

Material Behavior During High Velocity Impacts – Novel Numerical Approaches



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Saeed Rahmati

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Supervised by

Dr. Bertrand Jodoin

Co-supervised by

Dr. R.G.A. Veiga and Dr. A. Zúñiga, Federal university of ABC, Brazil

University of Ottawa, Ottawa, Ontario, Canada

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Abstract

The prediction of material behavior and its microstructural evolution during high velocity impacts has been investigated for decades. The application of this topic can be observed in various engineering applications such as the cold spray process.

Cold spray (CS) is an additive manufacturing method in which solid particles are accelerated using a low temperature supersonic inert gas flow, prior to their impact onto a substrate and adhesion/consolidation. In this process, unlike other thermal spray processes, the particles are kept well below their melting point prior to impact. This allows the CS process to be used for the manufacturing of high quality, specialized products at a low energy input.

In CS, the deformation and bonding processes happen in a very short time (less than 100 ns). With the current technology, in-situ investigation is almost impossible. In this situation, numerical modeling methods are the best alternative to study the deposition process. There are several factors influencing the particle deposition, such as particle/substrate material properties, particle size, material temperature, particle velocity and so on, but it has been shown that the particle impact velocity has the major role during the deposition process. In fact, despite the type of bonding, i.e., mechanical or chemical, particle is sticking to the substrate after experiencing severe plastic deformation that occurs upon the impact at high velocities. Therefore, in order to develop the understating of the CS process, investigating the deformation behavior of material during high velocity impacts, and also bonding mechanisms involved during particle deposition must be investigated.

Although numerous studies have been done to explore the mechanisms occurring during particle deposition, the details of this process are still unclear.

Therefore, the purpose of this research is to study the fundamental aspects of material behavior during the deformation and deposition processes with the aim of improving the understating of the CS process. Two different numerical approaches will be used to achieve the objective of the study, i.e., Finite Element Method (FEM) and Molecular Dynamics (MD) method.

FEM will be used to study the metallic bonding occurring between the particle and the substrate. A physically based model to predict this phenomenon will be implemented into ABAQUS/Explicit FEM software. MD simulations will be performed to investigate the microstructure evolution during high velocity impacts. In order to characterize the deformation behavior of materials at a fundamental level, analysis will be focused on the basic mechanisms of plasticity and hardening in metals, i.e., the multiplication, glide and locking of dislocations, and also solid-state amorphization that happens at high strain rate deformations.

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Chapter 1

Introduction

1.1 Background

Cold Gas Dynamic Spraying, or simply Cold Spray (CS) is a particle deposition method categorized as a thermal spray process. In CS, the particles are accelerated in a de Laval nozzle using relatively low gas temperature to rise their kinetic energy. Unlike other conventional thermal spray processes in which molten material is sprayed onto a surface to be coated, CS particles are well below their melting point prior to the impact with the substrate. CS was first developed as a coating method [1] but nowadays it is also used as an additive manufacturing process [2]. CS has the ability to spray a wide variety of materials and hence, it has the potential to be used in different applications. For instance, for metals on metals deposition, CS can spray from soft metal tin [3,4] to hard MCrAlYs [5,6]. Polymer

metallization or spraying polymers on metals [7,8], and even spraying metals on ceramics have also been achieved [9,10]. Due to this unique ability, numerous works have been done over the last decade to develop thorough understanding of the process fundamentals [11–28].

In CS, the high kinetic energy of the particles at impact causes a large plastic deformation at high strain rates, i.e. up to 10^9 s^{-1} [29–31], and allows the particles to adhere to the substrate [11,21,27]. Material plastic behavior during high deformation rates, as found in CS, has been the focus of studies for decades [32–48].

Since material deformation occurs over a very short period of time (tens of nanoseconds), in-situ experimental investigations of particle/coating deposition process are very difficult [49]. Experimental studies can usually only take place after the deposition process is completed. These studies rely on the microscopic observation of the as-sprayed cross-section of the coatings [50,51]. Therefore, numerical methods could be an alternative to study ‘in-situ’ the CS process in more details. Several studies have been performed using Finite Element Methods (FEM), such as Lagrangian [52–54], Eulerian [55–57], Arbitrary Lagrangian-Eulerian (ALE) [58], as well as Smooth-Particle-Hydrodynamics (SPH) [59–61] to study the particle and substrate deformation behavior during the impact. All studies show that intense localized plastic deformation happens at the particle/substrate interface [11,12,27]. Figure 1-1 illustrates the equivalent plastic strain and temperature distribution for a copper particle impacted to a copper substrate [62]. As can be seen, the deformation distribution is minimum at the flattened area at the interface where the particle hits the substrate and it is maximum at the particle/substrate edge. Due to the localization of the plastic deformation to the region surrounding the particle/substrate interface, a significant increase in the temperature can be observed in this region. By increasing

the particle impact velocity, the plastic deformation and subsequently the material temperature locally rises. This concentration of plastic deformation and high localized temperature result in a unique dynamic failure at the particle and/or substrate edge called adiabatic shear instability [11]. The occurrence of adiabatic shear instability is usually shown by the formation of material jetting at the particle and/or substrate edge [11], Figure 1-1.

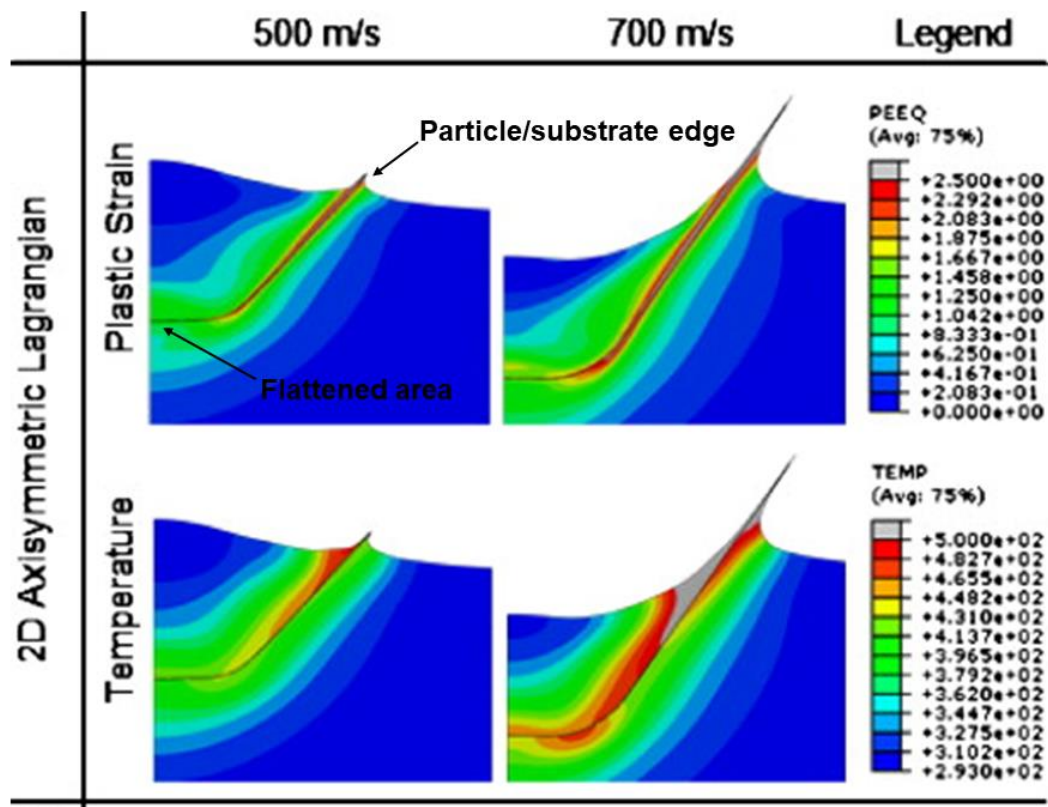


Figure 1-1 Numerical results from a 2D axisymmetric Lagrangian simulation displaying equivalent plastic strain (PEEQ) and temperature distribution just before rebound [62] (*Reproduced with permission of Elsevier*)

Mechanical anchoring and metallurgical (or metallic) bonding have been found as the two bonding mechanisms in CS. Mechanical anchoring occurs when particles interlock with the substrate intricate topology as they are physically trapped in it [63,64]. Metallurgical bonding is a chemical bonding mechanism that is usually

stronger than mechanical anchoring. This bonding mechanism requires intimate contact between oxide-free metallic surfaces and an appropriate localized pressure to allow the chemical bond to be established [65]. Materials are typically surrounded by a thin oxide layer. The necessity of removing this oxide layer during the particle deposition to allow the metal-to-metal contact is acknowledged in the CS literature but the in-situ details of this oxide removal process is still a point of disagreement. Numerous studies have indicated that adiabatic shear instability, leading to large local deformation levels is responsible for the oxide layer removal [11,12,21,27,29,54,66–68] whereas other studies have shown that the breakage in the oxide layer and creation of metallurgical bonding is not related to the occurrence of adiabatic shear instability as sufficient deformation levels can be achieved without it [69–71]. Moreover, studies have shown that partial melting in the contact zone is responsible for the local removal of the oxide layer and chemical bonding [72,73]. Despite the differences in the theories and beliefs about the oxide removal process, all studies agree that metallic bonding requires a minimum impact velocity (called critical velocity) to establish intimate contact between metallic surfaces.

Although FEM can be a predictive tool to study CS systems at the macroscopic level under the assumption of continuum mechanics, it is unsuitable to be used to study in details the microstructure evolution of material during the impact. In that case, Molecular Dynamics (MD) which is considered as an idealized computational experiment [74] could be a useful alternative method to investigate the material behavior at the atomistic level given the difficulty to get in-situ experimental data. MD simulates the time dependent behavior of a system of atoms. This method determines the time evolution of the set of interacting atoms (trajectories of atoms) by numerically solving Newton's equation of motion for the system [75]. Therefore, MD

is able to generate information at the microscopic level, which are atomic positions and velocities. In order to calculate the microscopic behavior of a system from classical mechanics' theory, MD requires a description of the interaction potential (or force field) as an input [75]. The results quality depends on the accuracy of the description of the interaction potential. Therefore, MD method acts as a computational microscope. This microscopic information is then converted to the macroscopic quantities such as pressure, temperature and stress using statistical mechanics. MD is a common simulation approach to predict and observe cross slip and dislocation nucleation/multiplication and especially helpful to study material deformation at strain rates higher than 10^6 s^{-1} [76,77], which is the case in the CS process, due to its high computational cost. Several studies have reported single-crystal impact simulation using MD [78–84]. However, the systems studied were too small (few hundreds to few thousands atoms) to be able to display the dislocation activity that is one of the main mechanisms in plastic deformation of ductile materials [85]. Consequently, it would make more sense to study systems that are larger to enable the display of dislocation activity that is the main mechanism of plastic deformation.

1.2 Motivations and Objectives

The motivation of this research lays on the importance of understanding the deformation/deposition mechanisms involved in the CS process. As mentioned in the previous section, the current experimental techniques are unable to track the material behavior during the CS process due to the extremely high deformation rate found in this process and the size of the system to be tracked. Therefore, for this study, the numerical simulation approach was chosen to understand the mechanisms affecting

the material deformation and to predict the material behavior during the CS process. Although numerous studies have been done using numerical methods as an alternative for experimental analysis, very few were able to implement and illustrate the physics of the process. In this research we aim to develop and implement numerical approaches which allow us to study the particle deposition in the CS process.

The particle deposition process can be analyzed on two subjects: the material behavior during the deformation and the occurrence of metallic bonding. In order to achieve the goals exposed previously, the following specific objectives are proposed:

1. Study the effects of particle/substrate material properties, particle size, material temperature, and oxide or hydroxide layer on the critical velocity of the particle.
2. Study the effects of oxide layer on the particle deformation behavior.
3. Study the failure mechanisms that can be involved in the CS process.
4. Study the material behavior at high strain rates deformation and mechanisms that govern the plasticity in that region.

1.3 Outline

This thesis has been formulated in six chapters. **Chapter 1** (the present chapter) describes the admissible information for the suggested research work. It is also shown the motivation for the studying and the purposes of this research.

In **Chapter 2**, the CS process will be explained and a review of the relevant literature about this process, material behavior during dynamic processes, and theories of adhesion and metallurgical bonding will be provided. In addition, the methodology of some important studies that used numerical approaches will be described. The capabilities of FEM and MD simulation methods will also be defined.

Chapter 3 will describe the main objectives of this research in detail. It will present the research interest as well as the importance of the hired methods.

Chapter 4 will provide a detailed of the methodology to follow and reach the proposed approach for this study. The research design will be described. The employed theory and assumptions will be defined in detail, and the implementation method will be explained.

Chapter 5 will present the results obtained by the numerical approaches described in Chapter 4. Four studies have been published in peer-reviewed journals and will be presented in their published form.

Finally, **Chapter 6** will provide the conclusion from each study, and highlighting the important outcomes. Several suggestions for future work will also presented in this chapter.

Chapter 2

Literature Review

2.1 Cold Gas Dynamic Spraying

2.1.1 Background

The CS process is a solid-state deposition process, which was first developed as a coating process in the 1980s by Dr. Anatolii Papyrin at Institute of Theoretical and Applied Mechanics of the Siberian Division of the Russian Academy of Science in Novosibirsk. Dr. Papyrin and his colleagues showed the feasibility of the CS process for various applications, successfully depositing a wide range of metals onto different substrate materials. US (also by Dr. Papyrin) and European patents of this process were issued in 1994, and 1995 respectively [86].

In the CS process, material deposition is achieved by accelerating small powder particle (5-70 μm) towards a substrate at high velocities (300-1200 m/s). Particles are accelerated by a supersonic gas flow that is always at a temperature lower than their melting point. Consequently, the undesirable effects experienced with traditional thermal spray processes, such as high temperature oxidation, melting, phase transformation and evaporation, are minimized or eliminated in the CS process. This makes the CS process a promising coating method for many materials.

Figure 2-1 displays a comparison between thermal spray processes based on the gas temperature and the particle velocity. As can be seen, the CS process operates in the lowest gas temperature and fastest particle velocity region. Consequently, CS relies on the severe plastic deformation of the materials in order to build up coatings. This gives the advantage of material deposition at low-temperature and also limits its capability in spraying materials that do not show any degree of plasticity [87].

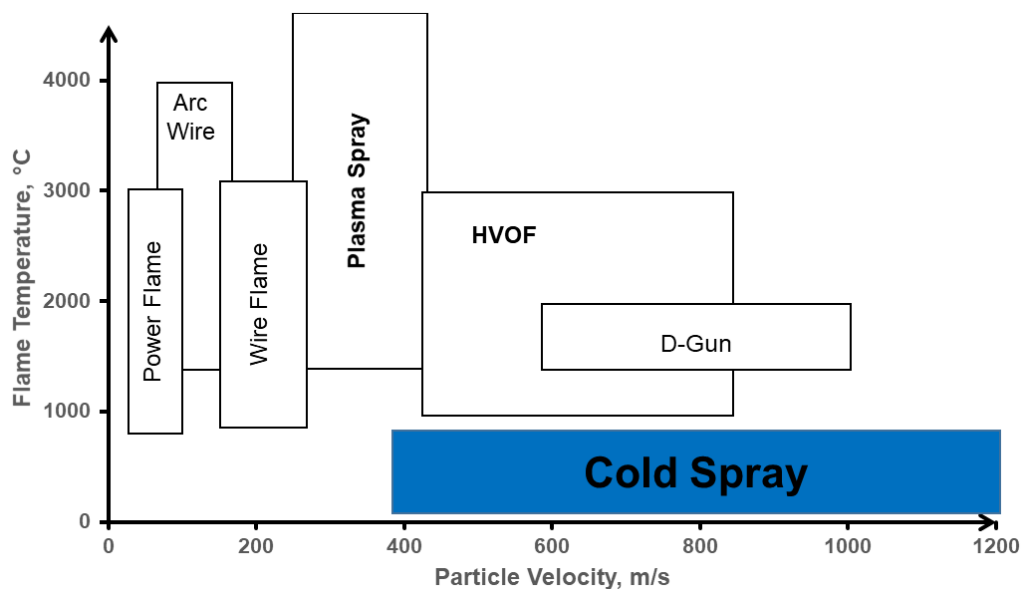


Figure 2-1 Cold spray working gas temperature, particle velocity, and substrate temperature in comparison to other important thermal spray processes [88]

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Since CS was introduced, an enormous amount of studies have been conducted on the topic [16,17,19,20,22–24,50,68,84,89–112]. These studies covered process fundamentals as well as applications. Although the CS process seems to be simple, the phenomenon involved are extremely complex. To fully understand the process at a fundamental level, it is necessary to consider gas dynamics, heat transfer, solid mechanics as well as surface and material sciences. Until now, not all aspects are fully understood, including material deformation behavior at high strain rates and the particle deposition process mechanisms.

2.1.2 Process overview

Figure 2-2 illustrates the CS process schematically. The driving gas can be air, nitrogen or helium. The high-pressure gas (from 500 kPa to 5 MPa) passes through an electrical heater to reach the process temperature (from room temperature to 1100 °C). The gas is then accelerated to supersonic speed (300-1200 m/s) through a convergent-divergent (de Laval) nozzle, which converts the gas thermal energy into kinetic energy. Powder particles are fed into the gas stream. The powder injection can be done before or after the nozzle throat. If the powder injection is upstream of the throat, the process is called high-pressure, and if the feeding is done downstream of the throat, the process is called low-pressure, because the pressure before the throat is relatively higher than after the throat. The particles are accelerated by the gas flow and exit the nozzle at a high velocity. Afterwards, the particles impact onto the substrate and adhere after a severe plastic deformation.

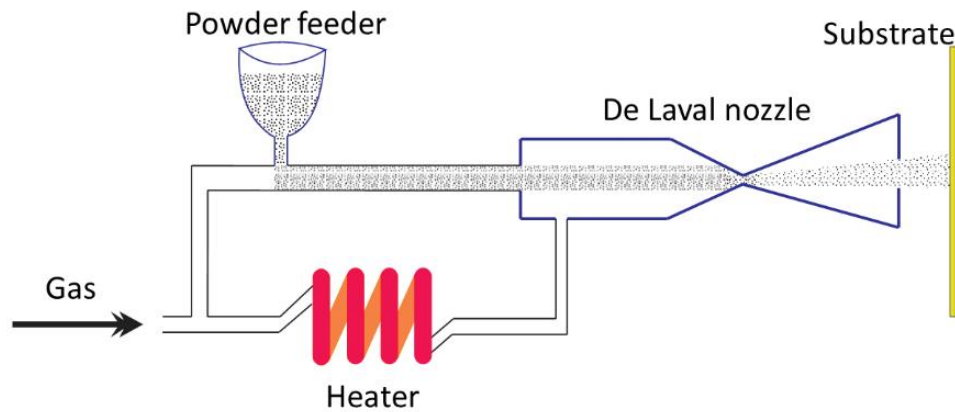


Figure 2-2 Schematic illustration of CS process [31] (*Reproduced with permission of Springer Nature*)

2.1.3 Deposition process

When a particle impacts onto the substrate, the particle high kinetic energy causes a large plastic deformation at high strain rates (up to 10^9 s^{-1}) in both the particle and the substrate [29,31]. Figure 2-3 shows a Scanning Electron Microscopy (SEM) image of a copper particle deposited onto a copper substrate [11]. As can be seen, severe plastic deformation occurred in both particle and substrate. About 90 percent of the dissipated energy during the plastic deformation is in the form of heat [113,114]. The deformation process is assumed to be an adiabatic process because it occurs over a very short time period (in the order of nanoseconds) [11]. Therefore, the energy dissipated has heat during the plastic deformation increases the temperature of the deformed regions locally and results in thermal softening in those specific areas [31]. Some studies have shown that this temperature rise could even lead to localized melting in some zones of the particle [115,116]. Other studies have reported that the temperature stays below the melting point and the deformation is completely a solid state process [26,117].

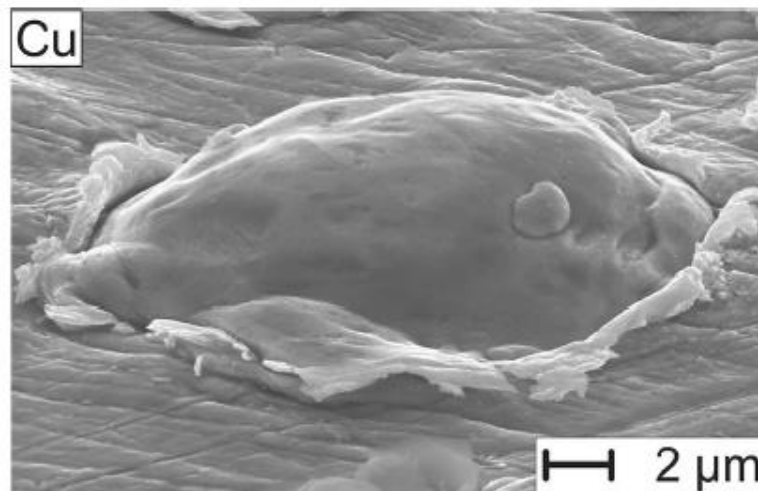


Figure 2-3 SEM image of a copper particle deposited to a copper substrate [11]

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Metallurgical bonding and mechanical anchoring are the two main mechanisms involved in the deposition of the particles in the CS process [112]. Mechanical anchoring is a bonding mechanism in which there is a nano/micro length scale mechanical interlocking between materials [63,64]. In this mechanism, the particles get trapped in the convoluted topology of the substrate, following the severe plastic deformation of the particle and/or the substrate during the impact [118]. Metallurgical bonding is a chemical bonding and is typically stronger than mechanical bonding. This type of bonding requires an intimate (atomic distance) contact between oxide-free metallic surfaces, which can be achieved by applying an appropriate localized pressure [65]. Almost all metallic materials (except few noble metals) have a native oxide layer on their surfaces. Therefore, the removal of this oxide layer to allow metal-to-metal contact for the creation of metallurgical bonding is mandatory. Numerous studies have suggested that adiabatic shear instability is responsible for removing this oxide layer [11,12,21,27,29,52,66,68], while some studies have shown that oxide removing can happen without the occurrence of adiabatic shear instability [69,70]. In

addition, studies have shown that partial melting in the contact region can cause the oxide removal and metallic bonding upon solidification [72,73]. The direct in-situ observation of oxide break-up and surface cleaning processes is not possible by the current experimental techniques [49]. For this reason, numerical approaches have been used to investigate the particle deposition process [53,84,91,95–97,104,119–125]. Despite the different theory about the oxide layer removal during the deformation, all studies agree that the particle requires a minimum impact velocity to adhere to the substrate, i.e., the critical velocity.

The critical velocity indicates the onset of creation of bonding in the CS process. It is dependent on the particle and substrate materials, particle size and materials temperature [29,98]. Hassani-Gangaraj et al. [49] adapted the experimental technique proposed by Lee et al. and Veysset et al. [47,126] to CS to assess precisely the critical velocity of different materials and particle sizes upon impact with polished substrates. Figure 2-4a [49] shows an example result taken for a 15 μm aluminum particle impacting onto an aluminum substrate below the critical velocity (at 765 m/s). At this velocity, both the particle and the substrate were deformed, but it can be seen that the particle rebounded. Figure 2-4b [49] displays another example taken for a 16 μm aluminum particle impacting onto an aluminum substrate at 825 m/s. At this velocity, the particle did not rebound, but instead adhered to the substrate, which shows this velocity exceeded the critical velocity.

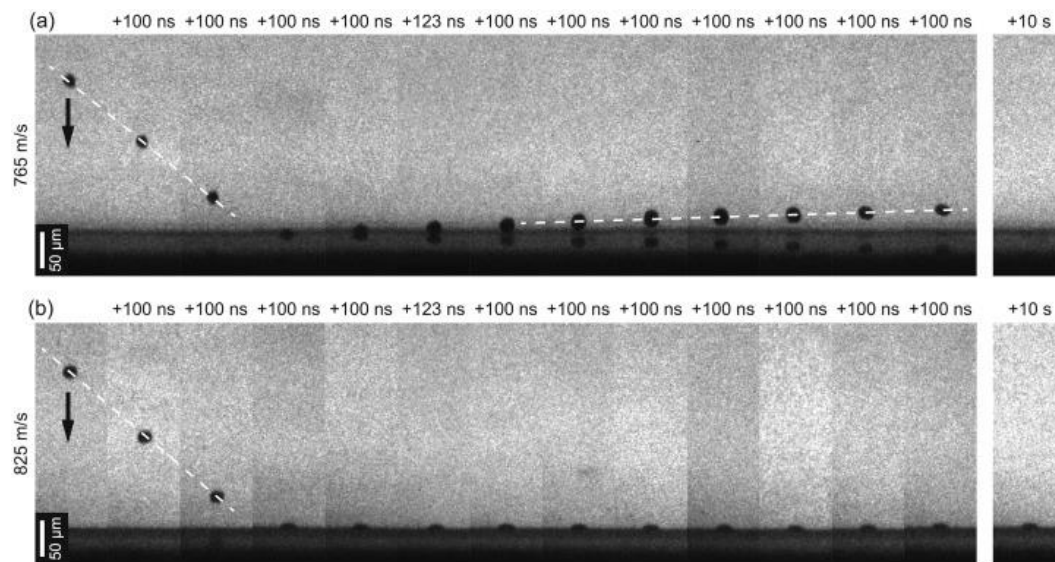


Figure 2-4 In-situ observation of 15 μm aluminum particles impacting to an aluminum substrate, a) when the impact velocity is lower than the critical velocity (765 m/s), b) when the particle impacted at the critical velocity that is 825 m/s [49]

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The possibility of depositing dissimilar materials and generating a composite coating is one of the advantages of the CS process. However, the study becomes more complex as the mechanical and thermomechanical properties of the particles and substrate usually differ. As shown in Figure 2-5 [21], four different deformation cases can be considered based on the material characteristics dissimilarity between particle and substrate.

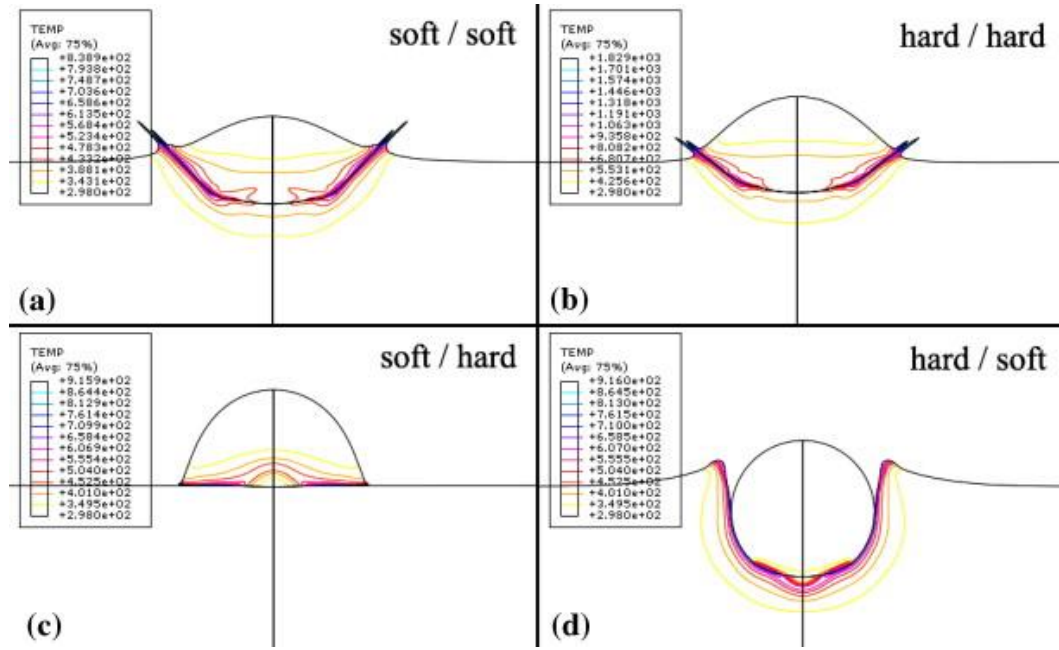


Figure 2-5 Four cases of particle impact on substrate. a) soft/soft, b) hard/hard, c) soft/hard, d) hard/soft [21] (Reproduced with permission of Elsevier)

2.2 Particle Impact Modeling

Up to now, several numerical works have been done to evaluate the critical velocity and/or simulate the particle deposition in CS [12,21,27,28,60,127–131]. Assadi et al. [11] showed that bonding can possibly be linked to adiabatic shear instability at the particle/substrate edges. They performed some simulations of copper particle impacting to a copper substrate at different impact velocities by using Johnson-Cook material model as the constitutive model. In Johnson-Cook model, the flow stress is defined through:

$$\sigma = (A + B\varepsilon_p^n)(1 + C \ln \dot{\varepsilon}_n^*) \left(1 - \left(\frac{T - T_r}{T_m - T_r} \right)^m \right) \quad (1)$$

where A , B , n , C , and m are material constants, ε_p is the equivalent plastic strain, $\dot{\varepsilon}_n$ is defined as the ratio between the plastic strain rate, $\dot{\varepsilon}_p$, and the reference strain rate,

$\dot{\epsilon}_0$, at which the material constants are obtained, and T , T_r , and T_m are absolute temperature, reference or transition temperature, and melting temperature, respectively. In this model, the stress is the product of three bracket terms. The first bracket calculates the strain hardening. The second bracket calculates the strain rate hardening and the third bracket represents the thermal softening in the material during the deformation.

For each simulation, Assadi et al. [11] found the element with the highest strain, and plotted the equivalent plastic strain (PEEQ), temperature, and stress histories of that element during the deformation, as shown in Figure 2-6. They concluded that the abrupt increase in the strain and temperature and consequently the drop in the stress are the signs of the occurrence of the adiabatic shear instability. However, Hassani et al. [71] showed that this sharp raise in the plastic strain is not related to the adiabatic shear instability phenomenon. They operated a simulation setup by eliminating the part that is responsible to calculate the thermal softening in the Johnson-Cook model, i.e., the third bracket in the Equation (1), and they illustrated that even without calculating the thermal softening, predicted results are similar to the ones that Assadi et al. [11] have obtained.

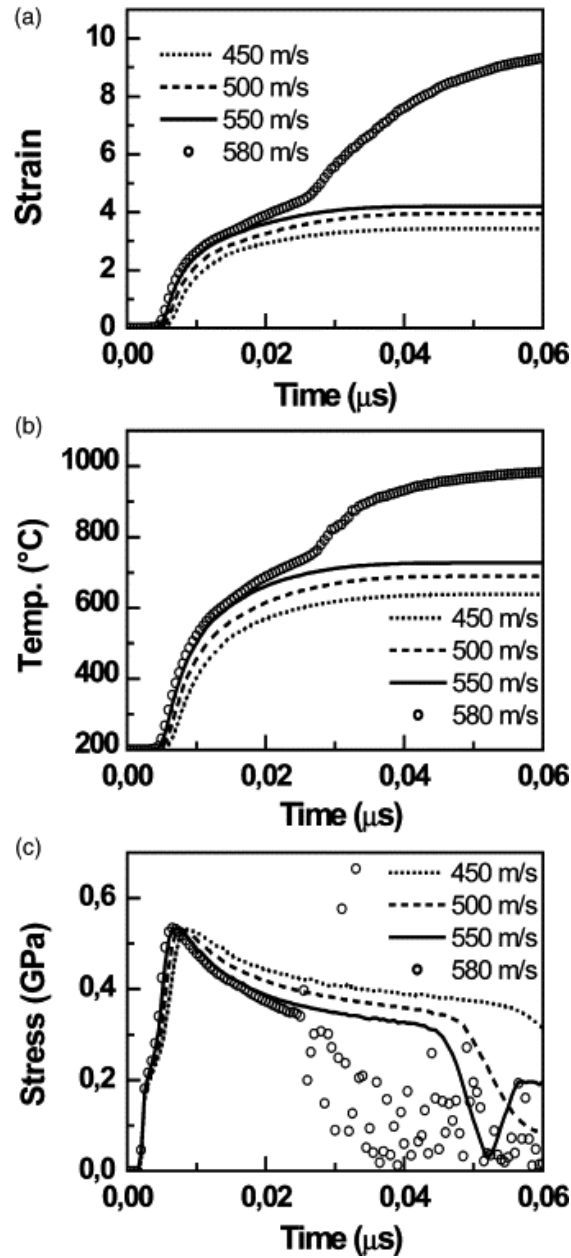


Figure 2-6 Simulation results of the particle's element with the maximum plastic deformation at different velocities a) plastic strain, b) temperature, and c) stress. [11]

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Assadi et al. [11] also proposed a semi-empirical equation to predict the critical velocity, v_{cr} , for different materials as follows:

$$v_{cr} = 667 - 14\rho + 0.08T_m + 0.1\sigma_u - 0.4T_i \quad (2)$$

Where ρ is the material density in g/cm^3 , T_m is the melting temperature in Celsius, σ_u is the ultimate strength in MPa , and T_i is the initial temperature in Celsius. This formula was obtained by using the experimental data for copper, and Assadi et al. emphasized that this formula is only valid for small changes of involved parameters, for instance it cannot be used for particles that are not made out of copper, while people have been using it for other materials.

Meng et al. [132] proposed a model based on the average equivalent plastic strain (PEEQ2) over all particle elements to calculate the critical velocity. They calculated the PEEQ2 for different particle/substrate systems, as shown in Figure 2-7. The solid lines in this figure indicates the critical velocity for each system. As can be seen, for velocities below the critical velocity, the PEEQ2 values first increase but quickly plateaus with a further increase at the impact time. In contrast, for velocities above the critical velocity, the PEEQ2 values continuously increase by increasing in the impact time. Meng et al. [132] also reported the temperature distribution of each particle/substrate system after impacting with a velocity lower than the critical velocity, close to the critical velocity, and relatively higher than the critical velocity, Figure 2-8.

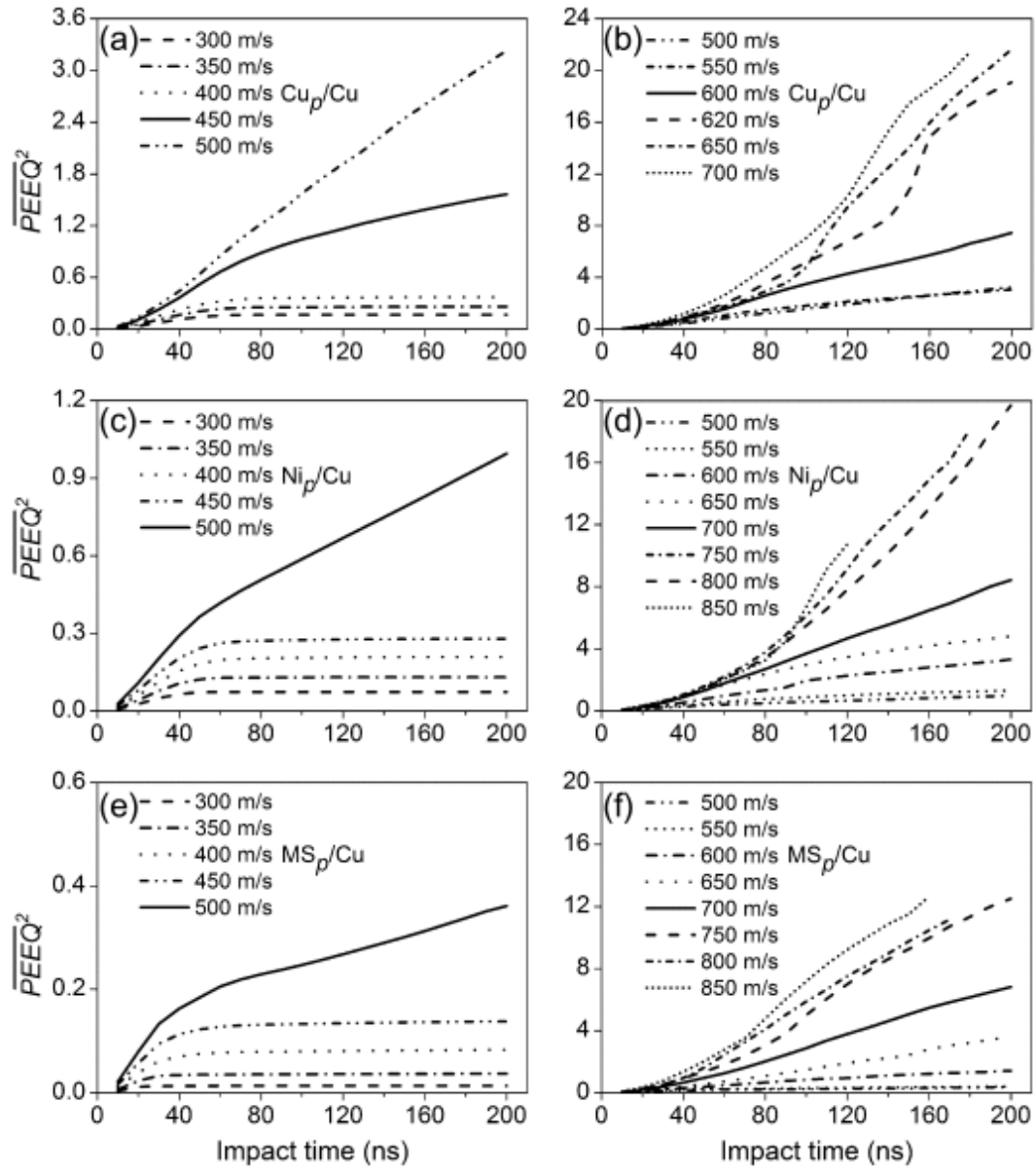


Figure 2-7 $\overline{PEEQ}^2$ evolution over the impact time for different particle/substrate systems [132] (*Reproduced with permission of Elsevier*)

As can be seen in Figure 2-8, when the impact velocity is close to the critical velocity (the column indicated by “Intermediate v_p ”), both particle and substrate were deformed severely and a large material jetting can be observed. However, it must be noted that Meng et al [132] used Lagrangian simulations and it is well-known that Lagrangian elements cannot represent this amount of plastic deformation. Therefore, this predicted jetting is due to the large distortion in elements at the particle/substrate

interface and is not related to any physical mechanisms like adiabatic shear instability.

This is the same misjudgment that Assadi et al. [11] made in their study.

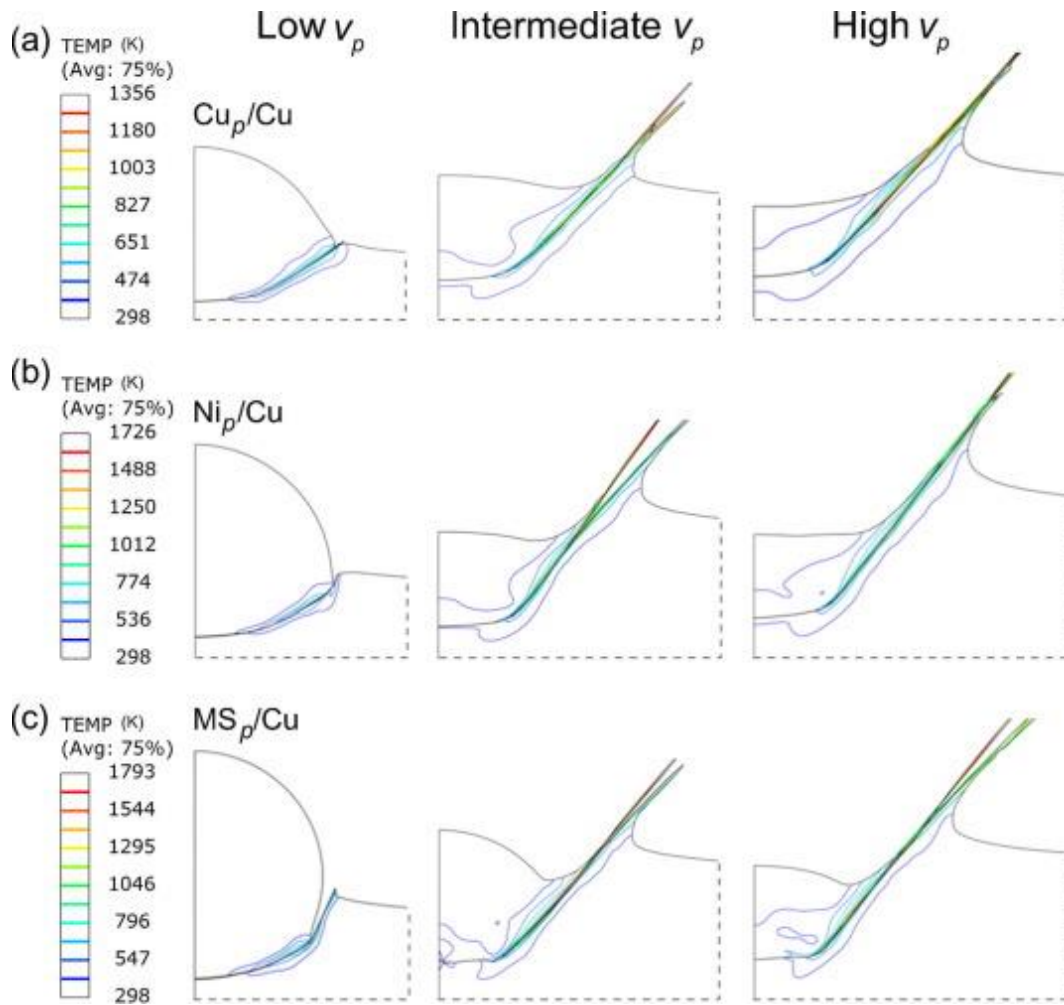


Figure 2-8 Temperature distribution of different particle/substrate system after impacting with a velocity lower than the critical velocity, close to the critical velocity, and relatively higher than the critical velocity [132] (*Reproduced with permission of Elsevier*)

Yildirim et al. [62] simulated the particle deposition by using a surface based cohesive behavior. Similarly, Profizi et al. [109] and Manap et al. [61] have also simulated the bonding in CS using two different cohesive zone models via the smooth particle hydrodynamics (SPH) method. Surface based cohesive behavior method is a simple way to model the cohesive interaction between two “sticky” surfaces (surfaces bond

after coming into contact) using a traction-separation constitutive model [133]. It should be noted that this method is unable to model the exact metallic bonding because the surface based cohesive method models the cohesion exactly like glue, thus the particles stick to the substrate upon the initial contact. Moreover, this method does not consider the necessity of breaking the oxide layer for bonding. As such, the overall bond strength between the particle and the substrate in this method relies on the glue strength which must be obtained by trial and error [133].

