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ULTRA-HIGH STRAIN RATE MECHANICAL STUDY OF METALS IN THE COLD-SPRAY PROCESS THROUGH LASER-INDUCED PROJECTILE IMPACT TEST

Swetaparna Mohanty
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ULTRA-HIGH STRAIN RATE MECHANICAL STUDY OF METALS IN THE COLD-SPRAY PROCESS THROUGH LASER-INDUCED PROJECTILE IMPACT TEST

A Dissertation Presented
by
SWETAPARNA MOHANTY
Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

May 2023
Mechanical & Industrial Engineering Department
ULTRA-HIGH STRAIN RATE MECHANICAL STUDY OF METALS IN THE COLD-SPRAY PROCESS THROUGH LASER-INDUCED PROJECTILE IMPACT TEST

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By

SWETAPARNA MOHANTY

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DEDICATION

To my parents, for their unconditional love and support.
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First and foremost, I would like to express my sincere and profound gratitude to my advisor and mentor, Professor Jae-Hwang Lee for believing in my abilities. This work would not have been possible without his invaluable guidance and support. He was instrumental in providing me with opportunities to learn and thrive and in inculcating a deep sense of scientific understanding in me. His enthusiasm, genuine curiosity and his passion for scientific research have always inspired me. His immense support, guidance and brainstorming sessions throughout my doctoral studies have made me a better researcher. He has made my doctoral journey interesting and worthwhile.

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Last but not the least, I would like to thank my closest friends from Michigan, Massachusetts, and California for all the invaluable memories. You have been my family away from home.
ABSTRACT

ULTRA-HIGH STRAIN RATE MECHANICAL STUDY OF METALS IN THE COLD-SPRAY PROCESS THROUGH LASER-INDUCED PROJECTILE IMPACT TEST

MAY 2023

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Cold spray is an additive manufacturing process that enables the deposition of metals, ceramics, polymers, and other materials below the melting point of the feedstock powder, resulting in a solid-state consolidation. Ultra-high strain rates in the orders of $10^6$ s$^{-1}$ and beyond are involved in this consolidation process. In recent years, this extreme process has been studied extensively to fundamentally understand the bonding dynamics and improve the deposition efficiency and performance of deposited materials. Furthermore, understanding the dynamic characteristics of the materials can extend our fundamental
knowledge of the materials at the ultra-high extreme strain rate regime. The current study investigates the extreme dynamic behavior of metallic systems through micro-ballistic single-particle collisions. The micro-ballistic collisions of the microparticles at these extreme strain rates are achieved by the advanced laser-induced projectile impact test (α-LIPIT). The high strain rate nonlinear dynamic response of the materials as a function of material and process parameters influencing the cold spray process, such as substrate oxide layer, oxide/hydroxide layer of the microparticles, and elevated temperatures, are systematically quantified through this controlled experimental study. The collision dynamics and dynamic response of the materials can help us understand the materials science occurring at the interface of both the feedstock powders and the target substrates. Additionally, as material properties and deformation dynamics are strain-rate-dependent, our studies are also performed to understand material response at a wide range of strain rates. Thus, our knowledge of the rate-dependent mechanisms is extended to ultra-high strain rate plastic deformation processes and the strength of metals at both the quasi-static and high strain rate regimes.
# TABLE OF CONTENTS

ACKNOWLEDGEMENTS.........................................................................................v

ABSTRACT..........................................................................................................vii

LIST OF FIGURES............................................................................................xii

LIST OF TABLES...............................................................................................xxii

CHAPTER

1. INTRODUCTION..............................................................................................1

   Metals: Structure and Properties.................................................................1
   Theory of metals at the atomic scale..............................................................1
   Mechanical behavior of metals.................................................................7
   Strain rate dependence of metals in terms of hardness..............................10
   Mechanical properties of metals at high strain rates...............................13
   Characterization of mechanical properties at high strain rates...............15
   Ballistic modeling......................................................................................17
   Hardness measurements and nanoindentation...........................................20
   A brief review of additive manufacturing.................................................24
   Cold spray additive manufacturing process.............................................26
   Motivation, significance, and overall goals.................................................29
   References..................................................................................................32

2. LASER-INDUCED PROJECTILE IMPACT TEST IN METALLIC SYSTEMS: A COLDSPRAY PERSPECTIVE ..............................................................................49

   References..................................................................................................71

3. TRANSITIONAL INELASTIC DYNAMICS OF ALUMINUM MICROSPHERES WITH ALUMINUM SUBSTRATES OF VARYING OXIDE THICKNESSES UNDER COLD SPRAY IMPACT CONDITIONS

   Abstract.......................................................................................................75
   Introduction.................................................................................................76
   Materials and Methods...............................................................................79
   Results and Discussion..............................................................................81
   Conclusion..................................................................................................88
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Comparison of experimental and modeling deformation textures of cold rolled T61…3</td>
</tr>
<tr>
<td>1.2</td>
<td>Schematic illustration of (a) dislocation line in crystalline and amorphous solids (b) shear transformation zone in amorphous metals (c) atomic jumps .......... 4</td>
</tr>
<tr>
<td>1.3</td>
<td>Hall-Petch relationship plot of some coarse grain metallic systems ....................... 6</td>
</tr>
<tr>
<td>1.4</td>
<td>Strain rate sensitivity in Al6061 .................................................................10</td>
</tr>
<tr>
<td>1.5</td>
<td>Strain rate sensitivity in copper ...............................................................11</td>
</tr>
<tr>
<td>1.6</td>
<td>Strain rate regimes and conventional instrumented methods for material characterization at that representative strain rate ........................................ 15</td>
</tr>
<tr>
<td>1.7</td>
<td>Penetration model as developed by Ravid and Bodner .................................. 19</td>
</tr>
<tr>
<td>1.8</td>
<td>Schematic illustration of a typical load-depth curve for an indentation method ...... 22</td>
</tr>
<tr>
<td>1.9</td>
<td>Micrographs of the indented area for different crystallographic orientations of Al through a Vickers diamond indenter ........................................ 23</td>
</tr>
<tr>
<td>1.10</td>
<td>Major metal additive manufacturing technologies .................................... 25</td>
</tr>
<tr>
<td>2.1</td>
<td>Deformation features at three impact velocities in PS-b-PDMS copolymer at high strain rates ................................................................. 50</td>
</tr>
<tr>
<td>2.2</td>
<td>a) LIPIT experiment with MLG membranes with a schematic of the penetration steps. (b) Post penetration MLG features .............................................. 51</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic illustrations depicting the evolution of the LIPIT system .......... 52</td>
</tr>
<tr>
<td>2.4</td>
<td>Schematic illustration of an advanced LIPIT system ................................... 53</td>
</tr>
</tbody>
</table>
2.5 Summary of recent studies by Jae-Hwang Lee’s group @UMass-Amherst through LIPIT system ..........................................................................................................................54

2.6 Dynamic deformation profiles of Ag microcubes post LIPIT impacts .................56

2.7 Phase transformation in Ag microcubes through LIPIT characterization ..........57

2.8 Observed 9R phase in ultra-fine-grained aluminum film ...................................57

2.9 Impact-induced deformation and localized melting .............................................58

2.10 Supersonic impact behavior of a range of metallic microparticles .................59

2.11 Jet formation and it’s correlation to critical adhesion velocity ..........................60

2.12 (a) Deformed shapes of the captured Al microparticles. (b) Flattening behavior of Cu and Al μPs ..........................................................62

2.13 Rebound, deposition and erosion behavior in the cold spray process through LIPIT studies ..............................................................................................63

2.14 Size effects as demonstrated by LIPIT experiments .......................................64

2.15 Delamination of surface oxide layer .................................................................65

2.16 Deformation regime and plot depicting impact ratio regime prediction ..........67

2.17 Summary of observed jetting regimes in Cu μP LIPIT impacts to a Cu substrate ....68

2.18 Observed melting features on steel-Sn impacts ..............................................69

3.1 Schematic illustration of the three experimental conditions with (a) native oxide, (b) 10 nm additional oxide layer, and (c) 20 nm oxide layer. (d) An example of ultrafast
stroboscopic image showing an accelerated Al6061 µP traveling at 760 m/s with kinetic energy of 4.5 µJ

3.2 Measured $v_r$–spectra of Al6061 µPs for an Al6061 substrate with (a) no additional oxide layer, reproduced from ref. 33. (b) 10 nm oxide layer, and (c) 20 nm oxide layer are shown with a trend curve of $2\sqrt{\bar{v}_r}$ (gray) and corresponding fitting curves (red). (d) – (f) CoR–spectra from the measured $v_r$–spectra are shown with the two curves corresponding to the curves in (a) – (c).  

3.3 Post-collision features of Al6061 substrate having a 20 nm additional oxide layer after 617 m/s collision of Al6061 µP. (a) SEM micrograph of the impact-induced crater. (b) Enlarged image of the crater highlighted section (red box) showing fine fractures of the oxide layer.

3.4 (a) Top reflection optical and (b) tilted SEM images of a 16.4 µm diameter Al6061 µP after 1,000 m/s collision to Al6061 substrate ($h_{\text{ALD}}=20$ nm). The two triangle markers indicate the same areas in both images. (c) Cross-sectional SEM images of the (d) magnified back-scattered electron micrograph of the top surface of Al6061 substrate.

3.5 Plastically deformed volume of the µP normalized with respect to the µP initial volume, shown as a function of $v_f$ for both Al-Al impacts.

4.1 Modification of the Laser Induced Projectile Impact Test: Schematic Illustration depicting the incorporation of the temperature chamber to the LIPIT system. The microballistic study of the coupled effects of elevated temperature on both the Al6061 µPs and the target substrate was studied by this system.
4.2 Temperature-dependent Al6061 µPs impacts on a Al6061 target substrate: COR spectra of Al6061 µPs impacts at (a) 23°C (b) 100°C (c) 200°C and (d) 300°C, respectively, color scaled with the diameter dependence of the Al6061 µPs. Semi empirical fit curve (red), reproduced from[31] shows the trend of Al6061 µPs impacts to Al6061 target substrates at room temperature……………………………………………………………………….103

4.3 Temperature-dependent Al6061 µPs impacts on a Al6061 target substrate: Rebound velocity spectra of Al6061 µPs impacts at (a) 23°C (b) 100°C (c) 200°C and (d) 300°C, respectively, color scaled with the diameter dependence of the Al6061 µPs. Semi empirical fit curve (red), reproduced from[31] shows the trend of Al6061 µPs impacts to Al6061 target substrates at room temperature……………………………………………..……107

4.4 Deformed shapes of captured Al6061 µPs: Representative SEM images of captured Al6061 µPs post impact to sapphire substrate at different experimental temperatures (room temperature, 100°C, 200°C and 300°C) over an impact velocity range of 50<v<1200m/s. The SEM images have been individually scaled to represent a collective scale bar of 10µm. The room temperature SEM micrographs have been reproduced from[28]………………………………………………………………………………...108

4.5 Deformation behavior in terms of Flattening ratio: Linear regression fitting of the specific diameter change (flattening ratio) as a function of impact velocity and temperature for captured Al6061 µPs post impact with sapphire substrate………………………………………………………………………………………………111

4.6 Material loss at elevated temperatures: Scanning electron micrographs showing mass loss from sub-critical radial crack formation in the jet region of the captured particle surface
with elevated temperature conditions. The inset shows the enlarged highlighted section (black box) of the under surface of the captured particle post collision with sapphire substrate.

4.5.1 Temperature-dependent Al6061 µPs impacts on a sapphire target substrate: Rebound velocity spectra of Al6061 µPs impacts at (a) 23℃ (b) 100℃ (c) 200℃ and (d) 300℃, respectively, color scaled with the diameter dependence of the Al6061 µPs. Unweighted 5 point averaging fit curve (blue), shows the trend of Al6061 µPs impacts on sapphire target substrates at their respective temperatures.

4.5.2 Temperature-dependent Al6061 µPs impacts on a sapphire target substrate: CoR spectra of Al6061 µPs impacts at (a) 23℃ (b) 100℃ (c) 200℃ and (d) 300℃, respectively, color scaled with the diameter dependence of the Al6061 µPs and with a trend curve (red) reproduced from [31] and fitting trend curves (blue) of the data at that particular temperature.

5.1 Schematic illustration of the fluidized bed reactors for treatments of the µPs.

5.2 Schematic illustration of the in-house electrochemical polishing setup for polishing of the aluminum substrates.

5.3 Velocity profiles of the high temperature exposed to dry air aluminum µPs: Measured \(v_i - v_r\) spectra for an aluminum µP impacting an aluminum target substrate. The aluminum target substrate was electrochemically polished prior to the single-particle experiments. The plots have been color scaled to the diameter dependence of the µPs.
5.4 Velocity profiles of the aluminum μPs subjected to humidity: Measured $v_l - v_r$ spectra for an aluminum μP impacting an aluminum target substrate. The aluminum target substrate was electrochemically polished prior to the single-particle experiments. The plots have been color scaled to the diameter dependence of the μPs.

5.5 Observance of scatter in the $v_l - v_r$ spectra for heat-treated and control group μPs. Surface morphology changes are denoted in terms of scatter in the $v_{cr}$ profiles of the μPs. The plots have been color scaled to the diameter dependence of the μPs.

5.6 Observance of scatter in the $v_l - v_r$ spectra for humidity-treated and control group μPs. Surface morphology changes are denoted in terms of scatter in the $v_{cr}$ profiles of the μPs. The plots have been color scaled to the diameter dependence of the μPs.

5.7 Trends of LSBP and HSUP for the heat treated and humidity treated μPs.

5.8 Post impact features of the bonded μP: Top view scanning electron micrographs of a bonded μP with (or without) different processing conditions. Arrow marks (white) indicate the presence of jet at the interface of the bonded μP and the target substrate.

5.8.1 Plot showing the distribution of the μP diameters as quantified from the optical micrographs.

6.1 Schematic illustration for (a) nanoindentation and (b) micro ballistic impact shown as a comparison along with the parameters associated with these experimental setups.
6.2 (a) Loading-unloading curves obtained from the LSR spherical nanoindentation. (b) Optical micrographs showing the residual impression from the LSR spherical nanoindentation...

6.3 (a) Micrograph showing impact and rebound of alumina microparticle (b) SEM micrograph showing the residual impression on Cu target substrate after alumina impact (c) Profile map of residual impression after alumina impact on Cu substrate with $h_{\text{max}}=6.7\mu m$...

6.4 Energy dissipation as a function of indentation volume for high purity aluminum and pure copper at LSR and HSR regime for a range of $v_i$. The slopes were obtained by fitting the linear portion of the $\Delta E$ curves.

