent SEM image for point 10 is provided in Fig. 6, with the defects highlighted at the vicinity of the indenter edges. These defects tend to reduce the material toughness which results in higher hardness reduction values that are not related to the heat treatment.

For these locations, the original values were replaced by the modified hardness reduction values as shown in Fig. 6. Each modified value is the average of four hardness reductions values at the vicinity of the point being modified, two points above and two points below, with an added tolerance of 5%. For example for point 4, the as-measured value of 47.58% was modified to 44.67% which is 1.05 times the average of values at points 2, 3, 5, and 6.

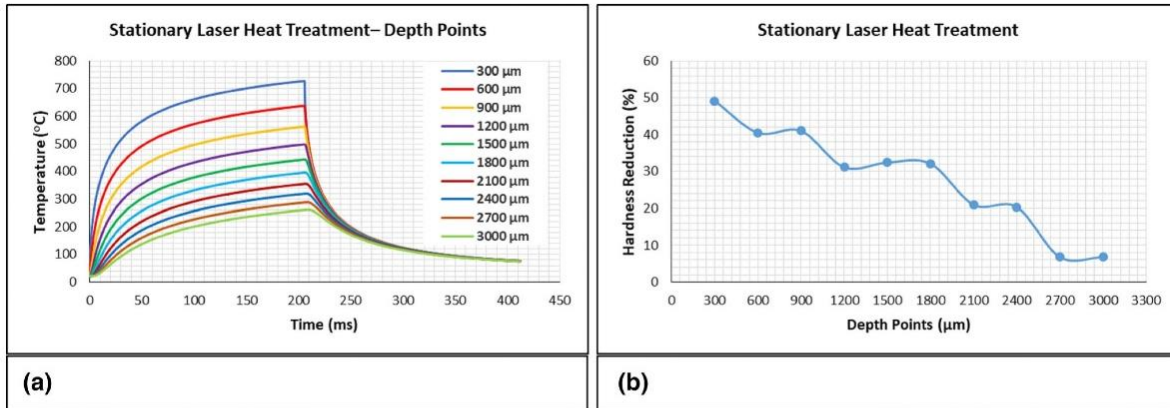


Fig. 7 Temperature and hardness profile for the stationary laser heat treatment, (a) simulated temperature histories at various depth points directly at the laser spot center, (b) measured depth hardness

reduction values. Laser power of 4 kW, laser spot size 1.8 mm, and laser heating duration of 200 ms, and cooling time of 200 ms

Results and Discussion

Stationary Heat Treatment

Figure 7(a) shows an example of the depth temperature profiles for the stationary laser heat treatment case with the laser beam power of 4 kW, and the laser spot size of 1.8 mm. The heating duration is 200 ms with an additional 200 ms for the cooling process. The measured hardness reduction values as a function of the depth at the laser spot center are presented in Fig. 7(b).

The sample initial temperature was 22 °C. When the laser beam touches the surface, the temperature starts to increase. The temperature rapidly rises until the end of the heating process, which in this specific stationary case is at 200 ms. The cooling process starts afterward, with the major temperature reduction occurring within the first 50 ms of cooling. By the end of 400 ms of the simulation, the sample temperature decreases over time and reaches nearly 100 °C at all points.

As seen in Fig. 7(a), the maximum temperature for the depth points decreases by increasing distance from the coating surface. For these depth locations, the maximum temperature drops from 730 °C at 300 μm to approximately 300 °C at 3000 μm. Similarly, as seen in Fig. 7(b), a decreasing trend is also observed in the hardness profile for depth locations by moving further from the heat source. Points that are distant from the heat source at a depth below 2400 μm barely experienced any hardness reduction. For these points, the reached maximum temperature is also below 350 °C. This reveals that to achieve a hardness reduction larger than at least 20% within the time range studied, it is necessary to reach a maximum temperature above 300 °C.

Moving Laser Heat Treatment

Figure 8(a), (b) illustrates the temperature profiles for depth and lateral points in a moving laser case with one laser scan. The heat treatment condition has been applied with a 4 kW laser power, 1.8 mm laser spot size, and 18 mm/s laser traverse speed. For this heat treatment test shown in Fig. 8, the temperature profiles were obtained at the points located at the lateral and depth in the middle of the laser path, shown schematically.

The initial sample temperature is 22 °C. Once the laser beam touches the surface and surface scanning starts, the temperature at the measurement points increases. This increase continues further as the laser beam approaches these points. As seen for both the depth and lateral points, the maximum temperature is higher for the points closer to the laser beam, and this maximum temperature drops by moving away from the laser. The temperature decreasing process starts with the laser moving away from the measurement points.

Figure 8(c), (d) shows the hardness profile for the depth and lateral points, respectively. Comparison between the depth and lateral hardness profile reveals that the hardness reduction values are higher than 30 % up to a radial distance of 4000 μm from the laser path. As seen in Fig. 8(c), a slow downward trend is observed for the depth points. A similar trend is also observed for the lateral points located at the distance up to 4500 μm from the laser path, shown in Fig. 8(d).

For the other lateral points after 4500 μm, the hardness reduction drops sharply. These lateral points experienced very limited ductility improvement after the laser heat treatment.

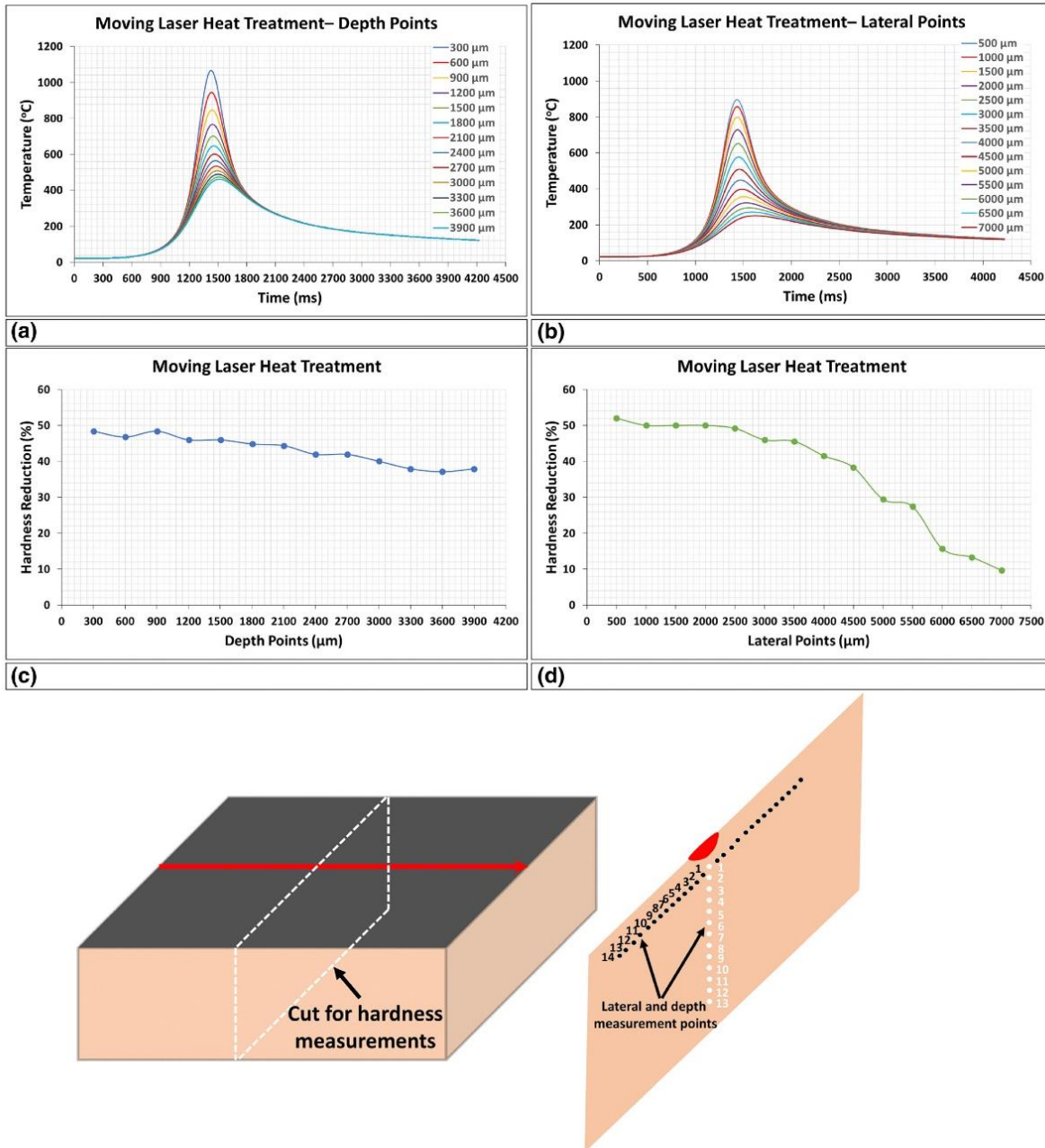


Fig. 8 Temperature and hardness profile for the moving laser heat treatment at a location in the middle of laser path shown in the schematic, (a) simulated depth temperature profiles, (b) simulated lateral temperature profiles, (c) measured depth hardness reduction

profile, and (d) measured lateral hardness reduction profile. Laser power of 4 kW, laser spot size 1.8 mm, and one laser path with the laser scanning speed of 18 mm/s. Schematic demonstrates the cut for hardness measurement and the measurement points

ANN Model Performance

The ANN model was trained using a dataset of 320 samples: 320 physical points where the microhardness values

were measured and temperature history computed. The best model accuracy has been achieved by using a neural network having 30 neurons in the hidden layer. The ANN

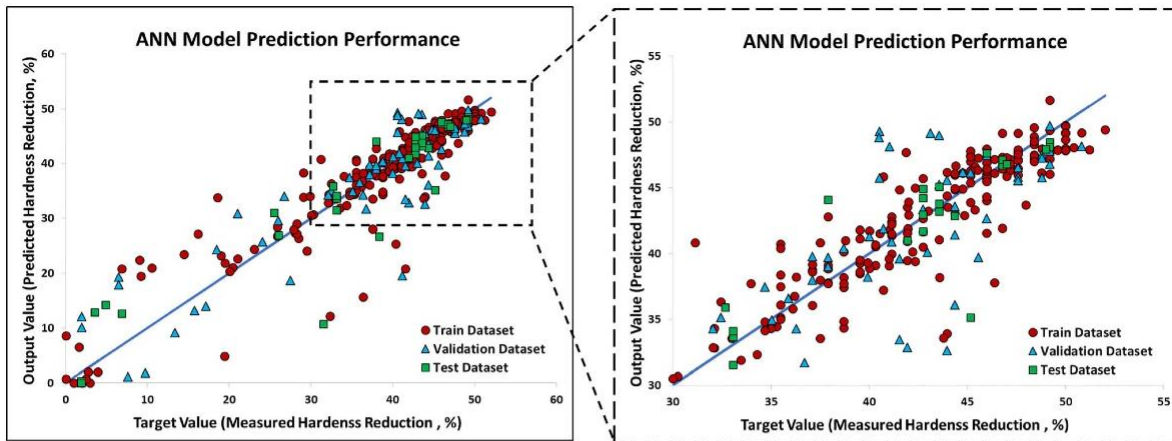


Fig. 9 Graph showing the distribution of predicted hardness reduction values (output value) with respect to the experimentally measured value (target value) for train, validation, and test dataset. The zoomed view of the region highlighted in the dashed box is shown on the right graph

Table 6 Proposed laser heat treatment conditions based on the ANN model

Moving short cylinder	Laser heat treatment conditions		
	Spot size (mm)	Laser Traverse Speed (mm/s)	Scan condition
Case 1	2.5	36	Lines with a step size of 2 mm
Case 2	1.8	31	Lines with a step size of 2 mm

model shows an overall accuracy of 92, 91, and 94% for training, validation, and test datasets, respectively.