Kurochkin et al. [134] 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. [135] 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. They could provide important information about the deposition process. However, their models lack 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.

2.3 Oxide layer removal mechanism

In CS, it is hypothesized that when a particle impacts on a substrate at a sufficient velocity, severe plastic deformation at high strain rates happens to both the particle and the substrate and leads to removal of the native oxide layer on the materials. This creates new oxide-free metallic surfaces, and if sufficient, the localized applied pressure causes the intimate contact between two fresh oxide-free surfaces and the

creation of metallurgical bonding. The bonding process of cold sprayed particles is displayed in Figure 2-9 schematically [136].

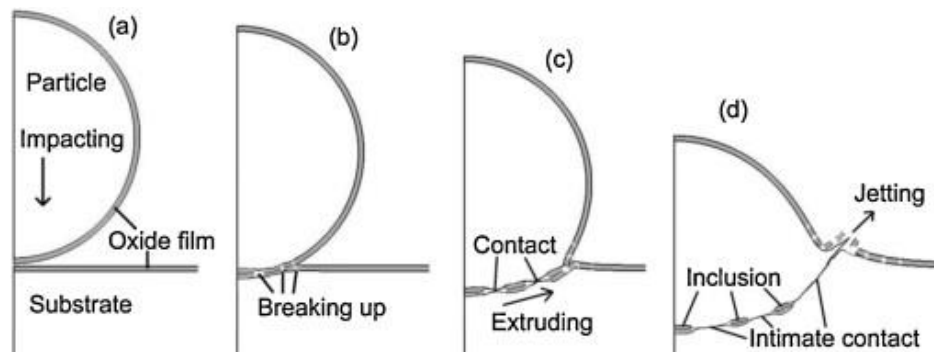


Figure 2-9 Schematic of metallic bonding process in CS illustrating the oxide breaking-up and fresh oxide-free material extruding as well as formation of jetting [136] (*Reproduced with permission of Elsevier*)

After Assadi et al. [11], several studies [12,21,27,66] have been done following the idea that adiabatic shear instability is the responsible mechanism to remove the oxide layer, and they suggested that this phenomenon is a sign of bonding in CS. However, some studies have shown that metallic bonding is not related to the occurrence of adiabatic shear instability [69–71]. For instance, Barradas et al. [70] analysed the interface of the cold-sprayed copper powders onto aluminum substrate using transmission electron microscope (TEM). They reported that the localized metallic bonding was formed only in the liquid phase. They also found some regions indicating the formation of adiabatic shear instability but they did not find any metallurgical bonding in those regions.

Xie et al. [69] proposed a new theory to explain the metal-to-metal contact and creation of metallic bonding. In order to show that the occurrence of adiabatic shear instability is not necessary for creation of metallic bonding, they studied the case of hard particles depositing onto soft substrate, e.g., nickel onto aluminum, where

particle deforms slightly without the formation of material jetting. Figure 2-10 displays the SEM images of cross-section of a single nickel particle and coating depositing on aluminum substrate after heat treatment. In Figure 2-10a, it can be seen that the particle is deposited with mechanical anchoring and at the interface, no intermetallic was formed that illustrate the absence of intimate metal-to-metal contact between the particle and the substrate. However, in the case of full coating deposition, they showed that the coating tightly bonded to the substrate by showing the formation of intermetallic layer at the interface, Figure 2-10b.

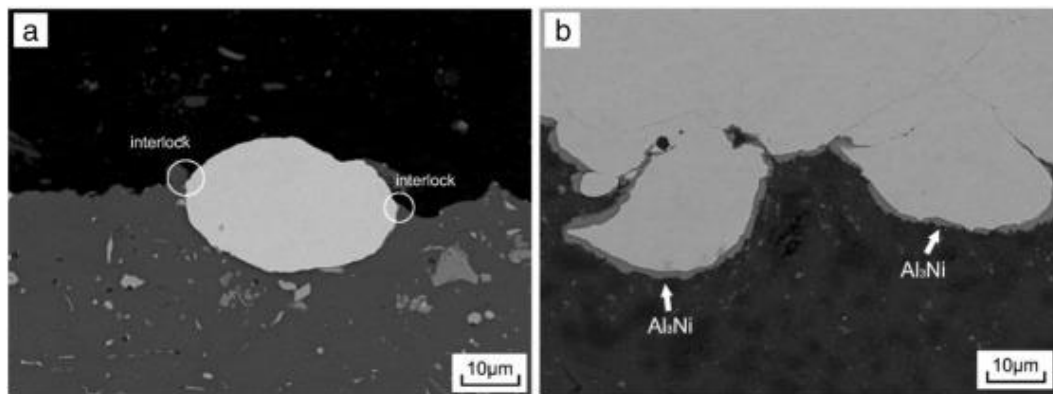


Figure 2-10 SEM images of cross-section of a) single nickel particle, and b) nickel coating depositing on aluminum substrate after heat treatment [69] (*Reproduced with permission of Elsevier*)

Xie et al. explains their theory by using the schematic of the coating/substrate interface evolution during the coating deposition process shown in Figure 2-11. When a single particle impacts onto the substrate at a high velocity, the native oxide layer of the particle and the substrate are broken and cracked. These cracked oxides form a bridge-like structure and results in many pores along the interface. These pores and bridge-like structure prevent the metal-to-metal contact. As more particles impact, the first layer of particles and the substrate deform more due to the peening effect and cause further cracks in the remained oxides. Therefore, the oxide layer breaks to many

nano-sized oxide debris and pores. By further deformation, most of these pores are then filled under a localized high interfacial pressure and a discontinuous metal-to-metal contact along the interface is achieved. Experimental studies reported nano-size oxide debris and pores at the particle/substrate interface which can help proving this theory [137,138].

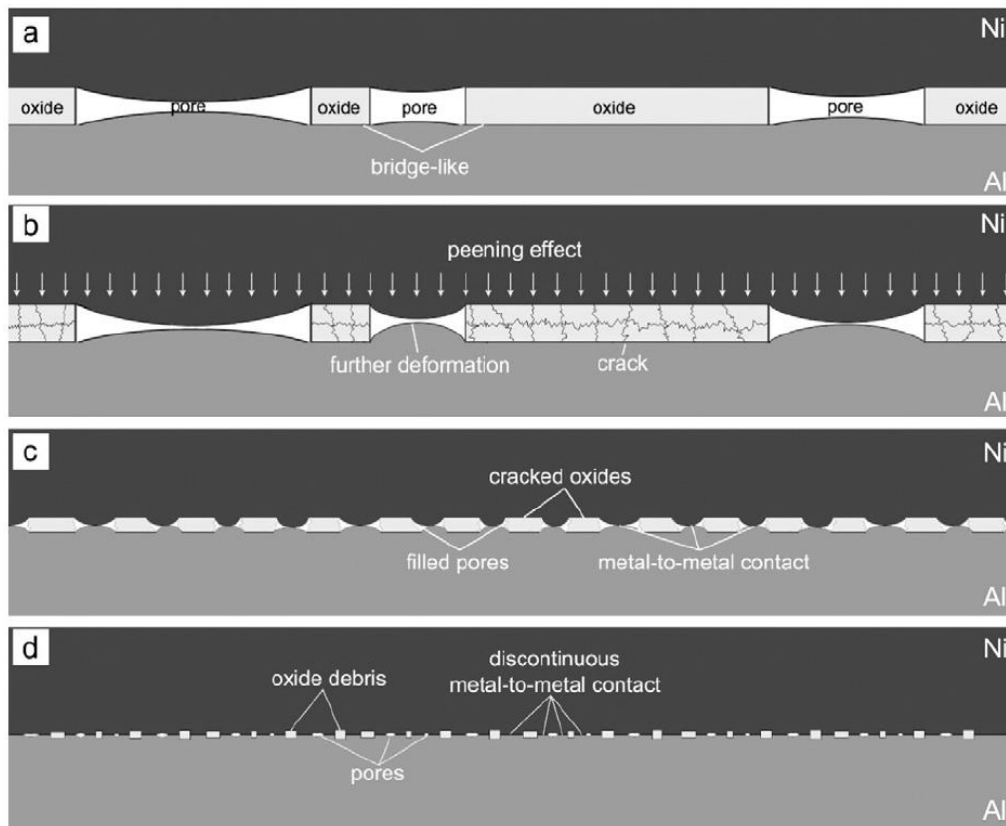


Figure 2-11 Schematic of the coating/substrate interface evolution during the deposition process [69] (*Reproduced with permission of Elsevier*)

The cold welding process is very similar to CS in the aspect of the creation of metallic bonding. Cold welding is a solid state process in which two metallic plates are joined together by applying a high pressure without heating or fusion at the interface [139]. It was shown that the native oxide film is broken into many debris during the deformation process and creates gaps (pores) that expose free-oxide surfaces on the metallic plates. The high applied pressure is also responsible to extrude the fresh

material through the gaps (fill the gaps), leading to the metallurgical bonding between the plates [139]. Clearly, this oxide removal process in the cold welding is similar to the pattern that Xie et al [69] suggested for CS.

2.4 Microstructure of cold sprayed material

The microstructure of CS coatings is dependent on the sprayed material, powders' shape/size, and spray conditions. One of the advantages of CS over other thermal spray processes is the fact that this method is a solid-state process. This ensures that the main microstructural features of the sprayed powders are retained after the deposition. Consequently, CS allows a better control of the coatings microstructure.

2.4.1 Dynamic Recrystallization

Even though the main feedstock powder microstructure features are retained in the coatings, there are still some microstructural evolutions in the sprayed particles and the substrate due to the severely plastic deformation that occurs at high strain rates. This rate of deformation causes the creation of a dense dislocation density in crystalline materials especially in grains near the particle/substrate interface [42]. These zones of high dislocation density, combined with localized high temperature from heat dissipation result in the occurrence of dynamic recrystallization (DRX) [17,30,42,140].

In dynamic recrystallization, unlike in static recrystallization, the nucleation and growth of new grains occurs during deformation and it is not an outcome of separate heat treatment [141]. The transformation kinetics during static recrystallization depends strongly on temperature and strain and not so much on strain rate. In contrast,

the kinetics of microstructure restoration after DRX is highly dependent on strain rate and also atomic thermal migration (temperature) [141]. Figure 2-12 shows EBSD maps inside a shear band in 304 stainless steel [142]. This EBSD map was taken after a heat treatment on a plastically deformed 304 stainless steel at a low strain rate. The equiaxed grains in the band indicates that these new recrystallized grains grow isotropically after nucleation, and those are not oriented along the shear deformation direction. Therefore, it can be concluded that these equiaxed grains should be the results of static recrystallization [142].

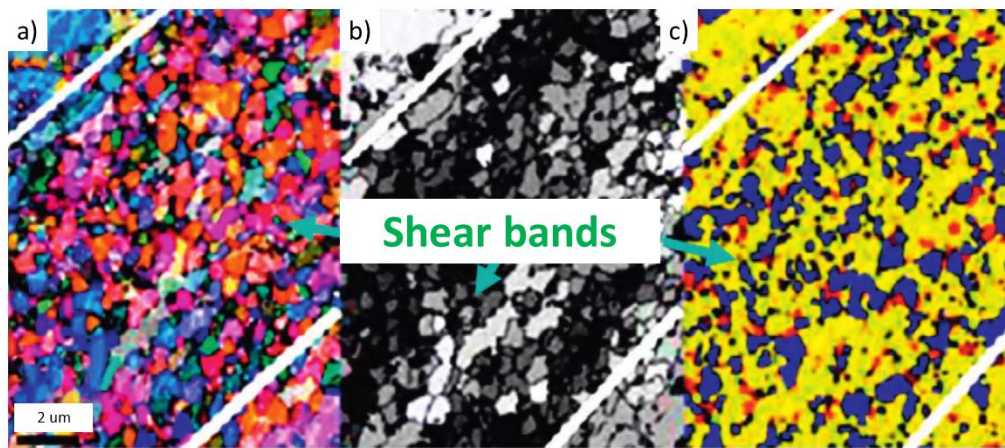


Figure 2-12 EBSD maps inside a shear band in 304 stainless steel, a) Euler contrast map, b) Kikuchi contrast map, and c) deformation map illustrating the equiaxed recrystallized grains in the band [142] (*Reproduced with permission of Springer Nature*)

EBSD maps in Figure 2-13 displays another mechanism of recrystallization inside a shear band in Fe-Cr-Ni monocrystal that is subjected to an explosive collapse loading observed by Yang et al. [142]. This figure shows elongated grains along the shear direction. This specifies that these elongated grains were developed simultaneously with localized deformation. In other words, after nucleation, the nuclei of the new

grains grow preferentially under the stress along the shear direction. Hence, these elongated grains are expected to be the results of DRX [142].

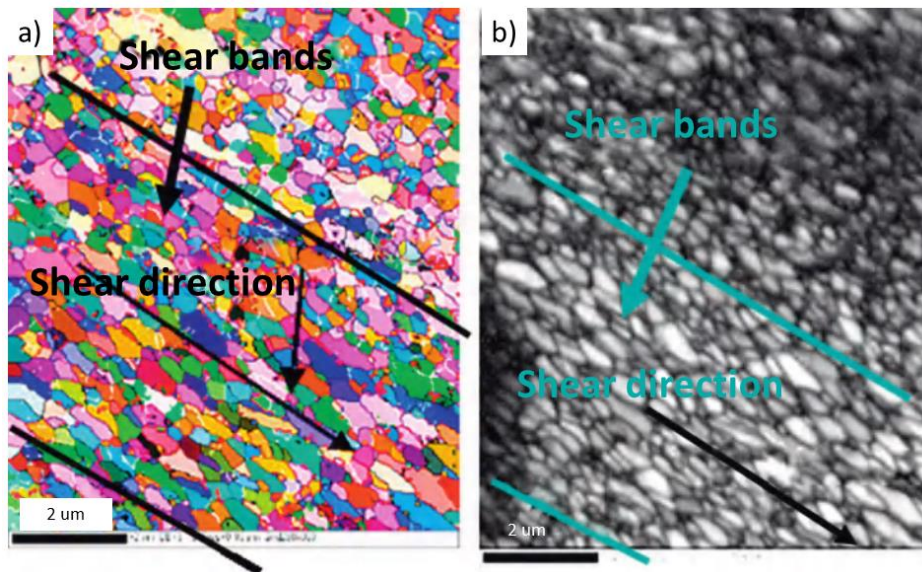


Figure 2-13 EBSD maps inside a shear band in Fe-Cr-Ni monocrystal subjected to explosive collapsed loading, a) Euler contrast map, and b) Kikuchi contrast map showing the elongated recrystallized grains along the shear direction [142]

(Reproduced with permission of Springer Nature)

Once DRX is initiated, the nuclei continue to grow even after the deformation is completed. This mechanism is recognized as metadynamic recrystallization [143]. As opposed to static recrystallization, metadynamic recrystallization does not need an incubation time, and it is due to the fact that this mechanism makes use of the formed nuclei during DRX. Subsequently, microstructures that undergoes DRX are subjected to rapid changes after unloading [143].

DRX in materials can occur in various forms [144], i.e. Geometric DRX (GDRX), Continuous DRX (CDRX), and Discontinuous DRX (DDRX). However, Derby [145] proposed that there are two different mechanisms that can cause DRX in materials, i.e. rotational and migrational DRX. Migrational DRX is most common for metals,

while, rotational DRX is prominent for geological materials such as quartz, and marble. However, the current observations including studies of Meyers and Pak [146] and Hines et al. [147] for titanium and copper, respectively, have shown that the deformation time for the creation of 100 nm size grains by rotational mechanism is lower by several orders of magnitude compared to the time required by the migration of boundaries. Therefore, in this case conventional migrational recrystallization is not the mechanism governing the dynamic recrystallization. The occurrence of the rotational recrystallization in metals begins by the dynamic recovery mechanism in which dislocations rearrange themselves into elongated dislocation cells. With increasing strain, the misorientation increases and these cells become elongated subgrains. This subgrain subdivision process continues as deformation increases; it occurs in different regions of the crystal and each region rotates to different directions. Thus, geometrically-necessary boundaries are created within the crystal [148–151]. Hughes and Hansen [150] showed that high-angle grain boundaries can be formed by these subdivision mechanisms. This process has been also reported by Sevillano et al. [152] for different metals subjected to high strains, and Meyers et al. [153] modeled this process using dislocation energetics.

As mentioned before, many researchers have reported that DRX is the main mechanism for the formation of fine-scale grains at the interface between a particle and the substrate or between two prior particles, but the exact details for DRX during CS are still unclear.

Zou et al. [30], Zhang et al. [42], and Meyers et al. [140] have shown some evidence that the unique microstructure in CS is formed by rotational DRX. For instance, Figure 2-14 and Figure 2-15 have been reported by Zou et al. [30] in which they explained the process of the formation of fine-scale grains by the rotational DRX mechanism.

Figure 2-14 shows the cross-section of the as-sprayed nickel coating, containing approximately 10 particles. They found a large number of 100-200 nm size grains in the region of particle/particle boundaries, Figure 2-14(a). As shown in Figure 2-14(b), the particle/particle interfacial regions have relatively lower pattern quality than the central regions of the impact particles. Pattern quality is a measurement of how sharp or blurry an analyzed pattern is; and a pattern taken from a volume of crystal with a higher number of defects, especially dislocations, will be less sharp. In addition, Zou et al. [30] calculated the pattern quality values of the center of the particles and the center of the fine-size grains. The lower obtained values for the fine-size grains indicated that there was relatively high defect density and/or lattice strain inside the fine-size grains in the particle/particle interfacial regions. Since the static recrystallization is almost strain/defect free, hence its EBSD map has a high pattern quality. Therefore, Figure 2-14 imply that the formation of fine-size grains is due to DRX, and it is not because of static recrystallization.

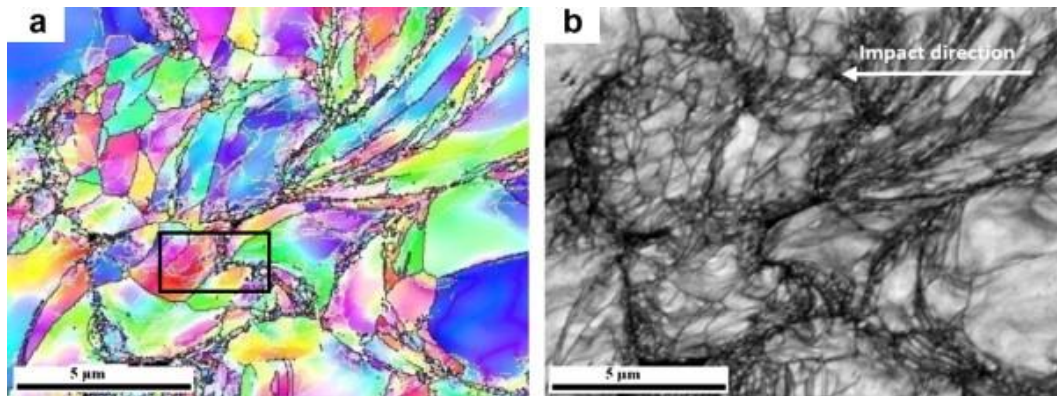


Figure 2-14 EBSD of the cross-section of the as-sprayed nickel coating, a) Euler angle map, and b) pattern quality map of the same area [30] (*Reproduced with permission of Elsevier*)

Figure 2-15(a) is the Euler-angle map corresponding to the area highlighted in Figure 2-14(a). Euler angles represents three successive rotations about specific directions to

align the crystal axes with the reference axes. Euler-angle map is used to illustrate the angular changes within the microstructure. The point-to-point and the point-to-region misorientations are plotted against the distance along path *ABCD*, which is from the particle center to its edge, as displayed in Figure 2-15(b). As can be seen, the misorientation gradient indicates three apparently distinct regions divided by points *A*, *B*, *C* and *D*.

From the center to the edge of the deformed particle, as marked from *A* to *B*, subgrains are not well formed and there are only a few of low-angle grain boundaries (LAGBs). The low misorientation in this region means low lattice strain and defect density. From *B* to *C*, the strain increases and some elongated subgrains can be observed. By continuing from *C* to *D* (at the particle/particle interface), the misorientation reaches to maximum and formation of highly misoriented fine-size grains can be seen, i.e., formation of high-angle grain boundaries (HAGBs) in this region.

Figure 2-15(c) illustrates the misorientation relative to the center of the particle, i.e., point *A*. In order to reveal the lattice rotation during the deformation within the crystal, the tolerance angle map is displayed using the color gradient from blue to red. As can be seen, the lattice is progressively rotated from the center to the edge of the particle. The lattice rotation along the path *ABCD* is also shown using the inverse pole figure, Figure 2-15(d). These results are adequate evidence showing that lattice, near the particle impact region, is gradually rotated until HAGBs are formed.

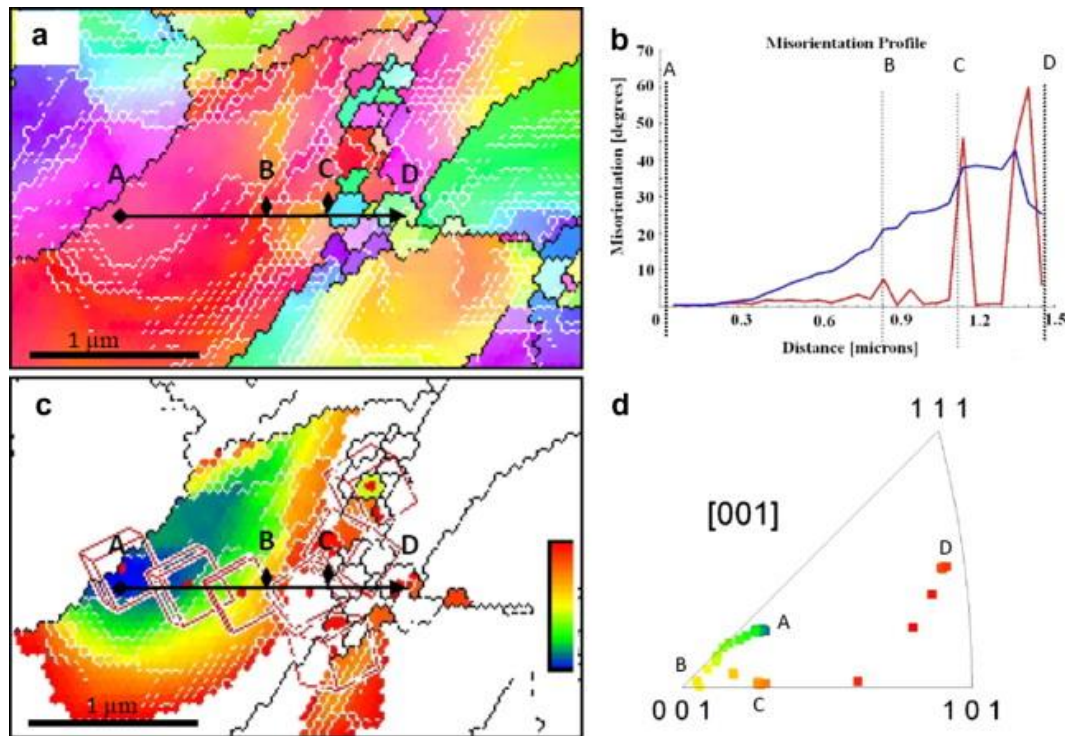


Figure 2-15 A close view of the highlighted box in Figure 2.9(a). a) Euler-angle map with four points (*A*, *B*, *C* and *D*) marked in a path from the center of the deformed particle to its edge. b) misorientation plot, showing the point-to-point (the blue curve) and the point-to-origin (the red curve) along the path *ABCD*. c) tolerance angle map (shown from blue to red). The cubes in the map illustrate the local crystal orientation. d) inverse pole figure of the points in the path *ABCD* [30] (*Reproduced with permission of Elsevier*)

Microstructural evolution in cold-sprayed material does not stop at the completion of the plastic deformation. Thevamaran et al. [154] have shown that the high elastic energy stored within the material (as residual stress) due to the high velocity impact triggers a continuous (static) recrystallization process, which takes place over the course of weeks at room temperature. They synthesized single crystal silver microcubes in a bottom-up seed-growth process. Then, they impacted those almost defect-free cubes onto a non-deformable substrate, using an advanced laser-induced

projectile impact testing, at 400 m/s. Afterwards, they analysed the cross-section of the deformed cubes using transmission electron microscope (TEM) and selective area diffraction (SAD) analyses 20 hours, 8 days, and 44 days after impact which are shown in Figure 2-16, Figure 2-17, and Figure 2-18, respectively [154].

Figure 2-16 shows a strong gradient in grain size along the height of the sample. The top region illustrates a single-crystalline diffraction pattern with negligible distortion, whereas the bottom region exhibits a nanocrystalline diffraction pattern. Thevamaran et al. [154] reported that the nanocrystalline grains at the bottom region are around 10 nm in size (20 hours after impact).

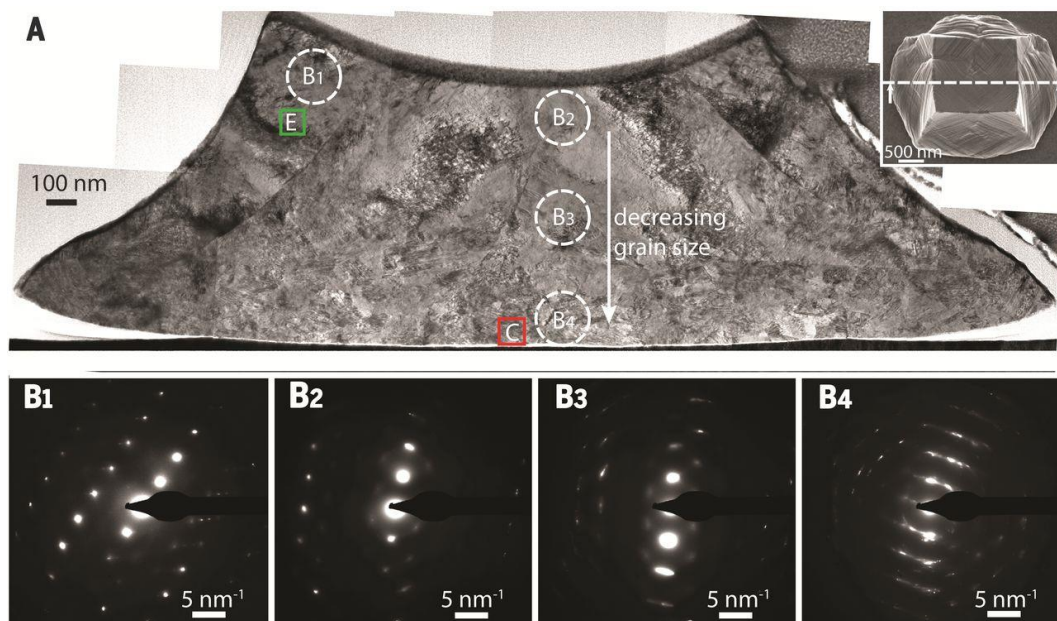


Figure 2-16 Gradient nanograined structure formation in impacted silver microcube, examined 20 hours after impact. A) a cross-sectional image of a silver microcube impacted along the [100] direction, (B1 to B4) SAD patterns taken along the progressively highly deformed regions indicated in (A) [154]

As shown in Figure 2-17, TEM analysis on a sample 8 days after impact showed substantial nanostructural recovery in the form of recrystallization. Two distinct

regions can be observed in Figure 2-17: the less-deformed region at the top and the recrystallized highly deformed region at the bottom. In this analysis, Thevamaran et al. [154] found 30 to 150 nm sized grains in the bottom region, which indicates the occurrence of recrystallization in this region (the sample investigated after 20 hours showed grains in the size of 10 nm). In addition, they found several subgrains and a high dislocation density in the bottom region that shows the system is still far from equilibrium.

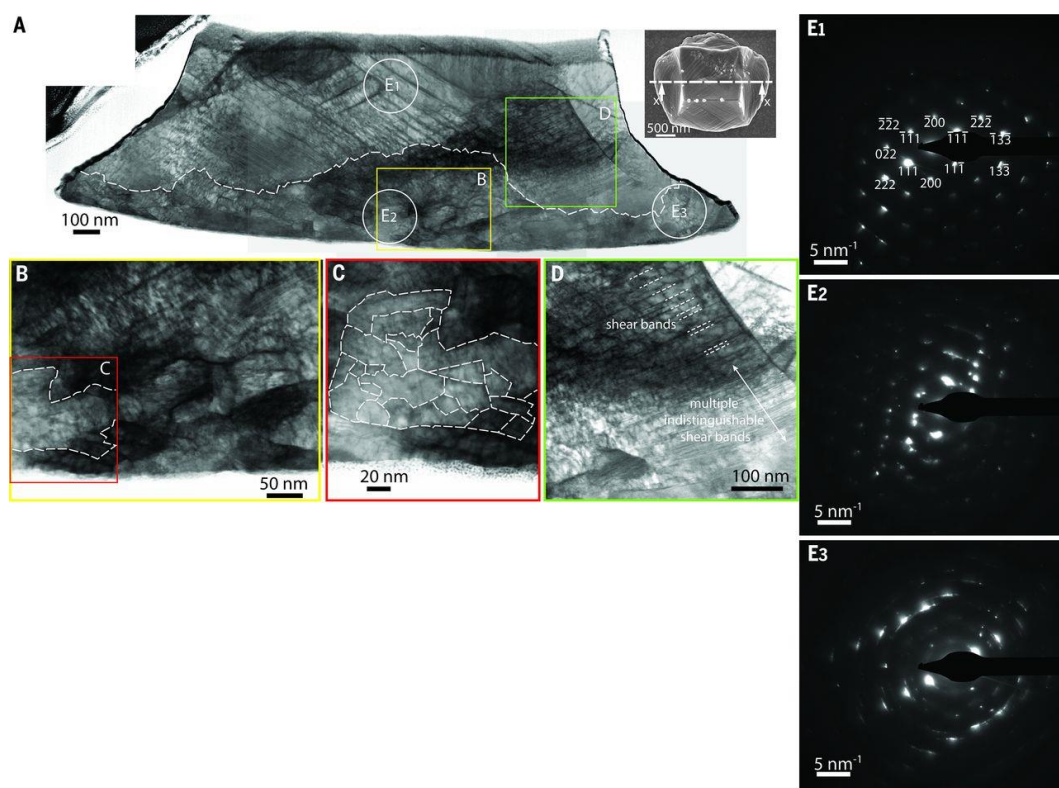


Figure 2-17 Partially recrystallized silver microcube, examined 8 days after impact. A) cross-sectional image of the silver microcube showing distinct less-deformed and highly deformed regions, separated by a white dashed line. (B to D) magnified views of the regions labeled “B”, “C”, and “D”, respectively. [154]

To further probe recrystallization, Thevamaran et al. [154] performed another TEM analysis 44 days after impact, shown in Figure 2-18. This figure displays much

showed that the deformed cubes were far from the equilibrium state, and hence, static recrystallization driven by the stored elastic energy happened in the material. This stored elastic energy (or residual stress) was confined within locally plastically deformed regions during the deformation in terms of crystalline defects. The high stored energy was the driving force for the static recrystallization to bring the material closer to its equilibrium state. Comparison between Figure 2-16 and Figure 2-18 shows how the microstructure was changed from being nanostructured after deformation towards micron sized grains later in time.

2.4.2 High Strain Rate Material Behavior

Material plastic behavior during high strain rates deformation and/or severe plastic deformations have been investigated for decades [155–159]. For instance, Xie et al. [160] studied the dynamic behavior and extreme plasticity of aluminum particles during high velocity impacts. In order to investigate the effects of the impact velocity on the particle deformation, the cross-section of deformed particles (with the size distribution of 19.3 ± 5.3 μm) after impacting onto a sapphire substrate with different impact velocities were analysed. Figure 2-19(a) shows the EBSD map of cross-section of an aluminum powder after the impact at 530 m/s. The equiaxed grains in the top region show that the deformation at the top region was negligible in contrast to the region near the bottom face (where the particle impacted to the substrate). Figure 2-19(b) displays the Electron Channeling Contrast (ECC) of an aluminum particle which impacted at 660 m/s. Compared to the 530 m/s impact velocity, the deformed particle at 660 m/s showed a significant change in deformation characteristics: almost all grains are largely flattened. Xie et al. [160] revealed that when the impact velocity of a 19 μm aluminum particle exceeds 580 m/s, a considerable portion of the volume

of the particle experienced an extreme pressure higher than its yield and this results in the structural collapse.

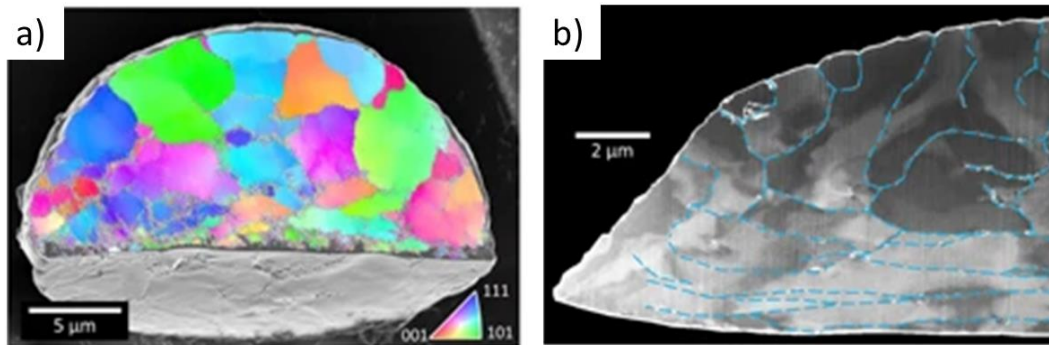


Figure 2-19 Plastic deformation of aluminum particles after impact to a sapphire substrate, a) EBSD map of the cross-section of deformed particle at 530 m/s, b) magnified view of the Aluminum particle with identified grain boundaries in blue dashed lines, with 660 m/s impact velocity [160]

In high deformation rate processes, in-situ observation of the microstructure evolution is a very difficult task to do. In the following, we will outline how MD simulations can help to study the microstructural evolution of material during CS:

MD simulation is a common method used to investigate the material behavior at the atomic level. Several studies have been performed using MD to capture material behavior at high strain rates [40,41,46,161–167]. Yaghoobi and Voyiadjis [41] 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 is negligible. In another study, Yaghoobi and Voyiadjis [40] 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. [165] 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. [168] explored the grain boundaries migration under shear deformation. They elaborated that grain boundary sliding occurs 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.

Chapter 3

Research Objectives

The main objective of this study is to clarify some mechanisms involved during material deformation/deposition and microstructural evolution during the CS process. The current research work aims at studying fundamental aspects of particle/substrate deformation to improve the understanding of the material behavior during CS impact, and study the metallurgical bonding mechanism of the CS process. The understanding of these mechanisms and material responses will help improving the coating quality and better usage of the CS process potential in different applications. The improvement in coating quality can be obtained by modifying the CS parameters such as particle velocity and temperature, which can be determined after a better understanding of the high strain rate deformation mechanisms and metallic bonding. Up to now, these phenomena have not been explained completely. It should be noted that this research is not aiming to reveal all underlying mechanisms

involved in CS. The main purpose of fundamental studies is to produce knowledge and understanding in relation to physical phenomena.

3.1 Simulation of Metallic bonding in CS

As mentioned in the previous chapter, numerous studies have been performed to simulate and/or explain the metallic bonding in CS, but none of them was able to show and track the occurrence of the metallic bonding in the contact zone. Most studies used indirect mechanical quantities such as stress, strain, temperature, etc. obtained by finite element analysis to explain the metallic bonding and/or particle deposition in this process [11,12,21,27,128]. In those studies, they were not able to directly simulate the particle sticking to the substrate. Nonetheless, there are few studies that used cohesive behavior contact method, which exist in the FEM software, to show particle deposition but they did not consider the most important factor in the occurrence of the metallic bonding which is the oxide layer cleaning from the metallic surfaces [109,119,122]. One of the objectives of this research is to develop a physically-based simulation method to predict the metallic bonding during cold spray. Understanding single particle deposition mechanism using a finite element simulation will help to understand the coating evolution behavior better. For further investigation in future, this model can be used to study the coating characteristics such as residual stresses, bond strength and porosity.

Xie et al. [69] suggested that the metallurgical bonding mechanism in CS is similar to the cold welding process. The bonding mechanism in cold welding has been explored experimentally [139,169–171] and the model proposed by Bay et al. [170] is an accepted theory in this field. For the first step in this research, this bonding mechanism

theory will be used and adapted to CS deposition in a finite element model to investigate the contact behavior and the deposition process of a single particle impacting on a substrate. This model would be the first step to simulate the particle deposition based on the physics of the process and will allow tracking locally the bonding process at the particle/substrate interaction zone.

In the second step, the native oxide layer will be modeled explicitly in FEM. It will allow to have an in-situ observation of the deformation/failure and the removal process of the oxide layer during the particle deposition in CS.

3.2 Prediction of microstructure evolution during the impact

Understanding the material behavior during deformation at high strain rates will help to develop the manufacturing process and increase the products quality in processes such as CS. It can be achieved by understanding the effects of each spray parameter on the deformation behavior of material. For instance, the effects of particle velocity, material temperature, material microstructure, and particle size during the deformation process. It is acknowledged that the main goal of simulation is to shed light on the underlying mechanisms, which control the process behavior. Fundamental studies using atomic-level methods such as MD can be used to investigate the mechanisms that exist at high strain rate deformations. MD simulations allow to study the microstructure evolution of the material and capture the underlying deformation mechanisms during the process. In principle, MD can predict the behavior of bulk material during different processes, but due to its expensive computational cost, this method is restricted to model the processes in nanosecond and nanometer scales. Despite the size of the system, the plastic deformation begins by atomic

movement/displacement, and the deformation mechanisms such as dislocation nucleation/movement is independent from the system size. Therefore, MD simulations can be used to study the material behavior during high velocity impact processes such as CS and capture some deformation mechanisms during the process, though the modeled system size is around 3 orders less than the actual system in CS.

Another objective of this research is to study in details the material behavior during the impact and reveal some mechanisms involved in the plastic deformation during the particle deposition at high velocities using MD simulations. Some of interesting topics to study in this research are listed below:

- a) Study the dislocation nucleation, interaction, multiplication etc. during the particle impact.
- b) Study the existence of solid-state amorphization mechanism which is one of the main deformation mechanisms in high strain rates deformation.
- c) Study the effects of grain boundaries on dislocation activities in polycrystalline metals.
- d) Study the dynamic recovery, crystallization, recrystallization, and grain growth during the deformation process.
- e) Study the crystal orientation effects on the plastic deformation.

Chapter 4

Methodology and Research Approach

The current chapter presents the methodology and research approach that will be used in this study. More specifically, it provides the description of the numerical models, i.e., Finite Element Method (or FEM) and Molecular Dynamics (or MD) method. These methods are chosen to achieve the objectives previously outlined in “Chapter 3”.

4.1 Finite Element Method

The commercially available finite element software ABAQUS/Explicit [133], commonly used in CS studies [28,52,103,121,131,172–175] is selected as the platform to model the behavior of a single particle impacting on a substrate. ABAQUS/Explicit uses an explicit integration scheme to solve highly nonlinear systems. It includes approaches allowing to model complex contact conditions. One of the main advantages of ABAQUS is that it grants the users to build and include “user subroutine”. User subroutines allow users to change and customize a wide variety of capabilities for particular applications [133].

4.1.1 Modeling Method

The behavior of a single particle impacting on a substrate is simulated in ABAQUS/Explicit using 2D axisymmetric and 3D model representations (see Figure 4-1). For the first study, 2D axisymmetric approximation is used because this allows to model the system with a smaller number of elements, and generates more accurate mesh, in comparison to a 3D model. All these will help to reduce the computational time. On the other hand, the purpose of the second study is to model the oxide layer explicitly with nanometer-size thickness. Therefore, for the second study, 3D model representation is used because this allows to model the oxide film with 3D shell elements. For both 2D and 3D models, it is assumed that the particle is perfectly spherical and impacts onto a flat substrate. The substrates are modeled as cylinders with a radius and height five times larger than the particle radius. It should be noted that in the previous study [31], the simulations results showed no sensitivity to larger dimensions of the cylinder.

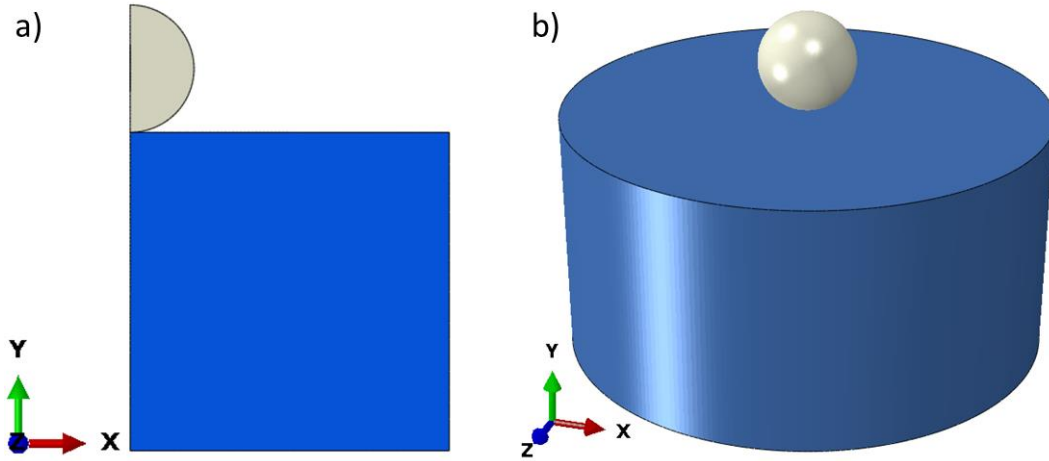


Figure 4-1 Finite Element models of single particle deposition process in CS a) 2D axisymmetric model, and b) 3D model

Due to the large plastic deformations found in CS, which cause severe element distortion when modeled, the Arbitrary Lagrangian-Eulerian (ALE) method [133] is used to remesh the model five times in each increment. In nonlinear analyses, such as high velocity impacts, the step time is divided into smaller increments so that the nonlinear solution path can be followed. In ABAQUS/Explicit, there is a stability limit for the time incrementation, which dictates the maximum time increment used by the explicit solver. An approximation of the stability limit, Δt_{stable} , can be expressed as the transit time of a dilatational wave across the distance defined by the characteristic element size, L_e :

$$\Delta t_{stable} = \frac{L_e}{c_d} \quad (1)$$

where c_d is the wave speed of the material and is defined as:

$$c_d = \sqrt{\frac{E}{\rho}} \quad (2)$$

where E is the modulus of elasticity and ρ is the material density. In ABAQUS/Explicit the time incrementation is fully automatic and does not need user intervention [133].