6.5 Energy dissipation profiles during (a) nano-indentation and (b) impact-indentation (micro-ballistic impacts) in FE simulation. The loading-unloading stages in nano-indentation and the particle impact-rebound stage in HSR impacts are separated by the dashed lines (black).

6.6 Comparative energy dissipation profiles during LSR indentations and HSR through experiments and simulation for both pure Cu and high-purity aluminum.

7.1. Schematic illustration of the new bilayer polymer launch pad for accelerating heavy microparticles.

7.2. CoR spectra of micro-ballistic impacts for Ta µPs to that of Ta and sapphire substrate.
7.3. $v_i - v_r$ spectra of micro-ballistic impacts for Ta µPs to that of Ta and sapphire substrate. The graphs have been color scaled to represent the diameter dependance of the high strain rate impacts. .................................................................172

7.4. Captured Ta particles post collision with a sapphire substrate show $v_i$-dependent plastic deformation.................................................................173

7.5. Top view SEM and cross sectional EBSD map of Ta µP bonded to a Ta substrate at $v_i=498$ m/s. The analysis shows the presence of slip bands and twinning. ..............174

A1. SEM micrographs of bonded µP post micro-ballistic impacts using LIPIT system: (a) conventional copper µP accelerated at 700 m/s(b) nano-agglomerate copper µP accelerated at 885 m/s.................................................................183

A2. Cross-sectional FIB micrographs of bonded µP post micro-ballistic impacts using LIPIT system: (a) conventional copper µP accelerated at 700 m/s(b) nano-agglomerate copper µP accelerated at 885 m/s.................................................................184

A3. Ultra-high strain rate LIPIT characterization of conventional copper µPs: Representative spectra color scaled with diameter (µm) (a) $v_i - v_r$ (b) CoR..............184

A4. Ultra-high strain rate LIPIT characterization of nano-agglomerate copper µPs: Representative spectra color scaled with diameter (µm) (a) $v_i - v_r$ (b) CoR..............185

B1. SEM micrograph of Al6061 µPs .................................................................186

B2. SEM micrograph of Alumina µPs.................................................................187

B3. SEM micrograph of Tantalum µPs.................................................................187
B4. SEM micrograph of “As received” HP Aluminum μPs…………………………….187

B5. SEM micrograph of RH 50% HP Aluminum……………………………………….188

B6. SEM micrograph of RH 95% HP Aluminum……………………………………….188

B7. SEM micrograph of HT Baseline HP Aluminum…………………………………..188

B8. Schematic illustration of the new bilayer polymer launch pad for accelerating heavy microparticles…………………………………………………………………………...190

B9. Schematic illustration showing (a) capturing of Al6061 microspheres and (b) transfer of the captured particle using an elastomer……………………………………………..192

B10. Illustration showing the calculation of flattening ratio of a captured Al6061μP post collision……………………………………………………………………………192

B11. Stroboscopic image showing capture of tantalum microsphere by a steel pinhole..193

B12. Schematic illustration showing the incorporated temperature chamber with the 4 heaters mounted. This addition does not affect the normal functioning of the LIPIT system…………………………………………………………………………………..195

B13. Modification of the Laser Induced Projectile Impact Test: 3D Schematic Illustration depicting the incorporation of the temperature chamber to the LIPIT system. The micro-ballistic study of the coupled effects of elevated temperature on both the Al6061 μPs and the target substrate was studied by this system………………………………………………….196

B14. Illustration of a spherical nano-indenter and the resultant loading-unloading curve. After complete unloading, the graph shows a residual impression of height h_c………………197
B15. (a) Optical micrographs of pure Cu and high purity Al showing the nanoindentation indents. (b) SEM micrograph showing the residual impression on Cu target substrate after alumina impact (c) Optical micrograph of a residual impression after alumina impact on a Cu substrate at $v_i \sim 400 \text{m/s}$ (d) Profile map obtained through laser profilometry of the residual impression after alumina impact on Cu substrate with $h_{\text{max}}=6.7\mu\text{m}$...........199

B16. Illustration of an electrochemical polishing setup...........................................200


## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 A list of fitting parameters. <em>Parameters are limited by the preset range (2 – 20) for stability of fitting.</em></td>
<td>85</td>
</tr>
<tr>
<td>5.1 Processing conditions of the high purity aluminum µPs.</td>
<td>127</td>
</tr>
<tr>
<td>6.1 Original values of bilinear Johnson-Cook plasticity model parameters</td>
<td>149</td>
</tr>
<tr>
<td>6.2 Parameters associated with the experimental setups of nano indentation and micro-ballistic impact</td>
<td>152</td>
</tr>
</tbody>
</table>
Metals: Structure and Properties

Metals are a class of materials that are characterized by their metallic bonding[1], high electrical and thermal conductivity, as well as their ductility and malleability[2]. Metals have a wide variety of applications, including in biomedical devices[3], construction[4], transportation[5], electrical and electronic devices[6] etc. Metals can also be combined with other elements to form alloys, so as to create new materials with tunable properties[7]. For example, steel (iron-carbon alloy) can be used to make corrosion resistant materials[8], and titanium alloys are commonly used in aerospace applications[9]. The properties of metals can also be modified through heat treatment[10] and other processes to improve their strength and toughness[11]. Overall, metals play a crucial role in our daily lives and are essential to many modern technologies and industries[12].

Theory of metals at the atomic scale

In a metallic system, the behavior of electrons can be described by the quantum theory of pure metals. Drude’s free electron model explains the electronic structure of metals by applying the kinetic theory of gases to a gas of conduction electrons[13]. This model along with the Wiedemann-Franz law[13] was able to explain the electrical and thermal conductivity of metals.

\[
\sigma = \frac{ne^2\tau}{m}
\]  

(1.1)
\[ K = \frac{\pi^2 n k_B^2 T}{3m} \]  \hspace{1cm} (1.2)

\[ \frac{K}{\sigma} = LT \]  \hspace{1cm} (1.3)

where \( \sigma \) is the electrical conductivity, \( K \) is the thermal conductivity, \( n \) is the number density of conduction electrons, \( e \) is the electron charge, \( \tau \) is the average time between collisions, \( m \) is the electron mass, \( T \) is the absolute temperature, and \( L \) is the Lorentz number.

This classical theory was later modified by Lorentz to form the Drude-Lorentz theory[13]. Additionally, metallic properties were later explained by the semi-classical theory by Fermi and Dirac in 1926. This theory described the behavior of electrons in a metal which obey the Pauli’s exclusion principle and behave like a gas of non-interacting or weakly interacting quasiparticles over different energy states[14]. Semi classical electron theory of metals was also put forward by Sommerfeld[13]. This work modified Drude model using new statistics to explain the electron theory of metals. Behavior of electrons in crystal lattices were explained by Bloch’s theory[15], as a solution to the Schrödinger equation in the potential energy function.

\[ \varphi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{\vec{r}}(\vec{r}) \]  \hspace{1cm} (1.4)

where \( \varphi_{\vec{k}}(\vec{r}) \) is the obtained Schrödinger equation wave function in the crystal and \( u_{\vec{r}}(\vec{r}) \) is the wave function[16]. This model could furthermore explain the optical properties, magnetic susceptibility, specific heat along with the electrical and thermal conductivities in the crystal lattice[15].

The properties and behavior of the metals are governed by the arrangement of the atoms in the lattice or the structure of metals. Different orders exist in their microstructures such as
crystalline, polycrystalline, single crystal, amorphous and nanocrystalline structure. Most metals have a crystalline structure, with the atoms arranged in a regular lattice pattern. The metallic crystal structures are body-centered cubic (BCC), face-centered cubic (FCC) and hexagonal close-packed (HCP)[17]. A metal or it’s alloy with a polycrystalline structure comprises of grains of different crystallographic orientations, sizes and shapes[18]. The deformation in polycrystalline metals has been explained by an extension of Taylor’s model[19] [20]and Sach principle[21]. Simulation studies based on the Taylor model such as VPSC model [22], ALAMEL model[23], work by Engler et al. [24] etc. have also addressed the deformation behavior in polycrystalline metals.

**Figure 1.1** Comparison of experimental and modeling deformation textures of cold-rolled T61[23]
In bulk single crystal metals, the deformation behavior is studied as a function of various factors such as its strength, hardening mechanisms, dislocation glides and susceptibility to creep, fracture, and fatigue[25]. In amorphous metals or metallic glasses, the deformation behavior is fundamentally different than that of crystalline metals due to the lack of a long-range order in the crystal structure [26]. The deformation mechanism in bulk metallic glasses is exhibited in the form of shear transformation zones[26], [27].

![Schematic illustration of (a) dislocation line in crystalline and amorphous solids, (b) shear transformation zone in amorphous metals, and (c) atomic jumps](image)

**Figure 1.2** Schematic illustration of (a) dislocation line in crystalline and amorphous solids, (b) shear transformation zone in amorphous metals, and (c) atomic jumps [26], [28]–[30].

In nanocrystalline metals, the grain size is in the order of tens of nanometers. These small grain sizes limit the dislocation pile up at the observed yield stresses[31]–[33]. Several MD and experimental studies have identified the deformation mechanisms in nanocrystalline metals[34] to be through grain boundary sliding[35], [36], deformation twinning[35], [37],
Thus, from the preceding section we can see the different deformation mechanisms that changes from coarse grain materials to nanocrystalline materials. The strength of a metal as a function of grain refinement or grain boundary strengthening is described by a behavior called as The Hall-Petch equation[39], [40]. This empirical equation states that the strength of a material increases as the average grain size decreases. The Hall-Petch relationship is mostly observed in polycrystalline grains. This work was based on the theoretical work of Eshelby, Frank, and Nabarro regarding the dislocation pile-up. [41].

The Hall-Petch equation is represented by the following equation[39], [40]:

\[ \sigma(d) = \sigma_0 + \frac{k}{\sqrt{d}} \quad (1.5) \]

Where, \( \sigma(d) \) is the yield stress, \( d \) is the average grain size, \( \sigma_0 \) is the lattice friction stress required to move individual dislocation and \( k \) is the material constant or Hall-Petch slope. However, when the grain refinement approaches nano scale in the nanocrystalline materials, a divergence in the Hall-Petch relationship is observed which is referred to as reverse Hall-Petch effect[42]. A pronounced softening effect is observed at smaller grain sizes, due to the accumulation of atoms at the grain boundaries[35].
Another size effect relationship was studied by Frank, Merwe[44] and later by Matthews[45]. The critical thickness theory by Matthews[45][46] established the maximum thickness for a given misfit. The equation is given by,

\[
h_c = \frac{b(1-v\cos^2\theta)}{8\varepsilon_0(1+v)\cos\lambda} \ln \frac{h_c}{b} \tag{1.6}
\]

where \( h_c \) is the critical thickness, \( \varepsilon_0 \) is the given misfit, \( b \) is the Burger’s vector magnitude, \( v \) is the Poisson’s ratio, \( \theta \) and \( \lambda \) are the angles between the slip plane, growth plane and the Burgers vector. The critical thickness theory by Matthews and-Blakeslee explained the stability of a thin film as a function of its thickness[47].

Dislocations are defects in the atomic structure of a crystal. They were first introduced by Taylor in 1934[48]. Plastic deformation is a result of the mobility of these defects[49]. They also play an essential role in determining the mechanical behavior of metals and
Thus, understanding the mechanical response of a material in terms of the dislocation behavior is crucial for the design and optimization of materials. Several models have been proposed to understand the behavior of dislocations in metals, such as the Peierls model, the Nabarro model, the Taylor model, and the Eshelby model. These models provide a theoretical framework for understanding the behavior of dislocations and their relationships in the microstructure of metals and alloys.

Several processing techniques such as cold working, annealing, heat treatment etc. can affect the structure of metals and alloys. They affect the microstructure which in turn affects the mechanical, optical, thermal, electrical etc. properties of the metals and alloys. For example, the strength and ductility of metals and alloys can be changed by heat treatment as it affects the size and shape of the crystals. Similarly, cold working can lead to changes in the strength and hardness of the metals and alloys. Additionally, presence of impurities, defects, and other factors such as temperature, pressure, and environment can also affect the properties of a metal/alloy.

**Mechanical behavior of metals**

The mechanical properties of metals refer to their ability to withstand loads and forces with respect to deformation and/or fracture. Some critical mechanical properties of metals include; tensile strength (the maximum amount of tensile stress a metal can withstand before fracture), yield strength (the amount of stress at which a metal begins to deform plastically), elastic modulus (the ratio of stress to strain or the resistance of a material to elastic deformation), hardness (the resistance of a metal to localized plastic
deformation), toughness (the ability of a metal to absorb energy before fracture), fatigue limit (the maximum stress that a metal can withstand without fatigue failure during repeated loading cycles), ductility (the ability of metal under tensile load to sustain a large permanent deformation without fracture), malleability etc. The mechanical properties of metals differ for different metals and their alloys. These properties determine their suitability to be used for different applications ranging from construction to aerospace. Several factors can affect the mechanical properties of metals, including but not limited to microstructure, presence of impurities, strain rate, temperature, corrosion, loading conditions, alloying, cold working, heat treatment, and age hardening[55]–[58].

Engel-Brewer theory[59], [60], Hume-Rothery theory[61], established the relationships between the structure of metals and alloys and their electronic parameters. Studies by Eberhart[62] sought to establish relationships between the bond directionality and elastic behavior in metals. They were able to correlate shear elastic constants with the bond directionality. Some of the main elastic properties of metals include[55], [56], [63], Young's modulus (the measure of the stiffness/resistance of a material to elastic deformation), Poisson's ratio (the ratio of transverse strain to longitudinal strain in a material), shear modulus (measure of rigidity of a material or the ratio of shear stress to shear strain), bulk modulus (the ratio of volumetric stress to volumetric strain or the resistance of material to compression). Plastic deformation can affect the elastic constants through lattice imperfections and through residual stresses and strains[63]. Grain orientations also influence the anisotropy in elastic behavior of metals[63]. This behavior was studied first by Green[64].

Green’s functions for 3D non-linear elastic solid is given by the differential equation[65]:

\[ \text{Green's functions for 3D non-linear elastic solid is given by the differential equation[65]:} \]
\[ C_{ijkl} u_{k,ij} + \delta(x) f_i = 0 \quad (1.7) \]

where, the Dirac delta function is represented by \( \delta(x) \). If the Zener anisotropy of elasticity approaches unity then the effects from grain orientation can be neglected.

The elastic behavior of single crystal and polycrystalline metals are affected by temperature. The temperature dependence is denoted by their temperature coefficients. The Young’s modulus is affected at elevated temperatures. This can be attributed to the softening of grain boundaries at elevated temperatures[63]. Elastic properties of metals are determined by its composition, microstructure and processing conditions[66].