Figure 9 presents a distribution diagram for the actual output values (target values measured experimentally) versus the output values predicted from the ANN model. This diagram is a plot of all the 320 samples studied in the current work. The solid line shows the pathline with the equal target and output values which is the ideal case (prediction accuracy of 100%). The main purpose of the work is to predict and test a laser heat treatment process that results in a hardness reduction of 30% up to approximately 3 mm depth into the copper sample. The hardness reduction measurements were mainly focused on depths where the hardness reduction was above the requested value. As observed, the vast majority of the 320 data points are distributed mainly above 30%. These are the lateral and depth measurement points located in the vicinity of the laser heat source. As seen in Fig. 9, the majority of these points are concentrated around the solid line which demonstrates the high performance of the ANN model and accuracy level close to 96% for the entire dataset.

The sparse distribution of the predicted points is only for the data point far from the laser heat source with a low hardness reduction value (which is not of interest for this

study). Only a few points (less than 15% of the total dataset) reach lower hardness reduction values, explaining why the model is not performing well for those lower hardness reduction due to lack of training in that region. However, these low hardness reductions are not a subject of interest in current work so it is not justified to gather more points in those regions.

ANN Model Application

As seen in the previous section, the trained ANN model demonstrated good prediction performance. This model is now used to find proper laser parameters to test on the cylinder. Different local temperature histories were obtained by running the thermal model using different laser heat treatment parameters such as laser traverse speed, laser spot size, and, different scanning lines in an effort to come up with the best design in terms of laser parameters to be used. The local temperature histories were then exported and prepared as input data for the ANN model to predict the resulting hardness profiles. Among all the simulations the two cases with the predicted hardness reduction values of at least 30% for up to 3 mm deep into the copper sample were selected to test on the cylinder.

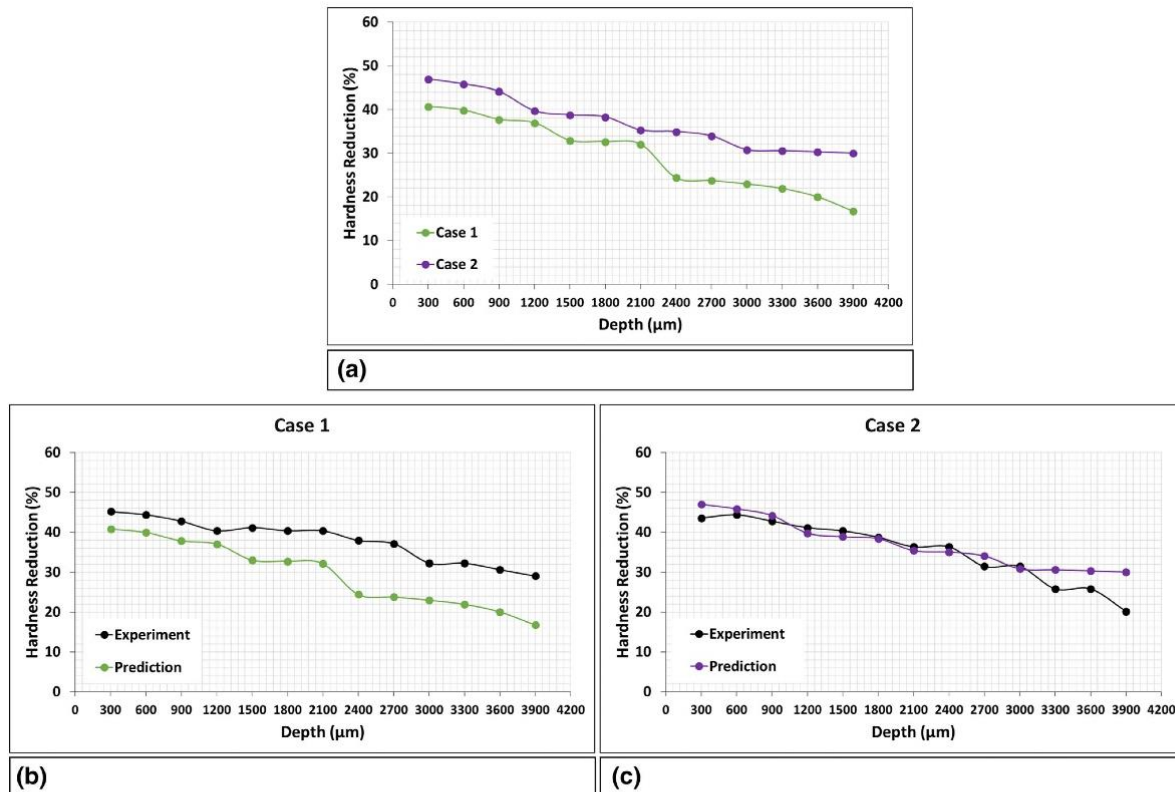


Fig. 10 Hardness reduction values (a) predicted for the proposed laser heat treatment conditions. Comparison between the ANN predicted values and the experimental measurement after applying the proposed laser condition for, (b) case 1, and (c) case 2

There are preliminary indications that this hardness reduction value is sufficient for the UFC to remain integral under the pressures that may develop in the underground repository (Ref 26).

The two laser parameters that were retained for testing are listed in Table 6. The laser power was kept at 4 kW and the laser angle is close to normal.

The hardness reduction values predicted by the ANN model for these two laser heat treatment conditions are shown in Fig. 10(a). These laser parameters were applied to the copper coating on the steel cylinder and microhardness values were measured experimentally. The comparison between the predicted values and the experimental values for case 1 and case 2 are provided in Fig. 10(b), (c), respectively.

As seen in Fig. 10(c), for case 2, the hardness reduction values from the prediction match the experimental measurements very well with an accuracy of 96%; however, for case 1, Fig. 10(b), the gap between the prediction and experiments is noticeable.

In order to investigate the reason for this behavior, different possible scenarios were studied; measurement errors (scenario 1), deviation from the proposed laser heat

treatment parameters when applied experimentally (scenario 2), and in the end, the effect of higher initial condition considering the effect of sample preheating by heat conduction (scenario 3).

In order to evaluate the possibility of measurement error (scenario 1), multiple measurements at different locations along the cylinder were performed. As illustrated in Fig. 11(a), all these measurements are in the same range, with a small deviation. This indicates that the difference in prediction and measured hardness reduction is unlikely to be related to measurement errors.

The second scenario is investigated by restarting the simulation using a smaller laser spot size (2.1 mm). The initial prediction was obtained using the simulation data for a laser spot size of 2.5 mm. The ANN predicted results for this case are shown in Fig. 11(b). The comparison between the new predictions and the initial predictions shows a higher hardness reduction prediction when using a smaller spot size; however, there is still a large gap between the experimental measurements and this new prediction.

The effect of laser preheating is studied using a higher sample initial temperature. For all the other simulations the initial temperature for the simulation was set at 22 °C. The

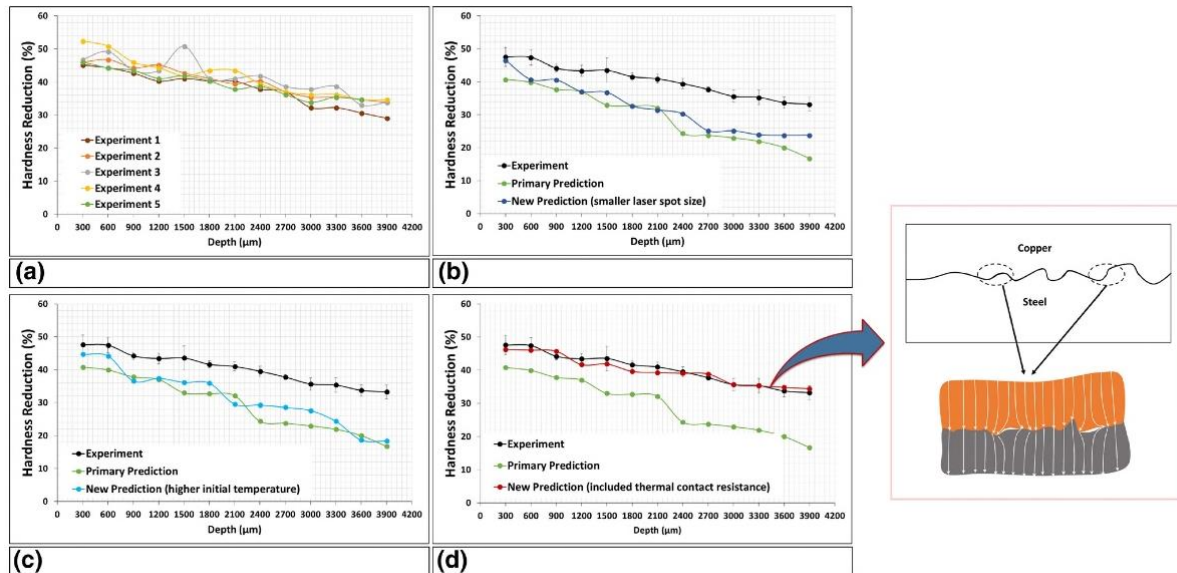


Fig. 11 Case studies to investigate higher hardness reduction measurements for case 1, (a) multiple hardness measurements, and comparison between experiment and prediction using (b) smaller laser spot size, (c) higher initial temperature (d) presence thermal

contact resistance at the interface. Schematic shows the presence of zones with thermal contact resistance and the way they interfere with the temperature diffusion at the interface

laser preheating effect is included by modifying the sample initial temperature to 100 °C. The predicted hardness reduction using the initial temperature of 100 °C is shown in Fig. 11(c).

As seen in Fig. 11(c), the initial prediction results and new predictions with higher sample initial temperature, are similar. This behavior was anticipated since in the ANN model, for the input, only temperature intervals above 150 °C were considered, and using the sample initial temperature of 100 °C has almost no effect on the ANN input values and eventually on the predicted data. It is known that the higher measured hardness reduction values presented in Fig. 10(b) are attributed to the higher heat accumulation in the copper part; however, none of the scenarios studied provides enough energy for such higher measured values.