Regarding the mesh size, according to the literature [11,31,68], solution convergence of the deformed particle shape is achieved when the mesh size is set to 1/50 of the particle diameter. However, in this research, the solution convergence based on the obtained critical velocity will be verified by using different mesh sizes.

4.1.2 Equation of State and Elastic Behavior

This section is a very brief introduction to the concept of equations of state (or EOS) and elasticity of solids. The equations of state determine the pressure, p , as a function of the density and the specific energy (the internal energy per unit mass), E_m [133]:

$$p = f(\rho, E_m) \quad (3)$$

The equations of state can also define how some of elastic properties of the material will change in response to expansion or compression.

Every material, when subjected to an arbitrary load, has the potential to change both its volume and its shape. Hydrostatic (or volumetric) behavior and deviatoric behavior are the material's response regarding the change in the material's volume (or density) and the material's shape, respectively.

The EOS defines only the hydrostatic behavior of the material. It means, by using an EOS, the material is assumed to have only volumetric strength (has no shear strength). Alternatively, by assuming that the deviatoric and volumetric responses are uncoupled, it is possible to define the deviatoric behavior of the material separately. In ABAQUS/Explicit, there are two available models for the deviatoric response: a

linear isotropic elastic model and a viscous model [133]. For this research, since an isotropic behavior is assumed for the materials, the linear isotropic elastic model is chosen to define the materials' deviatoric behavior. Therefore, in this research, the volumetric response of the material is governed by the equation of state, while its deviatoric behavior is governed by the linear isotropic elastic model.

The deviatoric stress-strain relationship is given by:

$$S = 2\mu e^{el} \quad (4)$$

where S is the deviatoric stress, μ is the elastic shear modulus, and e^{el} is the deviatoric elastic strain.

There are different available types of equation of state in ABAQUS/Explicit [133]. The Mie-Grüneisen equation of state is used to model materials at high pressure, and also is used to determine the pressure in a shock-compressed solid [133]. The EOS model which is used in this work is given by [133]:

$$p - p_H = \rho\Gamma(E_m - E_H) \quad (5)$$

where p_H and E_H are the Hugoniot pressure and specific energy per unit mass, and Γ is the Grüneisen ratio defined as [133]:

$$\Gamma = \Gamma_0 \frac{\rho_0}{\rho} \quad (6)$$

where Γ_0 is a material constant and ρ_0 is the reference density.

The Hugoniot (curve) is the location of all possible pressure-volume states of a material behind a shock. The Hugoniot can be defined when the internal energy is eliminated from the Equation (3) to obtain p versus $1/\rho$ or equivalently, p versus V (where V is the current volume). Thus, the Hugoniot pressure, p_H , is only a function

of density and in general, is defined from fitting experimental data. Moreover, the Hugoniot energy, E_H , is related to the Hugoniot pressure by:

$$E_H = \frac{p_H \eta}{2\rho_0} \quad (7)$$

where $\eta = 1 - \rho_0/\rho$ is the nominal (or engineering) volumetric compressive strain.

Elimination of Γ and E_H from the Equation 5 yields:

$$p = p_H \left(1 - \frac{\Gamma_0 \eta}{2}\right) + \Gamma_0 \rho_0 E_m \quad (8)$$

There is another equation (energy equation) which is coupled with the Equation (8) for pressure and internal energy. Abaqus/Explicit solves these equations simultaneously at each material point.

The energy equation equates the increase in internal energy per unit mass, E_m , to the rate at which work is being done via the stresses and also the rate at which heat is being added. In the absence of heat conduction, the energy equation can be written as [133]:

$$\rho \frac{\partial E_m}{\partial t} = (p - p_{bv}) \frac{1}{\rho} \frac{\partial \rho}{\partial t} + S : \dot{\epsilon} + \rho \dot{Q} \quad (9)$$

where $\dot{\epsilon}$ is the deviatoric part of strain rate, and $\dot{Q}$ is the heat rate per unit mass. The p_{bv} is defined as the pressure stress due to the bulk viscosity. In general, the bulk viscosity (or volume viscosity) is defined as a type of internal friction that resists the shearless compression or expansion of a fluid. The bulk viscosity become important when the calculation of energy during the shock wave is required. In a fluid, the stress is proportional to the rate of deformation over time ($\tau = \mu dy/dt$), while in an elastic solid, the stress is proportional to the amount of shear deformation. Many solids (even granite [176,177]) will flow like fluids, although very slowly, even under small

stresses. These materials are called viscoelastic solids in which they possess both elasticity (reaction to deformation) and viscosity (reaction to rate of deformation). As mentioned earlier, by using the equation of state, it is assumed that the volumetric and deviatoric behavior of the material are uncoupled, which is similar to the definition of viscoelastic solids. Thus, in this case, the bulk viscosity can be defined for the solid material.

The materials properties used in this work for aluminum, copper, and nickel are given in Table 4-1.

Table 4-1 Material properties [31,178,179]

Properties	Aluminum [179]	Copper [31]	Nickel [178]
Density (ρ_0), kg/m ³	2700	8960	8890
Specific heat (C_p), J/kg K	910	383	456
Melting temperature (T_m), K	934	1356	1728
Shear modulus (G), GPa	26	45	76
Grüneisen's constant (Γ_0)	2.14	1.99	1.93
Speed of sound (c_0), m/s	5292	3933	4650
Hugoniot slope (s)	1.4	1.5	1.45

4.1.3 Bonding mechanism implementation

Figure 4.2 illustrates the bonding model proposed by Bay et al. [139,180] for the cold welding process for two metallic plates joined together under high pressure.

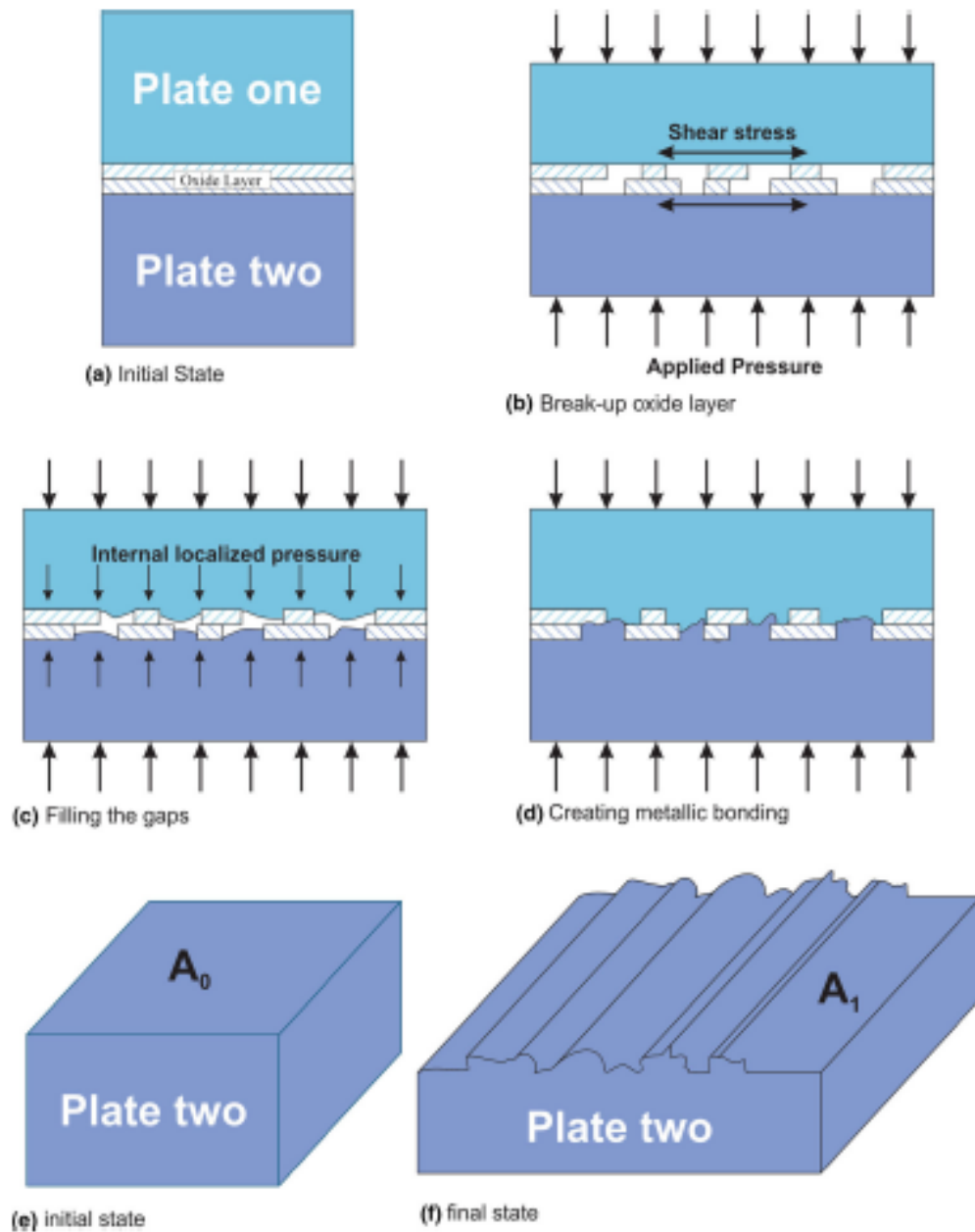


Figure 4-2 Schematic of the bonding model proposed by Bay et al. [139,180] for cold welding process

As displayed in this figure, there is an oxide layer on each metallic surfaces being put in contact at the initial state, Figure 4-2(a). Under the applied pressure, the shear stress developing at the interface induces plastic deformation in the metallic surfaces. If the applied pressure is high enough to create large deformation, the oxide layers eventually break up in parts due to their lower ductility, as shown in Figure 4-2(b).

Under the high-localized pressure at the interface, the freshly exposed metal is extruded through the gaps as illustrated in Figure 4-2(c). The metallic bonding occurs upon the contact of two clean metal parts under the high-localized pressure as shown in Figure 4-2(d).

Conrad and Rice [171] studied the adhesion of oxide-free surfaces of different FCC metals. They used metallic specimens previously fractured in an ultrahigh vacuum environment to avoid oxidation effects on their results. They showed that the bond strength obtained between those perfectly clean surfaces which joined together under a pressure (P) is approximately equal to the applied pressure:

$$\sigma_B \cong P \quad (10)$$

However, metallic surfaces generally have a native oxide layer and possibly contaminant film on their free surfaces resulting from manufacturing processes or simply handling operations. Thus, Bay et al. [170] showed that the bond strength obtained in an oxygen containing environment for typical metallic surfaces with native oxide layer is also related to the amount of clean surfaces available for bonding:

$$\sigma_B = P \cdot \Psi \quad (11)$$

where Ψ is surface expansion factor which indicate the ratio of available oxide-free surfaces for bonding to initial surface area:

$$\Psi = \frac{A_1 - A_0}{A_1} \quad (12)$$

where A_0 and A_1 are the initial and the final surface area, respectively (As shown in Figure 4-2e-f). Bay et al. [170] also illustrated that bonding is not obtained until a threshold has been achieved for the surface expansion factor, Ψ_{min} , which is material dependent.

The main difference between the cold welding and the CS process is the time scale. CS is a dynamic process, which operates at high strain rates, while cold welding is a quasi-static process. In the bonding theory proposed by Bay et al. [170], it is established that the required pressure allowing the material to flow through the gaps is dependent on the surface expansion and the material yield strength. The yield strength is a function of the strain, strain rate, and temperature. Hence, the required pressure must be obtained based on the instantaneous status of the material (or current-yield strength).

In CS, not all particles are successfully deposited. Some particles impact onto the substrate, creating temporary metallic bonding, but they debond from the substrate during the rebounding process. The rebounding process is due to the releasing of the stored elastic energy after the deformation process. Therefore, the deposition process can be summarized as follow: the metallic bonding is established during the particle deformation. Then, the stored elastic energy is released at the end of the deformation process and the rebounding process begins. During the rebounding process, the particle wants to detach from the substrate, hence, a localized negative pressure (or tension) is formed at the locations where the particle and the substrate are bonded together. At this moment, if the negative pressure on a specific location is higher than its bond strength, the bond will break, and if all metallic bonds break, the particle will detach completely from the substrate.

During the rebounding process, the strain rate is much lower than during the initial impact deformation process. Figure 4-3 shows a schematic illustration of true-stress-true strain curve at different strain rates [181]. As can be seen, by reducing the strain rate, the stress decreases. Based on the von Mises yield criterion [182], yield stress can be computed from the Cauchy stress tensor [133,182]. Therefore, if the strain rate

declines, the yield strength decreases as a consequence of reduction in the stresses (and also the applied pressure). The Equation (11) obtains the bond strength during the deformation process (high strain rate). Thus, due to the change in the strain rate from the deformation process to the rebounding process (high to low strain rate), the bond strength calculated by the Equation (11) must also change. In this research, a simple hypothesis was stated to update the bond strength instantaneously during the simulation. It is assumed that both pressure (normal stress) and yield strength vary with a same rate; hence, the Equation (11) can be rewritten as:

$$\sigma_B = P \cdot \Psi \cdot \left(\frac{\sigma_{y-c}}{\sigma_{y-h}} \right) \quad (13)$$

where σ_{y-h} is the yield strength at the moment of the bonding, and σ_{y-c} is the current-yield strength.

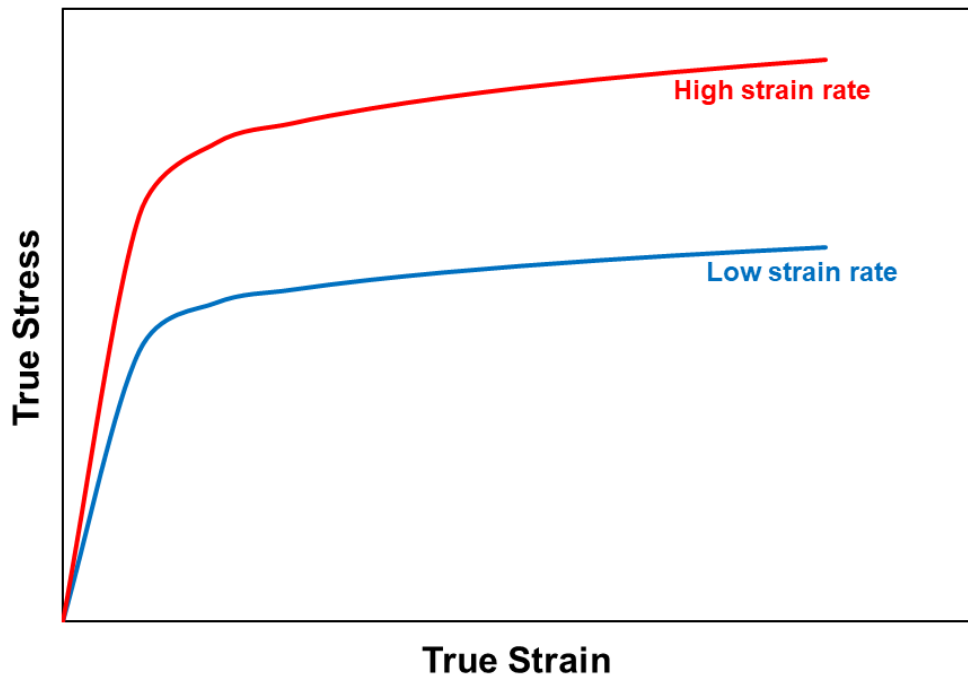


Figure 4-3 Schematic illustration of true stress-true strain curve at different strain rates [181] (*Reproduced with permission of Elsevier*)

During the single particle deposition, metallic bonding can occur in the interaction zone between the particle and the substrate. The “VUINTER” and the “VUINTERACTION” user subroutines are used to define the mechanical and thermal interaction between contacted surfaces through surface-to-surface and general contact methods, respectively [133].

For the first step, the bonding theory proposed by Bay et al. [170] was chosen to be implemented into a 2D axisymmetric ABAQUS/Explicit via a “VUINTER” user subroutine. The “VUINTER” was selected because this subroutine is usually a cheaper method with respect to the computational cost in comparison to “VUINTERACTION” subroutine for 2D simulations.

Error! Reference source not found. displays a simple 2D axisymmetric element with 4 nodes, i.e. A , B , C , and D . In a 2D axisymmetric model, the contact surface is modeled by only one edge, e.g., AB .

The expansion in the contact surface can be defined by measuring the strain applied on the contact edge. As can be seen in **Error! Reference source not found.**(a), the contact area represented by edge AB is $a \times b$. In addition, for this element, the logarithmic radial plastic strain, ε_r , and the logarithmic hoop plastic strain, ε_θ , can be defined as $\log\left(\frac{b_1}{b_0}\right)$ and $\log\left(\frac{a_1}{a_0}\right)$, respectively. Thus, Equation (12) can be rewritten as:

$$\Psi = 1 - \frac{A_0}{A_1} = 1 - \frac{1}{\frac{A_1}{A_0}} = 1 - \frac{1}{\frac{b_1}{b_0} \frac{a_1}{a_0}} = 1 - \frac{1}{e^{\varepsilon_r} e^{\varepsilon_\theta}} \quad (14)$$

where ε_r is the logarithmic radial plastic strain or the logarithmic plastic strain along the element direction obtained by using transformation equations for plane strain.

Furthermore, **Error! Reference source not found.** illustrates a schematic of the elements in the particle-substrate contact zone. Each element (denoted E_x) has two nodes (dots in the figure) in the contact surface, and each node is located between two nodes of a surface element belonging to the other solid surface. For instance, the “element one” (E_1) which belongs to the particle has two nodes, i.e., p_1 , and p_2 . These nodes are respectively between the nodes s_1 - s_2 , and s_2 - s_3 , which belong to the substrate elements, i.e., E_3 , and E_4 .

Figure 4-4 shows schematically the penalty contact method and the definition of bonding between nodes which is implemented in VUINTER subroutine [133].

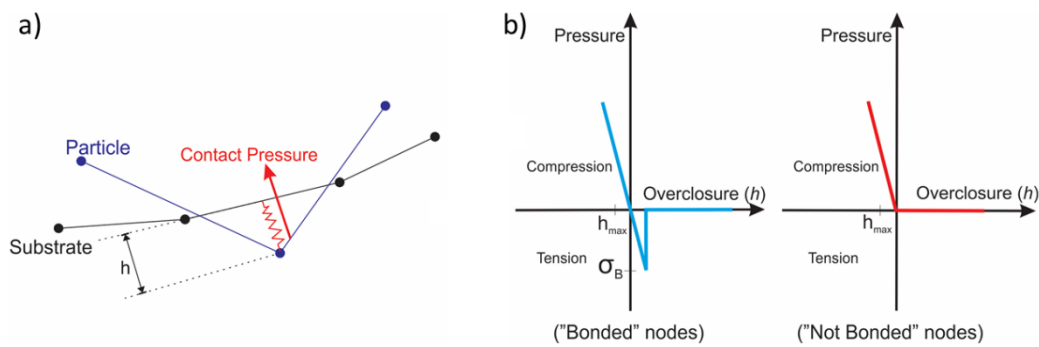


Figure 4-4 Schematic representation of a) penalty contact method and b) the behavior of “Bonded” and “Not Bonded” nodes in this approach

In this method, the interaction is defined via spring elements which model the contact stiffness. The surfaces can penetrate each other slightly in this approach. The interpenetration generates a contact pressure in the normal direction that aims to prevent more penetration of surfaces. The maximum allowed penetration, h_{max} , is achieved after several iterations to find an appropriate pressure and contact stiffness, Figure 4-4a. The difference between “Bonded”, and “Not Bonded” nodes is shown in Figure 4-4b. In the penalty method, the “Not Bonded” nodes come apart instantly when the contact pressure reaches zero. “Bonded” nodes cannot separate when the

contact pressure goes to zero. In order to come apart these nodes, a tension (or “negative” pressure) must be applied on these nodes and exceed the bond strength. Subsequently, “Bonded” nodes are allowed to be disconnected and contact pressure goes to zero, Figure 4-4b.

In this simulation method, there are two kinds of elements in the contact region, i.e., “Bonded” and “Not Bonded” elements. “Bonded” element means both nodes of the particle element are bonded to the substrate nodes, and “Not Bonded” element means at least one of the two nodes is not bonded. As shown in Figure 4-4b, “Not Bonded” elements separate instantly since the contact pressure is removed. However, “Bonded” elements are able to stand out against “negative” pressure (or tension) until the pressure value is larger than their bond strength. In the latter case, the element status is changed to “Debonded”. At the end of the deformation, the particle and substrate have been deformed at high strain rates and due to the high amount of work hardening, both particle and substrate behave like low ductility materials. Therefore, a fracture between the particle and substrate is assumed to be similar to brittle failure.

4.1.4 Material Model

In this research, the Preston-Tonks-Wallace (PTW) material model [183] was chosen to predict the material behavior during the impact process. It has been shown that this material model is one of the best models for predicting material behavior at high strain rate plasticity [31,43,44]. In this model, the flow stress is expressed by:

$$\sigma = 2 \left[\tau_s + \alpha \ln \left[1 - \varphi \exp \left(-\beta - \frac{\theta \varepsilon_p}{\alpha \varphi} \right) \right] \right] \mu(p, T) \quad (15)$$

$$\alpha = \frac{s_0 - \tau_y}{d} \quad \beta = \frac{\tau_s - \tau_y}{\alpha} \quad \varphi = \exp(\beta) - 1 \quad (16)$$

where ε_p is the plastic strain, $\hat{\tau}_s$ the normalized work hardening saturation stress, $\hat{\tau}_y$ the normalized yield stress, θ the hardening constant, d a dimensionless material constant and s_0 the value of τ_s at zero temperature. In addition, μ indicate the shear modulus and is assumed to be a function of temperature and density of the material. According to Banerjee [43], The MTS (Mechanical Threshold Stress) shear modulus model that is only function of the temperature can predict the shear modulus accurately. Thus, this model is preferred to be implemented instead of other complex models, given as:

$$\mu(T) = \mu_0 - \frac{D}{\exp(T_0/T) - 1} \quad (17)$$

where μ_0 is the shear modulus at 0 K, D , T_0 are material constants, and T is the temperature. τ_s and τ_y are defined as follows:

$$\hat{\tau}_s = \max \left\{ s_0 - (s_0 - s_\infty) \operatorname{erf} \left[k \hat{T} \ln \left(\frac{\gamma \dot{\xi}}{\dot{\varepsilon}_p} \right) \right], s_0 \left(\frac{\dot{\varepsilon}_p}{\gamma \dot{\xi}} \right)^{s_1} \right\} \quad (18a)$$

$$\hat{\tau}_y = \max \left\{ y_0 - (y_0 - y_\infty) \operatorname{erf} \left[k \hat{T} \ln \left(\frac{\gamma \dot{\xi}}{\dot{\varepsilon}_p} \right) \right], \min \left\{ y_1 \left(\frac{\dot{\varepsilon}_p}{\gamma \dot{\xi}} \right)^{y_2}, s_0 \left(\frac{\dot{\varepsilon}_p}{\gamma \dot{\xi}} \right)^{s_1} \right\} \right\} \quad (18b)$$

where $\hat{T} = T/T_m$, T_m is the melting temperature, s_∞ the value of $\hat{\tau}_s$ near the melting temperature, y_0 and y_∞ the values of $\hat{\tau}_y$ at zero and at very high temperature, respectively. Furthermore, γ , k , s_1 , y_1 and y_2 are all material parameters and

$$\dot{\xi} = \frac{1}{2} \left(\frac{4\pi\rho}{3M} \right)^{1/3} \left(\frac{\mu(\rho, T)}{\rho} \right)^{1/2} \quad (19)$$

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

4.1.4.1 Description of the PTW model:

The PTW model is a complex constitutive material model. However, this powerful model can be divided into simple parts in order to understand it better. Like other physically based constitutive material models such as Zerilli-Armstrong [184], Voyiadjis-Abed [185,186], and Gao-Zhang [45,187], this model was also formulated based on an Arrhenius equation:

$$\dot{\epsilon}_p = \dot{\epsilon}_0 \exp \left[-\Delta\phi(\tau) / k_B T \right] \quad (20)$$

where activation energy, $\Delta\phi$, is a decreasing function of the applied stress, τ , and $\dot{\epsilon}_0$ is proportional to the dislocation vibration frequency in the direction of the saddle point. The simple version of Equation (20) has some limitations. For instance, this equation is satisfied only if the potential barrier, $\Delta\phi$, is large compared to the thermal energy, $k_B T$, that is $\Delta\phi / k_B T \gg 1$. As the stress increases, $\Delta\phi / k_B T$ approaches zero, and the strain rate obtained by Equation (20) becomes less accurate. However, it should be noted that in high stresses, thermal activation is no longer the dominant mechanism in rate controlling; instead, dislocation drag mechanisms are expected to predominate. In the PTW model, the Arrhenius equation was modified to include the transition of rate controlling mechanism by joining onto a power-law dependence at very high strain rates, see Equations (18). In addition, Equation (20) gives an unphysical finite strain at zero stress. This failure occurs because this equation does not account for reverse motion of dislocation through the saddle points when the bias (stress) is removed; the reverse flow is exponentially suppressed at finite stress. The

PTW model introduced an inverse-error-function for $\Delta\phi$ to eliminate this deficiency of Equation (20) at high stresses.

Both work hardening saturation stress, $\hat{\tau}_s$, and yield stress, $\hat{\tau}_y$, in the thermal activation regime, Equations (18a-b), can be written in the Arrhenius form with $\Delta\phi(\hat{\tau}_c) \sim \text{erf}^{-1}[(c_0 - \hat{\tau}_c)/(c_0 - c_\infty)]$ where $c = s$ or y . The error function was chosen because it changes abruptly from nearly linear for $x \leq 1$ to a constant for $x \geq 1$. The same behavior cannot be obtained with rational functions unless extra material constants are added.

The work hardening law in the PTW model is also an extension of the well-known Voce behavior, i.e., a linear decrease in the work hardening rate as $\tau \rightarrow \tau_s$:

$$\frac{d\hat{\tau}}{d\varepsilon} = \theta \frac{\hat{\tau}_s - \hat{\tau}}{\hat{\tau}_s - \hat{\tau}_y} (\text{voce}) \quad (21)$$

The extension of Equation (21) in the PTW model is as follows:

$$\frac{d\hat{\tau}}{d\varepsilon} = \theta \frac{\exp\left[p \frac{\hat{\tau}_s - \hat{\tau}}{s_0 - \hat{\tau}_y}\right] - 1}{\exp\left[p \frac{\hat{\tau}_s - \hat{\tau}_y}{s_0 - \hat{\tau}_y}\right] - 1} \quad (22)$$

where p is a dimensionless material parameter. As mentioned before, $s_0 = \hat{\tau}_s(T = 0)$.

Thus, Equation (22) reduces to Equation (21) when $p \rightarrow 0$.

The flow stress in this model (Equation (15)) was obtained by integrating Equation (22) along a constant strain rate path (means keeping $\hat{\tau}_s$, and $\hat{\tau}_y$ constant) [183].

4.1.4.2 Material model parameters

The yield strength of pure aluminum and 1100-0 aluminum as a function of strain rate were reported by Casem et al. [34]. This result is plotted in Figure 4-5 to compare with the predicted result by the PTW model using parameters reported by Price et al.

[188]. This comparison illustrates that this set of parameters is not capable to predict the yield strength in a wide range of strain rates. Thus, for this research, a new set of parameters, which shows a better fit with experimental data, was obtained. The new parameters were found by modifying the reported parameters by Price et al. using the least square method. The least square method is a standard method in regression analysis to find the best fit for a set of data. The obtained results using the new parameters are also shown in Figure 4-5. It can be seen that these parameters are more suitable for modeling. The obtained parameters are shown in Table 4-2.

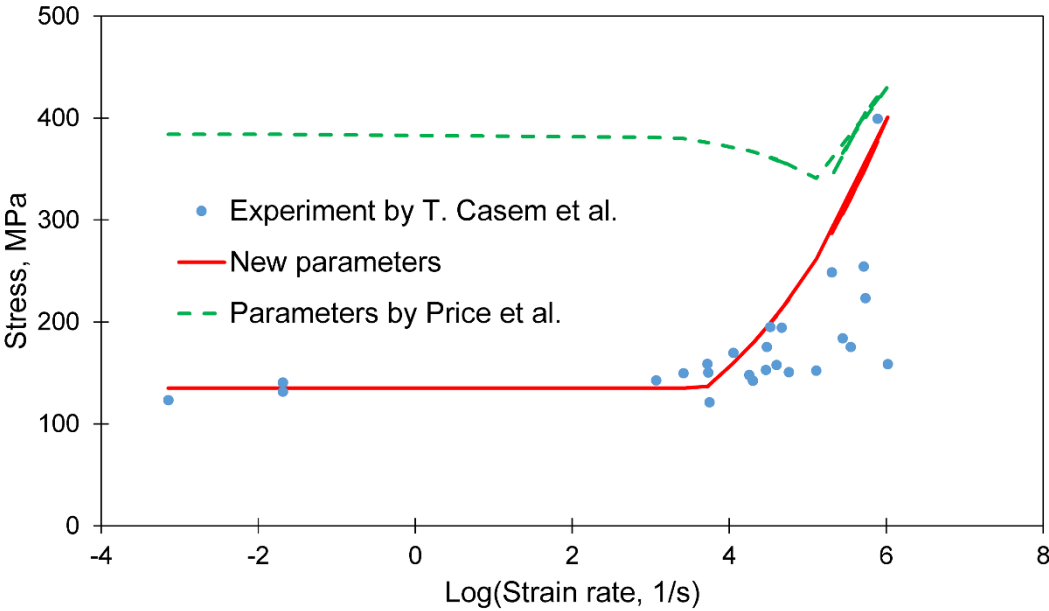


Figure 4-5 Comparison of calculated yield stress by PTW model using fitted parameters and parameters proposed by Price et al. [188] with experimental results [34]

The PTW material model parameters for aluminum, copper [31], and nickel [178] that are used in this study are shown in Table 4-2, respectively.

Table 4-2 PTW material model parameters for aluminum, copper, and nickel

PTW parameters	Aluminum	Copper [31]	Nickel [178]
Strain rate dependence constant (γ)	2.04e-5	1e-5	1e-5
Strain hardening rate (θ)	0.01156	0.025	0.01
Strain hardening constant (d)	3	2	2
Yield stress constant at 0 K (y_0)	0.0115	0.0001	0.0001
Yield stress constant at melting (y_∞)	0.002003	0.0001	0.0001
Medium strain rate constant (y_1)	0.0168	0.094	0.094
Medium strain rate constant (y_2)	0.2339	0.575	0.575
High strain rate exponent (s_1)	0.2034	0.25	0.25
Saturation stress at 0 K (s_0)	0.01489	0.0085	0.0045
Saturation stress at melting (s_∞)	0.002819	0.00055	0.00055
Temperature dependence constant (κ)	1.3	0.11	0.11
Atomic mass (M), kg	4.48039×10^{-26}	1.05521×10^{-25}	9.74627×10^{-26}
Shear modulus at 0 K (G_0), GPa	28.8	50	85.1
Material constant (D), GPa	3.44	3	9.13
Temperature material constant (T_0), K	215	165	269

4.2 Molecular Dynamics

To study the microstructural evolution of the material during the impact, Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) which is a MD program from Sandia National Laboratories [189] was chosen as the modeling platform. LAMMPS is free and an open-source software. This code has been used profusely in material modeling [190–204], and is able to model large-scale MD simulations up to 100 billion atoms [205].

4.2.1 Introduction

In MD simulations, the laws of classical mechanics [206] are used, in particular Newton's second law. In this section, we explain why it make sense to apply the laws of classical mechanics, even though one should use the laws of quantum mechanics.

In quantum mechanics, the Schrödinger equation [207,208] is taking the place of Newton's equations. The Schrödinger equation is a linear partial differential equation that predicts the future behavior of a quantum-mechanical system. It is a wave equation in terms of the wavefunction which predicts analytically and precisely the probability of the position of atoms. But the Schrödinger equation is so complex that it can be solved analytically only for a few simple bodies (or atoms). The direct numerical solution on computers is also limited to very simple systems with very small numbers of particles because of the high dimension of the space in which the Schrödinger equation is applied. Thus, approximation procedures are used to simplify this problem. These methods are based on the fact that the electron mass is much smaller than the mass of the nuclei [207]. The idea is to divide the Schrödinger equation, which defines the state of both the electrons and nuclei, with a separation approach into two equations. The influence of the electrons on the interaction between the nuclei is then obtained by an effective potential function [207,209]. As a further approximation, the nuclei are moved according to the classical Newton's equations using empirical potentials that have been fitted to the results of quantum mechanical computations or to the results of experiments. This approach is a classical example for a hierarchy of approximation procedures and an example for the use of effective quantities. In the following, the derivation of the MD method from the laws of quantum mechanics is presented.

4.2.2 Fundamentals

The atomic scale prediction of a real material needs the solution of Schrödinger wave equation for about 6×10^{23} nuclei (the number of atoms in one mole) and their electronic shells [210]. For a single particle, in a potential $U(r)$ with mass m and coordinates r and with the wave or state function $\Psi(r, t)$, the time dependent Schrödinger equation is [209]:

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(r, t) + U(r) \Psi(r, t) = i\hbar \frac{\partial \Psi(r, t)}{\partial t} \quad (23)$$

where $\hbar = h/2\pi$ and h is Plank's constant, and i denotes the imaginary unit.

MD simulations follows elementary atomistic path-dependent processes by solving the equation of motion of all particles. An exact answer of this many-body problem would require the formulation and solution of a Schrödinger wave equation for all atoms considering interactions among the charged constituents (nuclei, electrons) and their kinetic energies. It is obvious that this procedure is not manageable because of the large number of atoms involved ($\approx 6 \times 10^{23}$ particles). For this reason, in MD, instead of solving this huge system using Schrödinger equation, the interaction among the atoms is described by introducing interatomic (empirical) potentials and the classical equation of motion. It has been shown that the solution of this quasi-classical treatment of the atomic interactions is consistent with the solution of the Schrödinger equation [209].

The similarity between the full quantum mechanical treatment (Schrödinger equation) and the classical method (MD) of using empirical potentials and the equation of motion can essentially be justified on the basis of some assumptions. There are three main assumptions: the separation of the time-dependant solution from the time-

independent part of the Schrödinger equation, replacing the quantum mechanical momentum by the classical momentum, and using the Born–Oppenheimer approximation. Born–Oppenheimer approximation is the best-known mathematical approximation in MD in which the wave function can split into one part to describe the dynamics of the light electrons and another part to describe the dynamics of heavy nuclei [211].

From an electronic point of view, Born–Oppenheimer approximation is not necessarily straightforward [209]. Especially in the simulation of real materials, which contain lattice defects such as solute foreign atoms, dislocations, and interfaces, substantial fluctuation in the electronic structure can appear, due to changes in the local atomic configuration. However, in order to understand some basic physical concepts that occur in classical atomic ensembles, it is generally accepted that the fine details of the potential might not be crucial. For example, the fundamental relationship between the core structure of screw dislocations in body centered cubic (BCC) metals and their mobility was shown precisely by MD simulations using pair potentials [212,213]. Although these relatively simple functions provided only approximate information about the bonding in the real material, the results were of significant value in later understanding of the plasticity in BCC metals [214,215].

4.2.3 From the Schrödinger Equation to Molecular Dynamics:

In this section, the derivation procedure is gathered from [207,209].

Let us assume the state function Ψ is given as the solution of the Equation (23) (or Schrödinger equation):

$$i\hbar \frac{\partial \Psi(r, t)}{\partial t} = \mathcal{H} \Psi(r, t) \quad (24)$$

where $\mathcal{H}$ is the Hamilton operator. This operator, associated to the system of nuclei and electrons, is defined as the sum over the operators for the kinetic energy and the Coulomb potentials. Thus, the Hamilton (or Hamiltonian) operator is written as:

$$\mathcal{H} = T_e + V_{ee} + V_{eK} + V_{KK} + T_K \quad (25)$$

where T_e and T_K are the operators for the kinetic energy of the electrons and the nuclei, respectively. V_{ee} , V_{KK} , and V_{eK} denote the operators for the potential energy of the interactions (or Coulomb energy) between only the electrons, between only the nuclei, and between the electrons and the nuclei, respectively.

Now, if we assume that the state function can be written as $\Psi(r, t) = \psi(r) f(t)$, the right-hand side of the Equation (23) can be rewritten as:

$$i\hbar \frac{df(t)}{dt} \psi(r) = f(t) \mathcal{H} \psi(r) \quad (26)$$

Since the Hamilton operator $\mathcal{H}$ depends on the coordinates and impulses of the particles, it depends implicitly on time. Therefore, $\mathcal{H}$ does not act on $f(t)$. A division of both side by the term $\psi(r)$, and if $f(t) \neq 0$, yields:

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = \frac{1}{\psi(r)} \mathcal{H} \psi(r) \quad (27)$$

The left-hand side contains only the time coordinate, and the right-hand side contains only the coordinates in space. Both sides must be equal, hence the Equation (27) can be separated as following:

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = E \quad (28)$$

$$\mathcal{H} \psi(r) = E \psi(r) \quad (29)$$

where E is an eigenstate (i.e., a quantum-mechanical state corresponding to an eigenvalue of a wave equation) of energy.

The Equation (28) describes the evolution of the wave function over time. The general solution for this differential equation is:

$$f(t) = c e^{-iEt/\hbar} \quad (30)$$

The Equation (29) is the time independent part of the Schrödinger equation. It means to every energy eigenvalue E_n there is one (or in the case of “degenerate state”, several) associated state function ψ_n . In quantum mechanics, two or more different states of a quantum mechanical system are said to be “degenerate”, if they give the same value of energy upon measurement.

In addition, for every eigenvalue E_n , the Equation (30) gives a time dependent term f_n . Thus, the solution of Equation (24), i.e., the time-dependent part of the Schrödinger equation, can be obtained as a linear combination of the energy eigenfunctions ψ_n and the associated time-dependent terms f_n as following:

$$\Psi(r, t) = \sum_n c_n e^{-iEt/\hbar} \psi_n(r) \quad (31)$$

As shown in this section, the main objective of simplifying the Schrödinger equation is to find the relationship between the energy of an atom (or a molecule) with its coordination.

4.2.4 Interatomic Potential Functions

In MD, a pair potential or (potential function) is a mathematical function that is formulated to calculate the energy of atoms with respect to its interactions with other atoms in the space. The potential concept enables conducting nanoscale MD

simulations with as many as 10^6 - 10^9 atoms. Certainly, such quantities are still far from a full mesoscale modeling of material, but it is the best possible approach to reveal atomistic mechanisms and intrinsic structural properties. This information can be used at a larger scale to formulate and solve continuum mesoscale systems.

4.2.5 Molecular Dynamics for a Microcanonical Ensemble

Microcanonical ensemble is a statistical ensemble which defines the possible states of a mechanical system. The system is specified by the number of particles (or atoms), N , system volume, V , and system energy, E . Each of these is assumed to be constant in the ensemble. Therefore, microcanonical ensemble is also called NVE ensemble. The NVE ensemble is highly appropriate for dealing with a mechanical system completely isolated from other systems.

For a microcanonical ensemble, the methodology of MD can be simplified as follows:

For a system of N particles with coordinates $\mathbf{X}$ and velocities $\mathbf{V}$, Newton's law of motion can be written as:

$$\mathbf{F}(\mathbf{X}) = -\nabla U(\mathbf{X}) = M \dot{\mathbf{V}}(t) \quad (32)$$

$$\mathbf{V}(t) = \dot{\mathbf{X}}(t) \quad (33)$$

where $U(\mathbf{X})$ is the potential energy function of the system, which is a function of particle coordinates. As can be seen in Equation (32), the force $\mathbf{F}$ acting on each particle in the system can be calculated as the negative gradient of the potential energy function.

By having the initial position of particles (e.g., from theoretical knowledge) and their velocities (e.g., randomized Gaussian), MD can calculate all future positions and velocities.

When we have the initial positions and velocities of all particles, the force on each particle can be obtained by Equation (32). Afterwards, the new position and velocity of particles can be calculated by using Verlet integration [216] (or a more advanced version, i.e. the velocity Verlet algorithm) method. Verlet integration is a numerical method that is used to calculate trajectories (or flight path of an object as a function of time) of particles in MD. More details can be found in [207,209,217,218].

4.2.6 Modeling Method

In this research, the equations of motion were integrated using the velocity Verlet algorithm [217] with a time step of 1 fs. The interactions between the atoms were described by the widely used Embedded Atom Method (EAM) proposed by Daw and Baskes [219] as implemented in the interatomic potential developed by Mishin and co-workers [220]. In the EAM scheme, the total energy of a collection of atoms is described by the following equation:

$$E = \frac{1}{2} \sum \phi(r_{ij}) + \sum F_i \left[\sum \rho(r_{ij}) \right] \quad (34)$$

where r_{ij} is the distance between atom i and j . $\phi(r_{ij})$ is a pairwise interaction between atoms i and j , ρ is the contribution of atom j to the electron density at the location of atom i , and F_i is an embedding function that represents the energy required to place atom i into the electron cloud. In mathematics, the term “embedding” is used when an instance contains another instance in a mathematical structure, e.g., a group that is a subgroup.