In linear elasticity, Hooke’s law was correlated the strain tensor to the stress tensor in a homogenous body by[67], [68]

\[ \sigma^{ij} = c^{ijkl} \varepsilon_{kl} \quad (1.8) \]

where, \( \sigma^{ij} \) is the stress tensor and \( \varepsilon_{kl} \) is the strain tensor. Cauchy’s relations [67], [69] have been one of the governing equations for molecular models for elastic bodies,

\[ \nabla \cdot \sigma(x, t) + \rho_0 b(x, t) = \rho_0 \frac{\partial^2 u(x, t)}{\partial t^2} \quad (1.9) \]

The elastic properties of metals can be measured through different test methods such as tensile test, compression test, and bending test[70]. Young’s modulus of a material is used in various engineering fields such as mechanical engineering, aerospace engineering, civil engineering, and material science as it can be useful in prediction of the behavior of materials under different loads and conditions[71], [72].
Strain rate dependence of metals in terms of hardness

Strain rate is a measure of rate of deformation as a result of an applied load with respect to time. Metals exhibit strain rate sensitivity[73]. Propagation of stress wave and plastic wave front in metals can contribute to the strain rate sensitivity in metals. This dynamic behavior can be a result of plastic flow instability through the shock wave propagation within the microstructure[74].

![Strain rate sensitivity in Al6061](image)

**Figure 1.4** Strain rate sensitivity in Al6061 [75]
Strain rate sensitivity hardness in metals can be expressed in terms of yield stress ($\sigma$) and strain rate sensitivity parameter ($m$) as [74]

$$\sigma = C \dot{\varepsilon}^m$$  \hspace{1cm} (1.10)

$$m = \left( \frac{\partial \ln \sigma}{\partial \ln \dot{\varepsilon}} \right)_{T,\varepsilon}$$  \hspace{1cm} (1.11)

For quasi static strain rates, the dependence of metals on strain rates [74] through the microstructure of the metal in terms of activation volume ($V^*$) can be expressed by

$$m = \frac{\sqrt{3} k_b T}{\sigma V^*}$$  \hspace{1cm} (1.12)

Through motion of dislocations the strain rate can be expressed as [77], [78]

$$\dot{\varepsilon} = b \rho_m \bar{\nu}$$  \hspace{1cm} (1.13)
At high strain rates, the dislocation slip determines the dislocation velocity in terms of phonon drag $B_D$. The relaxation time $\tau_D$ dictates the dislocation motion thereby influencing the dislocation structure of the metal[74].

$$\tau_D = \frac{8\chi B_D}{3\rho D G b^2} \quad (1.14)$$

In aluminum and copper, the dislocations are controlled by this mechanism[79].

The onset of plastic yield criteria and strain rate dependence parameter ($m$) at high strain rates was proposed by Campbell[74], [80]

$$\int_0^{t_0} \left[ \frac{\sigma(t)}{\sigma_0} \right]^\alpha \, dt = C \quad (1.15)$$

$$\alpha = \frac{u_0}{k_B T} \quad (1.16)$$

$$m = \frac{1}{1+\alpha} \quad (1.17)$$

Several mechanisms contributing to the Hall Petch [39], [40] relationship have been proposed that includes dislocation pile up near the grain boundaries[81], presence of GNDs near the grain boundaries[82], behavior of GBs as dislocation sinks and sources[83]. The mechanical behavior of metals at high strain rates also leads to strain rate hardening that will be discussed in the next section.
Mechanical properties of metals at high strain rates

The mechanical properties of materials at quasi-static states are different from that of their behavior at high strain rates. Early studies on this phenomenon were done by Hopkinson [84]–[86] and Hopkinson through impacts of bullets[87]. Different quasi-static tests, such as that by Charpy [88] on the impact pendulum test, have also demonstrated this behavior. Early studies also established the plastic deformation behavior of copper and aluminum at a range of strain rates[89], [90]. The metals experience a phenomenon called strain rate hardening at high strain rates. Hollomon, Zener, Dieter, and Marin established the approximation of the stress-strain curve through strain hardening exponent (n)[91]–[93]:

\[ \sigma = K \varepsilon^n \]  \hspace{1cm} (1.18)

\[ n = \frac{d \left( \log \sigma \right)}{d \left( \log \varepsilon \right)} \]  \hspace{1cm} (1.19)

At a particular strain, the slope of the true stress-strain curve can give us a measure of the rate of hardening. In a metal, beyond the yield point the strain rate hardening behavior can be observed.

At high strain rates, the strain rate sensitivities of FCC metals such as Al and Cu can be explained by the phonon drag effect (Eq. 1.14). The average velocities of the dislocations experience a saturation which can make the flow viscous[94]. This was proposed by the kinematic equation by Orowan which correlated the dislocation velocity to the strain rate[95].
In metals, the plastic deformation under a given load is dictated by creep mechanisms and dislocations mediated mechanisms[96]. The creep rate at steady state is given by:

$$\dot{\varepsilon}_c = K\sigma^n e^{\left(-\frac{Q}{kT}\right)}$$  (1.20)

and the shear strain rate is given by

$$\dot{\gamma} = \dot{\gamma}_0 e^{\left(-\frac{\Delta G(r^*)}{kT}\right)}$$  (1.21)

There is an increase in fracture stress and the yield strength increases with an increase in strain rates as shown by Petch and Armstrong[97].

Several experimental approaches have been employed to measure the dynamic behavior of metals at high strain rates. In the quasi-static regimes, the metals typically exhibit a linear elastic behavior whereas, it can exhibit non-linearity at high strain rates [74]. This behavior is particularly pronounced at ultra-high strain rates, where the strain rates are in many orders of magnitude higher than at lower strain rates [74]. A greater adiabatic shear banding is observed in BCC metals as compared to the FCC metals with an increase in strain rates[98]. Deformation twinning increased for FCC metals with an increase in strain rates. For smaller grain size metals, there was a conversion of slip to twinning at higher strain rates[98]. Formation of dynamic recrystallization within the shear bands is also associated at higher strain rates[99].
Characterization of mechanical properties at high strain rates

**Figure 1.6** Strain rate regimes and conventional instrumented methods for material characterization at that representative strain rate[100].

Several experimental approaches have been employed to measure the dynamic behavior of metals at high strain rates. A few of the techniques are Split Hopkinson (Kolsky) Bar test[101], drop tower impact test[102], Taylor impact test[103], [104], Charpy test[105], plate impact test[106], shock tube test[107], gas-gun test[108], high speed tensile testing[109], dynamic compression testing[110]. In Split Hopkinson (Kolsky) Bar test [101], a striker bar is placed between two bars of the same material and is then launched at high velocity. The resultant stress wave that is transmitted through the bars is measured through strain gauges and sensors which can give a measure of the stress strain. In the drop tower test [102], a mass is raised to a predetermined height. With the release of the mass
onto the surface of a specimen that was clamped before, an impacting force is generated. Strain gauges and accelerometers are used to record force and duration of the impact. In Taylor impact test [103], [104], a cylindrical projectile is accelerated at high velocities towards a target substrate. The projectile is typically accelerated by using a gas gun launcher. During the impact, the projectile penetrates the target substrate which results in shock wave generation through the material. The profiles of the stress and strain waves are measured through strain gauges and sensors which can give a measure of the resultant stress and strain values. In Charpy test [105], a notched specimen is struck with a pendulum hammer. This leads to the fracture of the specimen. The material toughness is measured as a function of the energy required to fracture the specimen. In plate impact test [106], a bullet or a flyer plate is fired at a target specimen which generates shock wave that propagates through the target plate. This results in the deformation and sometimes fragmentation of the target plate. In shock tube blast test [107], a high-pressure gas is released rapidly to generate a shock wave that propagates through the tube attached to the diaphragm or membrane. In gas gun test [108], a high-pressure gas is used to accelerate a projectile to high velocities through firing of the projectile. In high-speed tensile testing[109], the specimen is subjected to a tensile load at high speeds through a specialized testing machine. The force applied and the displacement strain can be measured through sensors. These tests can measure the material behavior at strain rates below the ultra-high strain rate regime, which gives the necessity for ultra-high strain rate testing. One of the methods for ultra-high strain rate testing through laser induced projectile impact test (LIPIT)[111] has been described in Chapter 2. This experimental technique has launched the greater part of my dissertation studies.
Ballistic modelling

For a microparticle impact, Hertz contact stresses equations[112] predicted the maximum stress for a sphere when it impacts a plane target. This was independent of the sphere diameter. When the stress values exceed the threshold values, then material yields plastically. The mean contact pressure (P) from these studies were given by for Young’s modulus (E)[113]

\[ P^5 = \frac{1280}{243\pi^4} \rho v^2 \left( \frac{1}{f(E)} \right)^4 \]  

(1.22)

\[ f(E) = \frac{1 - v_1^2}{E_1} + \frac{1 - v^2}{E_2} \]  

(1.23)

However, the limitation of the study was that it was independent of the size of the impacting sphere. But it could predict the critical velocity at which the collision became purely plastic. Recently, different types of theoretical and analytical models have been developed to predict the ballistic impact response of materials.

Some of the analytical models for metallic targets are briefly summarized here[114].

The penetration dynamics of rigid projectiles were developed in Poncelet’s form:

\[ -\frac{dV}{dt} = A + BV^2 \]  

(1.24)

The solution of this equation yields the penetration depth in terms of velocity.

The hydrodynamic theory of penetration[115] analyzes the penetration of a projectile with initial velocity \( u \) and a penetration velocity \( v \). Here the model is assumed on a steady state, incompressible flow. The resultant equation is along the center line of the projectile and the target is given by
\[
\frac{1}{2} \rho_p (v - u)^2 = \frac{1}{2} \rho_t u^2
\]  
(1.25)

\[
u = \frac{v}{1 + \frac{\rho_t}{\rho_p}}
\]  
(1.26)

The hydrodynamic theory was later modified to include the velocity gradient in terms of resistance to plastic deformation \[114\], [116].

\[
\frac{1}{2} \rho_p (v - u)^2 = \frac{1}{2} \rho_t u^2 + \sigma_{Yt} - \sigma_{YP}
\]  
(1.27)

Using conservation of energy and momentum methods, Recht-Ipson \[117\] developed a model for finite targets with residual velocity \(V_r\) at normal impact angles

\[
V_r = \frac{M_p}{M_p + M_{sn}} (V^2 - V_{xn}^2)^2
\]  
(1.28)

In Walker Anderson model\[118\], the authors simplified the momentum balance in a semi-infinite target in the projectile and target penetration along the center line to Eq. 1.29 by modifying the Bernoulli theory of Tate\[119\].

\[
\rho \frac{\partial u_x}{\partial t} + \frac{1}{2} \rho \frac{\partial (u_x)^2}{\partial z} - \frac{\partial \sigma_{xz}}{\partial z} - 2 \frac{\partial \sigma_{xz}}{\partial x} = 0
\]  
(1.29)

The modified Bernoulli’s theorem as proposed by Tate\[119\] and Alekseevski \[120\] independently provides a model for an eroding penetration behavior with the critical velocity \(\nu\) where the penetration becomes zero, as a function of target’s resistance to penetration \(R\), dynamic flow stress \(\gamma\) and density of the projectile \(\rho_p\)

\[
\nu = \frac{2(R - \gamma)}{\rho_p}
\]  
(1.30)
In Ravid-Bodner model[114], [121], the penetration dynamics was explained in terms of several stages of penetration as shown in Fig. 1.7.

\[ \sigma = (A + B\varepsilon_P^n) \left[ 1 + C \ln\left(\frac{\dot{\varepsilon}_P}{\dot{\varepsilon}_0}\right) \right] \left[ 1 - \left(\frac{T - T_R}{T_m - T_R}\right)^m \right] \] (1.31)
For our studies, the JC model was incorporated to model the highly controlled single particle micro-ballistic impacts at ultra-high strain rates.

**Hardness measurements and nanoindentation**

Study of deformation behavior of materials through instrumented indentation has been used widely to measure material properties. One of the most investigated material properties that can describe the tribological characteristics of a material is hardness[123]. Hardness testing is a non-destructive method that has been used to measure the ability of a material to resist deformation. Indentation hardness gives us a measure of the material’s ability to resist local plastic deformation[124]. Deformation on the surface can be induced by mechanisms such as mechanical bending, scratching, indentation etc.[125]. In metals, plastic deformation has been related to the hardness[125]. Different types of hardness tests are used to find the hardness at different length scale, as the mechanical properties are believed to be scale dependent due to size effect and surface effects[125], [126]. Study of deformation behavior of materials through instrumented indentation such as nanoindentation can provide a measure of different material properties such as hardness[127]–[129], elastic modulus[127], [128], [130], hardening exponents[131], [132], creep parameters[133]–[135] and residual stresses of materials[136], [137]. The load–depth curves during the loading and unloading process of the indentation can give us a measure of the material’s ability against deformation. Results of indentation are dependent upon radius of the indenter tip, force applied from the indenter tip to the surface of the sample, the indentation depth, the surface tilt of the specimen and structural configurations such as grain boundaries in metals or crystallinity[138]. A factor that has
been shown to affect the hardness measurements is the strain rate of the indentation method[139]. The quasi static and dynamic hardness measurements can give us a measure of the strain rate sensitivity of the metal.

Hardness measurement was first done by Austrian mineralogist Friedrich Mohs[140]. Thereafter instrumented indentation was done by William Wade to measure the hardness from the load cavity[141]. Tabor laid out the theoretical foundation and model for indentation experiments[142], [143]. Indentation at nanoscales was introduced in the 1980s with the advent of microelectronics[129]. Some of the indentation tests that are carried out at the macro scale are the Brinell test[144], Meyer test[145], Vickers test[146], and Rockwell test[147]. Micro-indentations are carried out by the micro-Vickers test[148], Knoop test[149], and micro-IHRD test[150]. Indentation hardness and Young’s modulus from load depth curve was studied by Oliver–Pharr[127], [128] in which the hardness($H_i$) is defined as ratio of the peak indentation load to that of the area of the indenter impression.

\[
H_i = \frac{P_{\text{max}}}{A_i} \quad (1.32)
\]

where $P_{\text{max}}$ is the maximum load or peak indentation load and $A_i$ is the area of the indenter impression.
Studies by Korsunsky[151] showed that the energy dissipated or work of indentation can also be used to describe the hardness. They postulated that the total work done ($w_T$) is the integral of the area under the loading curve, and the work done from the elastic contribution is the integral of the area under the unloading curve. Thus, the plastic work done ($w_p$) is the difference in area between the loading and unloading curves. Stilwell and Tabor[152] calculated the energy dissipation when a conical indenter strikes an elastoplastic metal. Stilwell and Tabor's model is given by

$$H_i = \frac{P_{\text{max}}}{A_i} = \frac{w_p}{V_i}$$  \hspace{1cm} (1.33)
where \( w_p \) is the plastic work and \( V_I \) is the volume of indentation impression. These relationships have been the background of several experiments at low strain rates that have provided insight into material response such as material hardness.