The last investigation is done by adding a thermal contact resistance at the copper/ steel interface in the simulation. In order to study the influence of thermal contact resistance at the interface, the thermal transient simulation was restarted for the new case. In this case, thermal contact resistance of $2e-4 \text{ m}^2 \cdot \text{K/W}$ (or a conductance value of $5000 \text{ W/m}^2 \cdot \text{K}$) was applied at the interface. This value is an average interface conductance for copper-copper and steel-steel joints found in the literature (Ref 51). The new prediction is provided in Fig. 11(d). As seen in this figure, the predictions and the experiments match fairly well. This tends to confirm that the differences

between the prediction and experiments shown in Fig. 10(b), can be a result of heat accumulation in the copper part due to the presence of thermal contact resistance. It leads to a higher hardness reduction value as heat conduction from the copper layer to the steel substrate is reduced by the extra interfacial thermal resistance.

To validate whether the reason for case 1 not matching the experiments is due to the presence of thermal contact resistance, adhesion tests were performed. Examining the adhesion strength at the copper/steel interface provides information about interface characteristics that can be used to infer the bonding condition.

For adhesion testing, one-inch diameter specimens were extracted from the short cylinders using a hole saw tool after the laser heat treatment. Five specimens were extracted for both heat treatment conditions and were used for the adhesion testing. Coating thickness was machined down to $\sim 3 \text{ mm}$, giving a flat surface (the other end of the substrate was also machined flat). After machining, the samples were tested according to ASTM C633, using FM1000 epoxy glue. The tests were performed using an Instron 5582 universal testing machine (Burlington, Ontario, Canada) with a dynamic load up to 100 kN at a constant speed of 0.020 mm/s (1.2 mm/min).

The adhesion test results indicated a glue/adhesive failure for case 1 (adhesion strength $62 \pm 10 \text{ MPa}$) as opposed to case 2 where only the glue failed (therefore adhesion strength above $72 \pm 8 \text{ MPa}$). The lower adhesion

for case 1 might be a result of a weak bond or the presence of microscopic gaps at the interface. These gaps, if existing, would act as a thermal contact resistance at the interface, which interferes with the heat flow from copper coating to the steel substrate. It is thus assumed that it might be the potential cause for discrepancy between the ANN model and case 1 results, as one would not expect the ANN model to work for one case and fail for another case unless the physics of the problem had been changed, as proposed here.

Conclusion

In this work, the laser heat treatment process of CS copper coatings on steel substrates was modeled and the local temperature histories in the copper coatings following different heat treatment conditions were obtained. The local temperature history and hardness reduction data were used to develop and train an artificial neural network model. It was shown that this model predicts the hardness reduction from the temperature histories accurately.

The overall goal to design a laser heat treatment through appropriate laser parameters, to achieve hardness reductions of approximately 30% up to the depth of 3 mm from the surface in a steel cylinder coated with copper, was achieved. For that, multiple thermal simulations were performed and used by the ANN model to predict the associated hardness reductions. Among all the tested laser parameters, two heat treatment conditions resulting in the desired hardness reduction were tested experimentally. It was shown that for one case the prediction and the experimental measurements are close to each other and the model accuracy is 96%. For the other proposed case, a large gap between the predictions and the experiments was found. Many simulations and investigations were performed to find the source of this discrepancy and it was concluded that the likely cause of this behavior can be attributed to the interfacial characteristics at the copper/steel interface. The hardness reduction predicted from simulation including the presence of a thermal contact resistance shows an accuracy of 99%. This conclusion was further investigated and demonstrated by performing adhesion tests to support the theory that inadequate contact was the cause of the discrepancy. It is concluded that the ANN model is capable of predicting hardness reduction obtained from laser heat treatment and can also capture possible modifications that can interfere with the heating/hardness reduction of the part.

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5.4 Research Project 4: Enhancing Biofilm Inhibition and Antiviral Properties through Surface Texturing of Copper

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This work aims at understanding the differences in biofilm resistance of bulk copper, cold-sprayed, and shot-peened copper surfaces and identifying the major biofilm control mechanisms. The growth behavior of *P. aeruginosa* biofilm on modified surfaces was compared using stainless steel as a control, due to its prevalent use for touch surfaces. First, biofilm inhibition tests are performed on copper and two types of stainless-steel samples. Then the effect of surface microstructure is presented by a comparison between polished as-received (As-R) and cold sprayed (CS) copper surfaces. Last, the effect of surface roughness on the biofilm inhibition performance of copper is presented using three-shot peened samples as a comparison. The role of surface roughness and the grain size is illustrated and mechanisms affecting the biofilm inhibition properties of the surfaces are studied by performing complementary ion measurement tests using inductively coupled plasma optical emission spectroscopy (ICP-OES). Also, the antiviral performance of the copper cold sprayed and the shot-peened samples was also investigated. Using the best biofilm inhibition performance materials, the antiviral performance of these copper samples was compared with bulk copper and control samples using a lentivirus surrogate model of SARS CoV-2.

This peer-reviewed paper addresses the objectives presented in section 3.4.



Biofilm Inhibition and Antiviral Response of Cold Sprayed and Shot Peened Copper Surfaces: Effect of Surface Morphology and Microstructure

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Abstract Antibacterial properties of copper against planktonic bacteria population are affected by surface microstructure and topography. However, copper interactions with bacteria in a biofilm state are less studied. This work aims at better understanding the difference in biofilm inhibition of bulk, cold-sprayed, and shot-peened copper surfaces and gaining further insights on the underlying mechanisms using optical and scanning electron microscopy to investigate the topography and microstructure of the surfaces. The biofilm inhibition ability is reported for all surfaces. Results show that the biofilm inhibition performance of cold sprayed copper, while initially better,

decreases with time and results in an almost identical performance than as-received copper after 18h incubation time. The shot-peened samples with a rough and ultrafine microstructure demonstrated an enhanced biofilm control, especially at 18 hr. The biofilm control mechanisms were explained by the diffusion rates and concentration of copper ions and the interaction between these ions and the biofilm, while surface topography plays a role in the bacteria attachment at the early planktonic state. Furthermore, the data suggest that surface topography plays a key role in antiviral activity of the materials tested, with a smooth surface being the most efficient.

This article is an invited paper selected from presentations at the 2021 International Thermal Spray Conference, ITSC2021, that was held virtually May 25-28, 2021 due to travel restrictions related to the coronavirus (COVID-19) pandemic. It has been expanded from the original presentation.

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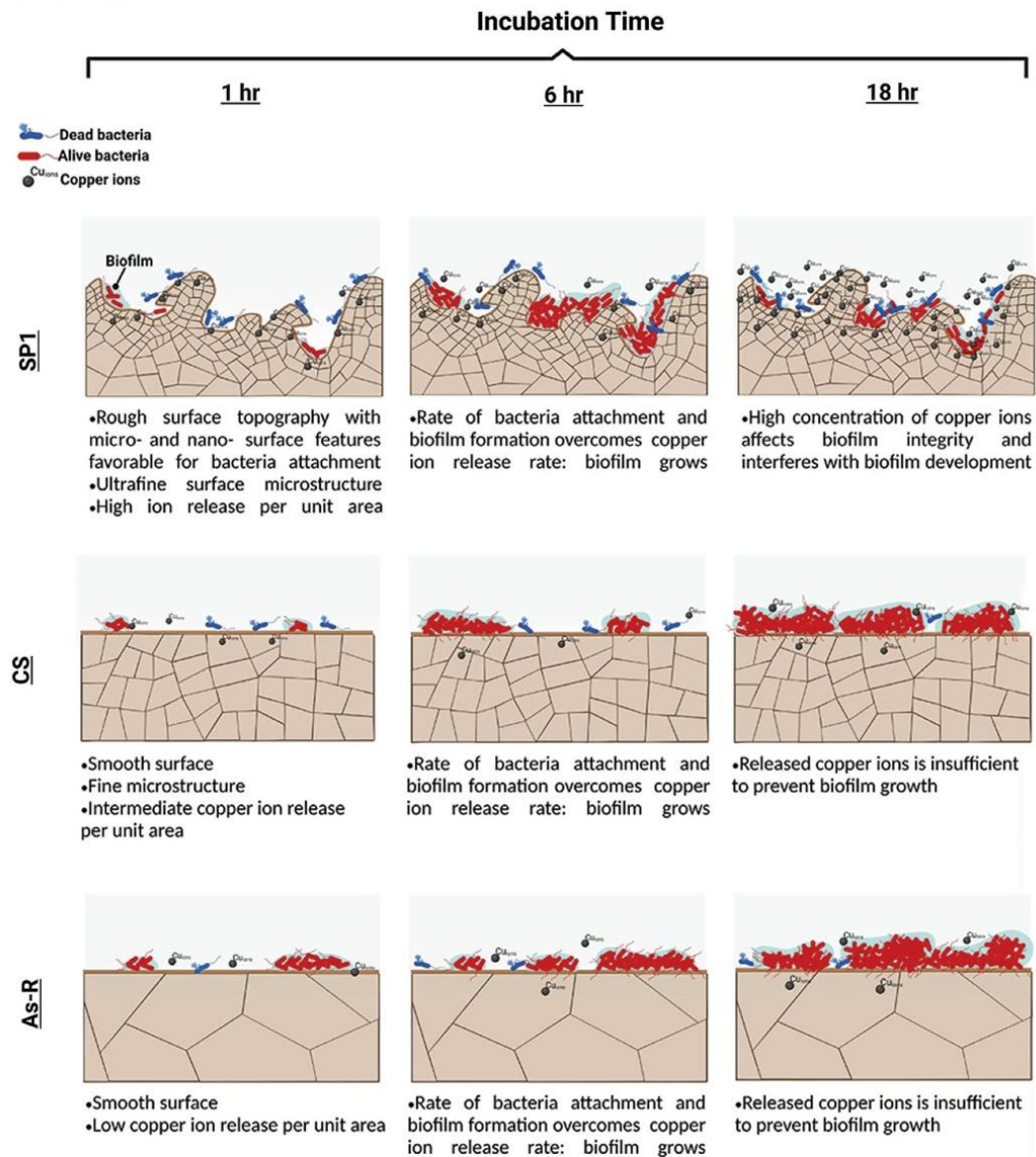
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Graphical Abstract



Keywords antiviral properties · biofilm inhibition response · cold spray · copper ion diffusion · shot peening · surface topography · surface microstructure

Introduction

The antimicrobial properties of copper surfaces have been extensively studied (Ref 1-4). It was shown that exposure to metallic copper can rapidly kill bacteria according to

several potential mechanisms (Ref 5). Many studies suggested that copper ions released from the copper surfaces cause a decline in the cell membrane integrity leading to leakage of cell nutrients causing loss of function of proteins (Ref 6). Other studies related the antibacterial activity of copper to its capacity to release ions which function as catalysts in reactions generating reactive oxygen species (Ref 7). DNA damage is also known as a secondary reason causing cell death (Ref 8). The inherent contact killing effectiveness of copper can be further improved by surface

modification processes such as cold spray (CS) or shot peening. CS is a solid-state deposition process in which the feedstock powder is accelerated at high speed towards a part to be coated. Upon impact, the powder undergoes severe plastic deformation at a temperature below their melting point and forms a coating (Ref 9). CS generally induces localized grain refinement and dynamic recrystallization of the sprayed material (Ref 10), as a result of the accumulation of dislocations during severe plastic deformation. These accumulated dislocations restructure and form subgrains that eventually turn into ultrafine grains (Ref 10, 11). The improved antibacterial properties of CS copper coating over bulk copper, at the planktonic state, have been explained by the presence of many favorable ion diffusion paths which enhance the surface copper ionic release (Ref 12–15).