As mentioned in “Chapter 3”, the system size has effects on the mechanisms involved in the plastic deformation. For the first step in the microstructural study, the size effect on the copper particles deformation during the impact was chosen to be investigated.

The purpose is to find a suitable system size for the study of fundamentals, which are the primary objectives of this research. The particles diameter is varied from 5 to 40 nm, labelled sequentially particle 1, 2, 3, 4, and 5, as shown in Table 4-3.

Table 4-3 Sizes of the model systems used in MD simulations

ID	Diameter, [nm]	Number of atoms in the particle	Number of atoms in the substrate
1	5	5,473	2,310,912
2	10	44,044	3,610,580
3	20	354,959	6,782,400
4	30	1,200,667	20,780,160
5	40	2,846,584	32,632,128

For each simulation, the particle is placed above the substrate with 1 nm separation, see Figure 4-6. Both particle and the substrate are oriented in the [111] direction; and an initial velocity of 1000 m/s is assigned to the particles.

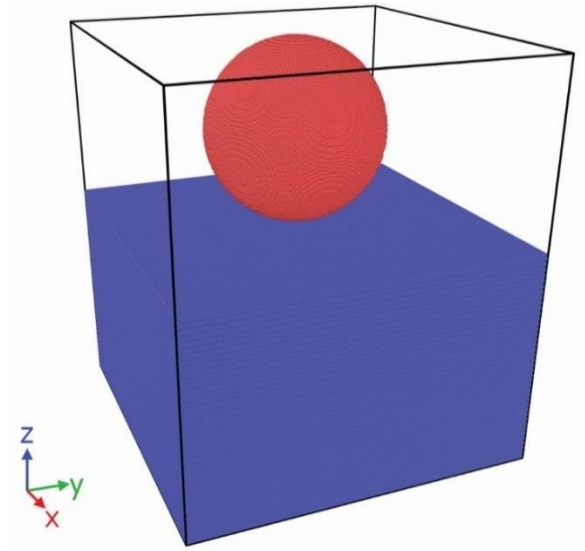


Figure 4-6 Model system used in MD simulations

In order to analyse the data obtained from MD simulations, the OVITO software [221] is used. This software includes algorithms such as Common Neighbor Analysis (CNA) [222], Polyhedral Template Matching (PTM) [223], Dislocation Extraction Analysis (DXA) [224,225], and grain segmentation [221] which allow to study the microstructure evolution of the materials during the deformation. CNA is able to classify atoms in the system according to the crystal structure they belong to. PTM provides a direct calculation of the local (per atom) lattice orientation. This algorithm identifies the local crystalline orientation by matching the local atomic order to determined structural templates. Moreover, the crystal orientation obtained by PTM can be mapped using RGB colors [226]. DXA is a computational method used to identify dislocations, including their types and line and Burgers vectors [224,225], and is used to investigate the dislocation evolution in our model systems. In addition, the grains are identified using the grain segmentation algorithm implemented in OVITO [221]. This algorithm is based on the PTM method to compute local lattice orientation. In contrast to the PTM algorithm, the grain segmentation method uses a

hierarchical clustering algorithm to explicitly group atoms into grains. This method can discriminate between grains and subgrains [221].

Chapter 5

Research Project Results

This chapter presents four peer reviewed papers published in international journals relevant to the current research. Two of which have been published in the Journal of Thermal Spray Technology (J. Therm. Spray Technol.) one in the journal of Computational Material Science, and one in the journal of Materialia.

5.1 Research Project 1

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The purpose of this project was to present the first steps of a modeling method, which allows predicting localized metallic bonding in CS. This model was the first physically based FEM model that could reproduce deposition mechanisms during the impact of a single particle onto a substrate based on the physics of the process.

The proposed model is based on cold welding (CW) bonding theory and its experimental data. All parameters used in this study were imported directly from the literature of CW. The reason for that was to illustrate the validity of the model to study the metallic bonding in CS.

In this paper, the impact process of a single particle onto a substrate was explained and it was shown that this process can be divided into two parts. The first part is the impact of the particle at high velocity, and involves plastic deformation at high strain rates for both particle and substrate. The second part is when kinetic energy of the particle approaches zero and most plastic deformation is done. This part is distinguished by releasing the stored elastic energy in materials mostly the substrate.

In addition, the implementation procedure and the penalty contact method in FEM was explained in details.

For the first time in CS literature, the localized metallic bonding process was illustrated in this peer reviewed paper. Critical velocity of three different metallic powders, i.e., copper, aluminum, and nickel, was calculated and it was shown that the proposed model could predict the deposition behavior of single particles relatively accurately with respect to the experimental observations.



William Lenling

President, TSS

9639 Kinsman Road, Materials Park, Ohio, 44073-0002 USA

440.338.5417 | Fax: 440.338.6614

www.asminternational.org

December 16, 2020

Dear Mr. Rahmati and Prof. Jodoin,

I am pleased to inform you that your manuscript “Physically Based Finite Element Modeling Method to Predict Metallic Bonding in Cold Spray” has been selected as an Editor’s Choice article for 2020 from the Journal of Thermal Spray Technology.

This selection is reflective of the comprehensive nature of your paper and its overall excellence. Only six papers are selected each calendar year as an Editor’s Choice article from among all of the articles published in the Journal of Thermal Spray Technology for that year.

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On behalf of myself and the team of associate editors of the Journal of Thermal Spray Technology, I congratulate you for the selection of your article as an Editor’s Choice article. Thank you for submitting your outstanding work to our Journal. We look forward to your continued contributions to the Journal of Thermal Spray Technology.

Sincerely,

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PEER REVIEWED

Physically Based Finite Element Modeling Method to Predict Metallic Bonding in Cold Spray

Saeed Rahmati¹ · Bertrand Jodoin¹

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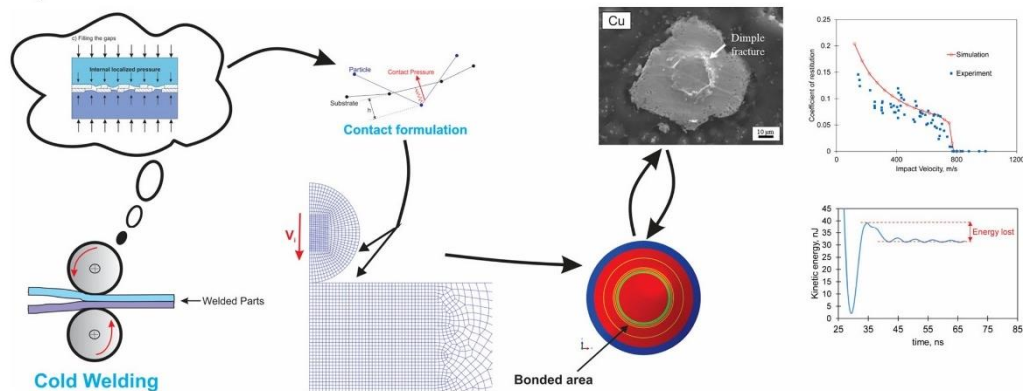
Abstract The cold spray (CS) process is unique due to its high strain rate deformation and particle deposition in solid state. In situ investigation of this process is challenging. Therefore, numerical methods have been used to simulate this process and provide a better ground for furthering the understanding of the process physics. Metallurgical bonding occurs during the deformation process at the particle/substrate interface during coating build-up. Up to now, several studies have been performed to predict the material behavior during this process. Although several studies have been done to predict the bonding in CS, none of them was able to show the occurrence of localized metallurgical bonding. In this study, a novel modeling method is

proposed to predict the occurrence and strength of localized metallurgical bonds in the CS process through finite element method. The process physics and implementation method are explained in details. Critical velocities of aluminum, copper, and nickel were predicted and compared with experimental data to validate the method. In addition, the proposed method is able to show the localized metallurgical bonding at the interface between particle and substrate. Comparison between the predicted bonding area with the proposed method and experimental data from the literature showed good agreement.

✉ Saeed Rahmati
sr_987@yahoo.com; saeed.rahmati@uottawa.ca

¹ Cold Spray Research Laboratory, University of Ottawa,
Ottawa, ON, Canada

Graphic Abstract



Keywords cold spray · critical velocity · metallurgical bonding · simulation

Introduction

Cold gas dynamic spraying or simply cold spray (CS) is a deposition method in which the particles are accelerated in a de Laval nozzle using a relatively low-temperature supersonic gas flow maintaining them below melting point prior to impacting and plastically deforming on the substrate (Ref 1). Although CS was developed first as a coating method (Ref 2), it is also used nowadays as an additive manufacturing process (Ref 2). CS offers potential in diverse applications due to its ability to spray a wide variety of materials. For instance, spraying metals on metals has been achieved from soft tin (Ref 3, 4) to hard MCrAlYs (Ref 5, 6). Metallizing polymers or deposition of polymers onto metals has also been achieved (Ref 7, 8), and even spraying metals on ceramics has been demonstrated (Ref 9, 10). This special ability of CS makes it a unique process and thus the development of a thorough understanding of the process fundamentals has been the topic of numerous works over the last decade and is still underway (Ref 1, 11–18).

The large kinetic energy of the sprayed particles prior to their impact onto the substrate leads to severely deformed particles occurring at high strain rates, i.e., up to 10^9 s^{-1} (Ref 19–21). Understanding the particle deformation/deposition behavior and the bonding mechanisms involved in CS has been the primary focus of scientific works for decades (Ref 1, 18, 19, 22–28). Mechanical anchoring and metallurgical bonding have been established as the two main bonding mechanisms involved in CS. Mechanical anchoring is a non-chemical phenomenon occurring when

particles are physically trapped in the substrate intricate surface topology and interlock with it (Ref 29, 30). By contrast, metallurgical bonding involves chemical bonds that are usually stronger than mechanical bonds. It requires oxide-free surfaces to allow intimate metal-to-metal contact and appropriate localized pressure to allow the chemical bond to be established (Ref 2). The necessity of removing the native oxide layer on particle–substrate surfaces for the creation of metallurgical bonding is widely acknowledged in the CS literature but the details of the in situ oxide layer removal process is still a point of contention. Numerous studies have indicated that adiabatic shear instability is the main mechanism responsible for the oxide layer breakup and cleaning away (removal) (Ref 18, 19, 22, 23, 31–34), while some have elaborated that metallurgical bonding in CS is not related to the occurrence of adiabatic shear instability (Ref 24, 35). In addition, partial melting in the contact region has also been deemed responsible for the localized oxide layer removal and chemical bonding upon solidification (Ref 36, 37). Despite these slight differences in the actual oxide removal process, all studies agree that the impacting particle requires a minimum velocity to adhere to the substrate, the critical velocity.

The critical velocity could be an indication of the onset of metallurgical bonding in CS, although adhesion solely attributed to mechanical anchoring also requires a critical velocity to be reached (Ref 2, 38–40). The critical velocity is dependent on the particle and substrate material properties, particle size, substrate and particle impact temperatures, and oxide or hydroxide layer thickness on both particle and substrate (Ref 19, 38, 41, 42). Since the deformation process in CS happens over only a few nanoseconds, in situ investigation on particle deformation and bonding mechanisms is a challenging task. Hassani-

Gangaraj et al. (Ref 43) have recently used an in situ observation technique derived from Lee et al. and Veyssset et al. (Ref 44, 45) and adapted to CS to assess precisely the critical velocity of different materials and particle sizes upon impact with a polished surface finish substrate. Prior to that several numerical studies have been performed to evaluate the critical velocity and/or simulate particle bonding in CS (Ref 18, 22, 23, 25, 46–52). For instance, Assadi et al. (Ref 1) have shown that the critical velocity can possibly be linked with the occurrence of adiabatic shear instability during the impact and suggested a semiempirical equation to calculate the critical velocity. Similarly, Meng et al. (Ref 53) proposed a model based on $PEEQ^2$, which is defined as the average equivalent plastic strain over all particle elements to calculate the critical velocity. They suggested that the critical velocity can be determined numerically when the slope of $PEEQ^2$ is changed significantly by increasing the initial velocity. To simulate bonding, Yildirim et al. (Ref 54) used the surface-based cohesive behavior option available in the commercially available finite element method (FEM) software ABAQUS/Explicit. In addition, Profizi et al. (Ref 55) and Manap et al. (Ref 56) also used two different cohesive zone models and have simulated the bonding in CS using the smooth particle hydrodynamics (SPH) method. Surface-based cohesive behavior is a simple way to model cohesive connections with negligibly small interface thicknesses using the traction–separation constitutive model. This method allows simulating cohesive interactions such as two “sticky” surfaces (surfaces can bond after coming into contact) (Ref 57). Although informative, a limitation of cohesive models lies with the fact that it is impossible to model the exact bonding behavior because the surface-based cohesive option acts exactly like a glue; hence, the particles stick to the substrate upon the initial contact. As such, this model does not include the requirement of breaking the native oxide layer and providing fresh surfaces for creating metallurgical bonding. In addition, the overall bond strength in this method relies on the glue strength [effective cohesive strength in FEM modeling (Ref 57)] which must be obtained by trial and error. Kurochkin (Ref 58) has developed a model to evaluate the relative bond strength between the particle and substrate based on the activation energy of the chemical bonds and the recoil coefficient. Wu et al. (Ref 59) further developed this idea and have shown the relationship between the particle velocities and the bond strength between particle and substrate. In this fundamental model, particle deposition can occur when the adhesion energy is higher than the rebound energy, providing important information about the adhesion process. However, there is a lack of information about the oxide layer removal process and inclusion in this model, and the adhesion energy is set as a function of

sublimation energy, which is potentially different from the fractured energy required to debond the atoms in solid phase. Xie et al. (Ref 60) calibrated an empirical model based on the experimental data and simulate the collisions of aluminum particles to an aluminum/sapphire substrate. Therefore, they could predict the extreme material behavior in high strain rate collisions.

The main objective of this study is to present the first steps of a new model that allows predicting localized metallic bonding in CS. The proposed model is taking into account the physics of oxide layer breakage. The model was used to investigate the bonding conditions of the local contact surfaces upon impact. The use of this model allows tracking closely the contact area during the deposition process. It divides the contact elements into three different groups: (a) elements which never met the required conditions for bonding during the impact process; (b) elements which met the bonding conditions at some point during the impact but fractured during the rebounding; and (c) elements which are bonded to the substrate at the end of the impact process. In addition, the critical velocity of aluminum, copper, and nickel powders with different diameters was predicted using the model and compared with experimental results available in the CS scientific literature for validation (Ref 43, 61).

Deformation Process During CS Impact

The deformation process during CS impact is presented in this section using FEM theory to describe the known process physics that helped develop the model proposed in this work

As mentioned before, particles require a minimum velocity, i.e., critical velocity, to adhere to the substrate. Particles with lower velocity than the critical velocity hit the substrate, deform plastically, and bounce off from the substrate. SEM images of deposited particles show severe plastic deformation, as shown in Fig. 1 (Ref 1). This large

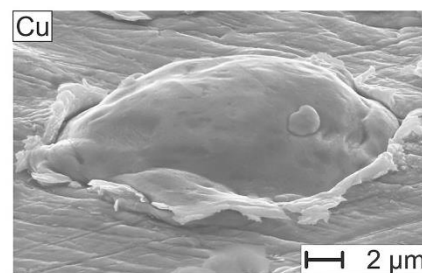


Fig. 1 SEM image of a copper particle impacted on a copper substrate (Ref 1)

plastic deformation is attributed to the large kinetic energy of the particle prior to impact.

At time zero, just before the impact with the substrate, the total system energy (one single particle and the substrate) is equal to the particle kinetic energy and particle and substrate internal energy. Based on energy balance, the system total energy must be constant. In FEM models, the total energy is typically defined as follows:

$$E_{\text{Total}} = E_I + E_V + E_{FD} + E_{KE} - E_W \quad (\text{Eq 1})$$

where E_I is the internal energy of the system, E_V is the viscous energy dissipated by damping mechanisms including bulk viscosity damping and material damping in the system, E_{FD} is the energy dissipated by friction, E_{KE} is the kinetic energy of the system, and E_W is the work done by externally applied load to the system. The sum of these energies should be constant, while in numerical models, it is approximately constant with an error of less than one percent (Ref 57). In the CS process, the external work is zero, and E_V and E_{FD} are negligible compare to the internal and kinetic energies. Therefore, the total energy can be assumed as the sum of internal and kinetic energy.

In FEM methods, the internal energy is described as follows:

$$E_I = E_E + E_P + E_{CD} + E_A \quad (\text{Eq 2})$$

where E_E is the recoverable elastic strain energy, E_P is the energy dissipated through the inelastic processes such as plasticity, E_{CD} is the dissipated energy through the viscoelasticity or creep that is zero in CS process, and E_A is the artificial energy which is primarily the energy dissipated to control hourglassing deformation that is used to avoid having nonphysical deformation for reduced integration elements in numerical methods (Ref 57). As long as the artificial energy is small compared to other internal energies, the results are reliable (Ref 57). In summary, the total system energy in CS can be shortened as follows:

$$E_{\text{Total}} = E_E + E_P + E_{KE} \quad (\text{Eq 3})$$

Figure 2 shows a typical time history (Ref 62) of total system energy, particle kinetic energy, and the total dissipated energy through the plastic deformation process in CS. According to the literature, about 90 percent of the dissipated energy through plastic deformation goes to heat (Ref 63, 64). This figure indicates that most of the kinetic energy is dissipated through plastic deformation. Although the recoverable elastic strain energy is small compared to the dissipated plastic energy, the particle can bounce off from the substrate due to this stored elastic energy.

Distribution of elastic strain energy during the process is mapped in Fig. 3. Following the particle impact, deformation happens in both particle and substrate, which causes elastic energy storage in both materials. In addition, as

soon as the particle hits the substrate, deceleration of the particle and acceleration of the substrate occur. It can be seen that the amount of elastic energy stored in the substrate is much larger than the elastic energy stored in the particle and that the particle bounces off from the substrate at the end of simulation. Both particle and substrate start to rebound together, while they are still in contact. The substrate then stops due to the boundary conditions and the particle detaches from the substrate. This rebounding is due to the releasing of elastic energy in the material. Conventional contact methods in FEM do not consider the bonding between two elements. Therefore, particles always bounce off from the substrate in FEM simulations. As stated previously, several studies have modeled the metallic bonding by using the cohesive element type, or surface-based cohesive contact method existing in FEM library (Ref 39, 55, 56, 65, 66). These methods were not developed to study and predict metallic bonding. The proposed method is employed instead of those methods to study and predict the metallic bonding in CS, with consideration of the oxide layer on both particle and substrate surfaces.

Modeling Method

The behavior of a single CS particle impacting on a substrate is studied using the commercially available FEM software ABAQUS/Explicit that has been used profusely in CS studies (Ref 67–71). An axisymmetric geometry is used by assuming the impact of a perfectly spherical particle on a flat substrate. The substrate geometry is modeled as a cylinder with a radius and height five times larger than the particle radius (Ref 21). It has been shown that simulating the large plastic deformation found in CS causes severe element distortion when using Lagrangian elements (Ref 33). To reduce the resulting computational errors, the Arbitrary Lagrangian–Eulerian (ALE) method (Ref 57) is used to remesh the model 5 times in each increment. According to the literature (Ref 1, 21, 34, 72), convergence of the final particle shape is obtained when the mesh size is set to 1/50 of the particle diameter. However, in this work, convergence for predicting critical velocity was checked by choosing different mesh sizes and the results showed that the mesh size should set to be 1/200 of particle diameter, as detailed in the “Results and Discussion” section. The particle and substrate material elastic behavior was modeled by a linear Mie–Grüneisen equation of state (EOS) which is adequate for impacts at high velocities (Ref 21, 73). In this study, three different materials were used to model particle–substrate, i.e., aluminum on aluminum, copper on copper, and nickel on nickel. The materials properties are given in Table 1. The initial temperature of

Fig. 2 History of particle kinetic energy, plastic dissipation energy for whole system, and total energy of system, for a 30- μ m aluminum particle impacting an aluminum substrate at 770 m/s

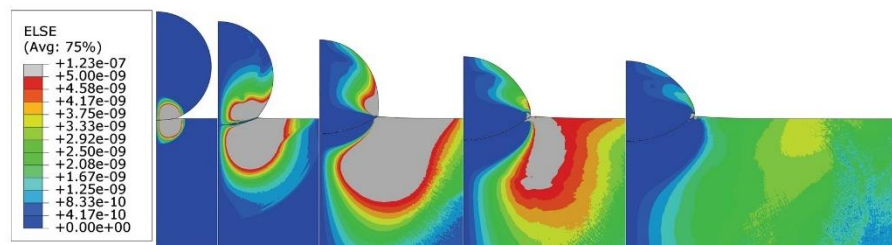
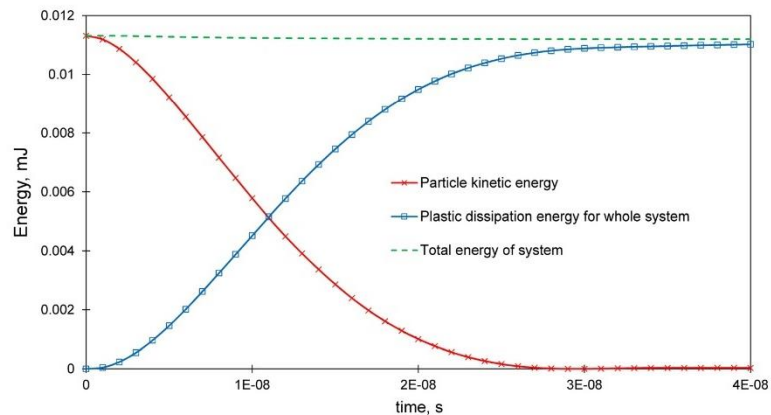


Fig. 3 Elastic energy distribution in 30- μ m aluminum particle and substrate during the whole deformation process, for initial impact velocity of 770 m/s

Table 1 Material properties (Ref 21, 72, 101)

Properties	Aluminum (Ref 72)	Copper (Ref 21)	Nickel (Ref 101)
Density (ρ_0), kg/m ³	2700	8960	8890
Specific heat (C_p), J/kg K	910	383	456
Thermal conductivity (κ), W/mk	237	386	91
Melting temperature (T_m), K	934	1356	1728
Shear modulus (G), GPa	26	45	76
Grüneisen's constant (Γ_0)	2.14	1.99	1.93
Speed of sound (c_0), m/s	5292	3933	4650
Hugoniot slope (s)	1.4	1.5	1.45

both the particle and substrate was assumed to be 300 K for all cases studied.

Material Model

The Preston-Tonks-Wallace (PTW) material model (Ref 74) which is one of the best models for predicting material behavior at high strain rates (Ref 21, 75, 76) was used to model the impact process. This model is expressed as follows (Ref 21):

$$\sigma = 2 \left[\tau_s + \alpha \ln \left[1 - \varphi \exp \left(-\beta - \frac{\theta \varepsilon_p}{\alpha \varphi} \right) \right] \right] \mu(p, T) \quad (\text{Eq 4})$$

$$\alpha = \frac{s_0 - \tau_y}{d} \beta = \frac{\tau_s - \tau_y}{\alpha} \varphi = \exp(\beta) - 1 \quad (\text{Eq 5})$$

where ε_p is the plastic strain, τ_s the normalized work hardening saturation stress, τ_y the normalized yield stress, θ the hardening constant, d a dimensionless material constant and s_0 the value of τ_s at zero temperature. Moreover, μ denotes the shear modulus and is assumed to be a function of temperature and density of the material.

According to Banerjee (Ref 76), the MTS shear modulus model which is only function of the temperature is able to predict the shear modulus accurately. Therefore, this simple model is preferred to use instead of other complex models, given as:

$$\mu(T) = \mu_0 - \frac{D}{\exp(T_0/T) - 1} \quad (\text{Eq 6})$$

where μ_0 is the shear modulus at 0 K, D , T_0 are material constants, and T is the material temperature. τ_s and τ_y are defined as:

$$\tau_s = \max \left\{ s_0 - (s_0 - s_\infty) \operatorname{erf} \left[k \hat{T} \ln \left(\frac{\gamma \dot{\xi}}{\dot{\epsilon}_p} \right) \right], s_0 \left(\frac{\dot{\epsilon}_p}{\gamma \dot{\xi}} \right)^{s_1} \right\} \quad (\text{Eq 7a})$$

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

where $\hat{T} = T/T_m$, T is the temperature, T_m the melting temperature, s_∞ the value of τ_s near the melting temperature, y_0 and y_∞ the values of τ_y at zero and at very high temperature, respectively. Furthermore, γ , k , s_1 , y_1 and y_2 are all material parameters and

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

where ρ is the density and M denotes the atomic mass. The PTW material model is not included in the ABAQUS library. In the previous study (Ref 21), this model was implemented into ABAQUS/Explicit via VUHARD user subroutine.

The yield strength of pure aluminum and 1100-0 aluminum as a function of strain rate were reported by Casem et al. (Ref 77). This result is shown in Fig. 4 to compare with the predicted result by PTW model using material model parameters reported by Price et al. (Ref 78). This comparison shows that this set of parameters is not able to follow the experimental yield strength in a wide range of strain rates. Therefore, the least square method which is a standard method in regression analysis to find the best fit for a set of data was used to modify the reported parameters by Price et al. to better fit Casem et al. experimental data. The predicted results using these new parameters are also plotted in Fig. 4 and show that these parameters are more suitable for modeling.

The PTW material model parameters for aluminum, copper, and nickel are shown in Tables 2, respectively.

Metallic Bonding in CS

In CS, it is hypothesized that when a particle impacts the substrate at sufficient speed, leading to localized high strain rates, the oxide layers on both the particle and substrate surfaces break up due to the extensive localized material deformation (Ref 2, 13, 79). This creates new freshly exposed metallic surfaces. The intimate contact between those fresh oxide-free layers causes metallic bonding (Ref 80). This bonding mechanism is assumed to be similar to the one experienced in the cold welding (CW) process (Ref 81–90). Figure 5 illustrates the bonding model proposed by Bay et al. (Ref 81, 82) for the CW process of two metallic plates pressed together to achieve cold welding.

In the initial state, Fig. 5(a), there is an oxide layer on each of the two mating surfaces being put in contact. Under the loading forces applied, the pressure developing at the

Fig. 4 Comparison of predicted stress by PTW model using fitted parameters and parameters proposed by Price et al. (Ref 78) with experimental results (Ref 77)

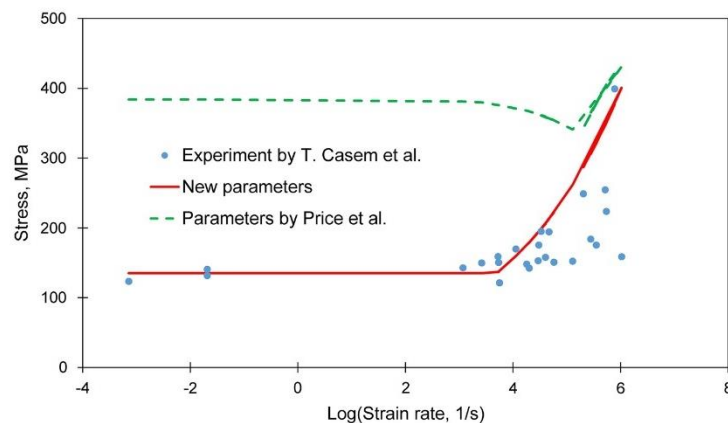


Table 2 PTW material model parameters for aluminum, copper (Ref 21), and nickel (Ref 101)

PTW parameters	Aluminum	Copper (Ref 21)	Nickel (Ref 101)
Strain rate dependence constant (γ)	2.04e-5	1e-5	1e-5
Strain hardening rate (θ)	0.01156	0.025	0.01
Strain hardening constant (d)	3	2	2
Yield stress constant at 0 K (y_0)	0.0115	0.0001	0.0001
Yield stress constant at melting (y_{∞})	0.002003	0.0001	0.0001
Medium strain rate constant (y_1)	0.0168	0.094	0.094
Medium strain rate constant (y_2)	0.2339	0.575	0.575
High strain rate exponent (s_1)	0.2034	0.25	0.25
Saturation stress at 0 K (s_0)	0.01489	0.0085	0.0045
Saturation stress at melting (s_{∞})	0.002819	0.00055	0.00055
Temperature dependence constant (κ)	1.3	0.11	0.11
Atomic mass (M), kg	4.48039×10^{-23}	1.05521×10^{-25}	9.74627×10^{-26}
Shear modulus at 0 K (G_0), GPa	28.8	50	85.1
Material constant (D), GPa	3.44	3	9.13
Temperature material constant (T_0), K	215	165	269

interface induces plastic deformation in the metallic plates. These deformations eventually become large enough, and the native oxide layers break up in parts due to their lower ductility, and move with the metallic parts they remain attached to, as shown in Fig. 5(b). Following this creation of gaps and under the high localized pressure existing at the interface, the freshly exposed metal is extruded into the gaps, as illustrated in Fig. 5(c). Upon contact with the other clean metal part and under the high localized pressure, a metallic bonding is created, as shown in Fig. 5(d).

Conrad and Rice (Ref 80) experimentally investigated the adhesion of clean fresh surfaces of different FCC metals. Using metallic specimens previously fractured in an ultrahigh vacuum (to avoid oxidation effects), they observed that the bond strength (σ_B) obtained between these perfectly clean surfaces put into contact under a pressure P (in the same ultrahigh vacuum environment) is approximately equal to this applied pressure, that is:

$$\sigma_B \cong P \quad (\text{Eq 9})$$

where P is the normal pressure applied to the surfaces.

However, metallic materials are usually used in oxygen containing environment. As such, they generally have a native protective oxide layer and possibly a contaminant film on their surfaces resulting from manufacturing processes or simply handling operations. Therefore, Bay et al. (Ref 81) introduced a surface expansion factor, Ψ , which shows the ratio of available fresh oxide-free surfaces for bonding to initial surface area:

$$\Psi = \frac{A_1 - A_0}{A_1} \quad (\text{Eq 10})$$

where A_0 and A_1 are the initial and the final surface area, respectively (Ref see Fig. 5(e) and (f)). It was established

experimentally that bonding is not obtained until a threshold has been achieved for the surface expansion, $\Psi_{\min}$, as shown in Fig. 6 (Ref 91) for copper-copper, aluminum-aluminum, and copper-nickel combinations.

Beyond this material-dependent threshold value, the bond strength increases quickly with Ψ . The bond strength eventually reaches the strength of the weaker of the two metals, with the required Ψ for this occurrence also function of the material (Ref 91). The bond strength is thus a function of Ψ ; hence, Eq (9) has been reformulated as follows (Ref 83):

$$\sigma_B = P \cdot \Psi \quad (\text{Eq 11})$$

The CW process is performed at low strain rates; hence, the strength of the materials is not changed significantly and remains below 250 MPa for copper (Ref 91). However, according to McQueen and Marsh (Ref 92), the ultimate tensile strength of copper can exceed 15 GPa under deformation occurring at high strain rate. Since the material deformation rate is high in the CS process, the material strength during CS can be much higher than during the CW process.

In Fig. 6, it is assumed that beyond $\Psi_{\min}$, surface expansion generates sufficient fresh metal areas available for bonding, and also that the contact pressure was enough to fill the created gaps by fresh metals. Moreover, Eq 11 allows determining the bond strength as a function of pressure. Therefore, in their original forms, both Fig. 6 and Eq 11 assume that the pressure is adequate for fresh metal to flow in the oxide gaps and merge.

However, a model refinement was implemented by determining the pressure which is required to allow material flowing through the gaps properly. It was found that this pressure is dependent on the surface expansion and the

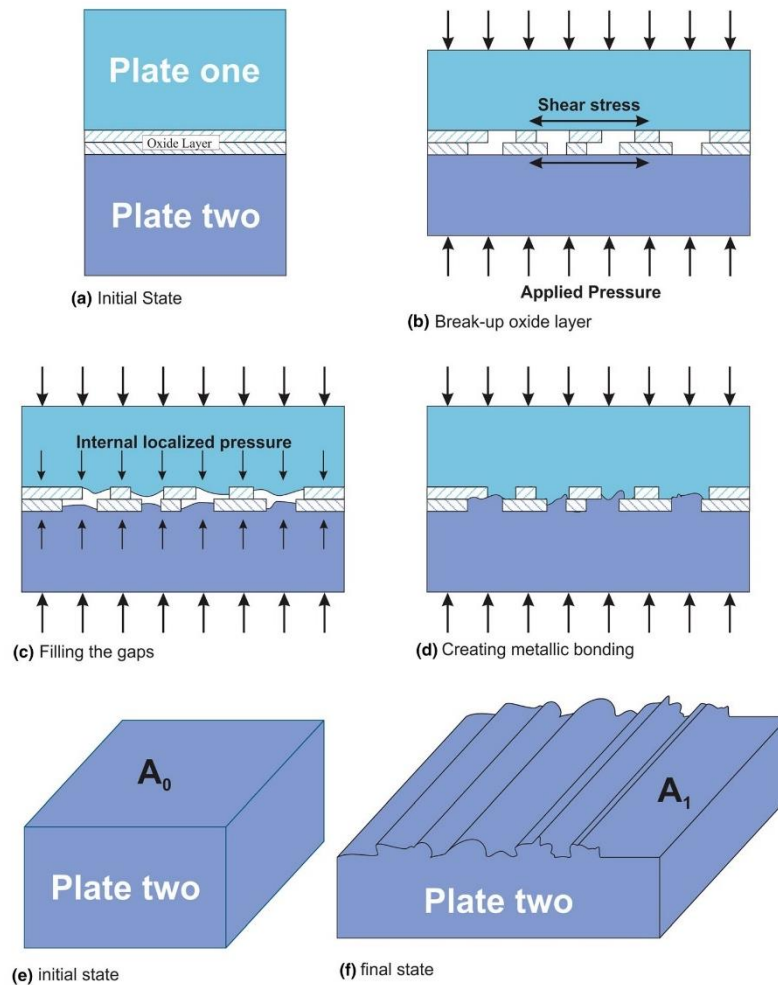


Fig. 5 Schematic of the bonding model in the CW process proposed by Bay et al. (Ref 81, 82)

material yield strength (Ref 81). Due to the work hardening during both CW, and CS by plastic expansion (or plastic deformation) of the surfaces, the material yield strength is increased. In addition, the yield strength is a function of the deformation rate. Thus, the required pressure must be obtained based on the instantaneous status of the material (referred to as current yield strength). Figure 7 (Ref 81) shows the relationship between the required extrusion pressure as a function of surface expansion, proposed by Bay (Ref 81) using Johnson's (Ref 93) and Hill's (Ref 94) slip line analysis of plane strain extrusion through square dies.

One can observe that the required (extrusion) pressure is decreased by increasing the surface expansion Ψ . It can be used for cases for which Ψ is larger than $\Psi_{\min}$ found in Fig. 6 to assess if the local pressure is sufficient to allow material flow through the gaps for achieving good metallic contact for bonding.

Another important difference between the CS and CW processes is the time scale. CW is a quasi-static process, while CS is a dynamic process operating at much higher strain rates. As mentioned earlier, the bond strength is strain rate dependent. In CS, surface expansion, material extruding, and merging are all occurring at high strain

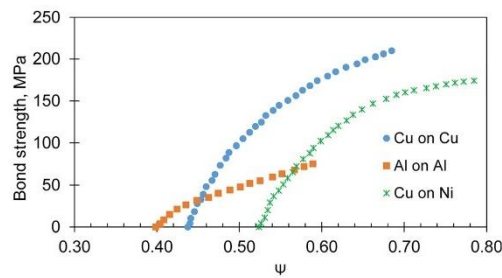


Fig. 6 Bond strength in rolling as a function of surface expansion, Ψ (Ref 91). $\Psi_{\min}$ for copper, aluminum, and nickel is 0.44, 0.4 and 0.52 respectively

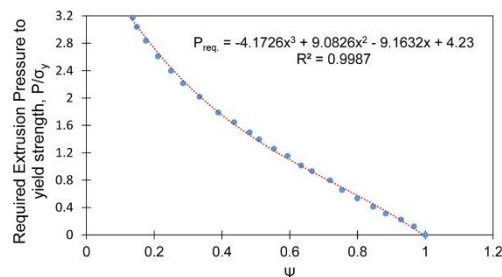


Fig. 7 Relationship between surface (Ψ) expansion and the ratio of required extrusion pressure (P) to instantaneous (current) yield strength (σ_y) (Ref 81)

rates. Since oxides are brittle materials, it is expected that the strain rate should not have a significant influence on their failure mechanism. Therefore, Ψ is defined the same way in CS than CW. During plastic deformation, the applied stress on the surfaces is equal to the instantaneous yield strength of the surface materials. In the CS process, the applied stress is due to the local pressure, which is caused by the impact. Therefore, the normal stress (P) on the surfaces is the pressure which induces the extrusion between the surfaces.

However, the bond strength (as defined by Eq 11) will be much higher than expected due to the high pressure (P) required for extrusion at these high strain rates. During the rebounding process, the strain rate is much lower than during the impact process, thus the bond strength during rebounding should be less than the bond strength in the impact process. According to the von Mises yield criterion (Ref 95), yield strength of materials can be computed from the Cauchy stress tensor (Ref 57, 95). Thus, if the strain rate decreases, the yield strength declines as a consequence of the reduction in the normal stress (or applied pressure). In a simple hypothesis, it is assumed that both pressure and yield strength vary at the same rate; therefore, the bond

strength during rebounding process would be changing at the same rate as the yield strength changes. Thus, Eq 11 can be rewritten as,

$$\sigma_B = P \cdot \Psi \cdot \left(\frac{\sigma_{y-c}}{\sigma_{y-h}} \right) \quad (\text{Eq 12})$$

where σ_{y-h} is the yield strength at the moment of the bonding, and σ_{y-c} is the current yield strength.

Implementation of Metallic Bonding Model

To implement the proposed bonding mechanism in FEM modeling, the simulation was divided into three steps. The steps are listed and then described: (1) simulating the first half of the impact; (2) post-processing to find the bonded elements; (3) restarting the rest of the simulation prior to rebounding.

As mentioned earlier, an axisymmetric geometry was chosen for this study. Figure 8(a) shows a simple axisymmetric element with 4 nodes, i.e., A, B, C, and D. In an axisymmetric geometry, the contact surface is modeled by only one edge, e.g., AB (2D axisymmetric). The expansion in the contact surface can be defined by measuring the strain applied on the contact edge. Therefore, Eq 10 is rewritten as:

$$\Psi = 1 - \frac{1}{e^{\epsilon_r} e^{\epsilon_\theta}} \quad (\text{Eq 13})$$

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 plastic strain. Furthermore, Fig. 8(b) shows a schematic of the elements in the particle–substrate contact region. Each element (denoted E_i) has two nodes (dots in the figure) in the contact surface, and each node is located between two nodes of a surface element belonging to the other solid surface. For instance, the “element one” (E_1) which belongs to the particle has two nodes, i.e., p_1 and p_2 . These nodes are, respectively, between the nodes s_1-s_2 , and s_2-s_3 , which belong to the substrate elements, i.e., E_3 , and E_4 .

Simulating the First Half of the Impact

In the CS process, bonding occurs in the contact region between particle and substrate surfaces. Therefore, the bonding mechanism has to be implemented via the contact subroutine applied for the simulation. The CS process can be divided into two parts. In the first part (or first half), the impact and plastic deformation occur at high strain rates. In the second part, the particle rebounds from the substrate due to the releasing of the elastic energy, at low strain rate. Thus, the bonding takes place in the first part but the

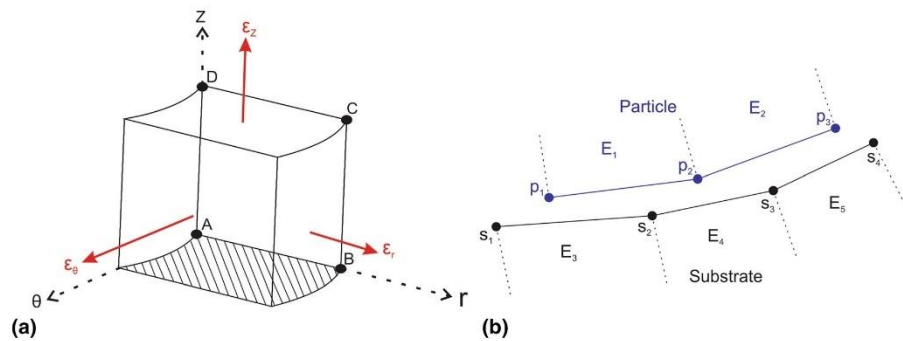


Fig. 8 (a) Schematic of an axisymmetric element (b) schematic of elements (E_1 and E_2 are particle elements, E_3 , E_4 , and E_5 are substrate elements) in contact zone

bonding quality (comparison between the bond strength and “negative” pressure (or tension) described in “**Metallic Bonding in CS**” section) is checked during the second part.

It is a challenging task to know the exact time needed for each part (impact and rebounding) of the simulation in advance. The exact simulation time for the first part is the time that particle kinetic energy reaches to zero but it is inefficient to do a pre-simulation and find the exact required time for each cases. Therefore, the simulation time was estimated based on the first conducted simulation, and the output and restart files were set to be saved for 100 intervals (100 times during the simulation). Saving the restart files for 100 times allows to check the results and starts the second part when the kinetic energy of the particle is close to zero and prior to rebounding.

Post-Processing to Find the Bonded Elements

Following the first step (simulation of the first half of the impact, before the onset of elastic energy release), post-processing was performed on the result file, i.e., *odb* file, by using a Python script. The algorithm flowchart is shown in Fig. 9. This script searches frame by frame both particle and substrate deformation to compute Ψ and the applied pressure on each node of each element. For clarity, the algorithm flowchart shows the post-processing for element E_1 in Fig. 8(b).