Study of deformation behavior of materials through instrumented indentation such as nanoindentation can provide a measure of different material properties such as hardness and elastic modulus[129].

Figure 1.9 Micrographs of the indented area for different crystallographic orientations of Al through a Vickers diamond indenter[153].
A brief review of additive manufacturing

Additive manufacturing, also known as 3D printing, is a process of creating a physical object from a digital 3D model data. It can be used to build a wide variety of objects layer by layer, from simple parts to complex[154]. Additive manufacturing was introduced in 1987 with the introduction of stereolithography (3D systems) by Charles Hull. This process has been extensively described by Jacobs[155]. Stereolithography was commercialized with the SLA-1 machine[156], [157]. A brief schematic of the metal additive manufacturing technologies has been outlined in Fig. 1.10[158].

Some of the key benefits of additive manufacturing include[159], [160] customization, high speed and efficiency, production of complex geometries, mass production system, high quality and low unit cost with applications ranging from aerospace industry[161], structural engineering[162], integrated assemblies[163], medicine[164], tissue engineering[165] and direct write technologies[166] Overall, additive manufacturing has the potential to create products with greater efficiency, innovation, and sustainability.
Some of the most common types of 3D printing technologies include [158] Fused Deposition Modeling [167], Stereolithography [167], Selective Laser Sintering [168], Binder Jetting[169], Material Jetting[170], Directed Energy Deposition [171], Laminated Object Manufacturing [172], Multi Jet Fusion [173]. Fused Deposition Modeling [125] works by heating and extruding thermoplastic filament through a nozzle to create a structure; Stereolithography [167] uses a laser to solidify liquid resin to create a structure; Selective Laser Sintering [168] employs a laser to melt the powdered materials to create a structure; Binder Jetting[169] uses a print head to deposit a binding agent on powdered materials to create the structure; Material Jetting[170] uses a print head to jet droplets of material to create a structure. Directed Energy Deposition [171] uses a focused energy source, either in the form of a laser or an electron beam, to melt or fuse metal powders to create the structure. Laminated Object Manufacturing[172] uses a laser to cut and bond.

Figure 1.10 Major metal additive manufacturing technologies [158]
layers of material to create the object. Multi Jet Fusion [173] uses heat and fusing agents to fuse together the plastic powders to make the structure.

A wide variety of materials can be used in additive manufacturing, including plastics, metals, ceramics, and composites, depending on the technology being used[174]. Some of the most notable trends in additive manufacturing are multi-material printing, metal printing, large-scale printing, hybrid manufacturing, bioprinting and smart manufacturing[175].

**Cold spray additive manufacturing process**

Supersonic particle deposition, or cold spray, is a deposition process of solid feedstock powders, employed in additive manufacturing processes to fabricate parts and structures with melting temperatures below that of the powder[176], [177]. In this process, a supersonic stream of microparticles are accelerated and subjected to microscopic collisions with a target substrate after passing through a de Laval nozzle with a convergent-divergent geometry. At these high speeds, the kinetic energy of the particles leads to extreme plastic deformation at the interfaces of both the microparticle and the target substrate, which eventually enables solid-state consolidation/adhesion at high strain rate[176], [178]. The microparticles adhere to the substrate after crossing the threshold velocity called the critical impact velocity. The uniqueness of cold spray is that it makes a deposition below the melting point of the feedstock material and the resultant coating is formed in the solid state. Some other advantages include, high deposition efficiency, high density coatings, coating temperature sensitive materials, high bond strength of the coating and low porosity[179].
Since the introduction of the cold spray process[177], various studies have been done to understand the basic principle[176], [180] governing it along with exploration of its applications in different fields[181]. Some of the applications of cold spray include the chemical, aerospace, biomedical industries[182].

Various thermal spray techniques with respect to particle impact velocity and process temperature have been studied by Ang et al.[183], [184]. Their study has shown that the temperature employed in cold spray techniques are far less in comparison to other thermal spray techniques, while still achieving the necessary high velocities for particle deposition. Cold spray has been of recent interest to the industry as it uses comparatively lower temperatures which avoids material modifications from phase transformation, high temperature oxidation, crystallization and building of residual thermal stresses[176], [185]–[189]. In the cold spray process, the compressive stresses instead of tensile stresses are the dominating factor for production of the coating[190]. This avoids the adhesion failure of the coatings. Cold spray reduces material modifications during the process as it uses kinetic energy for particle deposition instead of thermal energy. Several advantages of this process have led to greater interest in understanding the physical phenomenon associated with this process. One of the important parameters that determines the particle deposition is the initial velocity of the particle. The particles adhere to the substrate after crossing the threshold initial velocity called the critical impact velocity. The critical velocity of the particles is dependent upon the particle size, initial temperature, melting temperature and on the thermomechanical properties of the particle and substrate materials[191]–[195].
For a successful deposition, the feedstock powders should cross the critical impact velocity and bond to the substrate surface. Parameters affecting the successful deposition include propulsive gas parameters such as pressure, temperature, and type; feedstock powder parameters such as temperature, oxide/hydroxide layer; and nozzle parameters such as traverse speed, scanning step, standoff distance, spray angle and trajectory[196]. Therefore, to improve the deposition process, the deformation process along with the parameters influencing it must be understood.

Adiabatic shear instability at the particle/substrate interface has been attributed as the predominant bonding mechanism4 in cold spray process[191]. Under adiabatic conditions, thermal softening can be induced in the material through temperature rise and heat transfer during deformation. This has been observed experimentally and through simulations[195], [197], [198]. With increase in temperature during deformation, after a threshold, thermal softening dominates work hardening leading to formation of interfacial jets. Experimental and simulation[195], [197] studies have also shown that stress concentration along with temperature around the interface region can result in the formation of a jet. Another observation from these studies has been that of strongest bonding forming at the edges of the interfacial region. It has been observed that there is more interaction of the material in these locations due to the displacement of the oxide film, which forms the jet, allowing for pure material interaction[199].

Hussain et al.[200] through numerical simulations observed the presence of highly localized temperature rises at the interfaces, which were large enough to induce localized melting, thus influencing bonding. Therefore, the mechanisms commonly perceived as the
dominant mechanisms for the bonding in cold spray are mechanical interlocking by adiabatic shear interface instability and localized melting.

In cold spray an increase in temperature of the propellant gas has shown to influence the gas velocity inside the nozzle, which thereby increases the particle velocity and the particle impact temperature[177]. The increase in particle velocity and increase in particle impact temperature can influence the bonding characteristics by increasing the adhesion strength.

Several experimental and theoretical results have shown the dependency of the critical velocity at which particles permanently adhere, on powder and substrate properties. Apart from bonding mechanisms and factors influencing the deposition process, studying the material properties at these high strain rates can also provide us with information about the interfacial interaction between particles and substrates. Prior studies have shown the strain-rate-dependency of materials. In the cold spray process, the deformation strain rate of the sprayed particles is on the order of $10^6$ or higher[191]. These ultra-high rates of deformation are necessary in cold spray to achieve metallic bonding. Therefore, it is important to understand material behavior at these ultra-high rates.

**Motivation, significance, and overall goals**

Cold spray is a deposition process of solid powders, employed in the additive manufacturing process to fabricate parts and structures below powder’s melting temperature [176]. In this process, supersonic velocity impacts of microparticles to target substrates, leads the microparticles to experience ultra-high strain rate microscopic collisions leading to plastic deformation[176].
This research project is motivated by the need to understand the fundamental material science occurring at the interfaces of microparticles-substrates at ultra-high strain rates. Study of impact dynamics and bonding mechanism of these microparticles will help us in understanding the solid-state consolidation mechanism in a better way.

Conventional cold spray process is a bulk process, where a batch of particles are accelerated together. Therefore, an individual particle’s impact and bonding parameters can only be statistically estimated with errors. Several computational modeling studies have been conducted to understand this ultra-high strain rate collision event[191], [201]. Computational modeling studies at different spatial scales[192], [202] have predicted adiabatic shear instability and localized melting at the interfaces[188], [191]. However, validation of the numerical modeling results through experimental data at these ultra-high strain rates has been limited due to limited instrument capability. With an advanced laser-induced projectile impact test[111], a highly controlled single particle collision event at the microscale can be attained. We supersonically accelerate metallic microparticles for impacting metallic substrates to study the material behavior at these ultra-high rates. These controlled experiments of single particle impacts will help us in developing a simplified model to characterize the extreme plastic deformation of materials at ultra-high strain rates. Thus, the overall goal of this project is to study dynamic behavior of single particles at ultra-high strain rates and post impact microscale morphologies of metallic microspheres at these extreme strain rates.

In summary, reviewing the literature provided insight that despite the growing interest in understanding the deformation process and impact dynamics in the cold spray process, until now the studies have either been done through numerical simulations or in the bulk
process. Material response in this extreme collision event occurs at a high strain-rate regime. Individual particle’s impact dynamics at these high strain rates have not been vastly studied in literature due to limited instrument availability. Single particle experiments by advanced laser-induced projectile impact tests[111] can provide a way for fundamental studies at these extreme conditions. Laser-induced projectile impact tests can be very useful in cold spray related research because material and process parameters such as particle size, temperature, impact velocity etc. can be precisely controlled for each impact.
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CHAPTER 2

LASER-INDUCED PROJECTILE IMPACT TEST IN METALLIC SYSTEMS: A COLD SPRAY PERSPECTIVE

In ballistic experimental studies, prior work with several acceleration systems has demonstrated capabilities that can accelerate impactors to high strain rates. Projectile impact and/or penetration dynamics with representative targets is a multivariable and complex phenomenon. The shift in trends to micro and nano scales, driven by the need to have a better fundamental understanding of the collision dynamics and material science at extraordinary strain rates beyond $10^6$ s$^{-1}$, has led to the development of a unique characterization technique, Laser-Induced Projectile Impact Test (LIPIT).

The first Laser-Induced Projectile Impact Test or LIPIT was demonstrated by Lee et al.\cite{1} that could accelerate microparticles to ultra-high strain rates in the magnitude of $10^8$ s$^{-1}$ with the aid of laser systems. LIPIT provides flexibility on the type of material system (metals, polymers, ceramics, composites, fibers, 2D) that can be characterized. This system can accelerate microparticles to supersonic speeds up to 4km/s for silica microparticles (diameter~3.7µm). The first LIPIT characterization was done by Lee et al.\cite{1} in which the authors demonstrated high strain rate studies on PS-b-PDMS deblock copolymer (Fig. 2.1). This material exhibits periodic glassy rubbery layered nanostructure behavior. The experiments were done on two PS-b-PDMS copolymers with two molecular weights (22 and 24 kg/mol). The impact energy dissipation through layer kinking, layer compression,
flattening, segmental mixing and domain fragmentation was observed in this study. This study also concluded that the energy dissipation is a function of layer orientations.

Figure 2.1 Deformation features at three impact velocities in PS-b-PDMS copolymer at high strain rates [1].

In a separate study, Lee et al. [2] performed high strain rate studies on multilayer graphene with different thicknesses (Fig. 2.2). This study revealed high impact energy delocalization at high strain rates for multilayer graphene (MLG) membranes. The energy dissipation mechanism and deformation process was explained through a series of penetration steps in the MLG membrane. This study concluded that for multilayer graphene, the specific penetration energy is ~10 times higher as compared to steel sheets at high strain rates. In the next section, we will briefly discuss the evolution of LIPIT since its inception, along with the brief working principle of this system.
In the first and second generations of the LIPIT system (Fig. 2.3), the pulse delay was achieved by increasing the optical path[1], [2]. Therefore, both these generations of LIPIT had a fixed interframe time, 22ns for the first generation and 34.5s for the second generation. Also, the number of exposures for the first and second-generation LIPIT were capped at 2 and 3, respectively. This led to a limitation in the speed range and time span of the experiment[1], [2]. This limitation was later on overcome by the addition of a high frame rate CCD camera with 16 CCDs. Individual CCDs could be triggered independently, which can help in the acquisition of 16 images within a 3ns exposure time[3]. The first generation of LIPIT accelerated multiple microparticles at a time, whereas in the second generation of LIPIT, individual microparticles could be accelerated.
Figure 2.3 Schematic illustrations depicting the evolution of the LIPIT system[1], [2], [4].

The third generation of the LIPIT system (Fig. 2.3) has better performance capability as compared to the previous two generations in terms of image quality and availability of tunability for inter-frame time and the number of pulses. Together, it also supports the
added functionality of conducting high-strain rate single particle experiments in the vacuum and at elevated temperatures.

**Figure 2.4** Schematic illustration of an advanced LIPIT system.

Working principle of the advanced LIPIT system[1], [2], [4]: A Nd:YAG laser (Quanta-Ray INDI-40-10-HG, Spectra-Physics) was used to generate an ablation laser pulse (\(\lambda = 1064\text{nm}, \) pulse duration 5-8 ns). Simultaneously, a Ti:Sapphire oscillator (Mai Tai HP, Spectra-Physics) generates laser pulses (\(\lambda = 750\text{nm}, \) pulse duration <100 fs). Precise measurement of the pulse repetition rate (79.56 MHz) was done through a 500MHz oscilloscope (GDS-3504, Instek). The image acquisition is done through the triggering of a CCD camera (Hamamatsu Photonics, C11440-22C) for 10ms. The triggering of the camera was achieved by a digital delay generator (DG645, Stanford Research System). Launch pads for ablation are created by the method described in Appendix B. An individual \(\mu\)P is placed near the focal point of the ablation beam on the launch pad. After placing \(\mu\)Ps
on the launching pad, the gold layer below an aimed µP was ablated to expand the elastomer layer. As a result, the µP was propelled by the elastomer layer expansion. During this event, three serially aligned modulators (electro-optical) gated the Ti:Sapphire laser pulses. A photonic crystal fiber with supercontinuum conversion (SCG-800, Newport) capability is used to convert the gated laser pulses to white light. As ultrafast (< 1 ps) white light pulses produced a superimposed image (or a stroboscopic image) of the moving µP with a controlled inter-pulse time, accurate collision parameters, such as the impact velocity and rebound velocity, were acquired through the spatial calibration of the image and the inter-pulse time. A schematic illustration of the advanced LIPIT setup has been shown in Fig. 2.4.