The antiviral effectiveness of cold sprayed copper can be improved by using nanocrystalline copper powder (Ref 15). This was attributed to the increased grain boundaries and dislocation densities in the nanocrystalline copper coatings leading to higher ion diffusivity (Ref 15). Surface modification techniques, such as surface nanocrystallization (SNC), can be used to enhance surface ion diffusion by increasing surface dislocation densities and grain refinement. Shot peened surfaces present enhanced antibacterial properties over bulk copper (Ref 16).

Several studies have investigated the effects of surface roughness on cell attachment. It has been suggested that surface topography affects the ability of bacteria to adhere to the surface and to develop colonies. In one study, surfaces with similar surface chemistry but different surface roughness exhibited different bacteria retention abilities depending on the size of bacteria used (Ref 17). It was also reported that high surface roughness improves the antibacterial property of copper by improving its hydrophobicity (Ref 18). As opposed to many studies reporting hydrophobicity in favor of antibacterial effectiveness, others demonstrated higher bacterial adhesion on hydrophobic surfaces compared to hydrophilic surfaces (Ref 19, 20), with the mechanism still not understood. A different contact killing mechanism is considered when dealing with nanoscale surface roughness. It was proposed that the contact killing mechanism of nanotextured surfaces was mechanical rupture of cell membrane induced upon contact with the sharp nanofeatures (Ref 21, 22).

Many uncertainties are involved in identifying methodically and separately the effect and mechanisms of surface roughness on the bacterial attachment and inactivation. This makes the problem even more complicated when surface modification/treatment processes involving surface topography modifications also involve grain size modification at surfaces, creating a convoluted situation (Ref 23). Furthermore, examination of the literature (Ref

1, 2, 18, 24–28) on anti-pathogenic properties of copper surfaces reveals that almost all of these studies were focused on antibacterial properties in a planktonic state (Ref 1, 2, 18, 24–28), not as a biofilm (Ref 29–31).

Undesired biofilm represents a significant economic burden regardless of the industry or economic area and is a major threat to public health (Ref 32, 33). The development of biofilms occurs in five stages: Cell attachment, micro-colony formation, biofilm formation, biofilm growth and maturation, and eventually dispersal stage where the bacterial cells depart biofilms and can return to planktonic state (Ref 34, 35). The antibacterial properties of copper are commonly associated with the released copper ions that will cause cell damage (Ref 1, 2, 26). However, the copper interaction with biofilm is significantly different and the action of copper surfaces and copper ions will not only focus on cell interaction but will also interfere with extracellular polymeric secretions (EPS) (Ref 36). It was reported that exposure to CuO nanoparticles increased the production of loosely bound EPS on wastewater biofilms. These CuO nanoparticles altered the EPS structure and its chemical composition, affecting significantly the functional groups of proteins and polysaccharides of loosely bound EPS (Ref 29). CuO nanoparticles have been found attached to and embedded in an EPS matrix in wastewater biofilm (Ref 29). Developing antimicrobial surfaces with improved anti-biofilm and self-sanitizing performances is a critical task. This can be tailored by first understanding the mechanisms affecting the anti-biofilm response of the surfaces. Further, limited studies also reported the antiviral properties of metallic copper and copper ions (Ref 37–40).

This work aims at understanding the differences in biofilm resistance of bulk copper, cold-sprayed, and shot-peened copper surfaces and identifying the major biofilm control mechanisms. The growth behavior of *P. aeruginosa* biofilm on modified surfaces was compared using stainless steel as a control, due to its prevalent use for touch surfaces. First, biofilm inhibition tests are performed on copper and two types of stainless steel samples. Then the effect of surface microstructure is presented by a comparison between polished as-received (As-R) and cold sprayed (CS) copper surfaces. Last, the effect of surface roughness on the biofilm inhibition performance of copper is presented using three-shot peened samples as a comparison. The role of surface roughness and the grain size is illustrated and mechanisms affecting the biofilm inhibition properties of the surfaces are studied by performing complementary ion measurement tests using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Ref 41). Also, the antiviral performance of the copper cold sprayed and the shot-peened samples was also investigated. Using the best biofilm inhibition performance materials, the antiviral performance of these copper samples was

compared with bulk copper and control samples using a lentivirus surrogate model of SARS CoV-2.

Material Preparation and Surface Treatment

Coating and shot peening procedures were conducted using a commercially available EP Series SST cold spray system (CenterLine (Windsor) Limited, Windsor, Ontario, Canada). De-Laval tungsten carbide and steel nozzles were used for coating and shot-peening processes, respectively. These nozzles have throat and exit diameters of 2 mm and 6.6 mm, respectively, along with a diverging section length of 120 mm.

Discs of 10 mm diameter and 4 mm thickness were machined from as-received copper round bars (grade C101) as well as as-received stainless steel round bars (grade 316). The stainless steel discs were only used as control substrates for the biofilm inhibition response tests. The shot peening and cold spray processes were performed on copper discs.

In order to remove any machining imperfections and to standardize the substrate surface properties, all discs surfaces were grounded using a 220 grit ($\sim 63 \mu\text{m}$) diamond-grinding disc prior to each experiment.

The coatings were produced using as-received electrolytic copper powder (CenterLine (Windsor) Limited,

Windsor, Ontario, Canada). Figure 1(a) illustrates the feedstock powder morphology. These powders have an irregular shape with a purity of 99.7%, as specified by the manufacturer. The powder size distribution ranges from $5 \mu\text{m}$ to $45 \mu\text{m}$, as specified by the manufacturer. Powder cross-section images are shown in Fig. 1(b). As seen, these powders are dense and no internal pores or other defects are observed. The morphology of glass beads used for the shot peening process is illustrated in Fig. 1(c). These glass beads are spherical with an average particle size distribution of $88\text{--}149 \mu\text{m}$ and Mohs hardness of 4–5, as reported by the manufacturer.

The process parameters used to perform the cold spray and shot peening treatments are listed in Table 1. Three different peening parameters were used, i.e., SP1, SP2, and SP3. SP1 sample underwent the largest peening intensity and coverage. SP2 and SP3 samples experienced similar peening conditions except for the peening scan speed. These peening parameters were selected to produce refined grain sizes with different surface roughness values.

Biofilm Inhibition Test Methodology

The biofilm inhibition response of the various copper samples was evaluated using *Pseudomonas aeruginosa* bacteria (PA14). *P. aeruginosa* is a gram-negative rod-

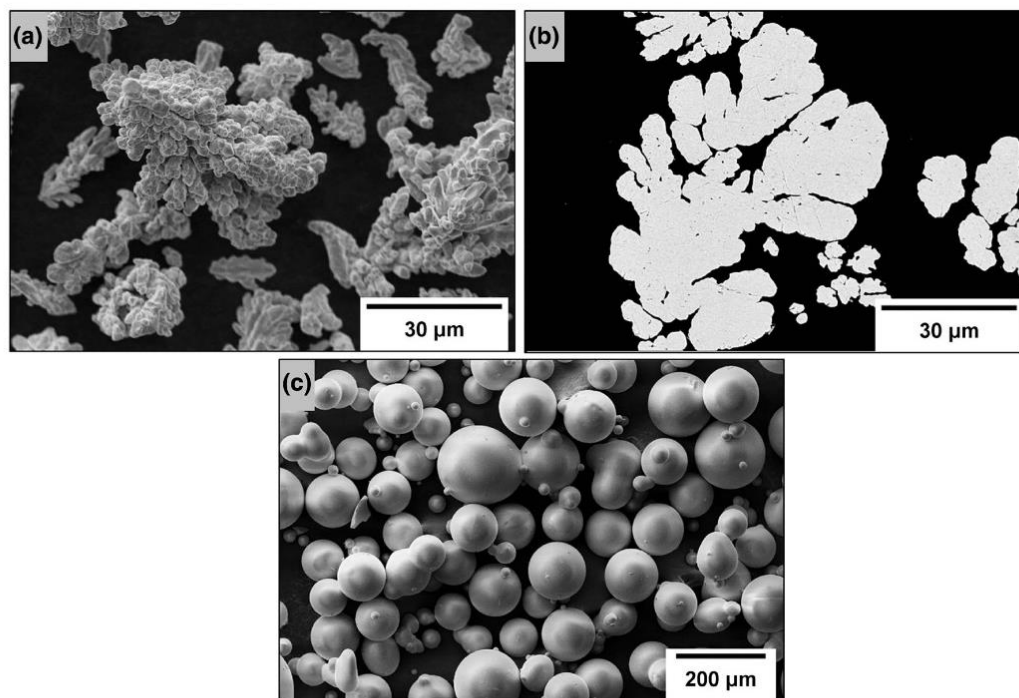
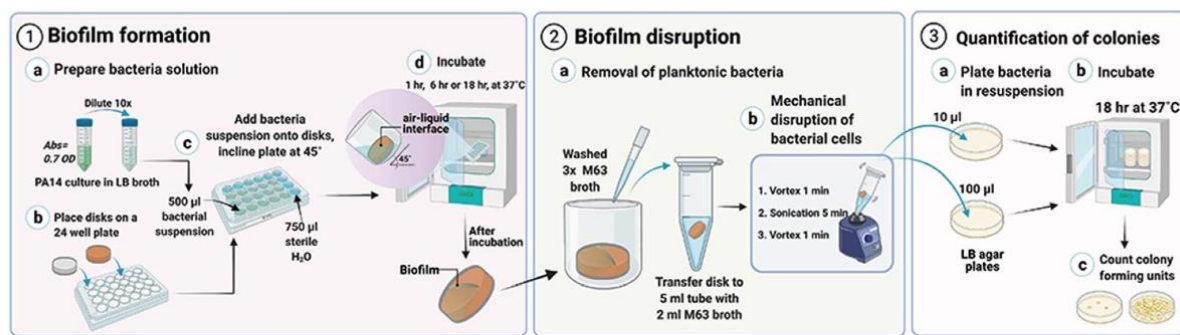


Fig. 1 Morphology of (a) loose copper powder, (b) powder cross-section, and (c) glass beads used in the shot peening process

Table 1 Coating and shot peening process parameters with the sample ID for each surface treatment listed

Surface Treatments		Gas Condition		Gun Traverse Speed (mm/s)	Powder Feed Rate (gr/min)	No. of Surface Scans	Surface Coverage	Particle Velocity (m/s)
		Pressure (MPa)	Temperature (°C)					
Copper Coating	CS	3.4	500	40	9.1	5	...	539±66
Shot Peening	SP1	0.7	25	20	34.8	5	10000%	208±32
	SP2	0.7	25	40	16.7	1	500%	
	SP3	0.7	25	200	16.7	1	97%	

**Fig. 2** Schematic of the biofilm inhibition test methodology conducted for the samples in this study

shaped pathogen with an average size of 0.5–3 µm (Ref 42). This pathogen uses several attachment organelles to adhere to surfaces and form biofilm (Ref 33, 35, 43). The schematic in Fig. 2 illustrates the biofilm inhibition response test. All experiments were carried out in a biosafety level 2 (BSL2). Experiments are divided into three stages; biofilm formation, biofilm disruption, and quantification of colonies.