As described in Fig. 8(b), each particle element has two nodes in contact surface, and each node is located between two nodes of the substrate element. In the flowchart, the subscripts p_1 and p_2 refer to the parameters associated with nodes p_1 and p_2 . In addition, the subscripts s_1-s_2 and s_2-s_3 refer to the averaged parameters for nodes s_1, s_2 and s_2, s_3 , respectively. The flowchart is divided into two columns. In each column, parameters of each particle node, i.e., p_1 (on the left column for the example illustrated) or p_2 (on the

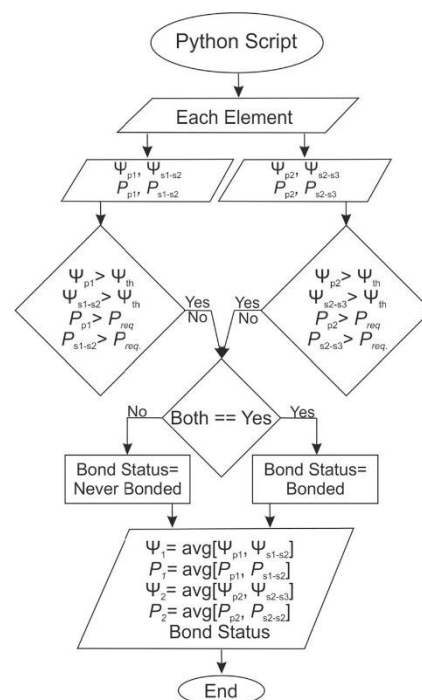


Fig. 9 Algorithm flowchart of the (Python) script

right column for the example illustrated), and the related substrate nodes, i.e., s_1-s_2 or s_2-s_3 , are checked.

For each column, a verification is made to determine if Ψ and P meet the minimum requirements for bonding (i.e., surface expansion threshold, Ψ_{th} , obtained from Fig. 6 and required pressure, P_{req} , obtained from Fig. 7). If the minimum requirements are fulfilled, the bond status of the

element is changed to “Bonded,” otherwise the bond status remains “Never Bonded.” Hence, this step allows determining which elements have achieved bonding to the substrate during the first phase of the impact process (prior to the rebounding/elastic energy release phase) and which one did not. At the end, the bond status of each element, the average surface expansion, and the average pressure between each node of the particle and the substrate nodes are saved in each frame, and the maximum is written in a data file to be sent to the next step.

Restarting the Rest of the Simulation

Afterward, the restart simulation is launched for the second part using the restart files from the first part and the data from the post-processing part.

Checking bonding quality, or comparison of the local bond strength and “negative” pressure (or tension), P_N , applied on each element during the rebounding process is made through a VUINTER user subroutine. The VUINTER subroutine is used to define the interaction between contact surfaces in ABAQUS/Explicit (Ref 57). The contact interaction is modeled by the surface-to-surface penalty contact method.

Figure 10 illustrates schematically the penalty contact method and the definition of bonding between nodes which was implemented in VUINTER subroutine (Ref 57). In the penalty contact method, the interaction is defined via spring elements which model the contact stiffness. The surfaces can penetrate each other slightly in this approach. The interpenetration causes a contact pressure in the normal direction that tries to prevent more penetration of surfaces. The maximum penetration, h_{max} , is obtained after several iterations to find the best contact stiffness and pressure. For details about penalty method and its implementation in FEM, the reader is referred to

(Ref 57, 96). The difference between “Bonded” and “Not Bonded” nodes is also shown in Fig. 10. In the penalty method, the “Not Bonded” nodes separate instantly since the contact pressure reaches zero, as shown in Fig. 10. On the contrary, “Bonded” nodes cannot separate when the contact pressure goes to zero. To make these nodes come apart, a tension (or “negative”) pressure (here, debonding pressure) must be applied on these nodes and exceed the bond strength (σ_B). Afterward, “Bonded” nodes are allowed to be detached, and contact pressure reaches zero (Fig. 10).

The bond strength σ_B of each bonded node is calculated by Eq 12, using the parameters obtained by the Python script. Figure 11 shows the algorithm flowchart of the VUINTER subroutine. The restart files from the simulation of the first part and data files obtained from the post-processing part are used to simulate the second part. In this simulation, we have two kinds of elements in the contact region, i.e., “Bonded” and “never Bonded” elements. “Bonded” element means both nodes of the particle element are bonded to the substrate nodes, and “never Bonded” element means at least one of the two nodes is not bonded. As shown in Fig. 10, “never Bonded” elements detach instantly when the contact pressure is removed, or in other words, these elements are not able to resist any “negative” pressure (tension). However, “Bonded” elements are able to stand out against “negative” pressure (tension) until the pressure value is larger than their bond strength. In the latter case, the element status is changed to “Debonded.” At the end of the deformation, the particle and substrate have been deformed at high strain rates and because of the high amount of work hardening, both particle and substrate behave like low ductility materials. Thus, a fracture between the particle and substrate is assumed to be similar to brittle failure.

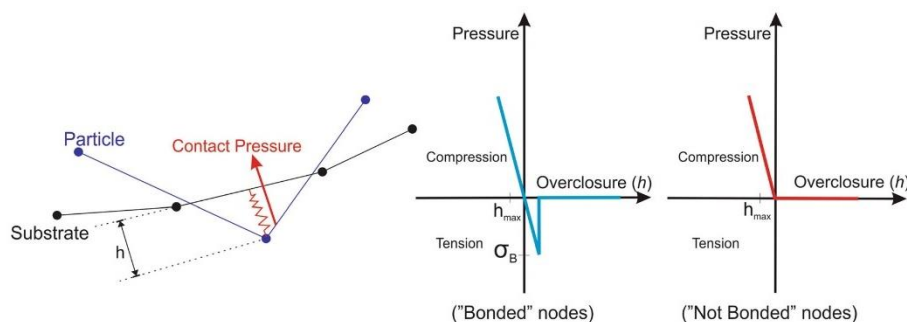


Fig. 10 Simple schematic of penalty contact method and relationship between contact pressure and overclosure of particle–substrate nodes in VUINTER subroutine

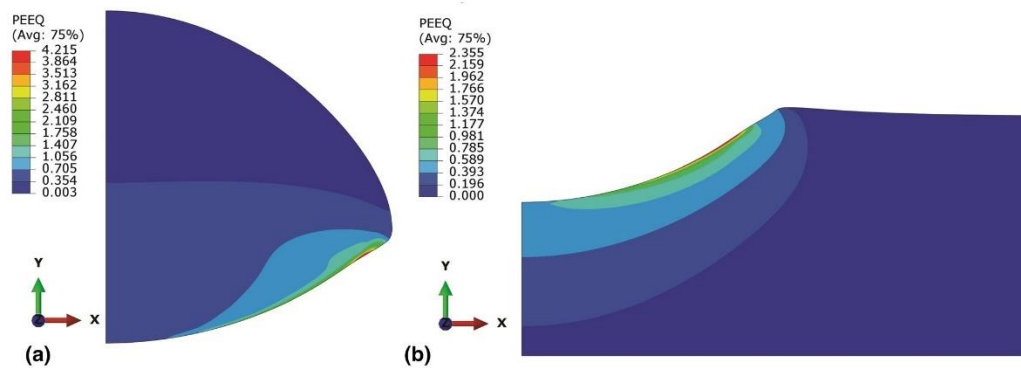


Fig. 13 Equivalent plastic strain for 30-um aluminum particle after the impact by 780 m/s to an aluminum substrate, (a) particle (b) substrate

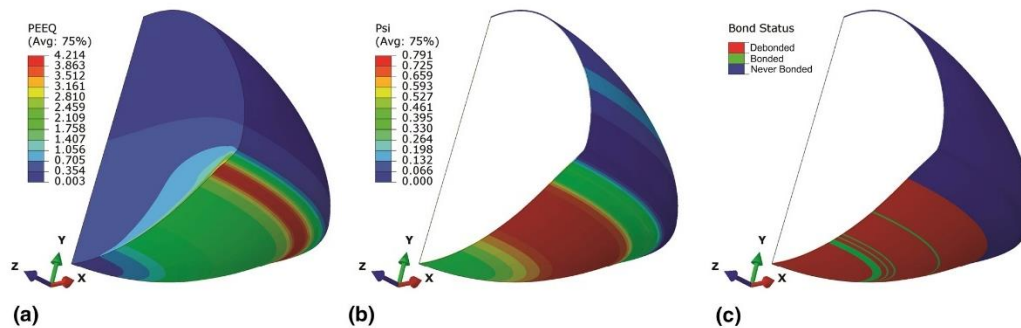
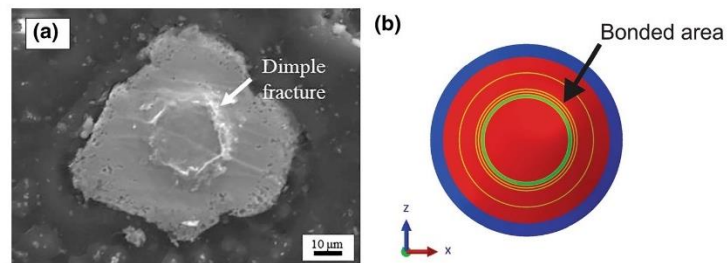


Fig. 14 (a) Equivalent plastic strain (b) surface expansion Ψ (c) status of bonding in elements, for 30-um aluminum particle with 780 m/s impact velocity

Fig. 15 (a) SEM image of bonded zone in CS, dimple fracture indicates the area of metallic bonding on copper particle, this figure was taken after detaching the deposited particle from substrate (Ref 61), (b) bottom view of Fig. 14c, bonded area is shown by arrow



(Ref 97), Kim et al. (Ref 98), and Vidaller et al. (Ref 99) showed similar results for Cu, Ti, and Ti6Al4V, respectively. Based on the published literature, there is no such study on aluminum. Therefore, qualitative comparison was made between the predicted results and the experimental results from copper (Ref 61). Figure 15 shows an SEM image of the bottom of a deposited copper particle (Ref

61). This image was taken after detaching the particle from the substrate. Dimple fracture which is shown by arrow indicates the area of the metallic bonding on the particle. As shown in Fig. 15(b), a similar qualitative behavior is predicted by the model, giving some confidence about the modeling approach.

Hassani-Gangaraj et al. (Ref 43) obtained the critical velocity of copper, aluminum, nickel, and zinc particles precisely and presented the coefficient of restitution (defined as the ratio between the rebound velocity and the impact velocity) as a function of impact velocity for those materials. Their experimental measurements have revealed a shift of the critical velocity from 825 m/s for 16 μm Al particles to 770 m/s for 30- μm Al particles (Ref 43), indicating that the smaller particles require lower velocities to deposit. The obtained results by the proposed model are in agreement with those results. The critical velocities were calculated to be 830 m/s and 780 m/s for 16 and 30- μm Al particles, respectively.

Figure 16(a) shows the comparison between the predicted coefficient of restitution (COR) for 30- μm aluminum particles and experimental results of aluminum powders with the diameters in range of 20–64 μm obtained by Hassani-Gangaraj et al. (Ref 43). To calculate the COR for

numerical results, the kinetic energy equation was used to calculate the rebound velocity, v_r , of the particle for each simulation as follows:

$$v_r = \sqrt{2 \frac{E_K}{m_p}} \quad (\text{Eq 14})$$

where E_K is the kinetic energy of the particle after complete detaching from the substrate, and m_p is the mass of the particle.

The COR is declining with the increase in the particle impact velocity in both numerical and experimental results, and it drops to zero at 780 m/s and 770 m/s, respectively. The critical velocity is the minimum velocity for deposition of particles, and it means that the overall bond strength between the particle, and the substrate was higher than the pressure on the bonded zone during the elastic energy restitution part of the impact. The creation of bonds between particle and substrate starts in velocities below the critical velocity. However, the particle detaches from the substrate because its overall bond strength is less than the pressure pulling on the bonded areas when elastic energy is restored. By looking at Fig. 16(a), it can be seen that the slope of the numerical results changes beyond the impact velocity of 720 m/s. This velocity, i.e., 720 m/s, is the minimum velocity at which some elements created bonding upon impact. For the sake of clarity, the scale of Fig. 16(a) is changed, and the results are redrawn in Fig. 16(b). Furthermore, four other simulations were performed with the impact velocities of 670, 720, 750, and 770 m/s without using the new bonding method. The computed COR are plotted in Fig. 16(b). At 670 m/s, no element was bonded during the simulation. Therefore, the COR of both methods (with and without bonding method) are exactly the same. By increasing the impact velocity, it can be seen that the difference between the computed CORs is increasing. This increase in the differences indicates that more and more elements bond by increasing the impact velocity.

The kinetic energy history of a 30- μm aluminum particle with the impact velocity of 750 m/s is shown in Fig. 17. As shown in this figure, the kinetic energy of the particle goes to zero (compared to the initial kinetic energy that was 0.01 mJ) around 30 ns, i.e., end of the “impact” process. It means the particle is almost stopped at this moment. Afterward, the particle starts to bounce off due to the releasing of the elastic energy. It can be seen that the kinetic energy is increasing and reaches a maximum at around 35 ns. This 5 ns period between 30 and 35 ns is the accelerating time during which the substrate and particle move together while they release their elastic energies. The time at the peak in this graph (35 ns) indicates the time at which the substrate was stopped because of its boundary

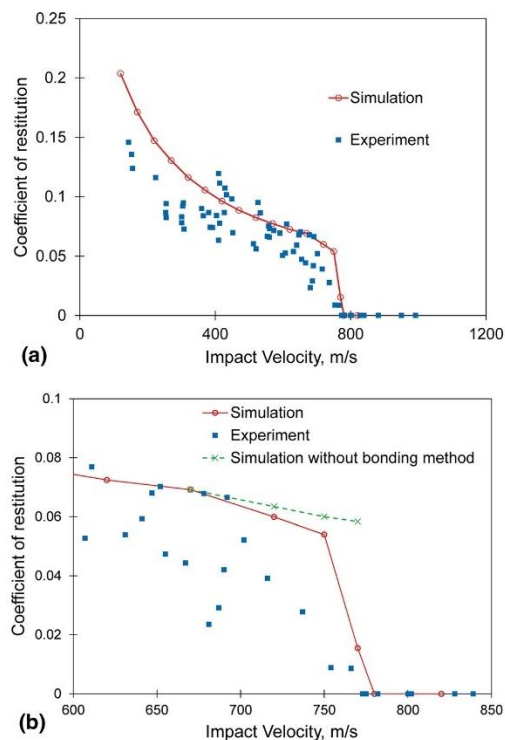


Fig. 16 (a) Coefficient of restitution as a function of impact velocity for aluminum, (b) redrawn of fig. a with changing in scales to have a better view for COR at velocities near the critical velocity of 30- μm aluminum particle and simulation results without using bonding method (ABAQUS default), experiment after Hassani-Gangaraj et al. (Ref 43)

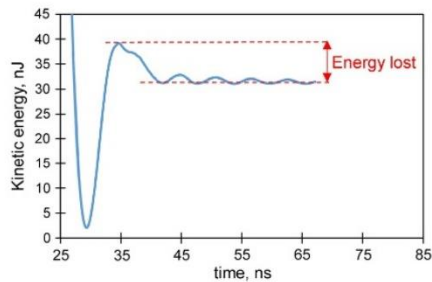


Fig. 17 History of kinetic energy of a 30-um aluminum particle with the impact velocity of 750 m/s during the rebounding process

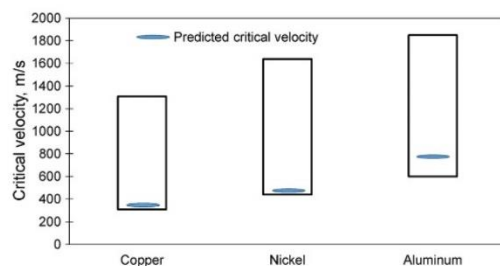


Fig. 18 Comparison of predicted critical velocity with experimental ranges of critical velocity for copper, nickel, and aluminum (Ref 1, 19, 38, 100)

conditions. At this velocity, the particle is bonded to the substrate by several elements. The decrease in the kinetic energy is due to the lost energy to break the bond between those elements. The overall required energy to debond all elements is shown in this figure as “energy lost.”

The same procedures were applied for 12 um copper particles and 12 um nickel particles to determine the critical velocity. Comparison of the calculated critical velocity with experimental data (Ref 1, 19, 38, 100) for each material is shown in Fig. 18. The obtained critical velocities were 370 m/s for 12 um copper, 780 m/s for 30-um aluminum, and 460 m/s for 12 um nickel. As it can be seen, the predicted results are in the range of critical velocities reported in the literature (Ref 1, 19, 38, 100). This large range of reported critical velocities is due to the differences in spray system setups (such as low-pressure or high-pressure CS system, nozzle material, and carrier gas type), different particle sizes and different particle oxygen content, with the latter having a dramatic effect on the particle critical velocity (Ref 38, 41). The reported critical velocity by Hassani-Gangaraj et al. (Ref 43) of 16, and 30-um aluminum particles are matched by the predicted critical velocities using the proposed method. Nevertheless, the obtained critical velocities for copper and nickel do not

match as well the results reported by Hassani-Gangaraj et al. (Ref 43). This difference is attributed to potential dissimilarity between modeled and experimental material properties. In other words, oxidation and impurity can change the mechanical properties of materials, and these were not included in the model material properties due to lack of available data.

Future research should be devoted to develop the understanding of the material behavior in the CS process. For instance, oxide layer thickness has a strong effect on the critical velocity of the particle and the occurrence of the bonding between materials. In addition, the second particle collision effects on the metallurgical bonding between the first particle and the substrate, and also studying the bonding behavior between particles are also interesting and important subjects for future work to explore.

Conclusion

In the present study, a novel FEM modeling method is proposed to predict and study metallic bonding formation mechanisms in CS. The bonding model is based on cold welding bonding theory and experimental data.

The modeling deposition process is divided into two parts. In the first part, the particle impact on the substrate is modeled, involving plastic deformation at high strain rates for both particle and substrate material. In the second part, characterized by the releasing of the particle and mostly substrate elastic energy, the particle rebounding status from substrate is modeled, comparing the local adhesion strength to the local debonding pressure.

The bonding zone at the particle/substrate interface was modeled and investigated locally and revealed that the preferential bonding zone differs from the jetting zone where the maximum plastic deformation occurs. Moreover, the comparison between the predicted bonding zone and experimental observation showed a good agreement. Furthermore, the coefficient of restitution 30-um aluminum particles was predicted and compared well with experimental data. The critical velocity for Al, Cu, and Ni were obtained using the proposed method and are in the range of experimental results reported in the literature.

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5.2 Research Project 2

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The main purpose of this project was to take one further step to improve the computational modeling of the fundamental process in CS, i.e., including the oxide layer and its breakage during the high velocity impact of a single particle onto a substrate. The following paper proposed a novel modeling method allowing modelling an explicit description of the breakage and partial removal of the nanometer-size oxide film that covers a micrometre-size metallic particle.

In this paper, the importance of the effective plastic displacement, an empirically adjustable parameter that is calibrated with experimental data, in modeling of the oxide behavior and its brittleness was shown. A direct relationship between the breakage and removal of the oxide layer and the critical velocity was also revealed.

In addition, a qualitative comparison was performed between a microscopic image and the numerical results, and it was shown that the final deformed shape of the simulated particle and the location of the metallurgical bonding were similar to the experiment. Moreover, the model was able to predict the gap between the particle and

the substrate around the south pole, which have been reported frequently in CS literature.



A Numerical Approach to Study the Oxide Layer Effect on Adhesion in Cold Spray

Saeed Rahmati¹ · Roberto G. A. Veiga² · Alejandro Zúñiga² · Bertrand Jodoin¹

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Abstract Due to the high strain rate deformation of particles in cold spray (CS), in situ investigation is challenging. It has been shown that metallurgical bonding is one of the main adhesion mechanisms of particles during coating buildup. Although several numerical studies have been done to study CS particle impact, very few were able to predict the occurrence of bonding based on the process physics. In this study, a novel finite element method is proposed to predict the occurrence of localized metallurgical bonding in the CS process that accounts for the native oxide layer which covers copper particles. The predicted critical velocity of was compared to experimental data to validate the proposed model. In addition, it was shown that the predicted bonding locations at the particle/substrate interface are consistent with experimental observations. The oxide removal process during impact was observed, and its effects on particle deformation/deposition were explained. Moreover, the effects of the oxide thickness and the impact velocity on the particle deposition were investigated and compared with experimental data. This comparison again illustrated the ability of the proposed model in predicting the material behavior during the deposition process.

Keywords cold gas dynamic spraying < processing · cold spray < processing · cold work < processing · finite element modeling < modeling · modeling of splat

formation < modeling · process modeling < modeling · particle velocity < processing

Introduction

Cold spray (CS) is a unique deposition method in which solid particles adhere to a substrate after high-velocity impact while maintaining relatively low temperature during their flight (Ref 1). It has been used as a cost-effective technique to produce dense metallic coatings, to repair damaged engine/aircraft parts and also as an additive manufacturing technique (Ref 2, 3). Metallurgical bonding and mechanical anchoring are the main adhesion mechanisms involved in CS (Ref 4). Mechanical anchoring occurs when the impacting particles are physically trapped in superficial imperfections of the substrate (Ref 5, 6). Metallurgical bonding, on the other hand, involves the formation of atomic bonds between the particles and the substrate. It requires that two oxide-free metallic surfaces be put in direct contact under a sufficiently high localized pressure (Ref 3, 4). Therefore, the innate oxide film on the metallic surfaces must be broken and at least partially removed for metallurgical bonding to occur (Ref 7).

In CS, it is widely acknowledged that the plastic deformation occurring at high strain rates (up to 10^9 s^{-1}) may result in partial removal of the native oxide layer. However, the detailed mechanisms of the in situ oxide layer removal process are still investigated. The large kinetic energy of the particles prior to the impact onto the substrate results in severe local plastic deformation of both the particle and the substrate. Metallic oxides are intrinsically brittle and therefore unable to undergo such large plastic deformation. As shown experimentally in the cold welding (CW) process (Ref 8), it is assumed that in CS, the

✉ Saeed Rahmati
saeed.rahmati@uottawa.ca

¹ Cold Spray Research Laboratory, University of Ottawa, Ottawa, ON, Canada

² CECS, Universidade Federal do ABC, Santo André, SP, Brazil

oxide layer is broken into many debris during the deformation, creating gaps that expose the fresh material (Ref 3, 4, 9–11). Numerous studies have suggested that adiabatic shear instability (ASI) is responsible for the oxide layer removal/clean up of the metallic surfaces (Ref 12–20) while some have shown that this cleaning allowing metallurgical bonding can happen without the occurrence of adiabatic shear instability (Ref 10, 21, 22). Experimental results from detached particles have established that bonding does not occur *a priori* in the jetting zone where ASI is predominant (Ref 23–26). It was suggested that the brittle layer removal process in CS follows a similar pattern as found in CW (Ref 10, 23, 27, 28). Despite the differences in theories about the oxide layer removal process, all studies agree that metallurgical bonding in CS requires intimate contact between oxide-free surfaces.

Direct observation of the oxide layer removal process during high-velocity impacts is beyond the capabilities of current experimental techniques. To circumvent these limitations, modeling appears as a good alternative for understanding the deposition process in CS. Up to now, several studies have been performed to include the native oxide layer on the particle using different numerical approaches such as Lagrangian (Ref 29, 30) and Eulerian (Ref 11). Due to the numerical limitations of these methods, the minimum thickness of the modeled oxide layer was between 30 and 100 times thicker than the real thickness of the native oxide film. In addition, only one element in the thickness direction was responsible to define the failure behavior of the oxide layer, which clearly affects the precision and resolution of the results. In a previous study (Ref 28), the effects of brittle layer on the metallurgical bonding were investigated using molecular dynamics (MD) simulations. In that work, a simplified, generic ductile core/brittle shell model was used to simulate at the atomistic scale the breakage and removal of a chemically inert, brittle shell and the subsequent adhesion of a metallic nanoparticle onto a metallic substrate due to the formation of atomic bonds. Although MD simulations provide valuable physical information about the adhesion process, the simulated particles must be small, orders of magnitude smaller than the actual particles in CS, for the simulations to be feasible. This hinders the use of MD as a predictive tool.

While finite element method (FEM) lacks the atomic resolution of MD, it allows modeling single particle impact in the micrometer scale found in CS experiments. If the material's parameters and the deformation behavior model are sufficiently accurate, FEM becomes a powerful computational technique to predict the evolution of the deposition process in CS (Ref 23, 31–37). In one study (Ref 38), the metallurgical bonding theory proposed by Bay et al. (Ref 8) was implemented in the FEM. The model did not

explicitly consider the oxide layer effect on the metallic bonding. The oxide film was modeled implicitly as the oxide layer removal was dependent on the surface deformation, and bonding was established only for elements reaching a prescribed deformation level (obtained from CW experimental data) while also experiencing a high localized pressure. All parameters used in that study were taken directly from the CW literature (Ref 8, 39). The critical velocity of aluminum, copper, and nickel particles was predicted, and it was shown that results matched well with the CS experimental data. In addition, the proposed model was able to predict and show the localized metallurgical bonding at the interface between particle and substrate. The occurrence of temporary atomic bonding was also revealed in that study. However, the model was unable to show the *in situ* breakage/removal of the oxide layer during the impact.

In this work, a step further is taken to improve the computational modeling of the elemental process of CS, i.e., including the oxide layer and its breakage and removal after high-velocity impact of a single metallic particle to a metallic substrate. The proposed FEM model provides an explicit description of the breakage and partial removal of the oxide layer that covers a micrometer-sized copper particle. This oxide removal in certain areas promotes local metallurgical bonding and ultimately dictates whether the particle adheres or not. A key aspect of the model is the parameterization of the brittle oxide layer in order to reproduce the available experimental data. Of special importance is the effective plastic displacement, an empirically adjustable parameter that is calibrated to model the oxide layer as mostly brittle. With the best set of material parameters and effective plastic displacement, the model allowed establishing a direct relationship between the breakage and removal of the oxide layer and the critical velocity. Moreover, a final deformed splat of the simulated particle that resembles the geometry and locations of metallurgical bonding of a copper particle as observed in microscope images is obtained. The effect of oxide layer thickness on adhesion was also addressed with the model.

Modeling Method

The deposition process of a single CS particle impacting on a substrate was studied using the commercially available FEM software ABAQUS/Explicit (Ref 40) with Lagrangian approach. A 3D geometry as shown schematically in Fig. 1 was used by assuming the impact of a perfectly spherical particle onto a flat substrate. The particle diameter was set at 12 μm . The oxide layer on the particle core is modeled using 3D shell elements with five integration points through the thickness. The oxide layer thickness was

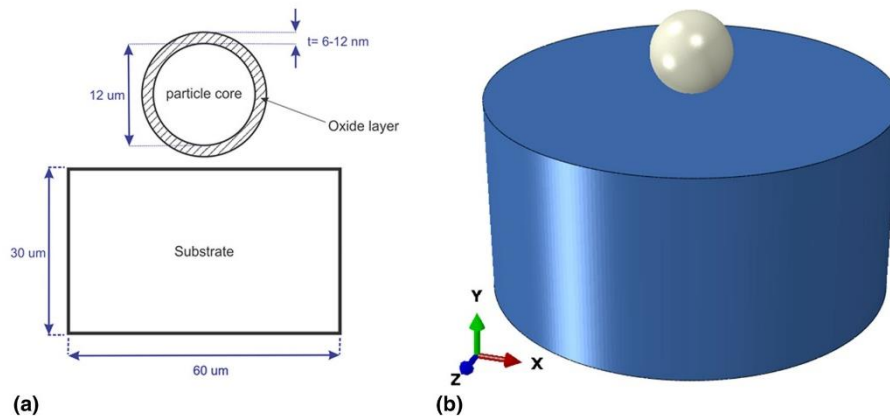


Fig. 1 (a) Schematic representation of the simulation setup, (b) The finite element model of single particle deposition in CS

set between 6 and 12 nm, as measured experimentally in (Ref 23). The substrate geometry was modeled as a cylinder with radius and height five times larger than the particle radius.

According to the literature (Ref 1, 19, 41), convergence of the final particle shape occurs by using mesh size equals to 1/50 of particle diameter. Therefore, the mesh size for the particle core and the substrate was set to 1/50 of particle diameter, while the element size for the brittle shell was set to 1/75 of particle diameter, to allow better resolution in displaying the brittle shell removal process.

The bonding between the particle core and the oxide layer was modeled using the tie constraint (Ref 40).

The native oxide thickness on the metallic particles is only few nanometers thick (Ref 23). In studies with atomistic views, it was shown that although this layer could not be plastically deformed easily like metals because of limited slip systems and also the strong directional covalent bonds of ceramics when compared to metallic bonds, it has some degree of ductility (Ref 42–44). Therefore, the oxide film possesses an important, non-negligible ductile character. Consequently, the Johnson–Cook failure model (Ref 45) was used as the damage initiation criteria (Ref 40) to simulate the failure of the brittle shell representing the oxide layers in this study. This method is the recommended technique for simulating progressive damage and failure of materials (Ref 40). For modeling the oxide response during the impact, the Johnson–Cook material model (Ref 46) which is available in ABAQUS/Explicit library is used. Furthermore, in a previous study (Ref 41), the Preston–Tonks–Wallace (PTW) material model (Ref 47) was implemented into ABAQUS/Explicit via VUHARD user subroutine (Ref 40). This subroutine is used to model the material behavior of the particle core and substrate.

Table 1 Material properties of copper (Ref 41)

Properties	Copper
Density (ρ_0), kg/m ³	8960
Specific heat (C_p), J/kg K	383
Melting temperature (T_m), K	1356
Shear modulus (G), GPa	45
Grüneisen's constant (Γ_0)	1.99
Speed of sound (c_0), m/s	3933
Hugoniot slope, s	1.5

In this study, both particle and substrate are assumed to be pure copper with the properties as shown in Tables 1 and 2 (Ref 41, 47). The materials parameters for the oxide layer were taken from (Ref 48). The initial temperature was assumed to be 300 K.

In order to model the damage behavior of the oxide layer, the Johnson–Cook criterion (Ref 40, 45) was used in combination with the linear damage evolution (Ref 40). The normal stress–strain behavior of a material experiencing damage is shown in Fig. 2(a). In this figure, σ_0 and E are the initial yield stress and the elastic modulus of the material, respectively, σ_{y0} and $\bar{\epsilon}_0^{pl}$ are the yield stress and the equivalent plastic strain at the onset of damage, and $\bar{\epsilon}_f^{pl}$ is the effective plastic strain at the failure, that is when the overall damage variable reaches the value $d = 1$. As illustrated in Fig. 2(a), for an elastic–plastic material with isotropic hardening, damage affects the material response in two ways: reduction in elastic modulus and reduction in the yield stress. The solid curve in this figure exhibits the damaged stress–strain behavior, while the dashed curve

indicates the material response in the absence of the damage.

The damage evolution law defines the rate of degradation of the material stiffness (Ref 40). The damage evolution was defined based on the effective plastic displacement ($\bar{u}^{pl}$) using the evolution equation as follows (Ref 40):

$$\dot{\bar{u}}^{pl} = L \dot{\bar{\epsilon}}^{pl} \quad (\text{Eq 1})$$

$$\dot{d} = \frac{L \dot{\bar{\epsilon}}^{pl}}{\bar{u}_f^{pl}} = \frac{\dot{\bar{u}}^{pl}}{\bar{u}_f^{pl}} \quad (\text{Eq 2})$$

where L is the characteristic length of the element, $\dot{\bar{u}}^{pl}$ and $\dot{\bar{\epsilon}}^{pl}$ are the effective plastic displacement rate and the equivalent plastic strain rate, respectively, $\bar{u}_f^{pl}$ is the effective plastic displacement at the point of failure, and $\dot{d}$ is the damage variable rate. In the linear damage evolution

law, the material stiffness will be fully degraded ($d = 1$) when the effective plastic displacement reaches the value $\bar{u}^{pl} = \bar{u}_f^{pl}$, as shown in Fig. 2b. The instantaneous failure (brittle behavior) will occur when $\bar{u}_f^{pl}$ is specified as zero (Ref 40). The case using $\bar{u}_f^{pl} = 0$ was tested, and the results are discussed in the “Results and Discussion” section. Application of the failure model for a given material requires the characterization of the $\bar{u}_f^{pl}$ (Ref 40). This parameter is mesh dependent, and its accurate value should be obtained experimentally. Finding the exact value for $\bar{u}_f^{pl}$ is beyond the scope of this study. The main objective is to propose an FEM method which is able to display the oxide layer removal process based on the physics of the process and be able to predict the particle critical velocity by considering the metallic bonding mechanism involved in the process. Therefore, several simulations were performed to find an acceptable range for this parameter. For this study, the range for $\bar{u}_f^{pl}$ was obtained between zero and 0.001. Results using this range were consistent with the literature: The thin oxide film is not purely brittle and the model should consider some ductility for this material. Overall, this parameter ($\bar{u}_f^{pl}$) has a significant effect on the failure and brittle behavior of the material. In the present study, the effects of this parameter on the failure behavior of the oxide layer are investigated.

Table 2 PTW material model parameters for copper (Ref 47)

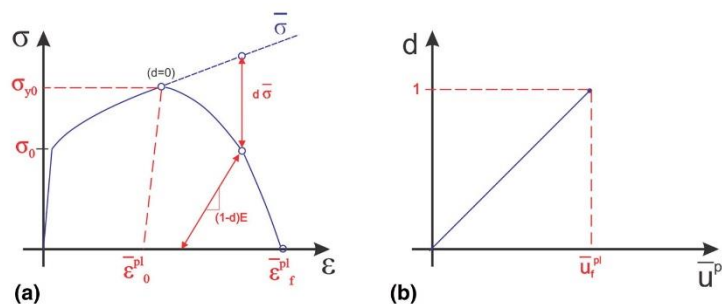
PTW parameters	Copper
Strain rate dependence constant (γ)	1e-5
Strain hardening rate (θ)	0.025
Strain hardening constant (d)	2
Yield stress constant at 0 K (y_0)	0.0001
Yield stress constant at melting (y_∞)	0.0001
Medium strain rate constant (y_1)	0.094
Medium strain rate constant (y_2)	0.575
High strain rate exponent (s_f)	0.25
Saturation stress at 0 K (s_0)	0.0085
Saturation stress at melting (s_∞)	0.00055
Temperature dependence constant (κ)	0.11
Atomic mass (M), kg	1.05521×10^{-25}
Shear modulus at 0 K (G_0), GPa	50
Material constant (D), GPa	3
Temperature material constant (T_0), K	165

Bonding Mechanism

In the current work, shell elements are selected to model explicitly a brittle shell representing the oxide layer around the particle. In addition, using the Johnson–Cook failure model allows to track the process of oxide cleaning on the particle surface.

Conrad and Rice (Ref 7) studied the metallurgical bonding between oxide-free surfaces of different FCC metals under an ultrahigh vacuum condition. They showed that the bond strength (σ_B) obtained between two perfectly

Fig. 2 (a) Schematic diagram displaying the stress–strain response of a material with progressive damage degradation (Ref 40), (b) Definition of linear damage evolution based on plastic displacement (Ref 40)



clean surfaces which are under contact pressure is approximately equal to that applied pressure, that is:

$$\sigma_B \cong P \quad (\text{Eq 3})$$

where P is the normal pressure applied to the surfaces.

The flow stress in the material is a function of strain rate. During rebounding, the strain rate is much lower than during the impact. Therefore, the bond strength during rebounding should be less than the bond strength in the impact process. According to the von Mises yield criterion (Ref 49), yield strength is a function of Cauchy stress tensor components (Ref 40, 49). Thus, if the strain rate decreases, the yield strength declines. It is assumed that both pressure and yield strength vary at the same rate as the strain rate. Consequently, the bond strength during the rebounding process can be assumed to change at the same rate as the yield strength. Thus, Eq. 3 can be rewritten as:

$$\sigma_B = P \cdot \left(\frac{\sigma_{y-h}}{\sigma_{y-c}} \right) \quad (\text{Eq 4})$$

where σ_{y-h} is the yield strength at the moment of the bonding, and σ_{y-c} is the current yield strength. For more detailed information regarding the bond strength formulation, see (Ref 38).

Implementation of Bonding Model

To implement the bonding mechanism into ABAQUS/Explicit, VUINTERACTION user subroutine which allows defining the interaction between contact surfaces is used (Ref 40). The contact interaction is modeled by the surface-to-surface penalty contact method. The definition of bonding in the penalty contact method was explained in detail in Ref. (Ref 38).

For the particle core, three kinds of elements in the contact region were defined, i.e., “Bonded,” “Never Bonded,” and “Debonded” elements. “Bonded” element means at least three out of four nodes of the element surface which is in contact are bonded. “Never Bonded” element means at least two out of four nodes of the element are not bonded. “Never Bonded” elements are not able to withstand any “negative” pressure (tension). However, “Bonded” elements are able to resist against “negative” pressure (tension) until the pressure is higher than their bond strength. When the pressure goes beyond the bond strength, the element status is changed to “Debonded.”

In the beginning of the simulations, the coordination of all shell elements was exported to an array with the dimension equals to the number of shell elements. During the simulation, for each iteration, when a shell element failed (local oxide degraded completely), the elements of the particle core surface which have similar coordination

were recognized and the normal pressure on those elements was checked. If the applied pressure on those elements was higher than their current yield strength, they were flagged as “Bonded” elements. The pressure must be higher than the yield strength to allow the fresh exposed material to extrude through the broken oxide film. The ratio between the normal pressure and the yield strength at the time of bonding (P/σ_{y-h}) of each flagged element was exported to an array. This ratio was calculated during the simulation to find the maximum strength during the deposition. The bonding quality (comparison between the bond strength and the negative pressure (or tension) as described before) was checked simultaneously during the deformation process when stored elastic energy of the elements is released (rebounding process).

The bond strength of each “Bonded” element is calculated by Eq. 4. Figure 3 shows the flowchart algorithm of the VUINTERACTION subroutine, and also the VUSLFD subroutine (Ref 40). The VUSLFD subroutine allows to have access to the material point data such as nodes’ coordination and stresses. During the rebounding process, due to the releasing of the stored elastic energy, a negative pressure (tension) applies on the bonded nodes (nodes of the “Bonded” elements). If the applied pressure is less than the bond strength of the nodes, the nodes remain as bonded nodes, otherwise, their status is changed to “Debonded” nodes. When at least two nodes of one “Bonded” element debond, the status of that element is changed to “Debonded” element.

Results and Discussion

Oxide Layer Effects on the Particle Deformation

The native oxide layer thickness on the particles is between few nm to tens of nm (Ref 23, 50). In order to study the effects of this thin film on the particle deformation, two simulation systems were performed; (a) one single particle impact without the brittle shell, and (b) one single particle impact with the (oxide) brittle shell. For the latter, the oxide layer thickness and the effective plastic displacement at the point of failure were set to be 6 nm and 0.001, respectively. The particle impact velocity was set to 500 m/s. After hitting the substrate, the particle undergoes significant flattening. Figure 4 displays the comparison between the final shape of particles and also the temperature distribution after the impact. As can be seen, the oxide layer did not have a noticeable effect on the final shape of the particles and both particles (with and without the oxide layer) exhibit similar plastic deformation and penetration depth. The temperature distribution is also similar for both

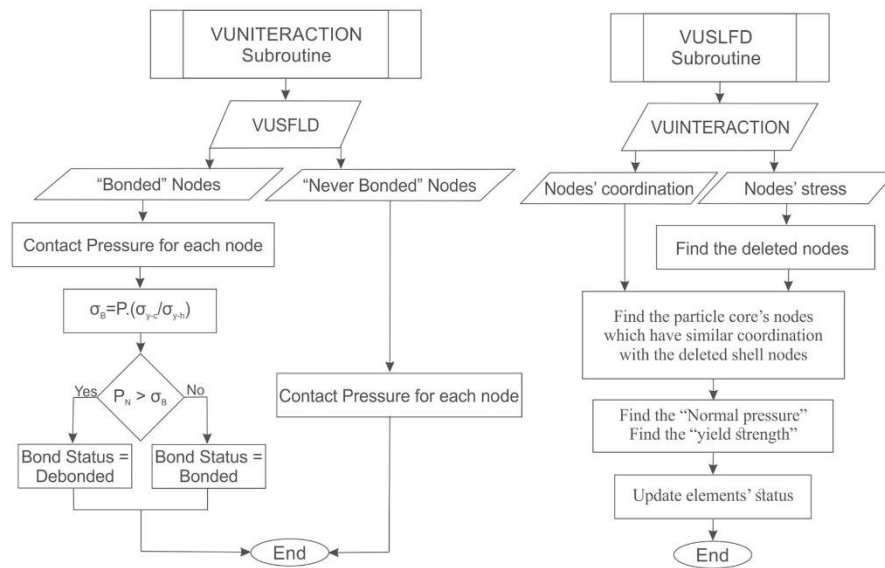


Fig. 3 Algorithm flowchart of the VUINTERACTION and VUSFLD subroutines

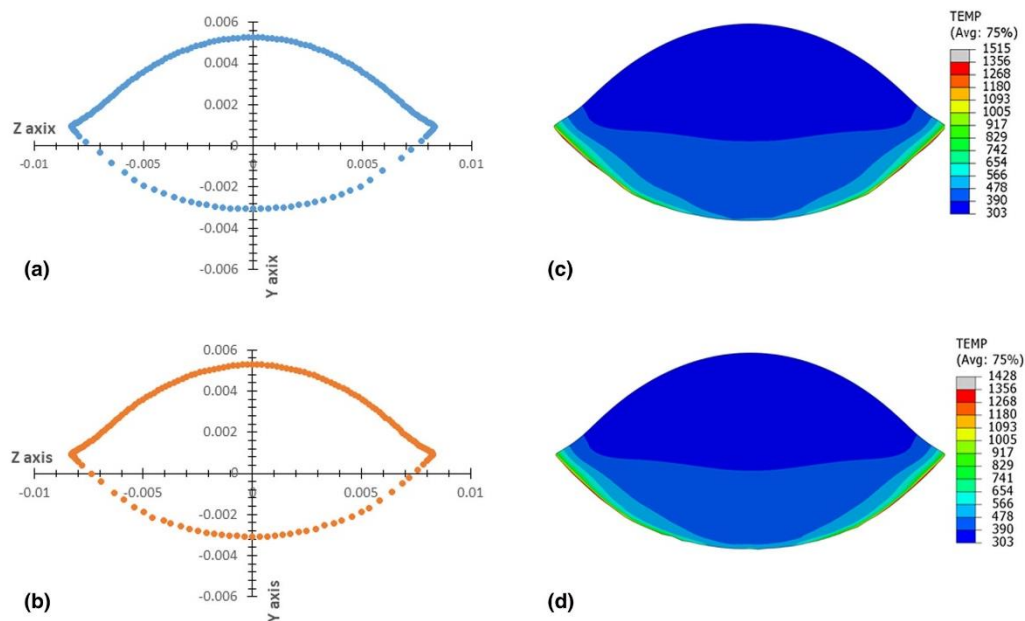


Fig. 4 Comparison between the final shape of (a) particle without the oxide layer, and (b) particle with the oxide layer, and temperature distribution for (c) particle without the oxide layer, and (d) particle with the oxide layer, after 40 ns after the impact at 500 m/s

particles at the end of the deposition process (Ref 40 ns in this case).