Figure 2.5 Summary of recent studies by Jae-Hwang Lee’s group @UMass-Amherst through LIPIT system [5]–[8].
Recent studies through the LIPIT system have produced a wide range of results that can be used for fundamental understanding of collision impacts and can be applied to various fields ranging from ballistics to cold spray applications. A few of the unique studies by Jae-Hwang Lee’s group (UMass-Amherst) through LIPIT impacts have been outlined in Fig. 2.5. Although LIPIT has the capability of characterizing several material systems, we will currently focus on metallic systems and a few of the studies that have been done with respect to metallic systems for several applications, including cold spray fundamental studies or otherwise.

Thevamaran et al.[9] demonstrated the deformation behavior of single crystal Ag microcubes when subjected to collisions against a Si target substrate at ~400m/s (Fig. 2.6). The impact-induced gradient was observed in the grain sizes. The study revealed that the heat generated during adiabatic compression led to dynamic recrystallization. Furthermore, the stored mechanical energy contributed to the continuous recrystallization within the microcubes. The nanostructural transformations were found to be dependent on the crystal and sample symmetries.
Phase transformations from FCC structure to an HCP structure was also observed by Thevamaran et al.[10] in Ag microcubes impacted at ~400m/s through LIPIT to a Si wafer in the [100] orientation (Fig. 2.7). This study concluded that phase transformation is orientation dependent.
LIPIT characterization studies by Xue et al.[11] observed a deformation induced 9R phase in UFG Al post impact at ultra-high strain rates (Fig. 2.8). The 9R phase was attributed to the shock induced rapid migrations of partials.

In additive manufacturing, impact-induced adhesion and localized melting have been established as contributing factors. LIPIT impacts studies on Al and Zn were done by
Hassani-Gangaraj et al.[12] to understand the adhesion mechanism in additive manufacturing through the melting perspective (Fig. 2.9). Their results on melting effects showed that impact-induced localized melting could instead act as a barrier for adhesion. Their study also observed that an increase in the melting rate did not result in adhesion. They found out that the solidification time was longer than the residence time of the microparticle on the substrate surface, which could prevent adhesion. This study provided a better understanding of the adhesion mechanism in additive manufacturing, which could in turn help in optimizing the material/process parameters of impact induced additive manufacturing techniques.

**Figure 2.9** Impact-induced deformation and localized melting[12]
After establishing that melting can hinder adhesion, Hassani-Gangaraj et al.[13], studied the supersonic impact behavior of a wide range of metallic microparticles in order to understand the bonding behavior (Fig. 2.10). The critical velocities, bonding events and material ejection through jet formation for these metallic systems were reported. This study reported the critical velocities of a range of metallic systems along with the observance of plastic deformation through jet formation. This study provided an understanding that jet formation contributes to the supersonic adhesion. The established critical velocities of the μPs through controlled LIPIT study can be used as a reference point for cold spray process of metallic systems in the bulk.

**Figure 2.10** Supersonic impact behavior of a range of metallic microparticles[13], [14]
In the previous supersonic impact studies, as material ejection and jet formation were observed during adhesion of the µPs, therefore through LIPIT characterization and FEA simulation, Hassani-Gangaraj et al. through a different study [15], [16] argued that bonding of the particles could be correlated with the hydrodynamic jet formation and that adiabatic shear instability was not a necessary condition for bonding. Instead, they put forward that bonding can be driven by jetting (Fig. 2.11). A proportionality between the critical adhesion velocity and the bulk speed of sound was established. This study provided an alternate mechanism of bonding apart from shear localization i.e., hydrodynamic pressure wave interaction leading to jet formation ultimately leading to bonding of the µPs.

**Figure 2.11** Jet formation and it’s correlation to critical adhesion velocity[15], [16]

During supersonic impacts, the µPs experience extreme plastic deformation. Studies on this deformation behavior can give us a better understanding of the bonding dynamics of the µPs. A unique perspective into the deformation behavior of Al6061 microparticles as a function of impact velocities was studied by Xie et al. [17]. The deformation dynamics was quantified through analysis of the deformed shapes of Al microparticles in the form of
flattening ratio (Fig. 2.12a). These deformed shapes were used to optimize the material modelling JC parameters. Experimental LIPIT characterization study of Ti microparticles by Wang et al.[19] was also used to optimize the modelling parameters in the JC model for LIPIT impact tests. Flattening ratio can provide a measure of the µP deformability during supersonic impacts. Flattening ratio of site-specific splats (Fig. 2.12b) were also used to quantify the deformation behavior by Tiamiyu et al.[18] The authors established different regimes of splat flattening that were characterized at different impact velocities. Through this study, the authors suggested that beyond certain impact velocities, the µPs had extreme penetrations into the target substrates, along with extensive petal formation, which could inversely affect the bonding behavior of the µPs. The µPs in this regime could de-bond and can cause erosion. This study can help optimize the process conditions of the cold spray process where the desired result is mostly formation of a coating instead of erosion.
Figure 2.12 (a) Deformed shapes of the captured Al microparticles[17]. (b) Flattening behavior of Cu and Al µPs[18].
Figure 2.13 Rebound, deposition, and erosion behavior in the cold spray process through LIPIT studies[20].

As a regime of de-bonding was shown in the previous study, which was then proposed as a source of erosion, therefore in a separate study, the supersonic impact-initiated erosion behavior was studied by Hassani-Gangaraj et al. [20] for the metallic system, Sn-Sn impacts. It was observed that beyond the bonding window, erosion or material loss was initiated at a threshold velocity called erosion velocity. This study defined a lower and upper bound in the deposition window for the cold spray process. As the cold-spray process is aimed at creating coatings, therefore optimizing the process parameters to accelerate the µPs below the erosion window can help in achieving that aim.

Several factors like process and material parameters can affect the bonding dynamics of the µPs. Studies related to the bulk cold-spray process have shown µPs size dependance of bonding behavior. Also, in the previous studies [13], [14], it has been seen that the Al µP size affected the critical velocity, therefore the effects of µP size on the bonding behavior in cold spray were done by Dowding et al. [21] through LIPIT experiments. They
established a power law scaling between the critical adhesion velocity and the µP size (Fig. 2.14). Impact by a larger µP size resulted in the temperature rise at the interface of the µP and the substrate which contributed to the overall decrease in spall strength thereby lowering the critical adhesion velocity. This study established a direct correlation between the µPs size dependence to that of the adhesion of the µPs. By controlling the material parameter like µP size, the cold spray process can be further tuned to obtain desirable results.

![Figure 2.14](image)

**Figure 2.14** Size effects as demonstrated by LIPIT experiments[21].

Studies have also shown that oxide layer can act as a barrier towards metallurgical bonding. Hassani-Gangaraj et al.[22] performed LIPIT experiments on a noble metal, Au (as a reference) and Al and Ag (with native oxide layers), to study the oxide layer effects on the adhesion. Further studies into the oxide layer of the metallic system was observed by Tiamiyu et al.[25] They observed delamination of the oxide layer (Fig. 2.15) near velocities that induce jetting. They proposed this behavior as an energy dissipation mechanism which
can lead to metal to metal contact ultimately leading to bonding. A separate study by Lienhard et al. [23] were also done to study the relationship between oxide-hydroxide layers in the µP with the critical adhesion velocity in the cold spray process. Analysis of the interfacial oxide chemistry in cold spray process through STEM maps of LIPIT impacted Cu µPs was done by Chen et al. [24]. Through these studies, it was observed that oxide/hydroxide layers can act as a barrier and can affect the bonding dynamics of metallic µPs in the cold spray process. Therefore, considerable efforts must be done to prevent the formation of these additional oxide/hydroxide layers.

Figure 2.15 Delamination of surface oxide layer[25]

Another process parameter that can affect the bonding dynamics in cold spray process is temperature. Substrate temperature effects on the bonding dynamics in the cold spray process were studied by Chaban et al. [26] through LIPIT experiments. They demonstrated that elevated substrate temperatures contributed to a lowering of the critical velocities. A
power law dependency of the critical velocities on the dimensionless temperature was suggested by Hassani-Gangaraj et al. [14]. Although elevating the temperatures might contribute to an earlier bonding of the µPs, but when the temperatures are elevated beyond a limit, they can also contribute to temperature induced oxide layer formation in metals which can ultimately counteract the effects of elevated temperatures for lowering of the critical velocities.

As in the previous studies, it was observed that extreme plastic deformation on both µPs and substrates leads to bonding. Therefore, in a study, Hassani-Gangaraj et al. [27] conducted supersonic impacts in-between several metallic systems to identify the regimes during this entire event of rebound to bonding. The study revealed that there is presence of three distinct deformation regimes. They identified the transition of how the plastic strain during the initial velocities is mainly on the µP (splatting regime), whereas with increase in impact velocities, the plastic strain is on both the µP (co-deformation regime) and the substrate and at sufficiently high impact velocities, when the µP bond, the plastic strain is mostly on the substrate (penetration regime). Through this study, an impact ratio based on material properties such as dynamic yield strength was proposed as a quantification method for the deformation regimes of splatting, co-deformation, and penetration (Fig. 2.16). Their study suggested that this ratio can be used to predict the impact and bonding regimes of other metallic systems, which can further help us in identifying and optimizing the cold-spray process.
Several theories of deformation mechanism [34] and bonding mechanisms in cold-spray process have been proposed. Previous studies by Hassani-Gangaraj et al. linked jetting to bonding[15], [16]. Their studies implied that for jet formation, adiabatic shear instability was not a necessary criterion. Instead, they observed the jet formation through interaction of hydrodynamic pressure waves during μP/substrate interaction. Their studies provided a different mechanism that correlated the bonding behavior to hydrodynamic plasticity without the need for shear localization. Furthermore, studies by Sun et al.[28], [29] have also enriched the knowledge of hydrodynamic jetting during the supersonic impacts and bonding. Although they observed the presence of ejecta and jets during bonding, but they also observed rebreaking of the jetting bonds in certain cases which led to rebounding of
the μPs. These studies provide evidence and shed a light on the overall jet formation mechanism and behavior which is proposed as a critical precursor for bonding.

To understand the conditions that lead to jet formation, jetting regimes in cold spray process were identified by Tiamiyu et al.[30] through LIPIT experiments on Cu μPs (Fig. 2.17). Plastic regime at low impact velocities with rebound of the μP, followed by emergence of substrate jetting near critical adhesion velocity followed by μP-substrate jetting at higher impact velocities ultimately leading to petalling of the μP-substrate have been identified through this study. Identification of different mechanisms during each impact velocity range can provide a systematic overview of the conditions that can ultimately lead to the successful deposition of the μPs. The cold-spray process parameters can be optimized by studying these mechanisms at each velocity range to accommodate maximum efficiency of the coating process.

Figure 2.17 Summary of observed jetting regimes in Cu μP LIPIT impacts to a Cu substrate[30].

The main target of cold spray process is to create a deposition on the substrate. But this process is sometimes accompanied by erosion which can further lead to substrate/coating degradation. During supersonic single particle impacts, erosion behavior was observed
previously [20] at high impact velocities beyond the bonding window. Further studies on erosion also identified onset of impact induced melting [31]. The authors [31] here then correlated the melting behavior (Fig. 2.18) to excess energy dissipation through an elastic plastic model and concluded that the melting contributes to only a small fraction of the excess energy loss. Beyond the upper limit of the bonding window, studies by Lienhard et al. [32] revealed jetting, melting, fragmentation and hydrodynamic penetration. Understanding the erosion phenomenon and identifying its characteristics and mechanisms can help us in applying different strategies to mitigate the erosion in cold spray process.

For example, as these studies [31] [32] have implied that erosion is material property and impact velocity dependent, therefore these two parameters should be precisely controlled to mitigate erosion in cold spray process.

![Figure 2.18 Observed melting features on steel-Sn impacts][31].

In the cold spray process, successful metallurgical bond formation is dependent on the bare metal-to-metal contact in between the μPs and the substrate. The presence of surface contaminants can significantly affect the adhesion of the μPs. The effects of surface contamination on the bonding dynamics in the cold spray process were studied through LIPIT impacts [23][33]. The authors observed that the presence of surface contaminants like oxides/hydroxides, amorphous carbon, and spherical oxide dispersoids hindered the
adhesion of the µPs. As these contaminants can be introduced during any of the stages such as from manufacturing to handling of the µPs/substrates or cold spray process itself, therefore, steps should be taken to minimize the introduction of these surface contaminants through surface preparation or process parameter optimization.
References


CHAPTER 3
TRANSITIONAL INELASTIC DYNAMICS OF ALUMINUM MICROSPHERES WITH ALUMINUM SUBSTRATES OF VARYING OXIDE THICKNESSES UNDER COLD SPRAY IMPACT CONDITIONS

This chapter focuses on the impact and bonding dynamics of aluminum microspheres when subjected to ultra-high strain rate microscopic collisions to aluminum substrates with systematically increasing oxide layer thicknesses. This paper has been published in Swetaparna Mohanty, Carmine Taglienti, David L. Gonzalez Arellano, Victor K. Champagne & Jae-Hwang Lee. “Journal of Thermal Spray Technology volume 31, pages1695–1701 (2022)”.

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Abstract
In the cold spray additive manufacturing process, supersonic collisions of metal microparticles with stationary metal target substrates create highly inelastic events within tens of nanoseconds. The rapid mechanical interactions, particularly at the microparticle-
substrate interface, produce adiabatic plastic deformation, eventually enabling solid-state consolidation. Since the extreme mechanical processes are inherently nonlinear and are significantly influenced by the materials’ conditions at the contact interface, controlled studies of impact and bonding dynamics of these microparticles help to better understand the solid-state consolidation mechanism. In this study, the extreme dynamic behavior of aluminum 6061 alloy microparticles (~20 μm diameter) impacting the aluminum 6061 alloy substrate as a model system is systematically investigated using the laser induced projectile impact test. The controlling parameters of these experiments are impact velocity (50-1,000 m/s) and substrate oxide film thickness (10 and 20 nm additional oxide layers prepared by atomic layer deposition). The influence of the substrate oxide layer on the dynamic responses of the microparticles is quantified as a semi-empirical function involving two characteristic transition points. Moreover, cross-sectional electron microscopy reveals that thickness-dependent fracture characteristics of the oxide layers support the origins of the transitional dynamics. Since the presence of a nanometer-thick oxide layer on a target substrate is realistically unavoidable, this controlled experimental study will enrich the understanding of the bonding dynamics influenced by the oxide layer in cold spray.