PA14 bacteria were allowed to grow in LB broth in an orbital shaker, at 37 °C and aerobic conditions. The absorbance characterization was performed on the bacteria suspension using spectrometer (SpectraMax M2). Bacteria suspension was adjusted to 0.7 optical density (OD) and then diluted by a factor of 10 using an LB broth (Fig. 2, Biofilm formation step a). From this solution, 500 µL of bacteria solution with initial concentration of $\sim 10^8$ colony-forming unit/mL (CFU/mL) was used for each disc. The 5 discs from each group were placed in a sterile plate and 500 µL of the bacteria stock solution was spread over each sample. Unused wells were covered with 750 µL of sterile H₂O to preserve the humidity (Fig. 2, Biofilm formation step b and c). Then the plate was placed in a humidity incubator at 37 °C at an inclination of 45° (Fig. 2, Biofilm formation step d). The discs were incubated for 1 hr, 6 hr, and 18 hr to allow bacteria colonization and

biofilm formation. Next, the biofilm was removed, see Fig. 2, and resuspended in M63 media, plated and survival colonies counted (18 hr incubation, 10–100 µL sample plated at 37 °C).

Anti-Viral Test Methodology

To evaluate the contact killing ability of copper samples when exposed to viral pathogens, a viral photoinactivation experiment was performed using a lentivirus surrogate model of SARS-CoV-2. The schematic of the antiviral test methodology is illustrated in Fig. 3. The test procedure is divided into four steps; cell preparation, virus preparation, cell/virus combination, and qRT-PCR analysis.

Cell Preparation

L929 fibroblasts were used. These cells were cultured in cell culture media DMEM/MEM supplemented with 1% Penicillin Streptomycin (PS), and 10% Fetal Bovine Serum (FBS). Cells were trypsinated, counted, and cell density adjusted to 15,000 cells/mL in 10 mL using DMEM. 100 µL of this cell solution were seeded into 96 wells and incubated for 24 hr at 37 °C.

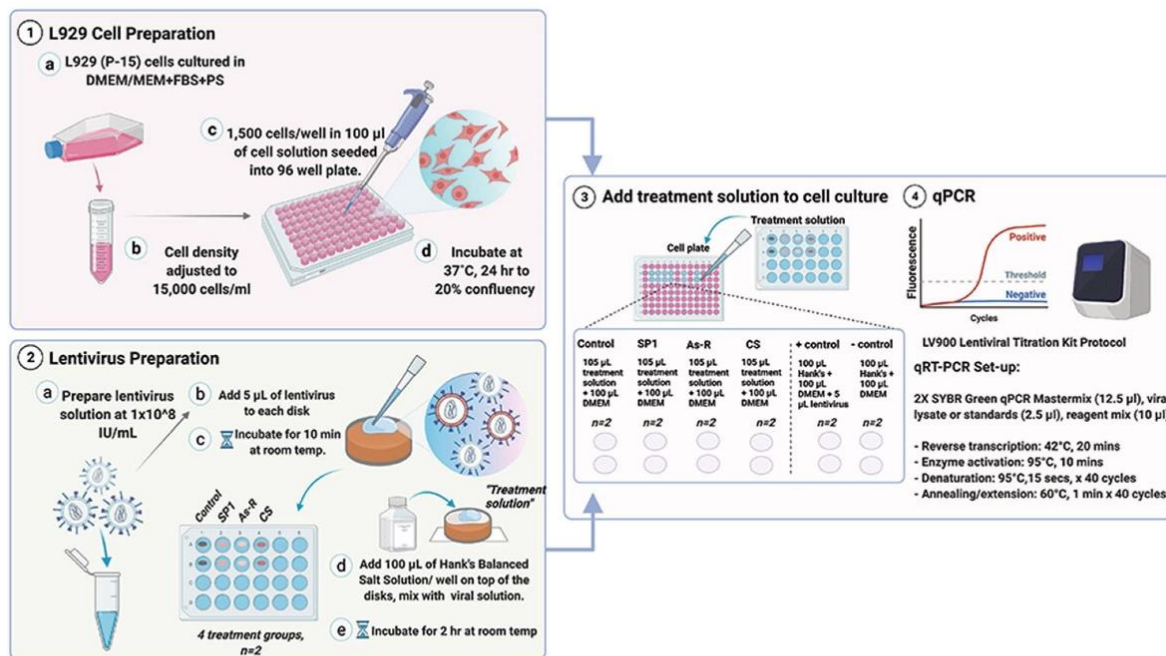


Fig. 3 Graphical protocol illustrating the viral test procedure. The “+control” is the virus-only group and the “-control” is the no virus (media only) group

Virus Preparation

The lentivirus (pLL-CMV-rFLuc-T2A-GFP-Puro Lenti-Labeler™ LentiVector, LL310VA-1, SBI System Biology) was diluted in saline solution and used at a viral dosage of 10^8 International units per milliliter (IU/mL), shown in Fig. 3. Discs (two discs from each copper group) were placed in a 24 well plate. A 5 µL drop of viral solution was placed on top of each disc (Fig. 3) and incubated for 10 min at room temperature (Fig. 3, Lentivirus Preparation, step c). After 10 min, 100 µL of Hank's Balanced Salt Solution (HBSS) was added on top of each disc, which mixed with the viral solution. HBSS is a buffer used for maintaining the physiological pH range and osmotic balance of the solution. This plate was incubated for 2 hr at room temperature (Fig. 3, Lentivirus Preparation, step e).

Cell/Virus Combination

First the culture media from the 96-well plate (Fig. 3, red well plate from L929 Cell Preparation part step d) was replaced with 100 µL of fresh DMEM/MEM cell culture media to provide enough nutrients to feed cells. Then 105 µL solution from each treatment well (Fig. 3, blue well plate from Lentivirus Preparation part step e) was added to the L929 cells plate. Positive control (100 µL of DMEM/MEM culture media + 100 µL of Hank's solution with 5

µL viral solution) and negative control (100 µL of DMEM/MEM culture media + 100 µL of Hank's solution) groups were also added to the L929 cells in the 96-well plate (Fig. 3, part 3). This 96-well plate was then incubated at 37 °C for 48 hr. Then, viral RNA was extracted and quantification analysis was performed.

Quantification Analysis

Quantitative RT-PCR (qRT-PCR), shown in Fig. 3 part 4, was performed for the qPCR Lentivirus Complete Titration Kit Cat#LV900 (Applied Biological Materials Inc, Canada). Samples from the 96-well plate were collected into 0.5 mL Eppendorf tubes individually and centrifuged at 2000 g for 5 minutes to remove cells/debris. 10 µl of viral supernatant and control samples were then mixed with 10 µl of Viral Lysis Buffer and incubated at room temperature for 3 minutes. The qPCR reaction was prepared by mixing 12.5 µl fluorescent dyes (2X SYBR Green qPCR Mastermix), viral lysate or standards (2.5 µl), reagent mix (10 µl) for a total volume of 25 µl per reaction. Real-time qPCR instrument (LightCycler 480, Roche) was programmed with reverse transcription at 42 °C for 20 minutes, enzyme activation at 95 °C for 10 minutes, denaturation at 95 °C for 15 seconds, and annealing/extension at 60 °C for 1 min - repeating the last two steps for 40 cycles. Melting/Dissociation Curve Analysis was then

performed at the end of the last annealing cycle by melting the product at 95 °C. The titer of the samples was calculated using the Ct values obtained from the LightCycler® 480 Software and the Lentiviral titer calculator tool at ABM's corresponding website as suggested by the manufacturer.

Surface Characterization

Microscope observation of sample cross-section was performed to study the samples microstructure after surface treatments. The cross-sections of the samples (As-R, CS, SP1, SP2, SP3) were ground with a 220 grit (~63 µm) diamond grinding disc and diamond paste solution down to 0.05 µm and etched for 5 s in a solution of 5g FeCl₃ + 25 ml HCl + 100 ml ethanol to reveal the grain boundaries. Optical microscopy observations were performed using an optical microscope (VHX—1000, Keyence Corporation, Osaka, Japan). The surface topography of the samples was also analyzed with an optical microscope. Ten 3D images per sample were taken to calculate sample surface roughness (Ra). This was done by extracting the surface topography using VHX-2000 3D Shape Measurement Software. A Matlab code (R2018b) was developed to measure the surface roughness from the exported data points.

Detailed observation of near-surface grain structure was done using scanning electron microscope (SEM) (EVO MA-10, Carl Zeiss AG, Oberkochen, Germany) equipped with secondary (SE) and back-scattering electron (BSE) detectors. Image J software was used to perform the grain size measurements of shot-peened and cold sprayed surfaces down to 20 microns deep. Prior to the analysis, all samples were cleaned ultrasonically with ethanol and dried with air to remove any surface contamination.

Copper Ion Release

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to measure and compare the copper ion release from the studied samples (SP1, SP2, SP3, As-R, CS). Prior to the experiment, the sidewall and base of all the discs were painted to prevent copper diffusion from these surfaces to allow comparing the copper ion diffusion of the modified surfaces only.

Copper discs from each studied group were placed in a 24-well sterile plate and covered with 500 µL of LB broth. This plate was then placed in a humidity incubator at an inclined angle of 45° and a constant temperature of 37 °C. These sample groups were incubated for 1 hr, 6 hr, or 18 hr. Next, discs were removed and the solution containing

copper ions was transferred to vials for quantification analysis.

The copper concentrations were determined for each sample using ICP-OES (Agilent Technologies Inc. 5110 ICP-OES) with the detection limit below 0.0006 ng/g or parts per billion (PPB). The weight of 0.1 ml of the solution was measured. This solution was then diluted in 1% HNO₃ solution with the dilution factor of 1:100. This diluted sample was used for the ion concentration measurement. Before each measurement, the calibration was done using the plasma calibration standard (Cu 1001 ± 5 µg/ml 4 % HNO₃). The concentration of copper in the solution is reported in µg/g.

Results and Discussion

Biofilm inhibition performance of copper is demonstrated by a comparison between bulk copper and stainless-steel samples, illustrated in Fig. 4. All sample surfaces were smooth and mirror polished prior to testing. Copper has significantly better biofilm inhibition properties when compared to stainless steel for all the incubation times.

The copper interaction with biofilm is significantly different from its interaction with bacteria cell in the planktonic state: the number of viable bacteria in the biofilm never reaches zero but rather increases. This is different from the antibacterial efficiency of copper reported using wet plating techniques studying exclusively the survival of bacteria in their planktonic state, where the number of bacteria drops as incubation time increases (Ref 2, 44, 45). As also seen in Fig. 4, there is a considerable difference in the values for copper and stainless steel after 1 hr, with this difference less significant at 18hr incubation time. This suggests that the biofilm inhibition efficiency of copper drops with time as the biofilm grows and thickens.