These results indicate that the particle core dominates entirely the deformation process: The material response (flow stress) of the oxide layer is not significant in the deformation of the oxide film because the kinetic energy of the particle core is sufficiently large that it can deform the oxide film easily and independently from the oxide material properties. The only parameter affecting the oxide failure behavior is the brittleness of the oxide, which is defined by the effective plastic displacement at the point of failure in FEM simulations. The effect of this parameter is studied and reported in the next section.

Brittleness Effect on the Oxide Failure

The effects of the effective plastic displacement at the point of failure, $\bar{w}^{pl}_f$, is investigated. As mentioned earlier, this parameter is the main factor affecting the deformation behavior of the oxide layer.

Oxides are well known to be brittle materials. Hence, for the first simulation setup, the $\bar{w}^{pl}_f$ is set to zero in order to impose a pure brittle behavior to the oxide layer. Figure 5 shows the oxide layer breakage and removal during the particle deposition at 350 m/s. As shown in this figure, the oxide film at the contact zone was almost removed completely at this relatively low impact velocity after 20 ns. This is not consistent with microscope observation of CS-deposited particles, where evidence of bonding is restricted to the vicinity of the edges of the particle–substrate contact zone, showing no bonding at the particle south pole. Being incompatible with experimental evidence, setting $\bar{w}^{pl}_f$ to nonzero values (and thus adding some ductility to the oxide layer) was necessary in our attempt to model the expected failure behavior of the shell.

Additional simulations were performed where $\bar{w}^{pl}_f$ was set to $\bar{w}^{pl}_f = 0.00025$, $\bar{w}^{pl}_f = 0.0005$, or $\bar{w}^{pl}_f = 0.001$. The predicted critical velocities were 385 m/s, 475 m/s, and 600 m/s for $\bar{w}^{pl}_f = 0.00025$, $\bar{w}^{pl}_f = 0.0005$, and $\bar{w}^{pl}_f = 0.001$, respectively. FEM results after 150 ns for impacts at 375 m/s for $\bar{w}^{pl}_f = 0.00025$ (thus at a velocity lower than critical velocity found for this value of $\bar{w}^{pl}_f$), 385 m/s for $\bar{w}^{pl}_f = 0.00025$, 475 m/s for $\bar{w}^{pl}_f = 0.0005$, and 600 m/s for $\bar{w}^{pl}_f = 0.001$ are shown in Figs. 6(a)–(d), respectively.

As shown in Fig. 6(a), no metallic bond was created with the substrate at this impact velocity, and the particle rebounded from the substrate, despite the fact that it significantly deformed, a feature already reported in a number of experimental studies (Ref 26, 51–54). By increasing the impact velocity to 385 m/s, the particle adhered to the substrate (the critical velocity for $\bar{w}^{pl}_f = 0.00025$), as shown in Fig. 6(b). It is interesting to note that increasing the ductile character of the oxide layer failure implies a higher critical velocity and, consequently, a higher level of deformation of the particle. For $\bar{w}^{pl}_f = 0.001$, both the jetting and the penetration in the substrate are much more pronounced than for $\bar{w}^{pl}_f = 0.00025$ and $\bar{w}^{pl}_f = 0.0005$. In principle, one could calibrate the effective plastic displacement at the point of failure to reproduce closely the experimental results with respect to the critical velocity. However, when direct comparison between modeling and experimental results is carried out, quantitative discrepancies may still arise from the assumptions used in the simulation setup that may not apply to a specific stock of powder particles used in the actual CS deposition. For instance, the oxide layer thickness of the powder particles can vary largely and be different from the shell thickness used in the model. In addition, the presence of impurities can change the mechanical properties of the powder material, which cannot be included in the simulations due to the lack of data. However, it is worthwhile to mention that the current simulated results (critical velocities), for all three values of $\bar{w}^{pl}_f$, are in the range of critical velocities reported in the literature (Ref 1, 17, 26).

Hassani-Gangaraj et al. (Ref 54) have measured precisely the critical velocity of copper powders upon impact with a polished surface finish copper substrate. They reported that the critical velocity of copper powders with the diameters in the range of 11–15 μm is 580 m/s. In addition, they presented the coefficient of restitution (COR), i.e., the ratio between the rebounding and the impact velocity, as a function of impact velocity. Fig. 7 shows the comparison between those experimental results and the predicted COR for 12 μm copper particles. The calculation method of the COR for numerical results was explained in detail in (Ref 38). As can be seen in Fig. 7, the proposed model was able to reproduce the material behavior trend similar to the experiment. The COR is

Fig. 5 Oxide layer deformation and breakage during the impact process at 350 m/s by using $\bar{w}^{pl}_f = 0$ (brittle behavior prediction)

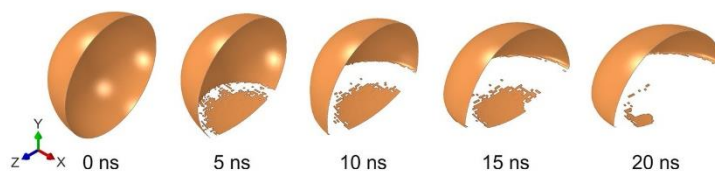


Fig. 6 FEM results after 150 ns corresponding to impact at (a) 375 m/s, where particle rebounded completely using $\bar{u}^{pl}_f = 0.00025$, (b) 385 m/s, particle bonded to the substrate using $\bar{u}^{pl}_f = 0.00025$, (c) 475 m/s, particle bonded to the substrate using $\bar{u}^{pl}_f = 0.0005$ and (d) 600 m/s, particle bonded to the substrate using $\bar{u}^{pl}_f = 0.001$

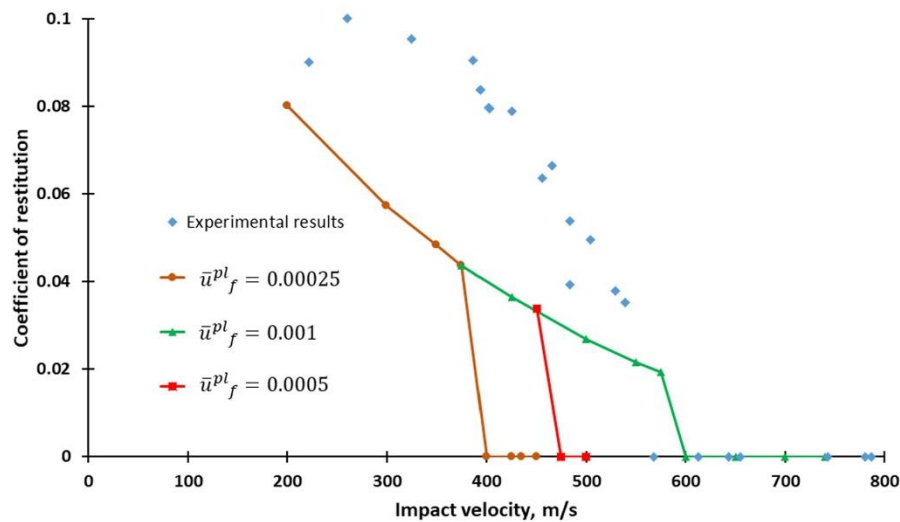
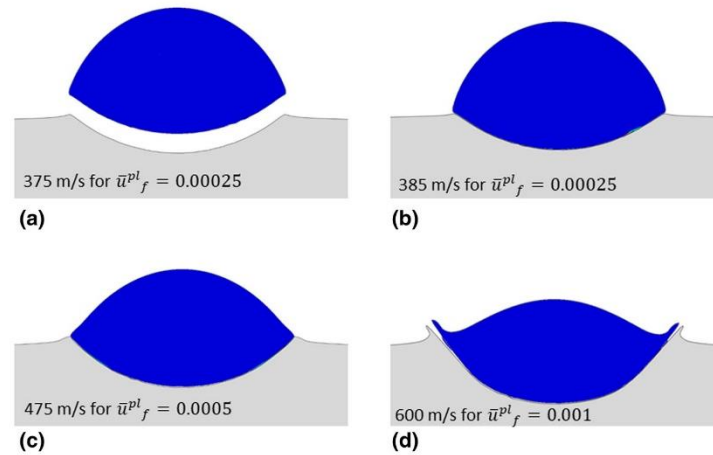


Fig. 7 Coefficient of restitution as a function of impact velocity for copper, experiment after Hassani-Gangaraj et al. (Ref 54)

decreasing with the increase in the impact velocity for both numerical and experimental results. The predicted COR values are not as accurate as for the case of aluminum particles (Ref 38), and this is attributed to the material properties used in the current work that are likely slightly different than the powder material properties. For the experimental results, the COR drops to zero at 580 m/s, and for the numerical results, it drops to zero at 600 m/s, 475 m/s, and 385 m/s for $\bar{u}^{pl}_f = 0.001$, $\bar{u}^{pl}_f = 0.0005$, and $\bar{u}^{pl}_f = 0.00025$, respectively. Figure 8 shows the comparison between the experimental value and the predicted

critical velocity using different $\bar{u}^{pl}_f$. As can be seen, the $\bar{u}^{pl}_f = 0.001$ could predict the critical velocity of the 12 μm copper particle relatively accurately with respect to the experimental result reported in (Ref 54). Visual inspection of simulation results, compared to microscopic images, can be an additional benchmark to assess the suitability of this model parameter to reproduce CS deposition of different materials.

The critical velocity of a material is undoubtedly one of the most important global parameters of the CS process. The ability to determine the critical velocity from material

parameters is therefore key to a computational model to be truly predictive. However, such a model, in order to

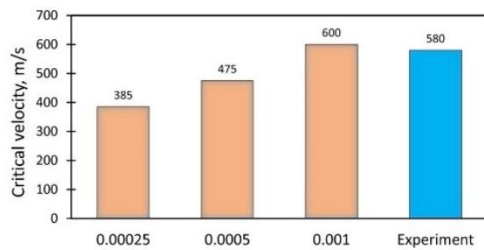


Fig. 8 Comparison of predicted critical velocities using different $\bar{u}^{pl}_f$ with experimental measured critical velocity for copper (Ref 54)

accurately describe the adhesion of a single particle to a substrate, should also be able to reproduce the geometry of the splat as observed in microscopic images. Figure 9(a) shows a scanning electron microscope (SEM) image of the cross section of a copper particle impacted onto a copper substrate (Ref 24). Figure 9(b) displays the FEM-simulated final deformed shape of a 12 μm copper particle after the impact to a copper substrate at 650 m/s, considering $\bar{u}^{pl}_f = 0.001$. Comparison between Fig. 9(a) and (b) suggests that the initial diameter of the experimental particle in Fig. 9(a) was also around 12 μm and according to King et al. (Ref 24), its impact velocity was around 650 m/s. By visual inspection, it is possible to see that not only the geometry of the simulated particle (due to the way it spreads over the substrate and penetrates it), but also its dimensions are in agreement with what is observed for the deformed particle after the actual impact. As one can see in

Fig. 9 High magnification views of particle/substrate interface, (a) SEM image a particle edge, (b) SEM image at particle south, (c) FEM image at particle edge, and (d) FEM image at particle south, experimental image after King et al. (Ref 24)

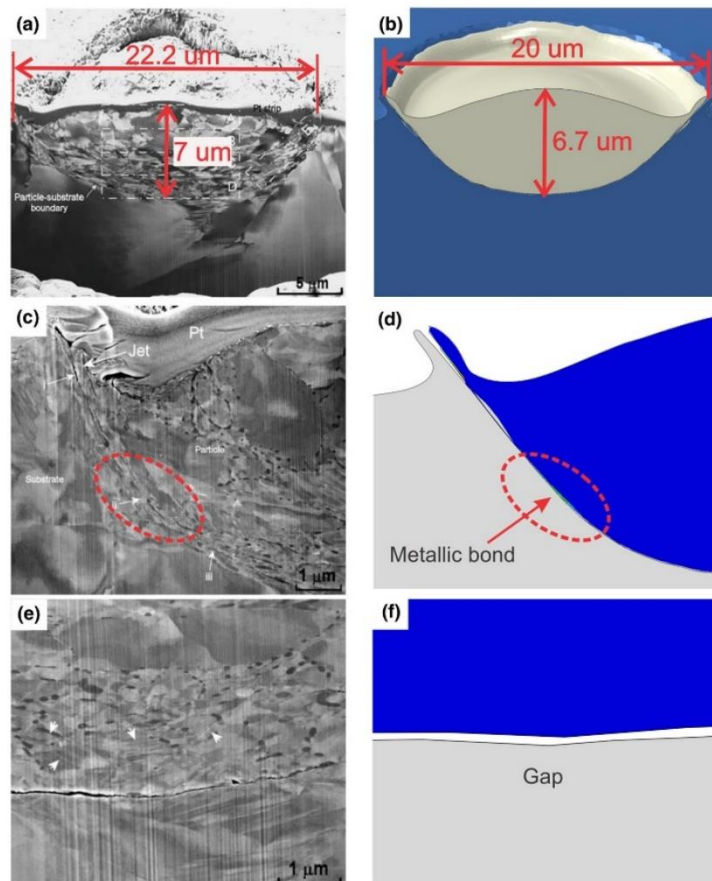


Fig. 9(c), metallic bonds formed near the edges of the particle–substrate contact zone. In Fig. 9(d), the bonding status of the elements in the simulated particle after the impact at 650 m/s also indicates that the region where metallic bonds were created is also near the edges of the contact zone, but not in the jetting, in agreement with the experimental results. Right at the particle south pole, a visible gap separating the particle surface from the substrate is shown in Fig. 9(e). This gap was also found in the numerical results, as see in Fig. 9(f), also in the center of the particle–substrate contact zone.

Another qualitative comparison between the predicted results and the experimental results from copper is presented in Fig. 10. Figure 10(a) shows the bottom view of a 12 μm copper particle after impacting onto a copper substrate at 700 m/s using $\bar{w}^{pl}_f = 0.001$. The bonded area and the oxide film remaining on the bottom of the particle are illustrated with arrows. Figure 10(b) displays an SEM image of the bottom of a copper particle (Ref 25). This image was taken after detaching the deposited particle from the substrate. The arrows in this image illustrate the dimple fracture and oxide film fragments on the bottom of the particle. Dimple fracture is an indication of metallic bonding on the particle bottom, and the pore-like area at the peripheral jetting zone shows the remaining oxide after the particle deformation. In Fig. 10, a similar qualitative behavior can be seen between the numerical results and the experimental observation which gives some more confidence about the proposed modeling approach. Moreover, other experimental studies investigating metallic bonding in CS also have reported similar results for the location of bonded area between the particle and the substrate (Ref 24, 55–57).

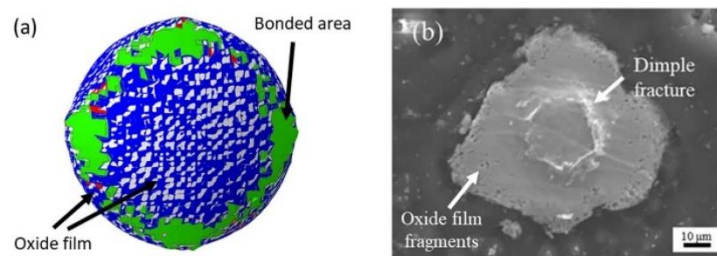
Removal of the Oxide Layer

Figure 11 depicts the mechanical response of a 12 μm copper particle after the impact onto a copper substrate at 650 m/s with $\bar{w}^{pl}_f = 0.001$. When the particle impacts the substrate at a high velocity, its kinetic energy ends up dissipated as heat, as well as resulting in severe

deformation at high strain rates. Upon impact onto the substrate, a shock wave arises at the particle/substrate interface. This shock wave creates a large pressure at the contact center (i.e., the particle south pole) and induces shear stress propagation along the lower half surface of the particle. Figure 11(a) shows the pressure distribution at the particle bottom at 0.5 ns after the impact. The pressure direction is normal to the contact center. As can be seen, the pressure at the particle south pole is higher than 8 GPa at that time. However, it is the shear stress that is responsible for the material deformation at the contact zone not the pressure (normal stress). As shown in Fig. 11(b), (c), by receding from the contact center to the particle edges, the shear stress is increasing. Therefore, the maximum deformation occurs at the particle edges. In addition, since the particle kinetic energy is decreasing with time, the shear stress decreases during the deformation, as shown in this figure. The resulting plastic deformation rises the material temperature, thus resulting in thermal softening of the material. Hence, it can be expected that, at the end of the deformation process, the maximum plastic deformation does not happen neither at the south pole nor at the particle edges: The maximum deformation occurs in a region where the ratio of the shear stress over material yield stress is maximum.

Maximum principal strain defines the maximum in-plane stretch of each element, while the equivalent plastic strain (or PEEQ) is a scalar quantity which is used to show the state of strain in an element when there is a multiaxial strain state (strain tensor). The maximum plastic strain (principal strain) distribution for the particle in Fig. 11 is displayed for the 6 nm oxide layer in Fig. 12(a), (b) using $\bar{w}^{pl}_f = 0.001$. The equivalent plastic strain (or PEEQ) is also shown for this particle in Fig. 12(c). The breakage in the oxide occurs where the deformation exceeded the failure threshold. As can be seen in Figs. 12(a)–(b), the oxide removal occurs in the region close to the particle flattened edges where the deformation is maximum but it is not exactly at that location where PEEQ is maximum (Fig. 12c), as also shown in (Ref 38). Therefore, PEEQ does not seem to be a criterion to locate the area where

Fig. 10 (a) Bottom view of a 12 μm copper particle after the impact with 700 m/s using $\bar{w}^{pl}_f = 0.001$ (bonded area and remained oxide film are shown with arrows), (b) SEM image of bonded zone and oxide film fragments (dimple fracture indicates the metallic bonding area on copper particle) (Ref 25)



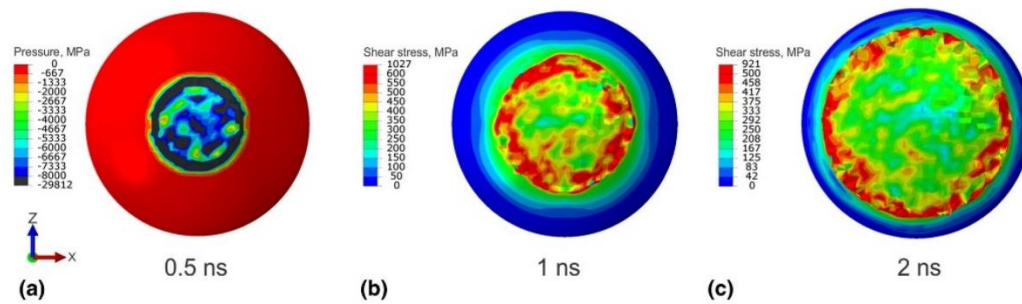
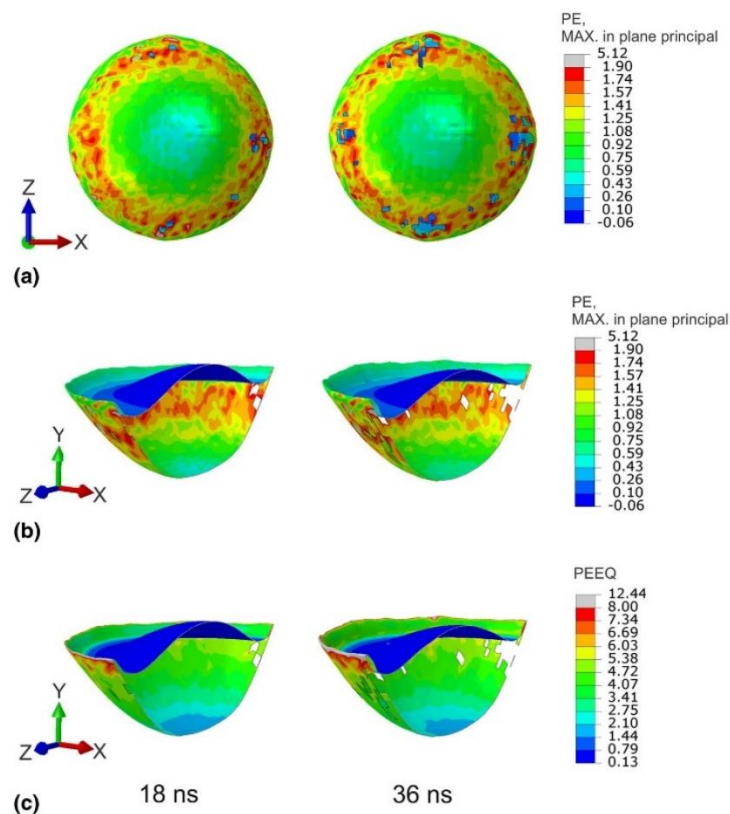


Fig. 11 (a) Pressure induced at the particle, (b, c) Shear stress distribution at the particle bottom

Fig. 12 Maximum principal in-plane plastic strain distribution inside the oxide layer, (a) Bottom view, and (b) Isometric view of the oxide layer, and (c) Equivalent plastic strain (or PEEQ) distribution inside the oxide layer, with 650 m/s using $\bar{w}^{pl}_f = 0.001$



metallic bonding is more favorable. In addition, the deformation at the particle south pole was not enough for breaking the oxide layer at this impact velocity.

The oxide layer removal process during the particle deposition is shown in Fig. 13(a). The impact velocity for this simulation was 650 m/s with $\bar{w}^{pl}_f = 0.001$, and the

oxide layer thickness was 6 nm (Ref 23). As can be seen, the oxide layer removal started very locally 12 ns after the impact. The oxide layer removal continued and produced an oxide-free ring-like region. However, the shell remained almost intact in the south pole of the particle, where the shear stress is minimum. This is consistent with

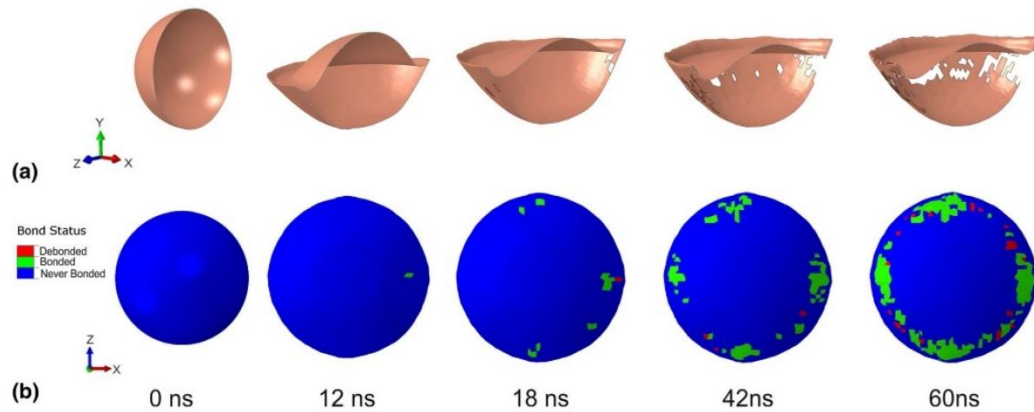


Fig. 13 (a) Oxide layer deformation and breakage during the impact process, (b) Status of bonding element on the bottom of the particle during the deposition process

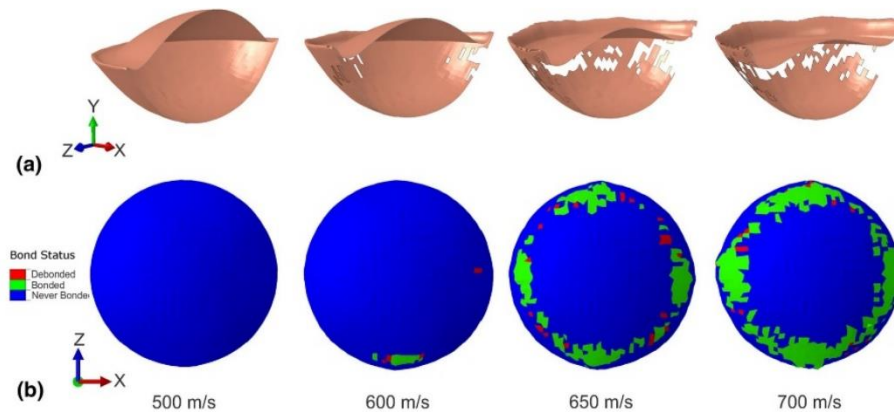


Fig. 14 The effect of impact velocity on particle deposition, (a) Equivalent plastic strain for the brittle shell, and (b) Status of bonding in elements on the particle surface at 40 ns after the impact

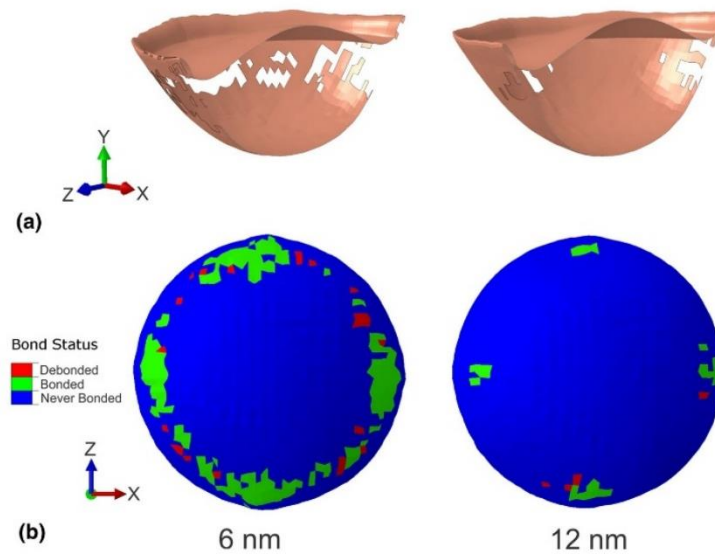
experimental observations that reported the absence of bonding at the particle south pole (Ref 23-25, 56, 57). Figure 13(b) shows the status of bonding at the contact zone on the particle surface. As illustrated, the bond strength of most elements was high enough to allow them to remain bonded during the rebounding process (green color). Only few elements created a temporary bond during the deposition and were debonded during the release of the elastic energy (red color). It means the pressure in the localized regions where the oxide layer was removed was high enough at this impact velocity to create a strong metallic bond between the particle and the substrate.

Figure 14 depicts the effect of impact velocity on the amount of breakage in the brittle shell 60 ns after the

impact. For these results, the thin film thickness and $\bar{u}_f^{pl}$ were 6 nm and 0.001, respectively. At 500 m/s, the deformation was not enough to break the oxide layer, and thus, the particle detached from the substrate completely with no metallic bonds. At 600 m/s, few oxide layer's elements (shell elements) were broken and the particle core could create some metallic bonds. By increasing the impact velocity, the oxide layer removal kept increasing, hence, more areas of oxide-free surfaces were available for metallic bonding, resulting in stronger adhesion between the particle and the substrate.

Razavipour et al. (Ref 23) studied the effects of oxide thickness (between 6 and 12 nm) on copper particle deposition. They showed that the critical velocity increases

Fig. 15 The effects of the brittle shell thickness on the particle deposition, (a) PEEQ distribution on the brittle shell, and (b) Status of bonding in elements on the particle surface



as the oxide layer becomes thicker. They also reported that the metallic bonded area on the particle interface (bond strength) decreases by increasing the oxide thickness. In CS, time is the limiting factor for material extrusion through the oxide gaps. The extrusion rate is a function of applied pressure over the material yield strength. Thus, in the case of thicker oxide, either the applied pressure at the contact zone must be higher or the area of the removed oxide film (oxide gap) must be larger (Ref 8, 23, 58). The kinetic energy for the deposition process only depends on the particle velocity. Increasing the impact velocity will rise both the applied pressure at the contact zone and the breakage area in the oxide layer. Figure 15 displays the bonding area for two 12 μm copper particles with 6 and 12 nm oxide thickness. The impact velocity for this simulation was 650 m/s using $\bar{\mu}^{\text{pl}}_f = 0.001$. As can be seen, the particle with the thicker oxide (12 nm) encountered less failure in the oxide layer and thus presents reduced bonded area compared to the particle with thinner oxide film, in agreement with the experimental findings.

Conclusion

A numerical model was used to investigate the effect of a thin oxide layer on the adhesion of copper particles to a copper substrate. By explicitly considering the presence of the innate oxide layer surrounding the metallic particles, known limitations of previous models are removed. The model provides insights on aspects of the adhesion process

in CS that are not directly accessible to experiments. A key parameter used to model the mechanical response of the oxide layer is the effective plastic displacement. With an appropriate value of this parameter, the model was able to reproduce the critical velocity and the final geometry of the splat of a micrometer-sized copper particle after impact and adhesion when compared to microscope images. A purely brittle oxide layer does not reproduce adequately experimental results; some level of ductility, as given by the choice of the effective plastic displacement, must be taken into account. Oxide breakage and removal allowed elements in the particle to be in contact with elements in the substrate, resulting in metallurgical bonding. The bonding zone is not located right at the flattened edges of the particle/substrate contact zone, where jetting is observed and the equivalent plastic strain is maximum. For the same velocity, with different oxide layer thicknesses, the breakage and partial removal of the oxide layer are hampered for the thicker oxide layer. As a consequence, adhesion requires a higher critical velocity, in agreement with experimental findings.

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5.3 Research Project 3

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The following project is the first step to study the microstructural evolution of FCC metallic particles during high velocity impacts using MD simulation methods. As mentioned in Chapters 3 and 4, the first objective was to find the required system size which allows to capture some mechanical quantities such as stress, strain and temperature that are meaningful for real materials. It was shown that nanoparticles larger than 10 nm began to behave similar to the micrometer size particles with respect to the mechanical responses. The predicted behavior was similar to the one that has been reported numerously in CS literature using FEM or other macroscale modeling methods.

In addition, it was shown that for particles larger than 10 nm, the onset of plastic deformation begins by heterogenous nucleation of Shockley partial dislocations at the particles' south pole, where particles impact onto the substrate. Dislocations' gliding, locking of the dislocations, and formation of a dense dislocation network by

increasing the plastic deformation which are the basic mechanisms of plasticity and hardening in metals were analysed and illustrated in this paper.

Moreover, the particle/substrate interface were investigated, and it was shown that the material jetting is formed in solid-state (below melting point), but due to the huge pressure that applied on that zone, which results a large plastic deformation at extremely high strain rates, this solid-state region behaves like a fluid.



Deformation of copper particles upon impact: A molecular dynamics study of cold spray



S. Rahmati^{a,*}, A. Zúñiga^b, B. Jodoin^a, R.G.A. Veiga^b

^a Cold Spray Research Laboratory, University of Ottawa, Ottawa, ON, Canada

^b CBCS, Universidade Federal do ABC, Santo André, SP, Brazil

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ABSTRACT

In this work, Molecular Dynamics simulations were performed to predict and provide detailed understanding of the deformation behavior of solid copper particles accelerated against a copper substrate. Simulations were carried out at an initial particle/substrate temperature of 300 K. The particles were assigned an initial velocity of 1000 m/s normal to the substrate surface, oriented in the [111] direction. The particles diameter was varied from 5 to 40 nm in order to assess changes in the deformation behavior due to size effects. For particles with diameters larger than 10 nm, the results showed well-defined patterns of dislocation activity associated with three distinct stages of deformation. The onset of plastic strain was localized at the flattened particles bottom, in the region of contact with the substrate, and characterized by the heterogeneous nucleation of Shockley partial dislocations. In the subsequent stage, a dense dislocation network was formed in the lower half of the particles, while the top of the particles remained undeformed. The plastic deformation of the top of the particles completed the process, resulting in the final flattened splat shape. High temperatures (above 1000 K) were observed at the particle-substrate interface, where fluid-like flow contributed to the formation of material jetting.

1. Introduction

Cold-Gas Dynamic-Spray or simply Cold Spray (CS) is a coating deposition method in which powder particles are accelerated towards a substrate by a relatively low temperature supersonic gas flow. Unlike thermal spray processes such as plasma spraying and HVOF spraying in which particle melting plays a vital role in material deposition, in CS the particles remain in the solid state throughout the coating formation process. Material deposition in CS is solely attributed to the high impact velocity of particles. The particle kinetic energy causes large plastic deformation upon impact at extremely high strain rates, i.e. around 10^9 s^{-1} [1–4]. It is generally accepted that successful particle bonding requires impact velocities higher than a critical velocity which depends on the temperature and material properties of both particle and substrate [1,5–7].

Since particle deformation occurs over a very short period of time (in the order of 10^{-9} s), in-situ investigations are very difficult [8]. In general, detailed experimental studies can take place only after the spray process is completed and usually rely on microscopy observations of particles cross-section in the as-deposited state [9–13]. Numerical simulation is a useful alternative to study “in-situ” the CS process in more details. Several Finite Element Analysis (FEA) approaches, such as

Lagrangian FEA [14–19], Eulerian FEA, Arbitrary Lagrangian Eulerian (ALE) [20–23] as well as Smooth Particle Hydrodynamics (SPH) [24–27] have been used to describe particle and substrate deformation behavior in order to provide enhanced understanding of the CS process. Many studies have shown that intense localized plastic strain, either with [1,2,5,28,29] or without [30] adiabatic shear instability, is necessary to achieve a substrate-particle metallic bonding. Moreover, highly localized interfacial melting can occur during impact [14], increasing metallurgical connectivity between particle and substrate.

Although FEA has been a useful tool to study CS systems at the microscopic level under the assumptions of continuum mechanics, it fully overlooks the mechanisms behind particle and substrate microstructure evolution that take place at the atomic scale. Therefore, if the goal is to shed light on those mechanisms, a different modeling approach such as Molecular Dynamics (MD) is required.

A few studies have reported single particle impact simulation using MD. Gao et al. [31,32] studied the factors influencing particle deposition in CS by modeling Au and Cu clusters with a few hundred atoms. They showed that higher initial velocity, temperature, and larger cluster improve the overall bond strength between the clusters and substrates. Moreover, Malama et al. [33] also concluded that increasing the particle size causes higher bond strength by modeling the impact of

* Corresponding author.

E-mail address: saeed.rahmati@uottawa.ca (S. Rahmati).

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Ti and Ni clusters onto the Ti substrate. The maximum number of atoms in the particle was about 2000 atoms in that study. Joshi and James studied the effects of spraying parameters also using small clusters with a maximum of 400 atoms as model systems and showed that, for impact angles other than 90 degrees, particles tend to rebound from the substrate [34,35]. Daneshian and Assadi [36] modeled with Lennard-Jones interatomic potential the impact of intrinsically brittle nanoparticles and indicated the role of particle size and particle impact velocity on deformation, fragmentation, and rebounding of the brittle particles.

Large plastic deformation [37–40] at extremely high dynamic rates makes CS a unique process to study. Copper, a ductile fcc transition metal, is a prototypical material in both CS experiments and multiscale models of single particle deposition. In this work, we report an atomistic investigation with MD of the impact of single copper particles at high velocities on a copper substrate. In order to characterize the deformation behavior of the copper particles at a fundamental level, our analysis focuses on the basic mechanisms of plasticity and hardening in metals, i.e., the multiplication, glide and locking of dislocations. Attention is also paid to the particle-substrate interface, where the high localized temperature leads to a different deformation mechanism.

2. Computational approach

Classical Molecular Dynamics consists of solving Newton's equations of motion for a system of discrete interacting particles [41], typically atoms. In this work, MD simulations were performed using the LAMMPS code [42]. The equations of motion were integrated using the velocity Verlet algorithm with a time step of 1 fs. The interactions between copper atoms were described by the widely used *Embedded Atom Method* (EAM) proposed by Daw and Baskes [43] as implemented in the interatomic potential developed by Mishin and co-workers [44]. In the EAM scheme, the total energy of a collection of atoms is described by the following equation:

$$E = \frac{1}{2} \sum \phi(r_{ij}) + \sum F_i \left[\sum \rho(r_{ij}) \right] \quad (1)$$

Here, $\phi(r_{ij})$ corresponds to the pairwise interaction between atoms i and j separated by the distance r_{ij} , F_i is the embedding energy of atom i , and $\rho(r_{ij})$ represents the contribution of atom j to the electron density at the location of atom i .

We considered in this study spherical, single-crystal copper nanoparticles. The atoms in the particles were arranged in a perfect face centered cubic (fcc) lattice with lattice parameter $a_0 = 0.36$ nm. In order to assess the influence of the particle size on the deformation behavior upon impact, the MD simulations were carried out for particles with diameters of 5, 10, 20, 30, and 40 nm (see Table 1), labelled sequentially particle 1, 2, 3, 4, and 5 henceforth. For each MD simulation, the particle was placed above the substrate with a separation of 1 nm. A model system in this initial condition can be seen in Fig. 1a. The substrate was also constructed as an fcc pure copper single crystal with its surface oriented in the [1 1 1] direction. As depicted in Fig. 1b, it was divided in three regions: (A) the top of the substrate, which consists of the surface directly exposed to particle impact and several atomic layers below it; (B) the bulk region in the middle, also comprising several atomic layers that could be maintained under the

condition of constant temperature throughout the simulations, therefore used for thermostating when necessary; and (C) the bottom of the substrate, a pseudo surface formed by six atomic layers of immobile atoms, which prevents the substrate to be rigidly displaced due to the particle impact. In addition, the thickness for regions A, B, and C are shown in Fig. 1b for particle 5. The thickness for regions A, and B are varied by particle size (smaller for smaller particles). Periodic boundary conditions were employed in the directions perpendicular to the substrate surface and open boundary conditions in the direction normal to it.

Before modelling the impact, each particle-substrate system was equilibrated in the NPT ensemble for 20 ps at 300 K and the pressure in the substrate in directions perpendicular to its surface was relaxed down to zero [45,46]. After equilibration, the velocity of the particle in the direction normal to the substrate was set to 1000 m/s. This velocity is expected to be above the copper critical velocity for adhesion and below the erosion velocity [2]. Moreover, according to Goel et al. who studied the impact of copper particle with different initial temperatures, this velocity is below the velocity for which the particle is expected to melt [47].

3. Results and discussion

3.1. Validating the adiabatic hypothesis

A predominant hypothesis in CS is that, due to the extremely high strain rate upon impact, the whole deformation process takes place without significant heat transfer [1,5]. In other words, it can be seen as a quasi-adiabatic process in which the particle-substrate system undergoes a rapid and localized increase in temperature. To verify whether this condition holds in the MD simulations, two different thermodynamic regimes were used to simulate the impact of the copper particle onto the substrate. In these preliminary simulations, particle 5 was chosen as the model system.

In the first simulation setup, the system was put in contact with a thermal bath maintained at 300 K through the region B shown in Fig. 1b. This thermally connected region (the “heat sink”) provided a way for the heat generated by the impact to flow out of the system. The equations of motion for the atoms in the region B were integrated in the NVT ensemble using the Nosé-Hoover thermostat [48], whereas the equations of motion of the particle and region A were integrated in the NVE ensemble. For the second simulation setup, an MD simulation was carried out in the NVE ensemble also for region B, therefore removing the thermal coupling and treating the entire system as thermally insulated. It aimed at simulating the particle impact as an adiabatic process. Since electrons are not explicitly treated by EAM potentials, thermal transport in the MD simulations was solely due to the phonon mechanism.

The particle and substrate temperatures were monitored for up to 100 ps after the impact. As a consequence of the high particle initial velocity (1000 m/s), the dissipation of the particle kinetic energy, besides significant deformation, also resulted in a rapid increase in the total temperature of the system. Fig. 2 shows little difference between the temperatures in the thermally connected and the isolated system. This implies that the system, in the first case, remained far from the thermal equilibrium with the thermal reservoir, thus strongly suggesting that the deformation process indeed behaves as a quasi-adiabatic one. Henceforth, all the subsequent MD simulations considered only the NVE ensemble for the whole particle-substrate system at an initial temperature of 300 K.

3.2. Mechanical response and dislocation activity

From a macroscopic perspective, plastic deformation is usually described in computer simulations by continuum models, such as the Johnson-Cook model [49], which are typically solved by FEM

Table 1
Sizes of the model systems used in MD simulations.

ID	Diameter, [nm]	Number of atoms in the particle	Number of atoms in the substrate
1	5	5473	2,310,912
2	10	44,044	3,610,580
3	20	354,959	6,782,400
4	30	1,200,667	20,780,160
5	40	2,846,584	32,632,128

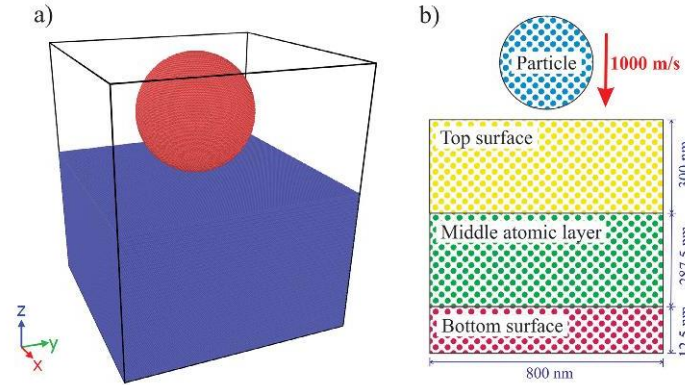


Fig. 1. a) Model system for particle 5 before impact and b) schematic representation of the MD simulation model for particle 5.

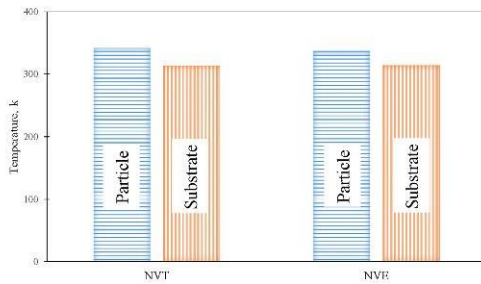


Fig. 2. Temperatures of the particle and substrate in MD simulations carried out in either the NVT or NVE ensembles.