**Keywords**

cold spray, additive manufacturing, oxide effect, extreme plastic deformation, shear instability, critical velocity

**Introduction**

In additive manufacturing, the construction of a macroscopic object is achieved through sequential deposition and consolidation of microscopic material elements by various
techniques. Among the additive manufacturing techniques, solid-state consolidation of metallic microparticles (µPs) can be achieved when the µPs are subjected to high-speed collisions with a stationary target substrate. This process enables a unique additive manufacturing method known as cold spray (CS) and has attracted growing attention in recent years for the fabrication, repair, or restoration of components. In CS, the kinetic energy of the µPs leads to extremely high-strain-rate (HSR) plastic deformation at the interface between the µP and the target substrate, which eventually enables solid-state consolidation/adhesion. Recently, CS has been of interest to the industry as it uses comparatively lower temperatures than typical thermal spray, avoiding material modifications from phase transformation, oxidation, re-crystallization, and buildup of residual thermal stresses. The advantages of this process have led to greater interest in understanding the physical phenomenon associated with this process.

One of the important CS parameters that determines the µP deposition is the impact velocity of the µP. The µPs can adhere to the substrate above the threshold initial velocity or the critical impact velocity, which is dependent on the µP size, temperature, melting temperature, and thermomechanical properties of the µP and substrate materials. Bae et al. studied the adiabatic-shear-instability-based bonding mechanism numerically by impacting many µPs onto a substrate and subsequently comparing the results to experimental data. Champagne et al. studied material mixing between copper particle and aluminum substrates as a result of adiabatic shear instability. In addition to the basic CS parameters, as an environmental effect, the presence of oxide layers on µPs and the substrate can play a significant role in the bonding process of a metallic µP to a metallic surface. This oxide surface may act as an undesirable barrier preventing the formation
of metallic bonds between the μP and the substrate. For example, the surface oxide layer of μPs has been shown to influence critical velocity,\textsuperscript{19,20} which is an important parameter of the CS process as it determines the bonding of the μPs onto the target substrate. Thus, bonding is largely related to the characteristics of the collision dynamics regarding removing this oxide barrier and exposing the pure metals to each other for metallurgical bonding. Material interlocking by interface instability, cohesive bonding, adiabatic shear instabilities, and local melting have been put forward as the fundamental bonding mechanisms of the CS process.\textsuperscript{5,9,21,22} Another hypothesis has been that extreme plastic deformation breaks the surface oxide layer, thereby exposing the native pure metals, leading to metallurgical bonding of the exposed surfaces.\textsuperscript{5,21,23} The strongest bonding at interfacial regions was also found as a result of more material interaction in these areas due to the displacement of the oxide films.

Various parameters of the CS process, such as oblique impacts, particle size, substrate hardness, the effects of oxide layers and surface conditions, as well as the impact of multiple μPs, have been simulated and observed.\textsuperscript{10,24–28} The generation of ultra-fine-grained structures (including dislocations, dislocation cells, and twinning) caused by the high velocity impact of μPs has also been extensively documented and related to bulk material properties.\textsuperscript{29–31} Since CS is a complex process involving collisions of a large number of μPs, experimental observations of the collision of a single μP can provide insight into the extreme materials science behind it. Previously, simulation-based studies on the role of oxide layers in the impact process of CS have been carried out by Hemeda \textit{et al.}\textsuperscript{32} Xie \textit{et al.} reported a single μP study characterizing the collision dynamics of aluminum 6061 alloy (Al6061) μPs with a target Al6061 substrate that has the native oxide
layer.\textsuperscript{33} While Lienhard \textit{et al.}\textsuperscript{34} investigated surface oxide and hydroxide effects on aluminum μPs, there has not been a systematic experimental study showing the effects of substrate oxide on the collision dynamics.

\section*{Materials and Methods}

Among the broad range of deposition materials used in CS, polycrystalline Al6061 have been used widely in many fields of industry, including defense and aerospace, due to its ability to form freestanding structures and repair existing structures.\textsuperscript{5,35,36} Typically, 2-5 nm of native oxide film is present on Al6061 when exposed to air at room temperature.\textsuperscript{37,38} To form a metallurgical bond, the oxide barrier must be removed by the collision, and the pure metal should be exposed.\textsuperscript{39} Al6061 μPs (obtained from the United Technology Research Center and annealed at 230°C for 1 hour) with diameters ($D_p$) of approximately 15-25 μm were used for the experiments. Al6061 target substrates (McMaster-Carr) were manually polished using grinding papers and abrasives. For a controlled experiment to quantify the effects of the oxide layer in the μP-target substrate collision dynamics, the additional oxide layers were deposited with different thicknesses ($h_{ALD}$) using the atomic layer deposition process (Savannah – Thermal ALD) (Fig. 3.1). We considered the Al6061 substrate with only the native oxide layer ($h_{ALD}$=0 nm) as a reference substrate. Alumina oxide layers were grown on Al6061 substrates by using trimethylaluminum (TMA, Al(CH)\textsubscript{3}) and water as precursors. Prior to deposition, the Al6061 substrates were cut into 5 mm × 5 mm areas. Using N\textsubscript{2} as the carrier gas flow, TMA and water were alternately introduced for deposition. One complete deposition cycle at 200°C was defined by a 15 ms H\textsubscript{2}O injection, 8 s reaction, 15 ms TMA injection, and an 8 s reaction. The flow rate of the
precursors in the carrier gas was 20 sccm. For a 5 nm thick oxide layer, 50 cycles of the reaction process were performed at a growth rate of 1.06 Å/cycle.

**Figure 3.1** Schematic illustration of the three experimental conditions with (a) native oxide, (b) 10 nm additional oxide layer, and (c) 20 nm oxide layer. (d) An example of ultrafast stroboscopic image showing an accelerated Al6061 µP traveling at 760 m/s with kinetic energy of 4.5 µJ.

The laser induced projectile impact test (LIPIT)\textsuperscript{33,40} was used to create precise µP collision events at extraordinary HSR on the order of $10^6$–$10^8$ s\textsuperscript{-1}. For a launching pad, silicone elastomer (Sylgard 184, Dow Chemical) was formed by spin coating an ~80 nm thick gold-coated glass substrate (Fisherbrand\textsuperscript{TM} Cover Glasses No. 2) and then crosslinking at 200°C for 1 h. After placing µPs on the launching pad, the gold layer below an aimed µP was
ablated to expand the elastomer layer. As a result, the µP was propelled by the elastomer layer expansion. As ultrafast (< 1 ps) white light pulses produced a superimposed image (or a stroboscopic image) of the moving µP with a controlled inter-pulse time (Fig. 3.1d), accurate collision parameters, such as the impact velocity ($v_i$) and rebound velocity ($v_r$), were acquired through the spatial calibration of the image and the inter-pulse time. All other technical details of LIPIT were the same as described in our previous study.33

Results and Discussion

Fig. 3. 2a - 2c shows the HSR dynamic response of the Al6061 µP-target substrate collision in terms of $v_r$ for the different oxide thicknesses. The $v_r$-spectra show that there is a considerable increase in the $v_r$ of the µPs with an increase in the target surface oxide thickness. This trend was also previously hypothesized by Yuji et al.16 As surface oxide increases, more energy is required to fracture and expose the native pure metal. Also, since the oxide layer is harder and more elastic than the native metal,41-43 less plastic deformation is produced in the oxide layer of substrate. Cohesive energy is present during the impact of a µP, whereas the rebounding of a µP from the surface gains energy from elastic recovery. Thus, with the introduction of the oxide layer, there is less interaction between pure metals, resulting in a higher rebound energy than cohesive energy. The critical velocities also change as a function of oxide thickness. A higher impact velocity is required for thicker surface oxide layers to achieve the critical velocity. This implies that a larger impact energy is required to overcome the increasing oxide layer barrier and to use against the rebound energy for bonding.
Figure 3.2 Measured $\nu_r$–spectra of Al6061 µPs for an Al6061 substrate with (a) no additional oxide layer, reproduced from ref. 33. (b) 10 nm oxide layer, and (c) 20 nm oxide layer are shown with a trend curve of $2\sqrt{\nu_l}$ (gray) and corresponding fitting curves (red). (d) – (f) CoR–spectra from the measured $\nu_r$–spectra are shown with the two curves corresponding to the curves in (a) – (c).

The mechanical interactions between an impacting µP and a substrate are separated into two stages: impact and rebound stages. The impact stage begins when the µP comes into contact with the substrate and ends when the relative motion of the µP to the substrate is stopped. Immediately after the impact stage, the rebound stage begins and then ends when the µP is separated from the substrate. At the end of the impact stage, the impact (or initial) kinetic energy of the µP ($E_I$) is equal to the sum of the plastically dissipated energy ($E_p$) and the elastically stored energy ($E_e$) if the energy transfer to mechanical waves is negligible; $E_I \cong E_e + E_p$. Note that $E_e$ and $E_p$ are from the whole collision system.
consisting of the µP and the substrate. In the rebound stage, as the material’s mechanical
deformation is elastic, $E_e$ is approximated to be the sum of the rebound kinetic energy ($E_r$) carried by the rebounding µP and the surface energy ($E_s$) needed to separate the µP and the substrate; $E_e \equiv E_r + E_s$. Vibrational energies of the µP and the substrate after separation are neglected in this model as the fraction of the kinetic energy dissipated through elastic waves is negligible ($< 3\%$). Additionally, we assume that the original mass of the µP ($m_p$) is unchanged during the two stages due to the ductility of Al6061 µPs. As $v_i$ and $v_r$ can be expressed by $v_i = \sqrt{\frac{2(E_p + E_e)}{m_p}}$ and $v_r = \sqrt{\frac{2(E_e - E_s)}{m_p}}$, coefficients of restitution (CoR) can also be approximated by:

$$\text{CoR} = \left( \frac{E_e - E_s}{E_p + E_e} \right)^{1/2} \cong \left( \frac{E_e}{E_p} \right)^{1/2} \left( 1 - \frac{E_s}{E_e} \right)^{1/2}$$

(3.1)

because $E_p \gg E_e$ for the entire range of $v_i$ in the study. In Fig. 3.2d-2f, for the lower range of $v_i$ ($< 200$ m/s), a common trend of $2v_i^{-1/2}$ is observed in CoR regardless of $h_{ALD}$, while this common trend appears in the $v_r$–spectra in terms of $2v_i^{1/2}$. The same trend of CoR was also reported by Wu et al. from the numerically-modeled impact of the macroscopic spheres in a slow range of $v_i$ ($< 150$ m/s). Since the aluminum oxide layer inhibits the formation of metallic bonds at the contact interface, the common low-$v_i$ trend, independent of $h_{ALD}$, is not supposed to be related to $E_s$ or the 2nd term in Eq. 3.1. Consequently, as the low-$v_i$ trend of $2v_i^{-1/2}$ is corresponding to $(E_e/E_p)^{1/2} \cong (E_e/E_i)^{1/2}$, $E_e$ and $E_p$ are approximately expressed by $E_e \cong 2m_p v_i$ and $E_p \equiv \frac{m_p v_i}{2} (v_i - 4)$, when $E_s/E_e \approx 0$. 

83
According to the numerical simulations in the previous study of Xie et al., nearly the entire volume of an Al6061 µP experiences plastic deformation when \( v_i > 200 \) m/s. While the deviation from the low-\( v_i \) trend of \( 2v_i^{-1/2} \) is related to the saturation of an elastically deformable volume of the µP, more severe plastic deformation starts near 300 m/s. We hypothesize that this severe plastic deformation results in partial interfacial bonding and then initiates shear instability followed by abrupt interfacial softening. We believe that the onset of the interfacial softening in the impact stage leads to a sudden increase in \( E_s \) in the rebound stage. To fit the low-\( v_i \) trend, partial bonding, and complete bonding, we introduce a semi-empirical fitting equation based on Eq. 3.1,

\[
v_r = 2\sqrt{v_i} \left[ 1 - \left( \frac{1}{c + e^{-(v_i-v_1)/\alpha_1}} \right) \left( 1 + \frac{1}{(c-1)^{-1}e^{-(v_i-v_2)/\alpha_2}} \right) \right]^{1/2}
\]

(3.2)

, where the two sigmoid functions represent the two bonding characteristics. Fitted \( v_r \)-spectra and corresponding CoR-spectra are shown in Fig. 3.2. Fitting parameters are in Table.3.1. The transition to fracture regime is represented by \( v_1 \) (the onset velocity of fracture) and \( \alpha_1 \) (sharpness of the transition), which increases as \( h_{ALD} \) increases. The relatively large errors on both \( v_1 \) and \( \alpha_1 \) for thicker oxide layers are primarily due to the less distinctive transitions in \( v_r \) because the fractured thick oxide layer can still hinder the metal-to-metal cohesive contact. In addition to the reduced adhesion, the adhesion and elastic rebound are more inconsistently competing as the oxide layer increases. Due to this inconsistency in the fracture and possible suppression of adhesion force, the fitting results tend to be statistically less credible for thicker oxide layers. Using LIPIT, Hassani-
Gangaraj et al. reported the CoR–spectra of pure aluminum µPs with a native oxide layer.\textsuperscript{47} In the study, the CoR–spectrum of the 30 µm diameter aluminum µPs also demonstrated a transition in the CoR trend between 200 and 400 m/s, which may be caused by oxide fracture. The transition to the bonding state is represented by \( v_2 \) (the onset velocity of bonding) and \( \alpha_2 \) (sharpness of the transition). \( c \) is introduced for the asymptotic trend of \( v_r \) (\( v_r = 0 \)) through coupling of the two sigmoid functions. The larger value represents a greater inelastic contribution from the 2\textsuperscript{nd} transition driven by the shear instability. Compared to \( v_1 \), all values of \( v_2 \) are well-defined without a large error since the bonding process is accomplished by abrupt evolution of interfacial conditions such as shear instability, making \( v_r \) become zero. However, for the thickest case (\( h_{ALD} = 20 \) nm), the transition to the partial bonding stage, specified by \( v_1 \) and \( \alpha_1 \), is statistically insignificant, as the thickest oxide greatly suppresses the partial interfacial bonding and the shear instability.

\textbf{Table 3.1} A list of fitting parameters. *Parameters are limited by the preset range (2 – 20) for stability of fitting.