Contact killing efficiency of metallic copper is affected by many parameters and this makes the comparison between studies challenging. Contact killing properties of copper are significantly affected by the bacteria type and morphology (Ref 46), temperature and humidity (Ref 24, 27), and even the test medium composition (Ref 2, 26, 28, 47). Nevertheless, in all cases, the inherent antibacterial advantages of copper were well demonstrated.

Figure 5 compares the surface topography and microstructure of the samples used in the current study. Cross-section images of shot-peened samples SP1, SP2, and SP3 are shown in Fig. 5(a,b,c), respectively. Fig. 5(d,e) illustrates the cross-section images of As-R and CS samples, respectively. The high magnification images of the highlighted zone in the CS sample are shown in Fig. 5(f). The SP1 sample experienced the most intense shot peening process among all shot peened samples. It presents the

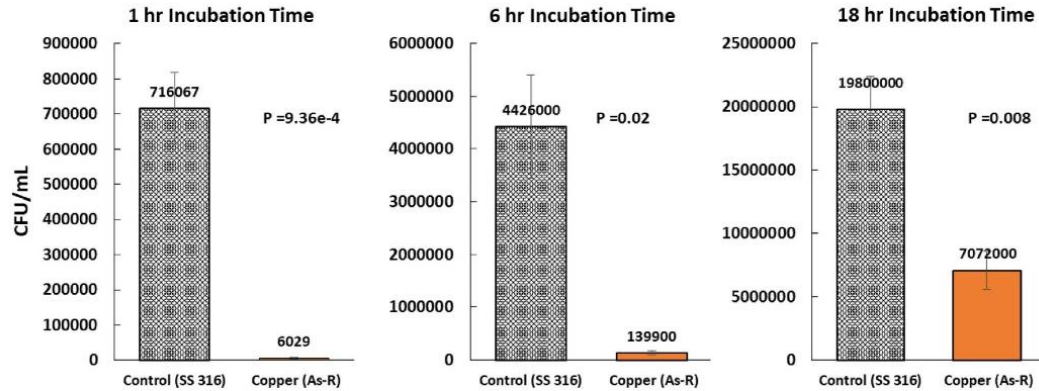


Fig. 4 Comparison between biofilm inhibition ability of bulk copper (As-R) with stainless steel substrates grade 316 (SS 316). The figure shows viable *Pseudomonas aeruginosa* bacteria in the biofilm formed on copper and stainless steel samples after 1, 6, and 18 hr

incubation time at 37 °C. Sample surfaces were polished and their surface roughness is nearly identical. P values calculated from t-students test vs. bulk copper (As-R)

roughest surface topography with the deepest affected zone highlighted in yellow, where the grain size was evaluated at $0.3 \pm 0.14 \mu\text{m}$. The cross-section of the SP2 sample presents a reduced depth zone of refined microstructure compared to SP1. Also, the surface topography comparison between SP1 and SP2 reveals that SP2 surface is smoother than SP1. The SP3 sample surface is the least rough among the peened samples. Shot peening parameter in SP3 resulted in less surface impingement and hence a non-uniform surface microstructure. The regions with detectable refined microstructure were highlighted in yellow. As seen, some parts of the surface barely experienced any microstructure modification. The As-R sample is characterized by coarse grains, with the coarsest surface grain sizes among all the studied samples. The cross-section of CS sample is shown with the copper coating and the substrate parts identified. The copper coating has a fine microstructure with an average grain size evaluated at $1.73 \pm 0.70 \mu\text{m}$ attributed to the fine microstructure of the feedstock powder used for the coating process and recrystallization caused by excessive plastic deformation. The magnified image of the highlighted region (blue box) in Fig. 5(e) is shown in Fig. 5(f). The powder boundary (black region) and the fine grains inside the deformed powders are observed.

Surface roughness comparison (Ra) for all samples is shown in Fig. 5(g). Both As-R and CS were mirror-polished hence have nearly identical surface roughness. For shot peened samples, the surface roughness differences are noticeable with the SP1 that has the largest Ra with the value of $9.59 \pm 2.7 \mu\text{m}$ and for the SP2 and SP3 the Ra values are $4.89 \pm 0.6 \mu\text{m}$ and $3.3 \pm 0.26 \mu\text{m}$, respectively.

Figure 6(a,c,e) compares the biofilm inhibition performance of modified surfaces (shot-peened and cold sprayed sample) with the bulk copper (As-R) sample at 1, 6, and 18

hr of incubation. The student's t-test was used to compare the antibacterial effect between the groups. The comparison is made between samples SP1, SP2, SP3, CS, and bulk copper (As-R). The p-values are reported in the figure. In all statistical tests, the significance level was considered as 0.05.

The results of copper ion diffusion, measured for these samples at the three incubation times, are also shown in Fig. 6(b,d,f). The p-value comparison demonstrates that the significance level between samples SP1, SP2, SP3, CS, and bulk copper (As-R) is all lower than 10^{-4} . The copper ion diffusion rate (CIDR) at 1, 6, and 18 hr was approximated by dividing the instantaneous copper ions concentration at these times by the time of measurement in hr and is reported in Table 2. These results reveal that the diffusion rate increases with time for all surfaces with the exception of CS which increases at 6 hr and then decreases. It also reveals that the diffusion rate for SP1 is much larger than for the other surfaces and that $\text{CIDR}_{\text{SP1}} > \text{CIDR}_{\text{SP2}} > \text{CIDR}_{\text{SP3}} > \text{CIDR}_{\text{CS}} > \text{CID}_{\text{As-R}}$ at all times except for $\text{CIDR}_{\text{CS}} < \text{CIDR}_{\text{As-R}}$ at 18 hr.

As shown in Fig. 6, when applied to a surface by cold spraying, copper exhibits better biofilm inhibition ability when compared to its bulk version (As-R) only for the 1 hr incubation time. The initial improved biofilm inhibition performance of CS copper compared to the as-received copper (As-R) is associated with enhanced ion diffusion and is explained by the effect of finer surface microstructure and increased dislocation densities typically found in cold spray coatings (Ref 10, 11).

Figure 7(a,b) compares the SEM cross-section images of As-R and CS samples. Fine-grain size is the characteristic of CS sample. It was shown that atomic diffusion in crystalline structure can be accelerated by the presence of defects such as dislocations, grain boundaries, and twinning

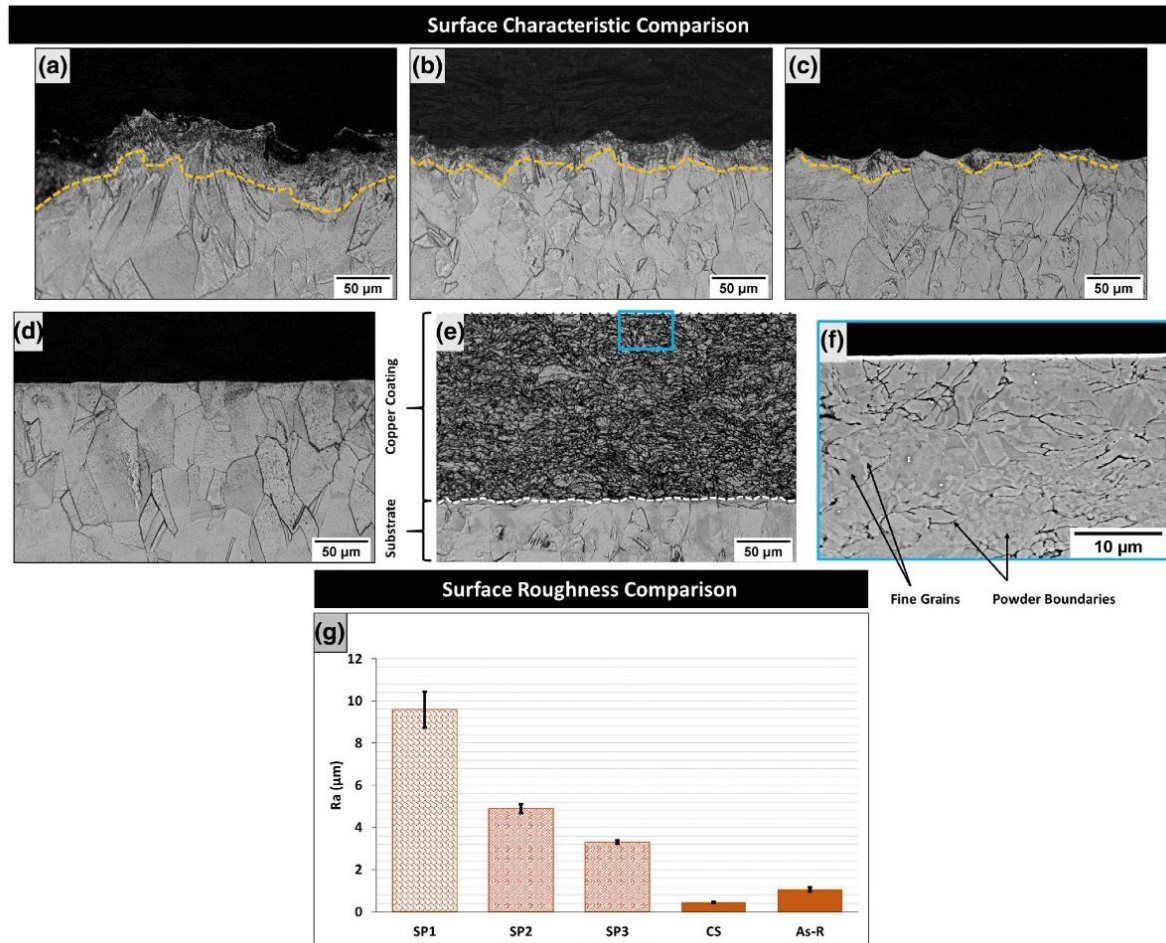


Fig. 5 Optical microscope etched cross-section images of the various copper samples. Shot peened samples (a) SP1, (b) SP2, (c) SP3, and surface polished samples of (d) As-R (bulk copper), and (e) CS. High magnification not-etched SEM image of the highlighted region in

figure (e) is shown in figure (f). Shot-peened affected zones were marked with yellow dashed lines. Surface roughness, R_a , comparison of the samples is shown in figure (g)

(Ref 13, 48). The improved antibacterial properties of CS copper coating over bulk copper, at the planktonic state, is explained by the presence of many favorable ion diffusion paths which enhance the surface copper ionic release (Ref 12–15).

As opposed to 1 hr incubation time, the enhanced inhibition ability of CS vs. bulk copper (As-R) decreases as the incubation time increases, as seen in Fig. 6(c,e). As presented, no significant differences are observed for CS and As-R for 6 and 18 hr incubation time with a p-value of 0.48. This seems to be independent of the ion release results for the As-R and CS samples. Despite the higher copper ion release from CS sample after 6 hr incubation time, illustrated in Fig. 6(d), the biofilm inhibition response of both CS and As-R are almost identical.