[1,4,14,16,50]. The final splat is usually compared with microscopy observations and they are often in good qualitative agreement [25,38,51,52]. In these continuum models, the abrupt stop of the solid particle deposited in the CS process leads to a distinctive deformation pattern, where one can see significant particle flattening, with material

jetting at the edges of the zone in contact with the substrate. This deformation pattern, in FEM models, is related to the development of a stress state inside the particle, which can be spatially mapped.

At the atomic scale, on the other hand, the local components of the stress tensor can be obtained by proper spatial averages of the virial stress associated with each atom. The per atom stress component is calculated for the i -th atom as follows:

$$\sigma_{ab} = - \left[m v_a v_b + \frac{1}{2} \sum_{n=1}^N (r_{ia} F_{ib} + r_{ia} F_{ib}) \right] \quad (2)$$

where a and b are the spatial components (x , y , or z), the first term represents the kinetic contribution and the second term is the virial itself, with the sum being performed over the N neighbors of the i -th atom. Note that the atomic virial stress in Eq. (2) is presented in energy units. In order to convert to pressure units, the value of a stress component associated with an atom was divided by the corresponding atomic volume, taken as the volume of the Voronoi polyhedron centered at the atom.

Although the equivalence between the virial stress and macroscopic stress descriptions in continuum mechanics, such as Cauchy stress, remains somewhat controversial [54–56], the virial stress has been widely used to characterize the mechanical response of materials in MD

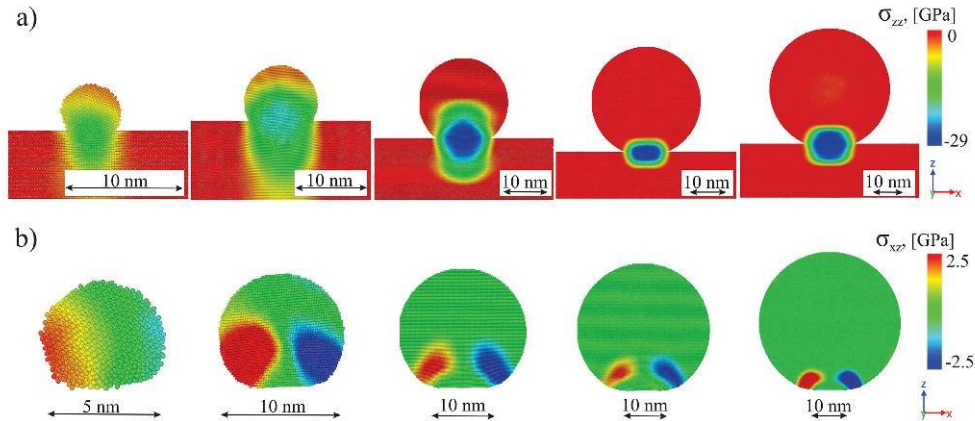


Fig. 3. a) Normal and b) shear virial stresses for particle 1 to 5, from left to right.

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simulations, provided that a proper spatial average is performed. The atomic stresses obtained with Eq. (2) were spatially averaged according to the procedure presented in Ref. [53]. Fig. 3 shows the distribution of the normal, σ_{zz} , and shear, σ_{xz} , stresses in particles 1 to 5 at 1 ps after the impact. As expected, a significant compressive stress with a magnitude of almost 30 GPa developed near the contact zone soon after the particle touched the substrate surface. Shear stresses also appear because atomic motion near the interface with the substrate is restricted in the normal direction but not in the directions tangential to the substrate. Fig. 3b shows the mapping of the shear stress in the particles, providing a clear picture of how it evolves depending on the particle size. By increasing the particle diameter, the largest shear stress becomes more localized near the edges of the particle-substrate contact region, a feature also observed in FEM simulation results of micrometer size particles [50].

When the high velocity copper particle impacted the substrate surface in our simulations, the first visible deformation it experienced was the flattening of its bottom surface in contact with the substrate, as can be seen in Fig. 3b. In order to characterize the onset of plastic straining expected at that location, the von Mises stress was calculated from the virial stresses by the well-known equation:

$$\sigma_{vM} = \sqrt{\frac{(\sigma_{11} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{11})^2 + 6(\sigma_{12}^2 + \sigma_{23}^2 + \sigma_{31}^2)}{2}} \quad (3)$$

The largest particle in this study was particle 5, with a diameter of 40 nm and comprising almost 3 million copper atoms. Fig. 4 depicts the evolution of the von Mises stress at the bottom of particle 5 just after the impact. Only the non-fcc atoms, as given by the Common Neighbor Analysis (CNA) algorithm [57], are shown for clarity. The highest von Mises stress value (around 27 GPa), which can be associated with the imminence of yield, was initially found at the edges of the particle-substrate contact zone and rapidly propagated inside the particle with further flattening. Its evolution is visibly accompanied by an increase in atomic disorder and the appearance of stacking fault defects (plaques of atoms identified as hcp by CNA) also localized at the bottom of the particle. These atomic level structural changes were another indication that the onset of plastic deformation occurred at the particle-substrate contact region, further corroborated by the dislocation structure analysis performed with the Dislocation Extraction Algorithm (DXA) [58,59] as implemented in the Ovito package [60].

As can be seen in Fig. 5, dislocation plasticity in particle 5 began within 1 ps after impact at the circular edge of its flattened bottom, where the heterogeneous nucleation of the very first Shockley leading partial dislocation segments with a Burgers vector of $1/6 \langle 112 \rangle$ was observed. These imperfect dislocations are known to be the main plasticity carriers in fcc metals with low and medium (the case of copper) stacking fault energies [61]. With increasing particle flattening, more partial dislocations were emitted from the particle surface and glided inside the particle. As the deformation proceeded at a very high strain rate, Fig. 5c and h shows that the bottom of the particle ended up fully occupied by a tangle of dislocations only 3 ps after it hits the

substrate. At this point, a large amount of dislocation junctions and several sessile segments, i.e., Lomer-Cottrell locks and Hirth dislocations with a Burger vector of $1/3 \langle 110 \rangle$, were produced by dislocation reactions, and other dislocation multiplication mechanisms were activated. Due to the high rate of dislocation creation in the vicinity of the contact zone, most of the crystal in the lower half of the particle deformed severely about 10 ps after the impact, resulting in a dense dislocation cloud, as one can see in Fig. 6. This high local dislocation density implied the reduction of the free path of glissile dislocations between obstacles to just a few Angstroms and contributed to strong localized strain hardening. In the final deformation stage, the upper half of the particle, which appeared as a perfect spherical dome over the dislocation forest and remained almost non-deformed until then, started to deform quickly too, with Shockley partial dislocations nucleating at different positions in the top surface and gliding downwards within the particle. Visually, significant deformation of particle 5 finished around 25 ps after impact. Fig. 7 shows that the initially spherical particle 5 ended up as a splat onto the substrate, with its interior filled by a dense dislocation network with an average dislocation segment length (taken as the ratio of the total dislocation length divided by the number of segments as given by DXA) of only 0.16 nm. Beneath the contact zone, associated with the emergence of a crater due to particle penetration, the dislocation structure in the substrate initially mirrored that of particle 5, and its evolution in the subsequent instants was related to the deepening of the crater.

As it can be seen in Fig. 8, the onset of plastic straining for particle 1, the smallest particle considered in this study, consisting of less than 5500 copper atoms, differed significantly from the largest one. The first dislocations, also Shockley leading partials, were observed arising at random locations at the particle surface and not at the edges of the flattened region where the particle impacted the substrate. A full dislocation network never established throughout the simulation time (20 ps), mainly because the leading partial dislocations, made of very short segments, were able to glide across the particle from one side to the other without encountering obstacles in their paths, disappearing at the particle surface before new dislocations were emitted. Therefore, particle 1 did not experience any significant strain hardening due to dislocation interactions. Additionally, the crystal structure of particle 1 was importantly modified by the introduction of planar defects by the leading partials, as seen in Fig. 9. Those stacking faults were not wiped out by the corresponding trailing partials which, most of time, did not have time to nucleate and glide. As a consequence, the planar defects, classified as hcp atoms, accumulated inside the particle in the course of the MD simulation as plaques parallel to $\{111\}$ fcc planes.

One can see in Fig. 10 the von Mises stress distribution in particles 2, 3 and 4 around 1 ps after the impact with the substrate. The highest von Mises stress was also found in the region where the bottom surface of the particles flattened in contact with the substrate, and their values were similar to the maximum von Mises stress in particle 5 at the moment it started to undergo plastic deformation. As discussed earlier for Fig. 3, a clear trend can be observed again in Fig. 10 in which the maximum von Mises stress in the first instants succeeding the impact

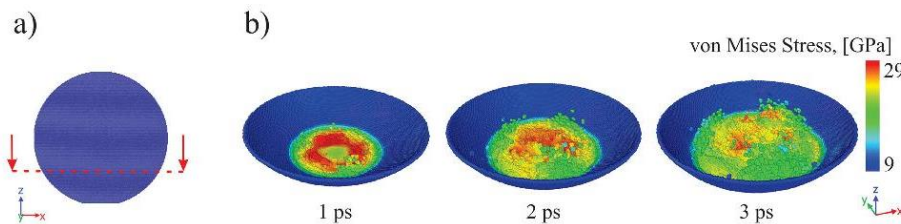


Fig. 4. The evolution of von Mises stress on atoms involved in the plastic deformation of particle 5 for the first 3 ps after the impact.

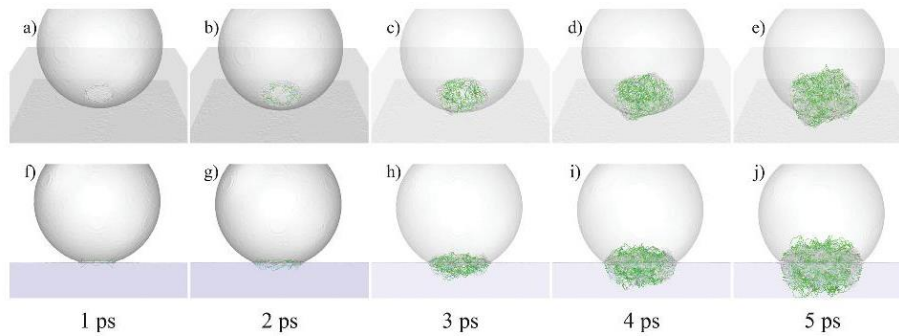


Fig. 5. Dislocation network evolution for particle 5 within 5 ps after the impact. From left to right, respectively: a-e) perspective and f-j) side views.

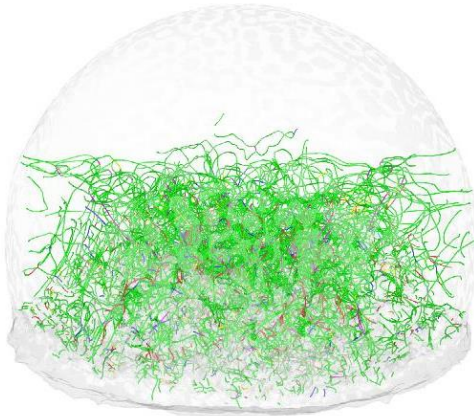


Fig. 6. Dislocation cloud at 10 ps after the impact for particle 5.

becomes more and more localized at the edges of the flattened bottom surface as the particle size increases, which is another clue for improving in spatial averaging by increasing the particle diameter (and, consequently, the number of atoms participating in the average). For particles 3 (around 355,000 atoms) and 4 (more than 1,200,000 atoms), the borders of the flattened bottom surface were also the sources of the first Shockley dislocations. It is noticeable, particularly for particle 5 but for particles 3 and 4 likewise, that a three-fold pattern developed in the stress distribution owing to the $[1\ 1\ 1]$ orientation of the particles

with respect to the direction normal to the substrate surface, as can be seen in Fig. 11. Once the particle deformation finished, particles 3 and 4 show flattened shapes with evidence of jetting in the border of the contact region as already shown for particle 5 and also as reported in FEM simulations for much larger particles. Seen from above, particles 3, 4 and 5 exhibited a three-fold shape, with three lobes, which was a consequence of the three-fold symmetry of the shear stress distribution. Particle 3 stopped flattening after about 14 ps of simulation, with an average dislocation segment length of 0.13 nm, whereas particle 4's average dislocation segment was 0.14 nm after reaching its final splat shape at 22 ps of simulation.

Somewhat more difficult is the characterization of the deformation behavior of particle 2 compared to the larger particles. For instance, the three stages of deformation upon impact that were described previously for particle 5 – and also observed in particles 3 and 4 – could not be clearly identified for particle 2. Indeed, particle 2 almost completely deformed just 1 ps after the impact. Regarding dislocation activity, as already observed for the largest particles, the very first leading Shockley partials also nucleated at the region in contact with the substrate as a consequence of the flattening of the particle bottom surface, as depicted in Fig. 12, though not exactly at the edges of the contact zone. Moreover, with about 44,000 atoms, the dislocation structure of particle 2 developed in a much more confined volume (about 1/64 of the volume of particle 5). In spite of the considerably high dislocation density in particle 2, the formation of a dense dislocation cloud with plenty of junctions, as seen for the largest particles, was not observed throughout the 20 ps of simulation. This is visually evidenced in Fig. 12 and might be a consequence of the short paths between the positions at the particle surface where several dislocation segments were emitted and annihilated without being temporarily blocked by other dislocation segments. Also by visual inspection, the particle stopped deforming around 7 ps after impact, when it reached its maximum flattening.

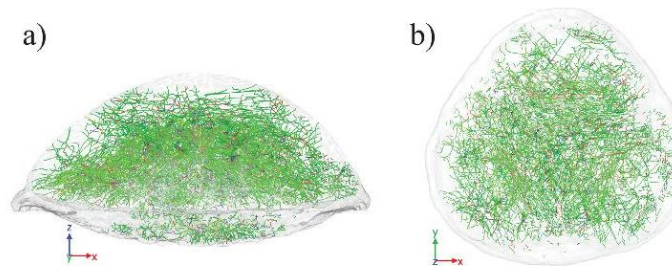


Fig. 7. Dislocation network at 25 ps after the impact for particle 5: a) side view, b) top view.

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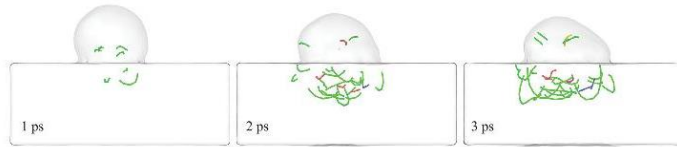


Fig. 8. Dislocation generation in particle 1 at 1, 2, and 3 ps after the impact.

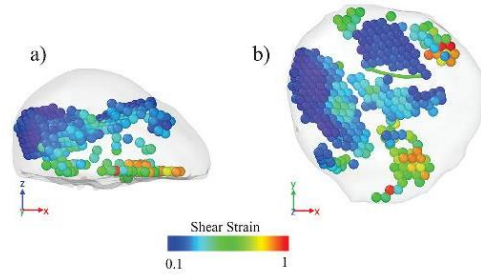


Fig. 9. Atoms in the stacking fault defects around 20 ps after the impact for particle 1: a) side view and b) top view.

Thereafter, the average dislocation segment length reported by DXA was about 0.11 nm. Compared to the largest particles, it confirms that, as one should intuitively expect, the larger the volume of a particle, the larger the average length of dislocation segments. Finally, Fig. 12e shows that the final three-fold shape, distinctive of the largest particles from a top view, was much less evident for particle 2.

According to DXA analysis, for all particles, around 80 percent of dislocation segments were Shockley leading and trailing partials bounding plaques of stacking fault defects. Fig. 13 displays the evolution of the dislocation density, taken as the ratio of the total dislocation length, given by DXA, with the volume of the particle, as a function of simulation time for particles 2 to 5. Particle 1 is not represented because, as aforementioned, a dislocation network never developed inside this particle throughout the MD simulation, only isolated dislocation segments. One can notice the very high dislocation densities – order 10^{17} m^{-2} – found inside the flattened copper particles after the saturation of their dislocation microstructures. This is compatible with the severe degree of plastic strain the particles experienced. Another important feature, directly related to the effect of particle size, is that the smaller the particle, the faster its dislocation structure saturates, with this saturation closely related to the end of particle flattening. Particle 5, for instance, attained its final shape about 25 ps after

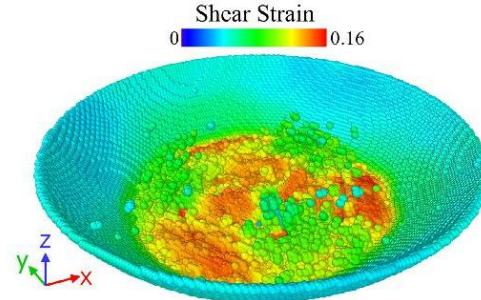


Fig. 11. Shear stress contour on atoms which are involved in plastic deformation after 3 ps for particle 5.

impacting the substrate, soon after it reached the highest dislocation density in the MD simulation ($4.4 \cdot 10^{17} \text{ m}^{-2}$). During the simulated time that followed this turning point, glissile dislocations continued to be able to glide and eventually annihilate either by arriving at the particle surface or reacting with other dislocations, while the number of new segments inserted in the particle volume decreased, thus resulting in a slow but seemingly constant decrease in the dislocation density.

3.3. Particle orientation effects

All particles, as previously stated, were oriented along the [111] direction with respect to the direction normal to the substrate, which seemingly had a strong influence on the final shape of the particles at the end of the deformation process. In order to examine the effect of the particle's crystal orientation on its plastic behavior, an additional MD simulation was carried out with particle 5 now oriented along the [100] direction, while maintaining the same initial velocity (1000 m/s). The substrate surface was kept in the [111] direction. The deformation behavior of particle 5 in this new orientation is displayed in Fig. 14, and it was characterized also by three stages. Due to the initial

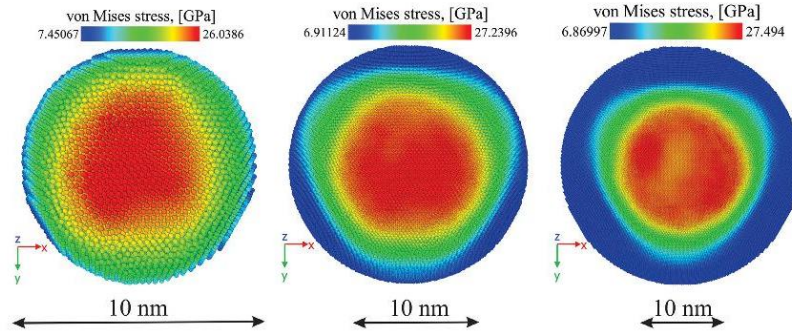


Fig. 10. von Mises stress distribution right after the impact for particle 2, 3, and 4, from left to right.

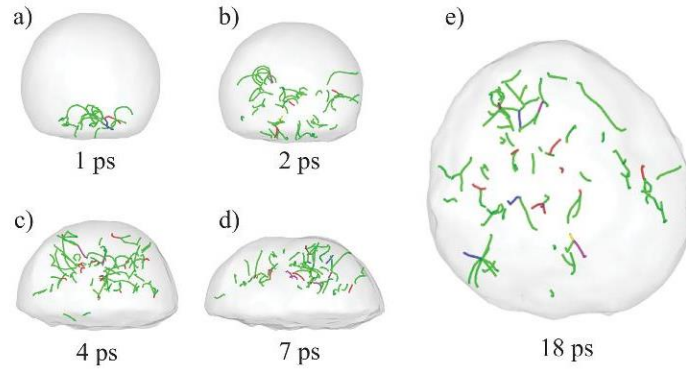


Fig. 12. Dislocation generation in particle 2 for a) 1, b) 2, c) 4, d) 7, and e) 18 ps after the impact. a-d are side view images and e is the top view image of the particle.

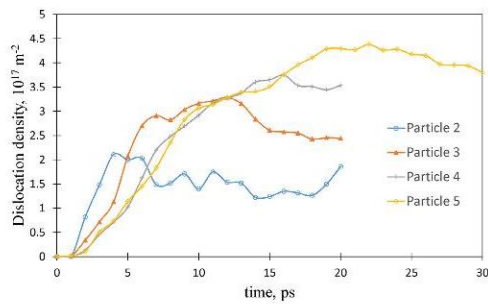


Fig. 13. Dislocation density as a function of time for particles 2 to 5.

flattening of the bottom particle surface, the first Shockley partial dislocations nucleated heterogeneously within the first picosecond after impact at the edges of the contact zone, where the particle touched the substrate. Next, with the increase in dislocation density caused by further flattening, the lower half of the particle became populated by a dense dislocation tangle. Finally, the upper half of the particle start to deform, and the whole particle flattened and spread onto the substrate.

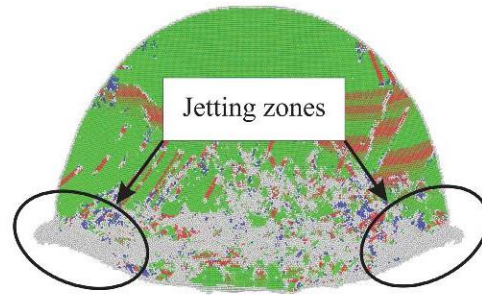


Fig. 15. Atomic structure around 15 ps after the impact. The colors show the atomic structures: green is FCC, red is HCP, blue is BCC, and white indicates atoms which do not have crystalline structure.

The deformation of reoriented particle 5 finished about 35 ps after impact and the maximum dislocation density, $3.6 \cdot 10^{17} \text{ m}^{-2}$, was lower than in the $[111]$ orientation. The change in orientation also changed the symmetry – now four-fold compared to the three-fold shape for the $[111]$ direction – of the shear stress distribution around the axis

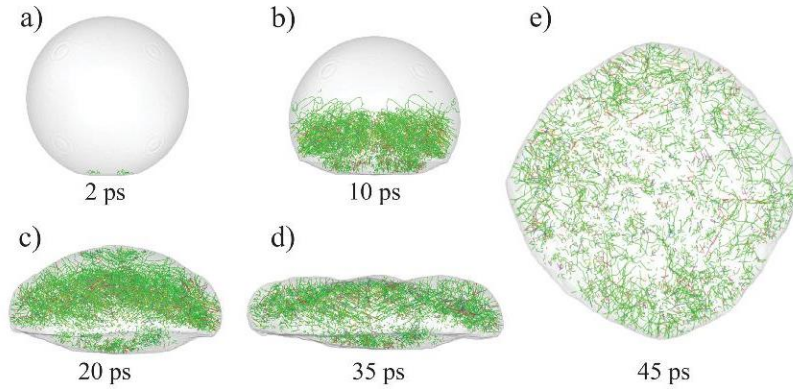


Fig. 14. Dislocation network in particle 5 oriented in the $[1\ 0\ 0]$ direction for a) 2, b) 10, c) 20, d) 35, and e) 45 ps after the impact. a-d are side view images and e is the top view image of the particle.

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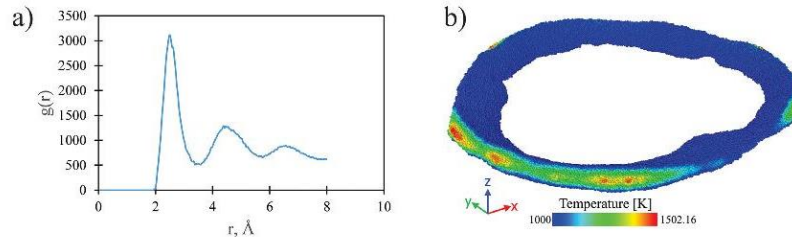


Fig. 16. a) Radial Distribution Function and b) temperature distribution for the jetting zone in particle 5 oriented in the [1 0 0] direction.

perpendicular to the impact direction, resulting in a final shape of the splat seen from above quite different from that of the particle oriented in the [1 1 1] direction, as one can see in Fig. 14e. From a side view, the shape of the reoriented particle 5 has remarkable differences with respect to the original orientation too.

3.4. Material flow at the contact zone

Taking particle 5 as the best representative of a CS particle in our simulations, we turn our attention to the evolution of the particle-substrate interface structure. As mentioned earlier, from the first moments of the impact, the highest deformation level is concentrated at the edges of the particle-substrate contact region. Upon impact, the atoms in the contact zone were subjected to severe forces, yielding relatively large displacements that cannot be related to normal plastic deformation. Indeed, as a consequence of such large displacements, the crystalline symmetry was broken in most of the particle-substrate interface. The atomic structure of the deformed particle around 15 ps after the impact is shown in Fig. 15. CNA shows that the jetting zone (white regions shown by arrows) is composed by atoms that do not have a crystalline structure identified by the algorithm. In addition to CNA, the Radial Distribution Function (RDF or $g(r)$) can also be used to verify the crystallinity of a collection of atoms and provide a global, averaged view of the atomic structure in the region of interest. The computed RDF for the jetting zone, seen in Fig. 16a, clearly indicates an amorphous structure. Fig. 16b in turn reveals that the highest temperatures, above 1000 K, were also localized in the jetting zone. By analyzing the atomic displacements over time, we observed that the atoms of the jetting zone started flowing much like in a fluid, with effective mass transport from the center of the contact zone towards the edges. This suggests that fluid-like flow might play a key role in the formation of the jetting zone during particle deposition. It should be mentioned that, in the short time simulated with MD, this amorphous jetting material was not able to recover a crystalline structure. Nevertheless, one should expect this to happen as the system slowly cools down and reaches thermal equilibrium.

4. Conclusions

In summary, MD simulations were performed to investigate the deformation of copper particles impacting onto a copper substrate to shed light on the basics of the CS process. Atomic interactions were described by an EAM potential. Both the particle and the substrate were thermally equilibrated at an initial temperature of 300 K. Five particles with diameters in the 5–40 nm range were assigned an initial velocity of 1000 m/s normal to the substrate surface. Analysis of the deformation behavior of each particle and underlying dislocation activity after the impact allowed us to identify, for the particles with diameter larger than 10 nm, three deformation stages. First, the onset of plastic deformation was characterized by the nucleation and glide of dislocations at the edges of the flattened particle bottom in direct contact with the substrate. Subsequently, with further deformation, a dense dislocation

network formed in the lower half of the particle, while the upper half remained almost undeformed. Finally, the top of the particle also deformed, resulting in the typical flattened shape of the splat, as observed in FEM simulations and microscopy observations. The maximum dislocation density in the severely deformed particles was very high, in the order of $10^{17}/\text{m}^2$. Temperatures higher than 1000 K were found at the particle-substrate interface, where local disorder and large atomic displacements provided an indication of fluid-like behavior, with material flowing from the center of the contact region towards its edges, ending up in a visible jetting zone.

CRediT authorship contribution statement

S. Rahmati: Investigation, Software, Validation, Visualization, Formal analysis, Writing - original draft, Writing - review & editing. **A. Zúñiga:** Conceptualization, Formal analysis, Validation, Writing - review & editing. **B. Jodoin:** Conceptualization, Funding acquisition, Writing - review & editing. **R.G.A. Veiga:** Conceptualization, Methodology, Formal analysis, Funding acquisition, Writing - review & editing.

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5.4 Research Project 4

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In this paper, MD simulations were performed to investigate the effects of crystal orientation and grain boundaries on plastic deformation of FCC particles during high velocity impacts. Two single crystal particles with different crystalline orientations, two simple polycrystal (i.e., bicrystal, and tricrystal) particles with inner walls (or grain boundaries) parallel and perpendicular to the shock wave, and a polycrystal particles with 64 randomly oriented grains were modeled.

The results showed that the deformation behavior and microstructural evolution of particles dependent directly on their initial microstructure. However, the interesting result was that the shear strain pattern was the same for all particles. This behavior indicates that the huge applied stress during high velocity impacts is such that it dominates the plastic deformation in the material and push the dislocations to move in some slip systems that are not the preferred ones.

In addition, it was shown that heterogenous nucleation of Shockley partial dislocations, and the solid-state amorphization are two main mechanisms in

deformation of particles. Moreover, phenomena such as recovery, crystallization, recrystallization, grain growth, twinning, and grain rotation were observed during the deformation of these FCC particles.

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Crystal orientation and grain boundary effects on plastic deformation of FCC particles under high velocity impacts

S. Rahmati^{a,*}, R.G.A. Veiga^b, B. Jodoin^a, A. Zúñiga^b^a Cold Spray Research Laboratory, University of Ottawa, Ottawa, ON, Canada^b CECIS, Universidade Federal do ABC, Santo André, SP, Brazil

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ABSTRACT

Material plastic behavior during deformation is affected by several parameters such as atomic structure, crystalline orientation, grain boundaries, impurities etc. In this study, molecular dynamic simulations were performed to provide a detailed understanding of the effects of grain orientation and grain boundaries on plastic deformation of FCC particles under high velocity impacts. Two single-crystal particles with different crystalline orientations, two simple polycrystal particles (bicrystal, and tricrystal) with inner walls parallel and perpendicular to the shock wave, and a polycrystal particle with 64 random grains were modeled. The results showed that the deformation behavior and microstructural evolution depended directly on their initial microstructure of the particles, whereas the resulting shear strain pattern was the same for all the particles. Phenomena such as recovery, crystallization, recrystallization, grain growth, twinning, and grain rotation were observed during the deformation of the particles. In addition, it was shown that heterogeneous nucleation of Shockley partial dislocations was the main mechanism at the onset of the deformation. Another important deformation mechanism was solid-state amorphization due to the densification of the dislocation network in certain regions of the particles, also associated with thermal softening effects.

1. Introduction

Material plastic behavior during high-velocity impacts, such as in the Cold Spray (CS) process has been investigated for decades [1–11]. CS is a coating method in which solid particles are propelled against a substrate at high impact velocities [12–14]. In CS, material deposition is only attributed to the kinetic energy of the powder particles, resulting in large plastic deformation on both particle and substrate at strain rates in the order of 10^9 s^{-1} [15,16].

Typical high strain rate experimental techniques such as gas guns, split Hopkinson bars, Taylor cylinder impacts, and plate impacts can explore high deformation rates up to 10^6 s^{-1} [17,18]. Remington [19] reviewed the high-energy pulsed lasers developed by Edwards et al. [20], which can be used to probe the material response at strain rates of 10^6 – 10^{10} s^{-1} and at pressures of hundreds of GPa up to several TPa [19]. However, in-situ experimental investigations on microstructural evolution of materials at high strain rates are very difficult to conduct. In this situation, molecular dynamics (MD), which is considered an idealized computational experiment [21], is a useful alternative to study material behavior in detail given the absence of experimental techniques. MD is a common method to predict cross slip and homogenous dislocation nucleation and is especially suitable to model the deformation at strain rates

higher than 10^6 s^{-1} [22,23] such as CS process. Up to now, several studies have been performed with MD to capture material response at high strain rate and high pressure regimes [24–33]. In crystalline materials, dislocation nucleation/movement controls the deformation mechanisms and the flow stress. Crystalline structures, and material defects (such as point defects, stacking faults, grain boundaries, twin boundaries, and volume defects [34]) are the main factors that affect the dislocation nucleation and movement. Yaghoobi and Voyiadjis [26] studied the underlying mechanisms of temperature and strain rate effects in FCC and BCC metals during high deformation rates. They showed that the dislocations interaction is the governing mechanism of material strength and that the effect of thermally activated dislocation motion is negligible in FCC metals. Moreover, Yaghoobi and Voyiadjis [27] studied the size effects of FCC crystals during compression deformation. Their results showed that the dislocation source length does not depend on the sample size in the extremely high strain rate deformation regime, and the related size effect mechanisms are not active anymore in that region.

Several studies have reported the single-crystal impact simulation using MD [1–3,35–41]. However, the systems used by Malama et al. [35], Joshi and James [36,37], Gao et al. [38,39], Oyinbo et al. [3], and Cheng et al. [41] were too small (few hundreds to few thousands

* Corresponding author.

E-mail address: saeed.rahmati@uottawa.ca (S. Rahmati).<https://doi.org/10.1016/j.mtl.2021.101004>

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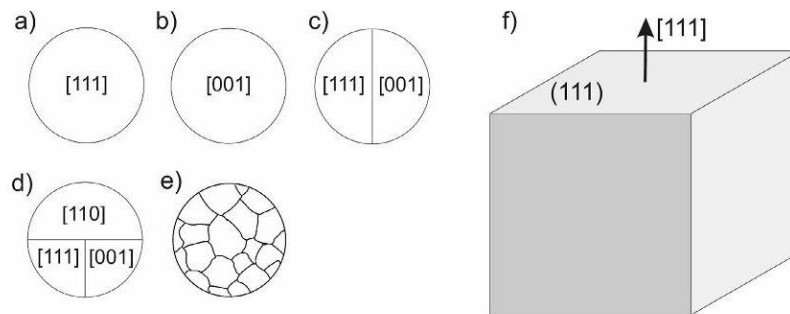


Fig. 1. Initial models for different particles and substrate used in MD simulations, a) particle [111], b) particle [001], c) bicrystal particle, d) tricrystal particle, e) polycrystal particle, f) substrate.

atoms) to be able to show the dislocation activity [1] which is the main mechanism for plastic deformation.

In CS, particle deformation is caused by the initial particle kinetic energy, with several parameters influencing the deformation behavior such as atomic structure, crystalline orientations, and material defects (impurities, dislocations, grain boundaries, etc.). In a previous study [1], the effect of particle size on the deformation of single-crystal FCC nanoparticles upon high velocity impacts were investigated. It was shown that for particles smaller than 10 nm, the deformation mechanism is not based on dislocation activities. In addition, the results showed that for particles larger than 10 nm, the onset of plasticity occurs by heterogeneous nucleation of Shockley partial dislocations from the particles bottom, in the region of initial contact with the substrate, followed by the evolution of a dense dislocation network. Moreover, plastic deformation at temperatures higher than 1000 K was observed at the particle-substrate interface; in this region, a fluid-like flow contributed to the formation of material jetting. In that study [1], the behavior of single-crystal particles was considered while in reality, particles are polycrystalline. Therefore, the main objective of this work is to investigate grain orientation and grain boundary effects on the deformation behavior of gold (FCC) particles in high-velocity impacts. In order to characterize the deformation behavior of the particles, we focused on the basic plasticity mechanisms, i.e. nucleation, multiplication, gliding and interaction of dislocations, and also amorphization during high strain rate deformation.

2. Computational approach

In this study, MD simulations were performed using the massively parallel code LAMMPS [42]. The velocity Verlet algorithm with a time step of 1 fs was used for the integration of the equations of motion. To describe the interaction between gold atoms, the interatomic potential developed by Grochola [43] was used in the simulations. This potential was implemented according to the formalism proposed by Daw and Baskes [44], the so-called Embedded Atom Method (EAM). EAM is widely used in MD simulations of metallic systems [1,2,24,26–28,30,32]. Gold is a noble metal that does not have a native oxide layer; consequently, the lack of an oxide layer surrounding the particle and covering the substrate has no impact on the results that will be presented in the next pages.

To investigate the effects of crystal orientation and grain boundaries on deformation mechanism, five spherical gold particles of diameter 40 nm impacting a gold substrate were considered. The gold atoms were arranged on an FCC crystal structure with lattice parameter 4.065 Å. Fig. 1 shows the substrate and the particles. Their orientations, when applicable, are shown with respect to the direction normal to the substrate. Two single crystal particles with [111] and [001] directions

parallel to the substrate's normal where modeled to study the effects of crystal orientation on particle deformation. In order to isolate the grain boundaries effect on plastic deformation, the simplest model of a polycrystal particle was used, i.e. a bicrystal particle, see Fig. 1. This particle was made of two hemispherical grains with the grain boundary oriented perpendicular to the substrate. For the sake of simplicity, the hemispheres were selected to have the same structural orientations as particles [111] and [001]. Therefore, the material behavior of those grains could be analysed individually (particles [111] and [001]) and then, the grain boundary effects can be illustrated by comparing the deformation behavior of the bicrystal with that of the single-crystal particles. Furthermore, the grain boundary in the bicrystal particle was almost parallel to the travel direction of the compression pressure wave induced in the material while being almost perpendicular to the wave itself. In order to study the effect of having a grain boundary perpendicular to the shock wave, another particle was modeled with three grains, the tricrystal particle. As shown in Fig. 1, the tricrystal particle has two inner boundaries, one perpendicular and one parallel to the substrate surface. The grains at the bottom of the tricrystal particle have the same orientation as the bicrystal particle. The top grain in this particle has a [110] orientation with respect to the direction normal to the substrate. Finally, a polycrystal particle was modeled with 64 random grains built by Voronoi tessellation to study the deformation behavior of a polycrystalline material upon impact. For each MD simulation, the particles were placed 1 nm above the substrate and given an initial velocity of 400 m/s normal to the substrate surface. The substrate was also constructed as an FCC pure gold single crystal, whose exposed surface was oriented in the [111] direction, as shown in Fig. 1. The total number of atoms for each modeled system was approximately 22 million atoms. Periodic boundary conditions were applied only to the directions perpendicular to the impact direction.

Each particle-substrate system was equilibrated in the NPT ensemble for 20 ps at 300 K before simulating the impact. Substrate pressure in the direction perpendicular to its surface was relaxed down to zero [45,46]. In order to simulate the impact, the ensemble was switched to NVE and the particle velocity was set to 400 m/s in the direction normal to the substrate. This impact velocity is within the range of spray velocities reported for gold [12,47].

In order to analyse the data obtained by MD [42], the OVITO software was used [48], which includes the following algorithms: Common Neighbor Analysis (CNA) [49], Polyhedral Template Matching (PTM) [50], Dislocation Extraction Analysis (DXA) [51,52], and grain segmentation [48]. CNA is able to classify atoms in the system according to the crystal structure they belong to. PTM provides a direct calculation of the local (per atom) lattice orientation. This algorithm identifies the local crystalline orientation by matching the local atomic order to determined structural templates. Moreover, the crystal orientation obtained by PTM

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can be mapped using RGB colors [50]. DXA is a computational method used to identify dislocations, including their types and line and Burgers vectors [51,52], and was used to investigate the dislocation evolution in our model systems. In addition, the grains were identified using the grain segmentation algorithm implemented in OVITO [48]. This algorithm is based on the PTM method to compute local lattice orientation. In contrast to the PTM algorithm, the grain segmentation method uses a hierarchical clustering algorithm to explicitly group atoms into grains. This method could discriminate between grains and subgrains [48]. For this study, the merge distance threshold parameter was chosen to be 19, value calculated by the algorithm in automatic mode.

The misorientation angle between the subgrains and the host grain was calculated by using the PTM algorithm. This algorithm was used to calculate the local lattice orientation for all the atoms. The computed lattice orientations are encoded as quaternions, where the first three components (x, y, z) represent the rotation axis and the last component (w) represents the angle of rotation around that axis. The PTM algorithm calculates the lattice orientation of each atom with respect to a template. Therefore, any changes in the orientation of the lattice during the deformation can be obtained by this method. The misorientation was determined as the angle between the rotation axis of each subgrain and the rotation axis of the host grain. The angle of rotation w was very similar for all the grains. The rotation axis of each subgrain was obtained by averaging the quaternion components of all the atoms of that subgrain (we averaged all the atoms due to the small size of the subgrains). For the host grain the rotation axis was calculated by only considering the atoms closer to the interface of each subgrain.

In order to calculate the temperature distribution in each particle during deformation process, for each atom, the velocity of the particle's center of mass was subtracted from the total atom velocity in order to avoid a spurious contribution from the translational motion of the particle. Afterwards, the local temperature at each particle point was estimated by a weighted tridimensional moving average over spherical volumes of diameter 3 nm centered at every atom in the particle. For each volume, the contribution of an atom was weighted according to its distance from the central atom.

3. Results and discussion

3.1. Total deformation

Each particle studied has a unique microstructure, which will affect its deformation behavior. Therefore, a simple way of comparing all different particles is by comparing their total deformation. The total deformation can be obtained as follows:

$$\epsilon_T = \frac{A - A_0}{A_0} \quad (1)$$

where A_0 and A are initial and final surface areas of the particle, respectively. The total deformation of each particle is shown in Fig. 2, illustrating the effects of crystalline orientation and grain boundaries on the total deformation. As it can be seen for particle [111] and particle [001], which are defect-free single crystals, the total deformation displays significant anisotropy, with the latter presenting a higher degree of deformation. Moreover, the amount of deformation for the bicrystal particle is in between that of the single crystal particles. This deformation behavior was expected since the bicrystal particle should show an average behavior of the two single crystal particles. The total deformation for the tricrystal particle is similar to the bicrystal particle. Finally, the polycrystal particle shows more deformation than the bicrystal and tricrystal particles. The differences in total deformation for each particle seems to be directly related to the internal structure of the particles (crystal orientation and presence of grain boundaries). Therefore, the effects of each factor is investigated in the next sections.

The temperature distribution on the cross section of each particle at 60 ps after the impact is shown in Fig. 3. Due to the high strain rate deformation after the impact, the generated heat associated to the plastic

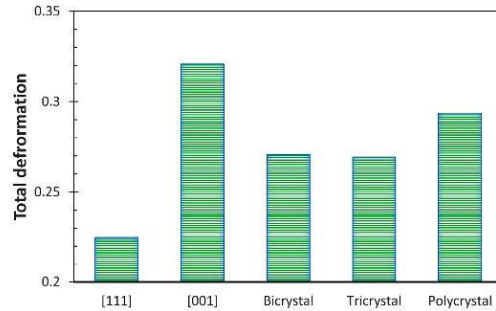


Fig. 2. Total plastic deformation for different particles.

deformation is not evacuated by conduction heat transfer. Regions with the highest temperature were found near the particle edges and close to the center of the particles. The top part of the particles was not yet deformed at 60 ps of deformation time, hence the temperature in these regions was not very affected yet by the deformation process.