<table>
<thead>
<tr>
<th></th>
<th>( h_{ALD} = 0 ) nm</th>
<th>( h_{ALD} = 10 ) nm</th>
<th>( h_{ALD} = 20 ) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c )</td>
<td>1.54 ± 0.04</td>
<td>3.96 ± 0.49</td>
<td>8.72 ± 5.04</td>
</tr>
<tr>
<td>( v_1 ) (m/s)</td>
<td>296 ± 11</td>
<td>366 ± 67</td>
<td>387 ± 228</td>
</tr>
<tr>
<td>( \alpha_1 ) (m/s)</td>
<td>20.0 ± 12.0*</td>
<td>20.0 ± 39.7*</td>
<td>6.8 ± 75.1</td>
</tr>
<tr>
<td>( v_2 ) (m/s)</td>
<td>841 ± 22</td>
<td>873 ± 7</td>
<td>871 ± 28</td>
</tr>
<tr>
<td>( \alpha_2 ) (m/s)</td>
<td>2.0 ± 8.1*</td>
<td>2.0 ± 2.9*</td>
<td>20 ± 6.2*</td>
</tr>
<tr>
<td>R-square (COD)</td>
<td>0.87</td>
<td>0.71</td>
<td>0.55</td>
</tr>
</tbody>
</table>
Fig. 3.3 shows two characteristic deformation features of the oxide layer \( h_{ALD} = 20 \text{ nm} \) coupled with the impact-induced plastic deformation of an Al6061 substrate. Near the perimeter of the crater, the oxide layer was fractured by out-of-plane buckling due to compressive in-plane stresses. In contrast, near the center of the crater, the oxide layer was fractured by tensile stresses, and nearly the entire oxide layer remained. Thus, metal-to-metal contact is possible through the narrow gaps between fractured oxide flakes. This observation is consistent with our hypothesis explaining the very limited deviation from the trend of \( 2\nu_i^{-1/2} \) of CoR, the representative character of this weak-adhesion post collision is also discussed in Fig. 3.2. Thus, the presence of the fragmented oxide layer at the impact site implies that fracture in the oxide layer may inconsistently prevent or allow adhesion.

**Figure 3.3** Post-collision features of Al6061 substrate having a 20 nm additional oxide layer after 617 m/s collision of Al6061 µP. (a) SEM micrograph of the impact-induced crater. (b) Enlarged image of the crater highlighted section (red box) showing fine fractures of the oxide layer.
As $v_i$ exceeded the critical velocity, $\mu$Ps remained on the substrate after collision, and evidence of shear instability can be seen in the form of jetting remnants (Fig. 3.4a and 4b). The jetting remnants showed lower specular reflection in Fig. 3.4a, and this can be originating from a strong scattering characteristic of aluminum nanoparticles in the visible regime. Thus, we supposed this observation supported the interfacial softening. A cross-sectional SEM micrograph (Fig. 3.4c) reveals deep penetration of the $\mu$P into the substrate, along with the presence of partial interfacial bonding. In contrast to the cross-sectional images corresponding to $h_{ALD}=0$ nm, the presence of considerable interfacial gaps between the bonded $\mu$P and the substrate also indicates the debonding that occurred during the rebound stage due to the insufficient metallurgical bonding originating from the oxide layers at the interface. The continuously varying brightness within the $\mu$P and the substrate region immediately below the $\mu$P is due to electron channeling effects from distorted crystal structures by extreme plastic flows. The enlarged section Fig. 3.4d clearly shows the presence of the aluminum oxide layer beneath the protective layer of platinum, corresponding to $h_{ALD}=20$ nm. In the presence of the strong bonding barrier, the bonding of the $\mu$P is accomplished significantly by mechanical arrest after deep penetration into the substrate rather than by metallurgical bonding, although the shear instability and interfacial jetting exist.
Figure 3.4 (a) Top reflection optical and (b) tilted SEM images of a 16.4 µm diameter Al6061 µP after 1,000 m/s collision to Al6061 substrate ($h_{ALD} = 20$ nm). The two triangle markers indicate the same areas in both images. (c) Cross-sectional SEM images of the (d) magnified back-scattered electron micrograph of the top surface of Al6061 substrate.

Conclusion

In conclusion, to better understand the underlying material science of the extreme deformation of the µPs, their collision dynamics was quantified by using LIPIT at extraordinary strain rates relevant to CS. Through individual impact tests of Al6061 µPs on Al6061 target substrates, with systematically increasing substrate oxide thickness, one of the important parameters of bonding, i.e., the effects of oxide layers on the critical velocity, were quantified. By analyzing the µPs-substrate interactions, two transition velocities were observed originating from the onset of oxide layer fractures and shear
instability. The common trend of $2v_i^{-1/2}$ was observed in CoR regardless of $h_{ALD}$ until the onset of oxide layer fractures for lower impact velocities. Deviation from this trend at higher impact velocities was attributed to severe plastic deformation resulting in partial interfacial bonding followed by shear instability. The overall trend of the collision dynamics was described using two sigmoid functions. The impact-induced crater’s interfacial microstructure revealed two distinctive oxide fractures: an out-of-plane buckling fracture near the perimeter and a tensile fracture at the center of the crater. Jetting remnants on the substrate’s surface correlated with the presence of shear instability during collision. The substrate-oxide-dependent collision dynamics with precisely controlled parameters will extend the knowledge of solid-state consolidation mechanisms of CS.

Acknowledgements

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Supporting Information

Figure 3.S1 Plastically deformed volume of the μP normalized with respect to the μP initial volume, shown as a function of $v_i$ for both Al-Al impacts.
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This chapter focuses on the impact and bonding dynamics of aluminum microspheres when subjected to ultra-high strain rate microscopic collisions to aluminum substrates at room temperature and at elevated temperatures. This is a manuscript in preparation.

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Abstract

Cold-spray additive manufacturing process is an emerging technology that can create particle coatings at relatively low temperatures. In this process, supersonically accelerated microparticles are subjected to microscopic collisions with a stationary target substrate at extremely high strain rates, ultimately leading to adiabatic plastic deformation at the contact interfaces of the microparticle and target substrate to create the coating. In recent years, this process has been studied extensively to fundamentally understand the bonding dynamics and improve the deposition efficiency and performance of these coatings. The deposition behavior and the bonding dynamics of these coatings have been shown to be influenced by several parameters. One critical factor influencing the cold spray process is
the temperature. In this study, we evaluate the effects of temperature on the bonding dynamics of the aluminum 6061 alloy microparticles (~ 20 µm diameter) onto a target substrate (aluminum 6061 alloy and sapphire) by using an advanced laser-induced projectile impact test (α-LIPIT). By modifying the α-LIPIT through incorporating a temperature chamber and systematically increasing the temperature within the chamber (room temperature, 100°C, 200°C, and 300°C), the synergistic effects of microparticle heating and target substrate heating on the deposition behavior in the cold spray process are studied in conjunction to each other. Our controlled experimental studies demonstrate lowering of critical velocities and thermal softening occurring at higher temperatures. The aluminum 6061 microparticles were also captured post impact and analytically defined through the measurement of the flattening ratio as a function of impact velocity and temperature. The understanding gained from this study can extend our knowledge on the bonding dynamics and particle deformation behavior at higher temperatures in the cold spray deposition process.

**Keywords**

Cold spray, advanced laser induced projectile impact test (α-LIPIT), temperature dependence, critical velocity, plastic deformation, thermal softening, jetting, radial cracks, flattening.

**Introduction**

Cold spray additive manufacturing process is a deposition process developed by Papyrin *et al.* that creates a deposition in the solid state below the melting point of the feedstock
powder[1]. Due to the lower temperatures involved in this process as compared to that of conventional thermal spray processes, it can avoid material changes such as oxidation, defects from residual thermal stresses, decomposition, and microstructural changes [2]–[5]. It is also suitable for creating coatings for temperature-sensitive materials[2]. Feedstock powders or microparticles (µPs) are accelerated to supersonic speeds by propelling them in the gas stream through the converging-diverging nozzle of the cold spray setup [2]. During the flight of these feedstock powders or µPs, there is an energy exchange between the µPs and the gas flow. The microscopic collisions of these supersonically accelerated µPs with the target substrate result in bonding after attaining a critical threshold impact velocity called critical velocity ($v_{cr}$) [1], [2]. Extra ordinary strain rates are attained during this microscopic collision event[6]. The kinetic energy of these accelerated µPs leads to adiabatic shear instability and subsequently leads to plastic deformation occurring at the interface of both the µPs and the target substrate. Bonding of the µPs is thereby achieved by this criterion[6]. Parameters such as particle material properties, substrate material properties, process parameters such as gas dynamics, spraying conditions, nozzle geometry etc. have been shown to affect the critical velocity of the accelerated µPs[2], [7], [8].

Several studies have been conducted to understand the parameters affecting the bonding dynamics along with the fundamentals that affect the underlying bonding mechanism [2], [6]–[8]. One of the prevalent theories has been that the interfacial shear instability followed by extreme plastic deformation leading to the bonding of the feedstock powder or µPs[6]. Localized thermal softening induced by adiabatic shear instability can help in the fracture of the oxide layer, thereby exposing the base material at the interface of both the powder
and the substrate for metallurgical bonding[7], [9]–[12]. Metallurgical bonding can also be due to metal-to-metal contact because of jet formation[13]–[15]. As the $v_{cr}$ is also influenced by operational conditions of the process, therefore, several studies have also been carried out to understand these effects in the cold spray process[2], [7]. One of the process parameters influencing the entire cold spray process is temperature. Prior studies have shown the $v_{cr}$ to be a function of µPs temperature and substrate temperature. Substrate temperature effect studies on the deposition behavior in the metal cold spray process have been carried out previously by different groups[16]–[18]. In addition, effects of elevated µPs temperature on the deposition behavior has also been reported previously [13], [19]–[23]. Effects of preheating on both the µPs and the substrate and their subsequent deformation behavior has also simulated[20]. Particle velocities are coupled with the velocity of the carrier gas. The velocity of the carrier gas is dependent on the temperature of the gas, therefore the $v_{cr}$ is also influenced by the temperature governing the carrier gas flow[21], [22], [24].

In the bulk cold spray process, several µPs are accelerated together and subjected to microscopic collisions. Therefore, understanding and correlating the effects of temperature on an individual µP behavior has been challenging. Through a micro-ballistic technique called as laser induced projectile impact test[25], individual µPs can be accelerated to extraordinary strain rates in a controlled experimental setup. This experimental technique of single µP study can help in isolating the effects of temperature in this extreme collision event similar to that in the cold spray process. This can help in understanding the underlying fundamental material science and bonding dynamics of µPs at an elevated temperature. Previous work by Chaban et al.[26] have shown the effects of an increasing
substrate temperature on the lowering of critical velocities through single-particle impacts. However, there has not been any experimental study that shows the synergistic effects of increasing the temperatures of both the µPs and the target substrates on the bonding dynamics through single particle studies. Thus, in our study, the effects of temperature (room temperature, 100, 200, and 300 °C) on both the µPs and the target substrate were investigated in conjunction with each other. The relationship between the preheating of µP and the target substrate to that of the \( v_{cr} \) has been quantified. Direct measurements indicate the non-linearity in lowering of the \( v_{cr} \) at elevated temperatures. Furthermore, the µP deformation behavior in terms of flattening ratio of the captured µPs post impact have also been demonstrated through this study. Based on the SEM micrographs of the captured µPs, an increase in material loss in the form of jetting has been established at elevated temperatures. These correlations can provide a better understanding of the fundamentals of the cold spray process.

**Materials and Methods**

Micro-ballistic collision events at ultra-high strain rates were achieved by a laser-induced projectile impact test (α-LIPIT) as described elsewhere[25], [27], [28]. The launching pad for this setup was created by spin coating silicone elastomer (Sylgard 184, Dow Chemical) on an ~ 80 nm thick gold-coated glass substrate (Fisherbrand™ Cover Glasses No. 2) and then curing it at 200°C for 1 hr. Polycrystalline aluminum 6061 µPs owing to its wide usage in cold spray applications[2] were selected as the impacting µPs. The Al6061 µPs (procured from the United Technology Research Center and annealed at 230 °C for 1 hr) with an average diameter of ~20 μm were used for the experiments. The Al6061 µPs were then dispersed on the launch pad. Individual Al6061 µPs were aimed and the Au film
beneath the targeted μP was ablated using a 1064 nm laser pulse. The expansion of the elastomer led to the acceleration of the μP towards the target substrate. Ultrafast (< 1 ps and controlled inter-pulse time) white light pulses produced a stroboscopic image of the acceleration of the μP, from which the impact parameters such as the impact velocity ($v_i$) and rebound velocity ($v_r$), were calculated through spatial calibration of the stroboscopic image.

Figure 4.1 Modification of the Laser Induced Projectile Impact Test: Schematic Illustration depicting the incorporation of the temperature chamber to the LIPIT system. The micro-ballistic study of the coupled effects of elevated temperature on both the Al6061 μPs and the target substrate was studied by this system.
Additional modification was done by introducing a temperature chamber (Fig. 4.1) to the LIPIT system, to expose both the µPs and target substrate to elevated temperatures. The temperature chamber was constructed of Al6061, allowing temperatures within the chambers to reach elevated levels. The chamber surrounded the site of collision without interfering with the normal functionality of the LIPIT system. Four-heaters were mounted on the inner walls of the temperature chamber and the temperature within the chamber was controlled by a positive feedback loop from the thermocouple attached to the inner wall of the chamber. The ablation stage and the target stage were equipped with two additional thermocouples. The temperature of the experiment was taken to be the average temperature between the thermocouple readings of the ablation and target stage as the flight path of the µPs was directly in between the two stages. Two different target substrates were employed in this experiment, Al6061 and sapphire. Al6061 target substrates (procured from McMaster-Carr) were manually polished using grinding papers and abrasives. Sapphire target substrates were procured from McMaster-Carr.