The reduction of ion diffusion rate for the case of CS after 18 hr is possibly explained by continuous microstructural evolution of CS samples after the deposition process (Ref 49). High elastic energy is stored in materials due to extreme plastic deformation during high-velocity impact. This stored energy triggers a continuous static recrystallization process that can take place over the course of weeks at room temperature (Ref 49).

The lower copper ion diffusion for CS compared to SP1 is attributed to surface microstructural differences between these two samples. As presented in Fig. 7(b,c), SP1 sample has finer surface grains compared to the CS sample. The intensive plastic deformation in SP1 sample resulted in this finer microstructure, with higher dislocation densities and hence larger ion diffusion ability. It should be noted that the induced increased surface area of shot-peened samples



Fig. 6 *Pseudomonas aeruginosa* bacteria survival in the form of microcolonies and biofilm reported in “CFU/mL” at (a) 1 hr, (c) 6 hr, and (e) 18 hr incubation time. The copper ion released from the samples reported in “µg/g” is shown at (b) 1 hr, (d) 6 hr, and (f) 18 hr

incubation time. Standard error of the mean value is shown. P-values were evaluated by t-test comparison between SP1, SP2, SP3, and CS vs. As-R

Table 2 Copper ion diffusion rate (CIDR) approximated at 1, 6, and 18 hr

	Diffusion Rate (µg/g.hr)		
	1 hr	6 hr	18 hr
SP1	73.7	107.7	507.4
SP2	43.1	58.0	149.9
SP3	38.4	44.6	43.7
CS	25.8	37.9	12.6
As-R	14.5	18.7	33.2

were calculated and only 5% increased area was observed for the SP1 sample. This increased surface was even smaller for the SP2 and SP3 samples with the value lower than for 2 %. These limited area increases cannot explain

the highly increased ion diffusion from the shot-peened samples. Therefore it is concluded that it is rather the refined microstructure and dislocation density that play a role in the high copper ion release. Shot peening induces severe plastic deformation that results in refined microstructure and high dislocation density at the surface and near-surface regions (Ref 50). As seen in Fig. 6(b,d,f), copper ion concentrations of shot-peened samples are consistently higher than As-R sample, for all the incubation times with this difference even more significant for SP1 sample at 18 hr. Also, as presented in Table 2, the copper diffusion rate is much higher for SP1 compared to As-R at all incubation times. Consequently, as shown in Fig. 6, an improved biofilm inhibition performance of shot-peened

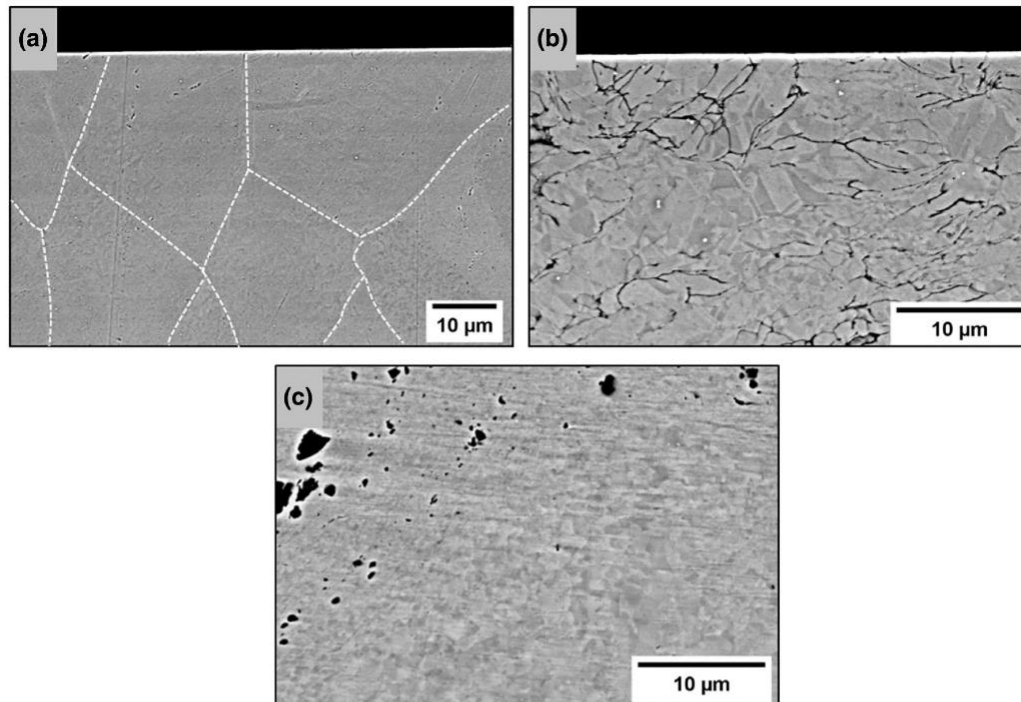


Fig. 7 Microstructure comparison for (a) As-R (bulk copper) and (b) CS samples, and (c) SP1. The SEM image shows the channeling contrast due to differently oriented grains. The grain boundary in the As-R sample is highlighted with the dashed line

samples over As-R sample is achieved with the observed improvement to be the most significant for SP1 at 18 hr of incubation time. For this sample, the biofilm inhibition response and the amount of copper ion concentration are directly correlated.

As presented in Fig. 6, the biofilm inhibition response of CS samples was similar to that of the SP1, SP2 SP3, and bulk copper samples for 6 hr incubation times, as p-values are all similar, despite lower copper ion diffusion of bulk copper at all incubation times. At 18 hr incubation time, the biofilm resistance performance of SP1 overcame that of CS and As-R.

The schematic in Fig. 8 illustrates an approximate model for bacteria attachment in planktonic state and biofilm formation in SP1, CS, and As-R samples at different incubation times considering the differences in surface topography and copper ion concentration. It illustrates that SP1 and CS initially presented better biofilm inhibition response compared with As-R sample. It also schematically explains the similar biofilm inhibition performance of CS and SP1 samples at 6 hr incubation time despite the lower copper ion release in CS. As already seen in Fig. 5(a), rough surface topography was induced by the peening process for the SP1 sample. This micro surface roughness plays a role in bacteria adhesion as well as the expected nano-roughness created by the peening process that was not

captured by the imaging resolution. Bacteria use different attachment mechanisms to increase the number of surface attachment points. Rod-shaped bacteria like *P. aeruginosa* have a large linear surface and this increases the area of contact. Besides, bacteria can create appendages, like flagella, to increase the area of contact and promote attachment. These flagella also help in the motility of bacteria to overcome hydrodynamic and surface repulsive forces and to maintain adherence (Ref 35, 46, 51). The combination of micro and nano roughness contributes to higher bacterial adhesion and increases the number of cell-to-surface contacts at the initial planktonic state for the SP1 sample. This explains the similar biofilm inhibition of polished CS surface and the rough SP1 sample for 6 hr incubation time despite their noticeable copper ion diffusion differences. However, the trend changes at 18 hr of incubation time as the whole biofilm formation process is dynamic. The enhanced biofilm inhibition characteristics and contact killing properties of the SP1 sample at 18 hr are explained by the increased copper ions concentration as a result of the larger copper diffusion ability from the finer grains.

As explained, SP1 is prone to bacteria attachment in the initial planktonic state due to its surface topography (Fig. 8, 1 hr incubation time). However, for this sample, due to its finer microstructure and dislocation density, the ion

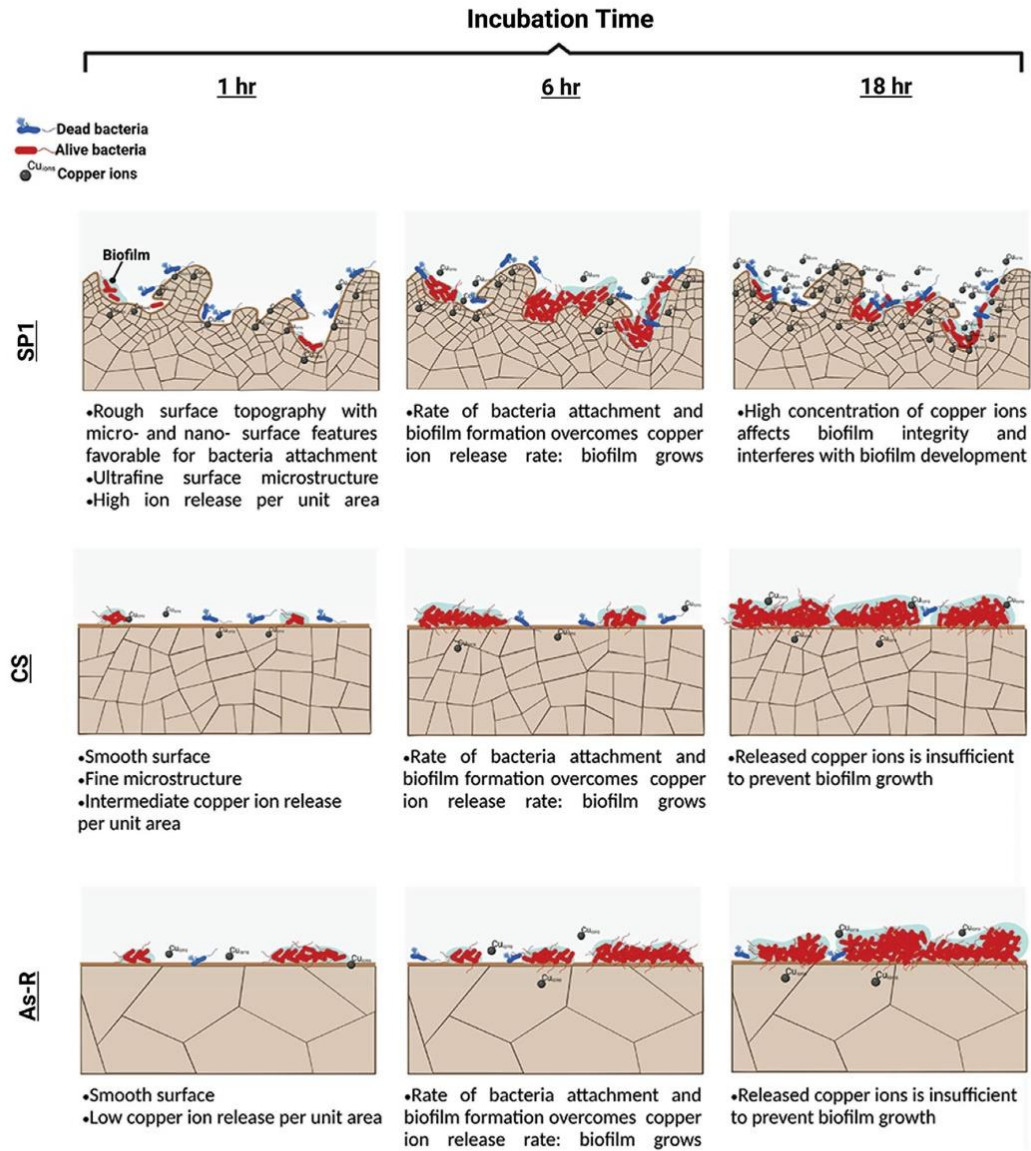


Fig. 8 Schematic comparing the biofilm control proposed mechanism of SP1, CS, and As-R samples. SP1 shot-peened sample with rough surface topography and very fine surface microstructure. CS sample, with smooth surface and fine microstructure. The As-R sample with

coarse grain and smooth surface. The copper ion concentration in $SP1 > CS > As-R$ at all incubation times with the exception at 18 hr incubation in which ion diffusion in $CS < As-R$

diffusion is significantly larger than for the CS sample. At 1 and 6 hr incubation time, the concentration of copper ion was not enough to kill a large number of bacteria in a planktonic state and prevent biofilm formation. As time evolves, copper ions travel over longer distances and this leads to progressively higher copper ions release from the surface (Fig. 8, at 18 hr incubation time). As discussed and illustrated in Fig. 6(f), for 18 hr, the ion concentration of the SP1 sample is sufficiently high to disrupt biofilm

structural integrity and decelerate any further bacteria proliferation and additional bacteria colonization. As observed in Fig. 6(e), a significant reduction of biofilm production is a characteristic of the SP1 sample. The destructive interaction of copper nanoparticles with biofilm was also reported in previous studies (Ref 31). It was shown that copper nanoparticles can effectively disperse the biofilm architecture by loosening the bacteria microcolonies.