Fig. 4 shows the atomic structure and shear strain distribution for particle [001] and the tricrystal particle at 60 ps. Green, and red colors indicate atoms with FCC, and HCP structures, respectively, while gray regions show atoms that have non-crystalline structure (or amorphous). Examination of Figs. 3 and 4 reveal that although the microstructural difference between the particles was large, the overall shear strain distribution (or shear strain pattern) were similar. It is well-known that the grain boundaries act as barriers to the dislocation movements [53–56]; however, it can be seen that they could not affect the overall shear strain pattern. In single-crystal particles (i.e. particles [111], and [001]), there is no boundaries or obstacle to inhibit the shear strain and the temperature distribution has an arrow-head shape in these particles. In the case of the bicrystal particle, the inner boundary was parallel to the initial shock wave travel direction, hence, it did not affect significantly the deformation pattern inside each grain. This resulted in a temperature distribution similar to that of the single-crystal particles. In contrast, the tricrystal particle has an inner boundary perpendicular to the travel direction of the initial shock wave; therefore, the shear strain pattern was localized more in the bottom grains. The polycrystal particle, which has more grain boundaries, exhibited a similar shear strain pattern to other particles. Multiple grain boundaries in this particle restricted the shock wave effects more, thus, the deformation is more localized near the impact zone.

3.2. Orientation effects on dislocation activity

The plasticity in FCC metals with low and medium stacking fault energies (as is the case of gold) is dominated by the glide of Shockley partial dislocations with Burgers vector $1/6 \langle 112 \rangle$ [34]. In our simulations, shortly after the impact, dislocation network evolution began by the nucleation of these Shockley partial dislocation segments from the bottom surface of the particle (where the particle hits the substrate), similar to what was shown in Ref. [1]. By continuing the deformation, more partial dislocations were emitted and glided inside the particle. As the deformation proceeds at a high strain rate, more dislocations were created and lead to the development of a dislocation network in the particle interior. Fig. 5a-b shows the dislocation networks for particles [111] and [001] after 130 ps (side and top views). Both single crystal particles ended up filled by a dense dislocation network. As already shown for the total deformation, the final shape of the single crystal particles also depends strongly on its initial crystalline orientation. From the side view, the top of particle [111] shows a hubcap shape while particle [001] exhibits a higher degree of flattening. From the top view, parti-

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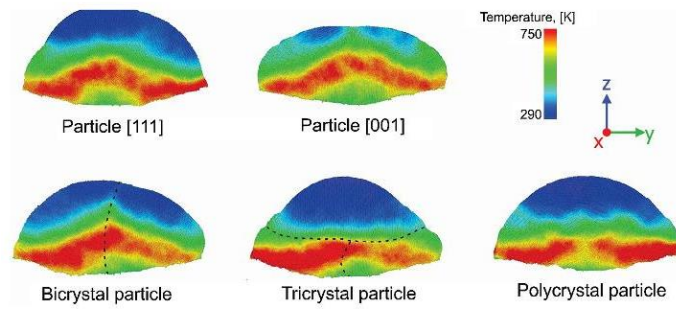


Fig. 3. Temperature distribution in particles at 60 ps after the impact (the maximum temperature in the polycrystal particle was around 830 K). Dotted lines show the grain boundaries in the bicrystal and tricrystal particles.

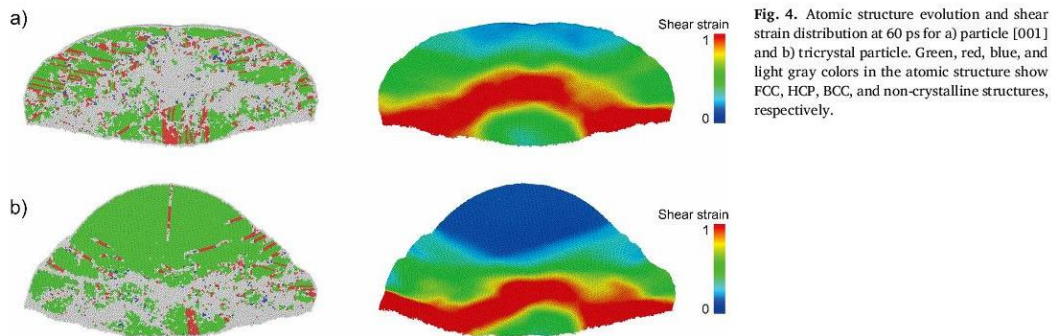


Fig. 4. Atomic structure evolution and shear strain distribution at 60 ps for a) particle [001] and b) tricrystal particle. Green, red, blue, and light gray colors in the atomic structure show FCC, HCP, BCC, and non-crystalline structures, respectively.

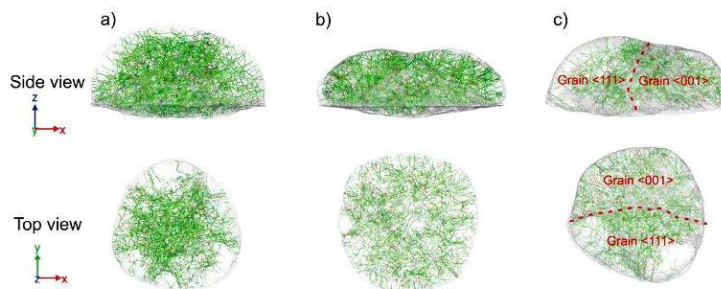


Fig. 5. Dislocation network and final particle shape after 130 ps for a) particle [111], b) particle [001], and c) bicrystal particle. Dotted lines show the grain boundaries in the bicrystal particle.

cle [111] has a three-fold shape, whereas particle [001] is more similar to a square. These manifestations of plastic anisotropy were expected owing to different orientations of the slip planes of the FCC metal with respect to the direction of the moving shock waves caused by the impact. The orientation-dependent plastic deformation of shocked single FCC crystals was extensively investigated with MD in previous works Refs. [57–59].

The final deformed shape of the bicrystal particle is shown in Fig. 5c. Taking each grain in separate, one can see that the deformation of one grain is significantly different from the other. This is a first hint that the deformation of individual grains in polycrystals may be greatly affected by their lattice orientation. From the top view of Fig. 5c, it can be seen that the [111]-oriented grain deformed into a three-fold shape, while the [001]-oriented grain deformed into a square shape, closely resembling the deformation geometry of their corresponding single crystal

particles. These results suggest that microstructure may play a crucial role in particle deformation and, consequently, adhesion.

In FCC crystals, the slip plane of Shockley partial dislocations is {111}. With respect to the direction normal to the substrate, particles [111] and [001] are orientated in $\langle 111 \rangle$, and $\langle 001 \rangle$ directions, respectively. Hence, {111} planes have different directions with respect to the substrate in these particles. Due to this, dislocations move in different directions with respect to the substrate normal direction. Fig. 6 shows the shear strain contour after 10 ps for particles [111] and [001], and the bicrystal (top view). For clarity, only non-FCC atoms (atoms involved in plastic deformation) are shown in this figure, which illustrates the effect of crystal anisotropy on the plastic deformation pattern. Shear strain in particle [111] has a three-fold pattern and a cross-sign pattern in particle [001]. By comparison between Figs. 5 and 6, it can be seen that the final shapes of particles [111] and [001] are related to their shear

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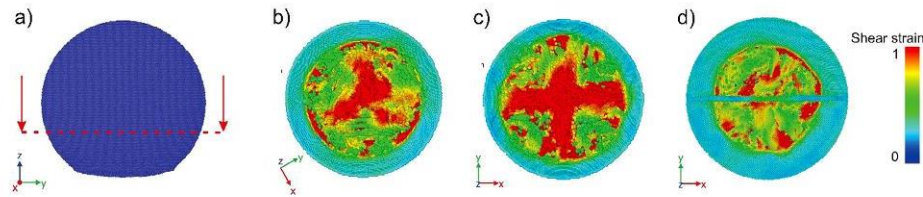


Fig. 6. Shear strain contour of atoms involved in plastic deformation after 10 ps. a) shows the cut line used for the top view of b) particle [111], c) particle [001], and d) bicrystal particle.

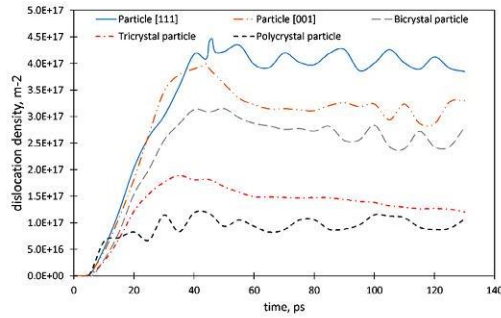


Fig. 7. Dislocation density as a function of time for each particle.

strain distribution symmetry. It is difficult to find a shear distribution symmetry for the bicrystal particle, Fig. 6c. However, Fig. 5c indicates that the inner boundary effect was not enough to change the shape of the individual grains when placed side by side with the corresponding single crystal particles.

The evolution of the dislocation density of all particles as a function of time is plotted in Fig. 7. The dislocation density is in the order of 10^{17} m^{-2} , which is large compared to quasi-static experiments. However, according to Yaghoobi and Voyiadjis [28], high strain rate deformation is mainly sustained through either large mobile dislocation densities or large mobile dislocation nucleation rates. High velocity impact results in shock waves propagating across the particle at or faster than the material sound velocity. When these shock waves reach the particle free surfaces or an obstacle like a grain boundary, they reflect into new waves. The new waves, which can be tensile (expansion) or compression waves, also propagated inside the particle in different directions. The encounter of two shock waves can result in constructive (increase the pressure) or destructive interferences (decrease the pressure). MD simulations reported in Ref. [60] revealed that a significant portion of the dislocations generated in shock compression is annihilated when the pressure decays, which can be the mechanism behind the oscillation of the dislocation density observed in Fig. 7. Dislocation density of particle [111] is higher than particle [001] while total plastic deformation of particle [111] is less than particle [001], as shown in Fig. 1. This means that there are other mechanisms involved in the deformation process as well. In a previous study [1], it was shown that large atomic displacements can occur during impact at high velocities. These large displacements cause local disorder and instability in the atomic structure, even resulting in the breaking of the crystal symmetry and the formation of an amorphous phase. Atoms in these amorphous regions of the system may show a fluid-like behavior when subjected to shear. This amorphization phenomenon can be induced by a high localized dislocation density, i.e., the disordered dislocation cores are so close to each other that the FCC crystal is locally destroyed [61–63]. The fraction of non-crystalline

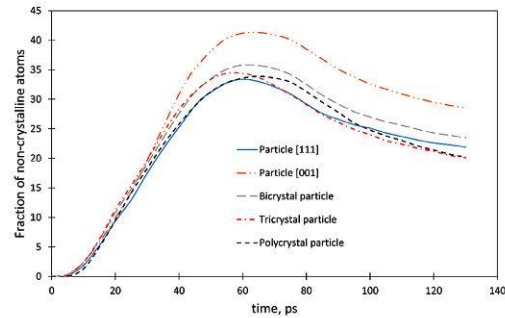


Fig. 8. Fraction of non-crystalline atoms during plastic deformation for each particle.

atoms during plastic deformation is shown in Fig. 8. As it can be seen in this figure, the fraction of non-crystalline atoms (or amorphous structure) increases with time until reaching a maximum (more than 30%) at around 60 ps for all particles and then starts to slowly decrease. This can be related to the localized density of dislocations, which could be high enough to directly induce solid-state amorphization [64,65]. MD simulations and theoretical methods have shown that a localized high density of dislocations can cause a significant atomic disorder and lattice strain, contributing to elastic softening and destruction of the crystalline structure [66–68]. Fig. 8 shows that the maximum difference in the fraction of amorphous atoms in particle [001] is around 8% higher than particle [111] at around 60 ps. As shown before, the plastic deformation is localized in the bottom part of the particles at this time. Therefore, this indicates that the large atomic displacements associated to the amorphous regions contributed more to the total deformation of particle [001]. For particle [111], it was dislocation nucleation and glide that had more allotment.

Figs. 9 and 10 show the atomic structure evolution of particles [111] and [001], respectively, during the deformation process. Permanent deformation began at the particle bottom and developed towards the center of the particle. Besides usual plastic deformation carried out by dislocations, a large non-crystalline region (in light gray) is observed during the deformation process for both particles. The deformation rate was higher in particle [001] than in particle [111]. As it was shown before, the dislocation density in particle [001] was higher than in particle [111] until 40 ps after the impact: more dislocations were nucleated and glided during the first moments after the impact in the particle [001], resulting in an extremely high dislocation density at the particle bottom. Consequently, a high local atomic disorder (amorphization due to a high density of defects) might have occurred. This amorphization also occurred in particle [111], but to a lesser extent compared to particle [001] since the deformation rate and the total deformation in particle [111] were lower compared to particle [001]. Af-

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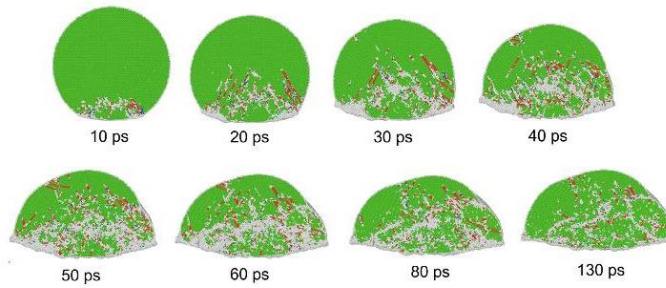


Fig. 9. Atomic structure evolution of particle [111] during impact. Green, red, blue, and light gray colors in the atomic structure show FCC, HCP, BCC, and non-crystalline structures, respectively.

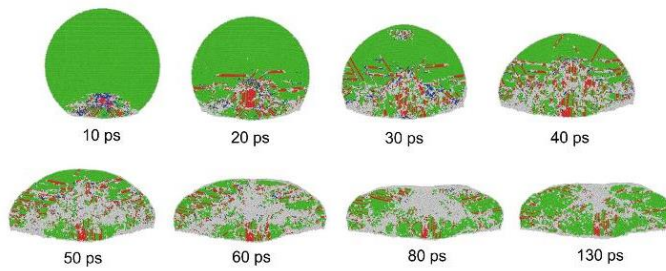


Fig. 10. Atomic structure evolution of particle [001] during impact. Green, red, blue, and light gray colors in the atomic structure show FCC, HCP, BCC, and non-crystalline structures, respectively.

ter 40 ps, the dislocation density in the particle [111] was higher than for the particle [001]. This can be related to the fact that more amorphous regions were created in the particle [001], implying that more dislocations were consumed in the deformation-induced amorphization process.

Fig. 10 shows that the concave shape at the top part of particle [001] was formed when the arrowhead peak of the amorphous region reached the top surface (around 80 ps after the impact). The large deformation, which happened in this amorphous region at high strain rates generated a large amount of heat and increased the temperature of this region. Therefore, this region became softer compared to other regions in the particle (with crystalline structure). Hence, more deformation was localized in this amorphous region (located at the middle-top region of the particle), thus creating the concave shape.

The bicrystal and tricrystal particles both have two grains with the same orientations in the initial contact with the substrate, as shown in Fig. 1; therefore, the plasticity onset of those particles at the contact region was similar. However, the overall evolution of the dislocation density in the tricrystal particle differed from that of the bicrystal particle due to the horizontal inner boundary in the tricrystal particle. As seen in Fig. 7, the dislocation density of the bicrystal particle is lower than that of both single-crystal particles, whereas the total deformation of the bicrystal particle is between the total deformation of both single-crystal particles. Moreover, the bicrystal and tricrystal particles exhibit similar values of total deformation, but the dislocation density of the tricrystal particle is lower than that of the bicrystal particle. Therefore, the total dislocation density seems to decrease as new internal interfaces area added to the system. In addition, the fraction of non-crystalline atoms is similar for both bicrystal and tricrystal particles till around 50 ps and then it decreases with a higher rate in the tricrystal particle. The tricrystal particle has smaller grains at the contact region compare to the bicrystal particle. Therefore, with the same plastic deformation, the internal energy of these grains in the tricrystal particle was higher than the one in the bicrystal particle. Thus, the rate of crystallization of the non-crystalline regions was higher for the tricrystal particle [69].

This crystallization phenomenon will be discussed in more detail later in Section 3.3.

3.3. Grain boundary effects on dislocation activity

As mentioned earlier, dislocation emission and glide as well as large atomic displacements of an amorphous phase are the two main deformation mechanisms operating in defect-free single-crystal particles upon high velocity impact [1,2]. In single crystal particles, the primary source and sink of dislocations is the external surface of the particle. When internal interfaces – grain boundaries – are present, as in some of the particles in this study, this significantly changes. Grain boundaries are known to interact with lattice dislocations in a number of manners [70]. Notably, grain boundaries are effective obstacles for dislocation glide, but they can also act as sources of dislocations. According to Grabski and Korsk [71], lattice dislocations can also be annihilated by reaching the grain boundaries. In our simulations, we conjectured that, besides the dislocation processes that also occur in single crystal particles, many emitted dislocations were absorbed by the internal planar defects in the polycrystalline particles (which were absent in the single crystal particles). As a consequence, the maximum dislocation densities in the bicrystal, tricrystal, and polycrystal particles were 3.15×10^{17} , 1.89×10^{17} , and $1.19 \times 10^{17} \text{ m}^{-2}$, respectively, which are lower than that of the [111] and [001] single-crystal particles with 4.47×10^{17} and $3.99 \times 10^{17} \text{ m}^{-2}$, respectively.

The evolution of the dislocation networks of the bicrystal and tricrystal particles is shown in Fig. 11 (the grains that impacted the substrate have the same orientations for both particles). Not surprisingly, the deformation began with the same behavior and continued until the dislocation network encountered the horizontal grain boundary in the tricrystal particle (between 15 ps and 20 ps). The grain boundary in the tricrystal particle acted as an effective barrier to dislocation gliding. Furthermore, the grain boundary itself started nucleating dislocations as soon as the dislocation network filled the lower grains, but due to the absorption of many dislocations by this horizontal grain boundary, the dislocation

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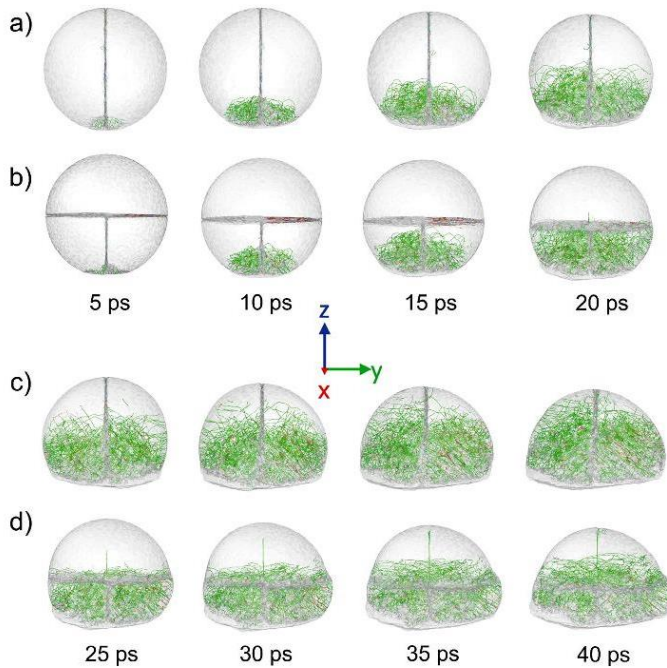


Fig. 11. Dislocation network evolution in a), and c) bicrystal particle, and b), and d) tricrystal particle.

density of the tricrystal particle was lower than that of the bicrystal particle.

3.4. Microstructure evolution

In CS, when a particle impacts a substrate at high velocity, it undergoes severe plastic deformation particularly at the zone of contact with the substrate. Part of the work done during plastic deformation is dissipated as heat, but a small portion is held in the material as stored energy (or elastic strain energy). If the temperature is sufficiently low, i.e. $T < 0.3T_m$, where T_m is the melting temperature, atomic mobility is reduced and the atoms are not able to rearrange to partially release this energy. This phenomenon is known as cold-working. However, if the material temperature is higher than $0.5T_m$, dislocations can rearrange themselves to lower energy configurations such as low-angle grain boundaries (LAGB), phenomenon known as recovery. These changes in the microstructure (which also include dislocation annihilation) cause softening in the material by reducing the dislocation density. Therefore, the material can deform more easily whenever recovery occurs [72].

The dislocation network of a 2 nm thick slice of particle [001] (which has been cut from the center of the particle) at 10 ps after the impact is shown in Fig. 12a. Due to the high velocity impact, the dislocation nucleation rate was high, hence the dislocation density at the particle bottom increased sharply (to approximately $2.85 \times 10^{19} \text{ m}^{-2}$ at the bottom quarter of the particle [001]). Fig. 12b shows the formation of LAGBs and subgrains in the same slice as in Fig. 12a. The temperature of this region was higher than 750 K, well above the equilibrium temperature of the system prior to the impact. This high temperature allowed the dislocations to rearrange themselves to release elastic energy, resulting in the formation of the LAGBs shown in Fig. 12b. As shown in this figure, the misorientation angle between the pink subgrain and the host grain,

and the gray subgrain and the host grain were 4.41 and 3.59 degrees, respectively.

As it was shown before, amorphization involved a large percentage of atoms in all particles during the deformation process. Crystalline structures, on the other hand, are in a lower energy state compared to their non-crystalline counterparts. Therefore, there is a thermodynamic driving force for crystallization of the amorphous phase. Since amorphization was more prominent in particle [001] compared to the other particles, this particle was chosen to analyze the occurrence of crystallization during the deformation process. Fig. 13a displays the local structural environment of each atom as determined by the grain segmentation algorithm (center of particle [001]) at 70 and 130 ps after the impact. The dislocation network in a 2 nm thick slice of the same central regions (at 70 and 130 ps) are shown in Fig. 13b. The grain segmentation algorithm assigned an amorphous structure to the light gray atoms circled in Fig. 13a at 70 ps. In addition, DXA also shows no dislocations for most of the same indicated region. This means that most of the atoms inside the circled region at 70 ps are indeed in an amorphous structure. On the other hand, both DXA and grain segmentation algorithms identified the appearance of crystalline structures inside the same circled region at 130 ps. With further evolution, the crystalline regions indicated by arrows in Fig. 13a began to grow, while other crystal clusters also appeared, indicating the occurrence of crystallization during impact (shown by the arrow in Fig. 13a).

The presence of grain boundaries played an important role in the microstructural evolution during impact. High-angle grain boundaries (HAGBs) are barriers for dislocation glide. Since the emitted dislocations could not cross easily those grain boundaries, they started piling up and the dislocation density increased. Fig. 14 illustrates the microstructural evolution in the bicrystal and tricrystal particles analyzed using the grain segmentation algorithm. The microstructural evolution of both

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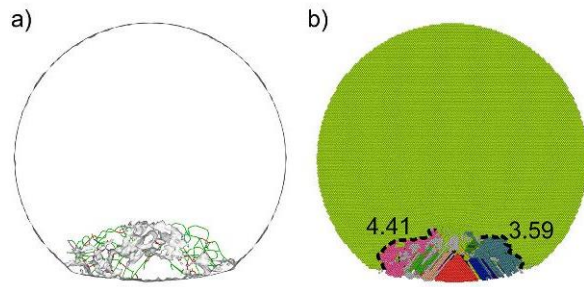


Fig. 12. Low-angle grain boundaries formation at 10 ps in particle [001] a) dislocation network, b) grain segmentation (different colors indicate different grains).

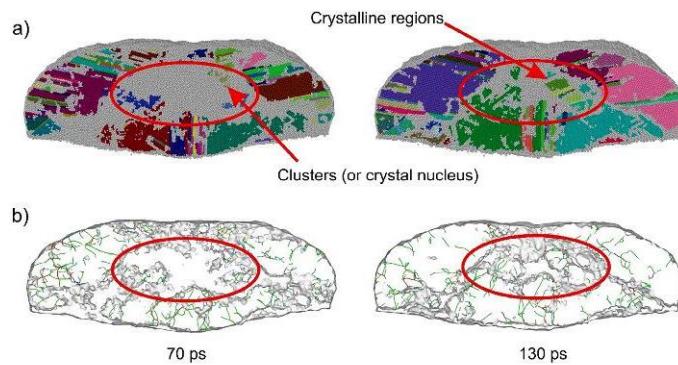


Fig. 13. Crystallization during the deformation process in particle [001] a) grain segmentation (different colors indicate different grains), b) dislocation network.

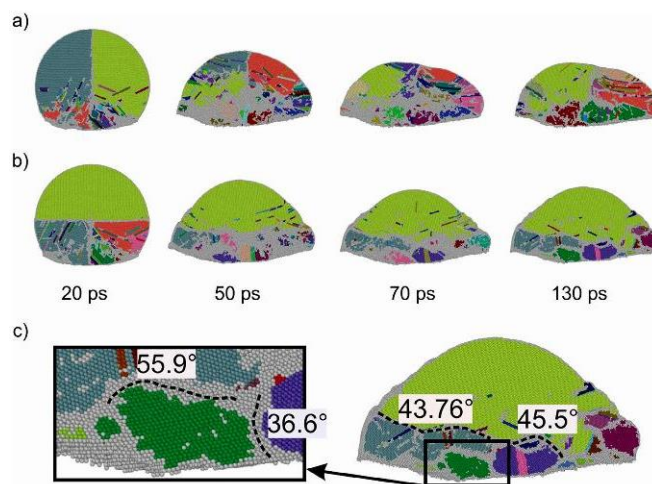


Fig. 14. Grain segmentation evolution during deformation for a) bicrystal, b) tricrystal particles, and c) misorientation between HAGBs in the tricrystal particle at 130 ps, different colors indicate different grains.

particles is roughly the same until the deformation front reached the horizontal grain boundary in the tricrystal particle. At 70 ps, both particles have almost reached their maximum deformation. Both grains in the bicrystal particle are filled by a dense dislocation tangle and defects. In the tricrystal particle, on the other hand, the deformation is localized mostly in the two bottom grains, while the top grain is less deformed and exhibits less dislocation activity. From 70 ps onward, the overall shape of both particles did not change significantly. However, the microstruc-

ture transformation of the particles is noted. By comparing the results for 70 and 130 ps, it is evident that most of the amorphous atoms went back to a crystalline structure (crystallization). The amorphous atoms mostly crystallized in a lattice direction similar to that of their neighbors. Simultaneously, many subgrains also merged. All of these phenomena resulted in larger grains with HAGBs at 130 ps. The same procedure for calculating the misorientation between subgrains was conducted to obtain the angle between some grains in the tricrystal particle, as

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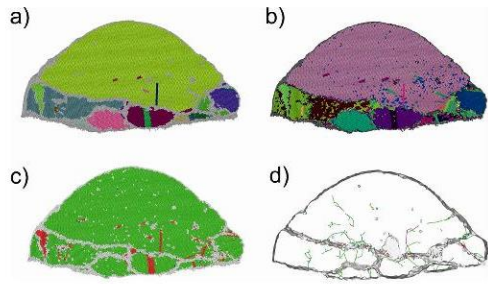


Fig. 15. Formation of HAGBs in the tricrystal particle at 420 ps after the impact a) grain segmentation, b) PTM, c) CNA, and d) DXA algorithms. Green, red, blue, and light gray colors in the atomic structure show FCC, HCP, BCC, and non-crystalline structures, respectively. In (a-b) different colors indicate different grains.

shown in Fig. 14c. The results indicate the formation of HAGBs in this particle after 130 ps. Moreover, grain growth process could be observed for the top grain (light green grain) in the tricrystal particle between 70 to 130 ps.

In order to study the microstructural evolution of the tricrystal particle in more detail, the simulation was extended to 420 ps after impact. To complete the validation of the grain segmentation algorithm as a tool to display HAGBs, the data at 420 ps was also analyzed using other methods available in Ovito [48], such as the PTM, CNA, and DXA algorithms, as shown in Fig. 15. All methods rendered similar results, indicating the formation of HAGBs. By comparing the results at 130 and 420 ps (Figs. 14 and 15), it can be seen that recovery and recrystallization have continued. The reduction in the fraction of non-crystalline atoms from 20.1% at 130 ps to 13.6% at 420 ps indicates more amorphous regions crystallized. Also, grains boundaries are better defined, and the grains contain less defects. Moreover, dislocation analyses showed a slight decrease in the dislocation density from $1.87 \times 10^{17} \text{ m}^{-2}$ at 130 ps to $1.56 \times 10^{17} \text{ m}^{-2}$ at 420 ps.

3.5. Deformation behavior of the polycrystalline particle

The impact of a polycrystalline gold particle consisting of 64 grains, with average grain size of 10 nm, was also simulated. Taking into account that the grains were equiaxial and randomly oriented, the polycrystalline particle can be seen as an isotropic material. According to the inverse Hall-Petch effect, the material strength decreases with de-

creasing grain size for grain sizes smaller than 20 nm [73]. Nonetheless, Giraldez et al. [74] showed that the grain size effect is negligible during high pressure (>100 GPa) and high strain rate ($>10^7 \text{ s}^{-1}$) plastic deformation, as is the case of high velocity particle impacts. Fig. 1 shows that the total deformation of the polycrystalline particle was larger than that of the bicrystal and tricrystal particles. The density of lattice dislocations, on the other hand, was lower. Since the amount of non-crystalline phase in the polycrystalline particle was similar to that of the bicrystal and tricrystal particles, then other deformation mechanisms might be operating in the polycrystalline particle in order to account for the larger total deformation. Two of such mechanisms are grain sliding and grain rotation, in which very small grains are able to slide and rotate on each other instead of undergoing internal deformation. These mechanisms are particularly effective at low strain rates (e.g. the top region of the particle). For instance, Fig. 16 shows three grains, labeled A, B, and C at the top region of the polycrystalline particle. It can be observed that the color of grains A, and C changed with time while the color of grain B did not change. The color changing in grains A, and C indicates that the orientation of these grain with respect to the template also changed with time, i.e., there was grain rotation. Another mechanism that could be contributing to the total deformation of the polycrystalline particle is twinning, which is expected to occur in materials with low stacking fault energies subjected to high strain rate deformation [75–78]. The occurrence of twinning in the polycrystalline gold particle is indicated by arrows in Fig. 16, including some grains which were not deformed severely during the impact. It has also been shown experimentally that some grains inside polycrystalline particles do not deform as much as their neighbors during high velocity impacts [79,80]. This is due to the crystalline orientation and misorientation of those grains in relation to their neighbors, which can make such grains much harder to deform.

The grain segmentation algorithm was also used to analyze the microstructure evolution of the polycrystalline particle during the deformation process (Fig. 17). In order to better track the microstructure evolution inside the grains, the grain boundaries are not shown in Fig. 17. Due to the severe plastic deformation at the particle bottom, as well as the amorphization of some atoms (colored in light gray), the algorithm could not identify grains at the impact zone near the edges. However, the algorithm could detect some small grains nucleating in the heavily-deformed circled zone at 30 ps, indicating recrystallization. As time continued, the deformation inside the particle increased, resulting in the amorphization of some grains. At 70 ps, the overall deformation was completed and the particle began to reduce its internal energy. After this point the amorphous regions began to crystallize (clusters and small new crystallized grains can be seen at 100 ps). Finally (at 130 ps), the small grains began to merge creating larger elongated grains, particularly at the impact zone. It is worth noting that elongated grains par-

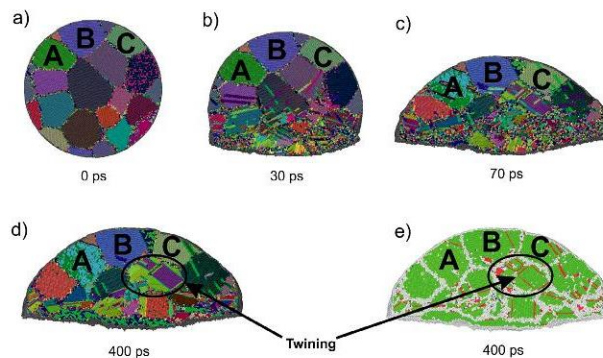


Fig. 16. Grain rotation and twinning during deformation for the polycrystal particle, a-d) PTM, and e) CNA algorithms. Green, red, blue, and light gray colors in the atomic structure show FCC, HCP, BCC, and non-crystalline structures, respectively. In (a-d) different colors indicate different grains.

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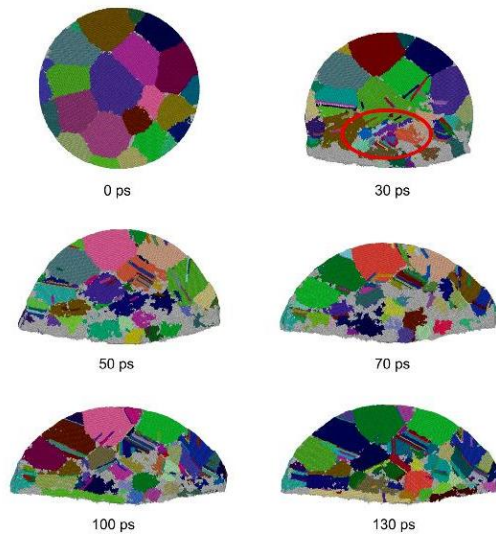


Fig. 17. Analysis of the microstructural evolution of the polycrystal particle during deformation using grain segmentation algorithm, different colors indicate different grains.

allel to the impact zone have been observed experimentally [79–81]; therefore, our simulations successfully reproduced this microstructural feature.

4. Conclusion

In the present study, MD simulations were performed to investigate the effects of crystal orientation and grain boundaries in the microstructural evolution of gold (FCC) particles impacting a gold substrate with a velocity of 400 m/s. The results showed that the deformation onset began by the heterogeneous nucleation of Shockley partial dislocations with a different rate for each grain orientation. Subsequently, the high emission rate of dislocations caused solid-state amorphization within the particles. Due to the high temperature in the amorphous phase, a large amount of plastic deformation occurred in these amorphous regions. It was also shown that most of the amorphous atoms went back to a crystalline structure (crystallization) when the deformation rate decreases. Nucleation, multiplication, gliding, and interaction of dislocations were also analysed; and the effects of vertical and horizontal grain boundaries on the dislocation movement were revealed. The grain segmentation and PTM algorithms in the OVITO software were used to show the formation of LAGBs, and HAGBs, grain rotation, and twinning processes during the deformation for different particles. In addition, analysis of the results showed that the shear strain pattern is independent of the microstructure of the particles and is similar for all particles.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Chapter 6

Conclusion and Future Work

6.1 Conclusions

The general purpose of this study was to improve the understanding of particle deposition mechanism and microstructural evolution of materials during high velocity impacts. For that reason, the research was divided into two different parts considering two different approaches, i.e., a) Simulation of metallic bonding in CS using FEM, and b) prediction of microstructural evolution during the impact using MD method.

6.1.1 Simulation of metallic bonding in CS using FEM

For this part, the metallic bonding, which is one of the two main mechanisms for deposition of metallic powders in CS, was studied.

In the first step, the cold-welding bonding theory which has been established to be the metallic bonding mechanism in CS was implemented in ABAQUS/Explicit. The parameters used in this study was imported into FEM directly from the literature of CW (without any modification). Critical velocities for aluminum, copper, and nickel particles were obtained. It was shown that the predicted results are in the range of critical velocities reported in the literature. In addition, the predicted coefficient of restitution (COR) for 30 μm aluminum particles was compared with experimental results of aluminum powders with the diameters in the range of 24-64 μm . This comparison indicated the capability of the proposed model to reproduce the material behavior during CS. Moreover, this model was also able to show the formation of temporary metallurgical bonds, which mostly occur when particles impact onto a substrate with velocities close but below their critical velocities.

After proposing the first physically based model that was able to predict the deposition behavior of materials during the CS process, we took it a step further in the computational modeling stage of this process, i.e., including the oxide layer and its failure behavior after high velocity impacts of a single metallic powder onto a metallic substrate. This novel FEM model provides an explicit description of the innate oxide layer that covers a micrometer-sized particle, and allowed us to simulate the breakage and partial removal of the oxide film during the particle deposition process in CS. The simulation results provided insights on aspects of the adhesion process in CS that are not directly accessible to experiments. A key parameter used to model the failure

behavior of the oxide layer was the effective plastic displacement. It was shown that by calibrating this parameter with experimental data, the model was able to reproduce the critical velocity, the location of metallic bonding, and also the final geometry of the splat of a copper particle after the impact and adhesion when compared to microscopic images. Oxide breakage and its removal allowed elements in the particle to be in contact with elements in the substrate, and in case of existence of an adequate pressure, resulting in a metallic bonding. In addition, simulation results indicated that the preferred zone for the creation of metallic bonding is not at the jetting zone where the equivalent plastic strain is maximum. The effect of oxide thickness on the critical velocity of the particle was also studied and it was shown that adhesion requires a higher critical velocity by increasing the oxide film thickness.

6.1.2 prediction of microstructural evolution during the impact using MD method

Developing in the understanding of particle deposition in CS cannot be achieved without fundamental investigation on microstructural evolution of material during the deformation. In order to study the material behavior during CS, i.e., deformation at high strain rates, MD simulation method was used. MD method is known as the best possible numerical approach to investigate the underlying mechanisms involved in high strain rate deformations where the experimental methods are incapable.

For the first study, MD simulations were performed to investigate the deformation behavior of copper (FCC) particles after impacting onto a copper substrate to elucidate the basics of the CS process. Five single crystal particles with [111] direction parallel to the substrate's normal were modeled. The particles' diameter was in the range of 5 to 40 nm, and the impact velocity was assigned to 1000 m/s normal to the substrate

surface. Analysis of the results showed that, for particles larger than 10 nm, the onset of plasticity began and was localized at the flattened particles bottom where particles impacted to the substrate (south pole), and characterized by heterogeneous nucleation of Shockley partial dislocations. By continuing in the plastic deformation, a dense dislocation network was formed in the lower half of the particle, while the upper half remains almost undeformed. Finally, the top part of the particle was also deformed and shaped the typical flattened surface of the splat, as has been observed in microscopic images. In addition, temperatures higher than 1000 K were found at the particle/substrate interface. Local atomic disorder along large atomic displacement in this region indicated a fluid-like behavior which resulted a visible material jetting at the end of the deformation.

In the second study, the effects of grain boundaries and grain orientation on deformation behavior of gold (FCC) particles during high velocity impacts were investigated. Two single-crystal particles with different orientation, two simple polycrystal particles (i.e., bicrystal and tricrystal), and a polycrystal particle with 64 randomly oriented grains were modeled. The impact velocity was chosen to be 400 m/s, to reduce the plastic deformation and allowing to track the microstructural evolution easier. The results showed that the onset of plasticity began with heterogeneous nucleation of Shockley partial dislocations with a different rate for each grain orientation. The high emission rate of dislocations caused an intense increase in the local dislocation density, resulting solid-state amorphization within the particles. It was shown that by decreasing the deformation rate, most of the amorphous atoms went back to a crystalline structure (or crystallization). The effects of horizontal and vertical grain boundaries on the dislocation movements were revealed. Moreover, formation of low-angle grain boundaries (LAGBs), and high-angle grain boundaries

(HAGBs), recrystallization, grain rotation, and twinning mechanisms during the deformation for each particle were shown. In addition, analysis of the results indicated that although the deformation behavior of each grain is different, the shear strain pattern is independent of the particle microstructure and is similar for all particles.

It is important to note that unlike FEM which is a predictive tool for engineering applications, MD simulations aim to enhance the understanding of the fundamental process. MD simulations can provide a detailed atomic level of information about the process which has been investigated. In MD simulations, the only input is the description of the interatomic interactions, and because there is no assumption needed to be made in the model, MD method is used to discover new physics or mechanisms. Due to the high computational cost of this method, the particles modeled in this study were two order smaller than the real particles in CS. Although, it is known that the deformation behavior can be affected by the material size, but the involved plasticity mechanisms can be common in all scales.

In other words, MD simulations can suggest the deformation behavior and the involved mechanisms, which can enable researchers to explain their experimental observations, and also this method can recommend the important mechanisms which must be looking for in the experiments. For instance, it is well known that dislocations are the defects responsible for the plastic deformation of metals. In this study, the evolution of the dislocation network has been shown by increasing the particles' deformation. However, the results also suggested the existence of another plastic deformation mechanism during high velocity impacts, i.e., solid-state amorphization. In addition, it was shown that the solid-state amorphization is a transitory process for pure materials (like copper) and due to this reason, this deformation behavior has not been observed experimentally from the microscopic images which are taken after the

spray is done. This outcome is something that must be studied further experimentally and numerically in future and also can be used to answer some of doubts which exist regarding the adhesion mechanism in CS.

6.2 Future Works

Several follow-up studies that would improve the understanding of the deposition process in CS process can be undertaken. In the following list, some potential future investigations are proposed:

1. In order to develop the FEM bonding model, the oxide layer on the substrate should also be modeled. This gets more crucial when the deposition process of dissimilar materials is studied, because dissimilar materials have different deformation responses and hence, have different oxide failure and oxide removal behavior.
2. The proposed model for predicting metallic bonding during the impact of a single particle onto a substrate illuminated the elemental features of the deposition process. This model can be developed easily to model the impact of multiple particles and study the coating build-up process in CS.
3. Both proposed FEM methods (2D and 3D models) can be used to investigate the coating characteristics such as residual stresses, bond strength, and porosity.
4. The Johnson-Cook failure model that was used to describe the failure of the oxide layer provided relatively good results with respects to the experimental observations, but the model can still be modified by implementing more developed failure models which consider more failure mechanisms in their calculations.
5. adiabatic shear instability (ASI) is still an unclear phenomenon in CS. Unfortunately, most of the time the large deformation at the particle periphery that causes severe distortion for elements in that region is referred to as ASI which obviously is not correct. The formation of material jetting (i.e., resulted

by ASI) should be studied in FEM using some constitutive material models that are capable to capture this mechanism.

6. There are still lots of unclear mechanisms which can be studied by MD methods. For instance, studying the deformation behavior of alloys that can be broken down to uncountable researches.
7. MD can be used to reveal the effects of particle and/or substrate preheating on the deformation behavior of materials.
8. The effects of post heat treatment on the material can be analysed by MD.
9. Study the effects of different crystalline structure, i.e., FCC, BCC, and HCP, on the deformation behavior.
10. Multiscale modeling is an advanced method in which the parameters for one scale can be found from another scale. Hence, multiscale modeling is a self-determining method. In processes that experimental measurements are challenging, like CS, this method can be helpful, especially for modeling complex systems like TWIP (twining-Induced-Plasticity) steels or high-entropy-alloys.

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