The SP2 sample follows a similar trend with similar mechanism as the SP1 sample. The SP2 sample is smoother and has a less refined microstructure than SP1. The smoother surfaces provide fewer bacteria attachment points while the less refined microstructures lead to less ion diffusion than SP1. Eventually, with time, when ion diffusion increases, it regulates the biofilm development behavior resulting in improved biofilm inhibition properties. However, no statistically significant biofilm inhibition improvement was noticed for SP3 sample.

The copper samples with the best biofilm control abilities for 1 hr incubation, i.e., CS and SP1, and 18 hr incubation, SP1, were selected to assess their antiviral effects as well. The bulk copper (As-R) and stainless steel control substrate were also included in the test as references for comparison purposes. The qRT-PCR test results for these samples are reported in Fig. 9. The values are presented in relative expression meaning that the antiviral response values were normalized to the kit's standard virus concentration value and reported in percentage. As seen, both the control sample and the virus only show similar values meaning that the control sample has no antiviral properties. SP1 sample demonstrates a slightly lower value than the control sample, with values of 69.5% and 52.4% for control and SP1, respectively. No detectable viruses were observed for As-R and CS samples. This suggests that these two samples have effective virus deactivation properties over a short contact time. It is evident that surface topography contribution in virus adhesion is dominant. Even in the presence of a reduced concentration of copper ion, the antiviral response of a flat and smooth surface is immediate while for the time frame considered it is not the case for the rougher SP1 surface despite its ability to deliver more copper ions at the surface.

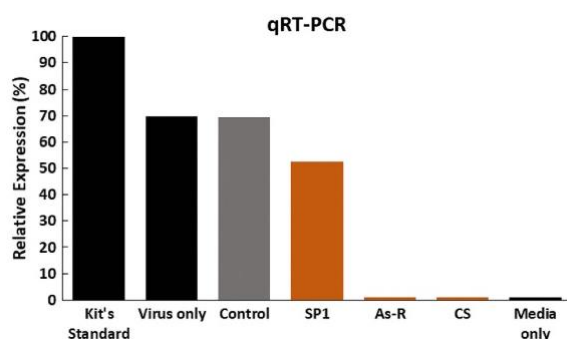


Fig. 9 qRT-PCR test results for control, SP1, As-R, and CS samples. The test results were normalized to the kit's standard virus concentration value. Kit's standard is the calibration kit used for the test. Virus only is the virus solution added to the assay without any treatment and the media only group is the media with no virus. Media only group is the control to ensure there is no virus contamination in the media

Conclusion

Biofilm inhibition and the antiviral response of bulk copper, copper cold sprayed, and shot-peened samples were investigated. It was found that the biofilm inhibition ability of copper surfaces is different from their interaction with bacteria in the planktonic state: the number of bacteria count in the biofilm always increases with time. The as-received bulk copper sample is the least effective sample in preventing biofilm formation at all incubation times. Biofilm inhibition effectiveness of cold sprayed copper, while initially better, decreased with time and resulted in almost identical performance than as-received bulk copper. Shot peened samples demonstrated the best biofilm inhibition properties at 18 hr incubation, which was attributed to significantly higher copper ion concentration and its interaction with the biofilm. In summary, the surface topography, including both nano and micro surface texture, can facilitate the adhesion of bacteria at the planktonic state. However, if the surface modification process is accompanied by induced grain refinement and increase of dislocation densities, it results in an increase in the copper ion release rate. The latter takes over the initial adherence enhancement property of the surface and results in improved biofilm inhibition properties by interfering with the biofilm structural integrity and reducing the biofilm formation. The antiviral properties of SP1 and CS sample were compared to the As-R and stainless steel samples. It was shown that it is rather the surface topography that plays the main role in antiviral properties than ion diffusion. A smooth surface is the best antiviral choice even when exposed to low copper ion concentration.

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6. Conclusions and Future Work

The primary goals of this thesis encompassed enhancing copper coatings deposited through the cold spray process, with a specific emphasis on two areas where copper is frequently employed. These areas include copper coatings for nuclear fuel containers and copper coatings for applications related to antiviral and biofilm formation inhibition.

The emphasis of this research was placed on copper, a material of significant interest within the additive manufacturing community. This study also drew upon the existing knowledge base in the field of cold spray technology to further advance our understanding and application of copper in this context.

This motivation was satisfied by conducting four clear research projects, each addressing a critical roadblock in the adoption of the technology. The primary objectives initially focused on enhancing the application of cold spray copper coatings.

Before applying copper, coatings and conducting any additional post processing, it is crucial to understand how various powder storage conditions may affect the spraying process and the quality of coatings produced over an extended period. Additionally, the utilization of a robust material model capable of predicting high strain rate deformation becomes an invaluable asset in this research endeavor. Consequently, substantial attention was dedicated to areas where fundamental analysis was lacking. Particularly, the emphasis was placed on developing a precise material model capable of predicting high-velocity impacts in cold spray procedures. By leveraging advancements in imaging technology and newly acquired experimental data, we accomplished the development of an enhanced material model, enabling a more profound understanding of the bonding mechanisms within cold spray applications. The newly developed material model now facilitates predictions of impact and deformation that closely align with real-life observations. This advancement significantly enhances the possibilities for further investigations into the dynamics of impact and bonding within cold spray

processes.

The next segment of this thesis, represented by the second paper, centered on examining the surface characteristics of copper at its fresh state compared to when it is stored. Additionally, it delved into identifying the type of surface oxide formed and measuring its thickness. By incorporating this data into a numerical model alongside the appropriate material model, we achieved a more profound comprehension of the influence these parameters exert, ultimately enhancing the deposition process. Our in-depth analysis revealed a direct correlation between prolonged exposure of powders to ambient conditions and increased particle oxide thickness, resulting in reduced deposition efficiency and poor particle bonding. Notably, this oxide growth was most significant within the initial thirty days of ambient exposure, with limited effects observed on particles exposed for an additional thirty days. Furthermore, we observed a transformation in the nature of the oxide layer from Cu_2O in the as-received state to CuO after the first thirty days of exposure. Our FEM results demonstrated that as particle oxide thickness increased, the extent of particle surface cleanup marginally decreased. Consequently, achieving proper oxide cleanup for bonding required a slightly higher impact velocity, thereby increasing the critical velocity. We found that substrate deformation levels emerged as the primary limiting factor in the bonding process, with softer particles undergoing more extensive deformation than the harder substrate. Additionally, our observations revealed that the point where maximum surface oxide cleanup and pressure (and consequently bonding) occurred differed from the location of maximum equivalent plastic strain (PEEQ), suggesting that PEEQ might not be a suitable variable for predicting bonding. The modeling results also shed light on the absence of metallic bonding at the initial particle impact point and the vicinity of particle jetting zone.

These first two fundamental studies enable the accurate prediction of optimal particle impact conditions for achieving high-quality coatings, while also shedding light on the critical significance of proper

storage conditions in ensuring consistent coating quality. This deeper insight into single particle behavior enhances our understanding of the process.

The third phase of the research, as presented in the third paper, was dedicated to addressing the common issue of low ductility and hardness in copper coatings generated through cold spray process, especially when applied to larger components. To improve the hardness and ductility of cold-sprayed copper on steel substrates, a laser heat treatment process was developed. The ANN model was employed to effectively predict hardness reduction from temperature data. While one experimental case closely aligned with predictions (96% accuracy), a discrepancy in another case prompted further investigation, revealing interfacial characteristics and thermal contact resistance as the probable root cause contributing to the discrepancies. In summary, the ANN model showcased its capability to forecast hardness reduction.

The last paper demonstrated the adaptability of the cold spray system for enhancing the surface characteristics of copper, making it more effective for antimicrobial applications. Biofilm inhibition and antiviral response of various copper samples, including bulk copper, copper cold sprayed, and shot-peened samples were investigated. Notably, the ability of copper surfaces to inhibit biofilm formation differed from their interaction with planktonic bacteria, with biofilm bacterial counts increasing over time. Initially, cold sprayed copper demonstrated superior biofilm inhibition, but its effectiveness declined, ultimately matching that of as-received bulk copper. Shot-peened samples exhibited the best biofilm inhibition by time, which attributed to higher copper ion concentration and its interaction with the biofilm. In summary, surface topography, including nano- and micro- textures, influences initial bacterial adherence, while induced grain refinement and increased dislocation densities enhance copper ion release, improving biofilm inhibition by disrupting biofilm integrity. In antiviral properties, surface topography outweighs ion diffusion, with a smooth surface proving effective even at low copper ion

concentrations.

Future work

Several follow-up studies could be proposed to expand upon this work and improve our current understanding.

- The research demonstrated that the laser heat treatment process effectively decreases the hardness of coatings generated through the cold spray process. However, it remains to be explored whether this process can also improve the ductility and tensile strength of the coating and whether any potential drawbacks are associated with this heat treatment procedure.
- The developed ANN model, when integrated with thermal modeling, serves to establish laser heat treatment parameters necessary to achieve a specific desired reduction in hardness. To further enhance this process, additional refinement is required to create a parameter window that offers optimized settings for achieving the desired outcome.
- The material model, designed to anticipate extreme impact scenarios, was created, and applied to conduct a foundational analysis of individual particle impacts. However, the utilization of this model to foresee the bonding process during coating production remains pending.
- It was evident from the study that the duration of powder storage can have adverse effects on both deposition efficiency and the quality of the deposit. To address this issue comprehensively, further research is essential to establish the specific environmental conditions that ensure powder preservation. The goal is to develop a preservation method that can be universally applied to various types of powders, regardless of their morphology and characteristics.

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