In order to study the deformation behavior of the µPs, they were captured post impact and surface morphological studies were done on them through SEM (FEI Magellan 400). For capturing the Al6061 µPs, a conical shaped aluminum foil is placed over the target substrate impact area with the opening hole in line with the focal point of the ablation laser. Al6061 µPs travel through the hole and impact the sapphire substrate; the impact velocity is measured before entering the cover through the spatial and temporal calibration of the stroboscopic images. The captured particles post collision were then recovered from the target substrate surface with an elastomer for further studies.
Results and discussions

High strain rate dynamic response of Al6061 at elevated temperatures

Quantification of the dynamic response of Al6061 at elevated temperatures was conducted by incorporating a temperature chamber into the LIPIT system and observing the material response as a function of both impact velocity ($v_i$) and temperature ($T_p$). Al6061µPs were accelerated over a broad range of velocities ($v_i$) at different temperatures ($T_p=$Room temperature, 100ºC, 200ºC and 300ºC) to observe their dynamic response. Study by Summers et al. [29] at quasi static loading, have shown a mechanical degradation in the integrity of aluminum alloy at temperatures greater than 250ºC. However, in the cold spray process, the accelerated µPs bond to the target substrate at sufficiently high strain rates. The temperature of the accelerated µP ($T_p$) was taken as the average between the thermocouple readings at the upper and lower stages of the chamber as expressed in the equation, $T_p = \frac{T_1 + T_2}{2}$ where $T_1$ is the upper stage temperature and $T_2$ is the lower stage temperature. In order to correlate the impact induced plastic deformation with the $v_i$ and elevated temperatures, the scope of this study has been to study the bonding dynamics and the plastic deformation occurring at (a) both the µPs and target substrate side and (b) isolating the deformation to the µPs by impacting them to sapphire substrates. We speculate as found in literature, a decrease in $v_{cr}$ at elevated temperatures. At elevated temperatures thermal softening will allow for greater movement of the dislocations within the material[30].This can lead to a considerably higher plastic deformation at elevated temperatures. However, as the cold spray process involves high strain rates, therefore, together with thermal softening, strain rate hardening will also play into effect at these
temperature ranges. So, the current study will examine the extent of effects of elevated temperature at these extreme strain rates coupled to that of thermal softening effects. Here $v_{cr}$ is measured when the μPs starts to bond to the target substrate surface ($v_r = 0$).

**Impacts of Al6061 μPs to Al6061 target substrates at ultra-high strain rates**

![Figure 4.2 Temperature-dependent Al6061 μPs impacts to an Al6061 target substrate: COR spectra of Al6061 μPs impacts at (a) 23°C (b) 100°C (c) 200°C and (d) 300°C, respectively, color scaled with the diameter dependence of the Al6061 μPs. Semi empirical fit curve (red), reproduced from[31] shows the trend of Al6061 μPs impacts to Al6061 target substrates at room temperature.](image-url)
The nonlinear response of the Al6061 µPs impacts have been plotted in Fig. 4.2 that shows the coefficient of restitution \((\text{COR} = \frac{v_r}{v_i})\) spectra of the collision events at room and elevated temperatures. The \(\text{COR}\) is zero when µPs adhere to the target substrate or \(v_r = 0\).

Prior experimental work conducted by Chaban et al. [26] through single particle impacts, have established a lowering of \(v_{cr}\) with increase in substrate temperature. But their work differs from our current work, as their work involved preheating of only the target substrates, whereas the current scope of our work focused on elevated temperatures on the coupled behavior of both the µPs and the target substrates. As in these experiments the material of the µPs is similar to that of the target substrate, there will be elastic and plastic deformation at both the systems along with microstructural changes at elevated temperatures. Our results (Fig. 4.2) have quantified the effect of temperature on the critical velocity \((v_{cr})\) of the µPs. As seen in Fig. 4.2, the initial \(v_{cr}\) of the Al6061µPs at room temperature was found out to be 830 m/s whereas it increased to 855 m/s at 100°C, 800 m/s at 200°C and 685 m/s at 300°C. Simulation studies carried out by Yokoyama et al. have also predicted this type of behavior[32]. When a µP impacts a target substrate, the kinetic energy of the impacting µPs leads to extreme plastic deformation at the interface of the µPs. The collision dynamics of the µPs leads to removal of any oxide layer, ultimately leading to metal-metal contact for metallurgical bonding. At elevated temperatures, there is greater energy and momentum exchange in between the µPs, thereby increasing the kinetic energies of the accelerated µPs. A larger impacting energy at elevated temperature might also be contributing to the early onset of fracture of the native oxide layer, thereby decreasing the \(v_{cr}\). Another possible explanation of this behavior is that at sufficiently
higher temperatures there is an early onset of internal viscous flow and thermal softening [13] in both the µPs and the target substrate. An increase in thermal softening can lead to an increase in plastic deformation ultimately leading to bonding. At these extreme strain rates, the plastic strain is sufficiently high thereby also leading strain rate hardening in the materials. From our studies, we can observe that at 100ºC the \( v_{cr} \) increases instead of decreasing as predicted by Gangaraj et al.[33] and observed by pre heating of the substrates by Chaban et al.[26]. Even though there might be an increase in the kinetic energies of the µPs, yet strain rate hardening induced by greater impacting energies from the elevated temperatures on both the µP and target substrate side might have overcome the thermal softening effects and contributed to the increasing of the \( v_{cr} \) at 100ºC. The \( v_{cr} \) follows a lowering trend as predicted in the literature for 200ºC and 300ºC studies. Study by Arabgol et al. have concluded that increasing the substrate temperature also increases the porosity of the microstructure, thereby increasing the deformation behavior, which can lead to lowering of the \( v_{cr} \) [34]. Increase in the jetting behavior at both the particle and substrate side can also increase the metallurgical bonding thereby lowering of \( v_{cr} \)[35]. In dynamic deformation, adiabatic shear instability can lead to the formation of jets at the interface of particles and substrate[4], [6], [36]. As predicted by Xie et al. [28] and Gangaraj et al.[33], through FEA simulations a distinct jet formation was observed in all the bonded particles at room and elevated temperatures which is essential for bonding of the µPs to the target substrate. Gangaraj et al.[33] in their study explained the hydrodynamic behavior of the µPs on impact. They showed that there was a presence of material ejection in the form of jet formation above the \( v_{cr} \). They also developed a scaling behavior that correlated the \( v_{cr} \) with that of the temperature. Our results also attribute the lowering of the \( v_{cr} \) through jet
formation as can be observed from the micrographs of the captured µPs in the later sections. Furthermore, simulation studies carried out by Yu et al. [20] have also shown that the effects of preheating both the particle and substrate have led to an increase in contact area between the particle and the substrate along with a sharper and longer jet formation.

Fig. 4.3, represents the $v_l - v_r$ spectra of the Al6061 µPs- Al6061 target substrate impacts at room temperature and at elevated temperatures. We can observe that for all the cases of temperatures, a linear increase in the $v_r$ at lower $v_l < 200\,m/s$. A transition zone appears at near 200m/s for $T_p = 23^\circ C$ and 100$^\circ$C. The $v_r$ associated with 100$^\circ$C are higher as compared to other temperatures. The appearance of a transition zone can be hypothesized to absorption of a large fraction of the impact energy and onset of severe plastic deformation leading to partial interfacial bonding as studied in literature[31]. For 200$^\circ$C and 300$^\circ$C impacts, the transition zone is difficult to distinguish. However, a decrease in $v_r$ is observed when the temperature increases from 200$^\circ$C to 300$^\circ$C. The decrease in rebound velocity from 200 to 300$^\circ$C can be attributed to the onset of internal viscous flow and thermal softening at this temperature range. The initial transition zone is followed by entirety of the µPs experiencing extreme plastic deformation which subsequently leads to adherence at $v_r = 0$. 
Figure 4.3 Temperature-dependent Al6061 µPs impacts to a Al6061 target substrate:
Rebound velocity spectra of Al6061 µPs impacts at (a) 23°C (b) 100°C (c) 200°C and (d) 300°C, respectively, color scaled with the diameter dependence of the Al6061 µPs. Semi empirical fit curve (red), reproduced from[31] shows the trend of Al6061 µPs impacts to Al6061 target substrates at room temperature.
Morphological studies of Al6061 µPs impacts to sapphire target substrates at ultra-high strain rates: The high rigidity modulus of sapphire as compared to that of Al6061 makes it a near ideal substrate to study the impact induced deformation of the Al6061 µPs. By impacting the Al6061 µPs to a sapphire substrate, the high strain rate deformation can be restricted to the µP side. This allows for a strain rate dependent deformation study of the µPs. Through the LIPIT setup, a sequence of µPs subjected to microscopic collisions with the sapphire substrate at different temperatures were captured to observe the extent of deformation as a function of temperature and \( v_i \) (Fig. 4.4).

**Figure 4.4 Deformed shapes of captured Al6061 µPs:** Representative SEM images of captured Al6061 µPs post impact to sapphire substrate at different experimental
temperatures (room temperature, 100°C, 200°C and 300°C) over an impact velocity range of 50<v_i<1200m/s. The SEM images have been individually scaled to represent a collective scale bar of 10µm. The room temperature SEM micrographs have been reproduced from[28].

The stroboscopic images did not visually identify any deformation during the capture of the µPs. However, from the SEM micrographs (Fig. 4.4) µP deformation morphologies have been observed. Through visual observation studies of the SEM micrographs, it is determined that Al6061 µPs impacting below v_i<350 m/s tend to maintain their initial spherical shape, but with increasing impact velocity (v_i > 650m/s), the Al6061 µPs display a globally flattened shape. Near the v_{cr} v_i > 650m/s, values at different temperatures (Al6061 µPs-Al6061 target substrate collisions), extensive plastic deformation is observed. However, we can observe a significantly deformed µP for T_p = 300°C at v_i~830m/s. As the deformation behavior is dictated by dislocations. Therefore, it is inferred that at this elevated temperature, thermal softening coupled with extreme strain rates might be contributing to the presence of dislocation loops, which can further the plastic deformation[37].

D_o is defined as the initial diameter of the µPs prior to any impacts. Through optical microscopy and through the LIPIT system, the initial shape of the µPs were visually investigated and the D_o measured. In the subsequent study, the effect of temperature on the deformation behavior was further quantified by measuring the D_o of the particle and the height of the captured particle post-collision, to calculate the specific diameter change or flattening ratio (∆D /D_o), which can provide a measure of the plastic deformation occurring
in the microparticle w.r.t the $v_i$ and temperature. It should be noted that diameter change calculations are accompanied with an error as the SEM micrographs (side view images) cannot represent the entire volume of the captured µPs. Therefore, any non-uniformity in the flattening of the surfaces can give rise to errors in measurement. Fig. 4.5 shows the flattening ratio for particles at different temperatures and impact velocity ranges. Linear regression fitting of the data shows a linear increase in the flatting ratio with increase in $v_i$ for all cases of experimental temperature, which correlates well to the conclusion from Xie et al.[28] A steeper slope is observed for 100˚C impacts, which might be indicative of temperature induced thermal softening of the material leading to greater flattening or deformation. Normalized specific diameter change of greater than 0.5 is observed above $v_i > 600$ m/s, where the majority of the µPs experience extreme plastic deformation. This correlates well with the observance of transition zone followed by subsequent bonding as shown in the $v_i - v_r$ plots of the Al6061 µPs-Al6061 substrate impacts.
**Figure 4.5 Deformation behavior in terms of Flattening ratio:** Linear regression fitting of the specific diameter change (flattening ratio) as a function of impact velocity and temperature for captured Al6061 µPs post impact with sapphire substrate.

**Figure 4.6 Material loss at elevated temperatures:** Scanning electron micrographs showing mass loss from sub-critical radial crack formation in the jet region of the captured
particle surface with elevated temperature conditions. The inset shows the enlarged highlighted section (black box) of the under surface of the captured particle post collision with sapphire substrate.

Fig. 4.6 (a)-(d), show that for $v_i > 600\text{m/s}$, the µPs began to form a jet region around the outer rim which has been associated with bonding of the µPs[33]. The enlarged SEM images of the under surface of the captured µPs, in the highlighted boxes provide evidence of substantial material loss from sub-critical radial crack formation in the jet region. The material loss has been shown to increase with an increase in the temperature and $v_i$. This can again be attributed to the onset of thermal softening at elevated temperatures. At sufficiently high $T_p$, the µPs experience internal viscous flow and thermal softening, leading to ejection of material in the form of jetting. Although LIPIT measurements are limited in providing direct measurements of the material being ejected, yet through visual inspection of the underside of the captured µPs at increasing temperature (Fig. 4.6(a)-(d)) we can observe the presence of extensive radial cracks thereby indicating greater material loss at elevated temperatures. Thus, we can infer that at elevated temperatures, the plastic flow increases which can contribute to the lowering of $v_{cr}$.

**Conclusion**

In summary, the bonding dynamics of Al6061 in relation to one of the major cold spray process variables; temperature was studied through micro ballistic impact studies. Al6061µPs and target substrates together were systematically exposed to elevated temperatures and the resultant interfacial dynamics in the form of critical velocities ($v_{cr}$)
was observed. The collision dynamics showed a non-linear lowering of $v_{cr}$ at elevated temperatures. This was attributed to the onset of an internal viscous flow and thermal softening at sufficiently elevated temperatures. In the subsequent studies the Al6061µPs were captured post collision with a sapphire target substrate and the deformation dynamics was quantified as a function of temperature and impact velocities ($v_i$) in the form of flattening of the µPs. Morphological studies of the captured µPs through quantification indicated an increase in the deformation of the µPs with increasing temperatures and $v_i$. Visual inspection of the underside of the captured µPs also indicated significant material loss and the presence of extensive radial cracks in the jet region at elevated temperatures. Elevated temperatures might have contributed to the increase in plastic flow of the materials thereby resulting in earlier bonding of the µPs. The experimental observation of the collision dynamics and the coupled effects of µP and substrate heating at extreme strain rates can further enhance our understanding of the cold spray process.

**Acknowledgements**

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Figure 4.S1 Temperature-dependent Al6061 µPs impacts on a sapphire target substrate: Rebound velocity spectra of Al6061 µPs impacts at (a) 23°C (b) 100°C (c) 200°C and (d) 300°C, respectively, color scaled with the diameter dependence of the Al6061 µPs. Unweighted 5 point averaging fit curve (blue), shows the trend of Al6061 µPs impacts on sapphire target substrates at their respective temperatures.
Figure 4.52 Temperature-dependent Al6061 µPs impacts on a sapphire target substrate: CoR spectra of Al6061 µPs impacts at (a) 23°C (b) 100°C (c) 200°C and (d) 300°C, respectively, color scaled with the diameter dependence of the Al6061 µPs and with a trend curve (red) reproduced from [31] and fitting trend curves (blue) of the data at that particular temperature.
References


CHAPTER 5

ULTRA-HIGH STRAIN RATE DYNAMIC CHARACTERIZATION
OF ALUMINUM MICROSPHERES WITH OXIDE/HYDROXIDE
LAYER FOR DETERMINATION OF CRITICAL VELOCITY
PROFILES

This chapter focuses on the impact and bonding dynamics of aluminum microspheres with varying oxide and hydroxide thicknesses when they are subjected to ultra-high strain rate microscopic collisions to aluminum substrates. This study can provide an understanding of the effects of environmental and storage conditions on the dynamic behavior of metallic systems at ultra-high strain rates.

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Abstract

Cold spray is a material deposition process which can lead to the formation of the coatings through the plastic deformation occurring at the interfaces of the microparticles and the substrates. Several parameters can influence the critical bonding velocity of accelerated microparticles including the process parameters and the material properties of both the
microparticles and the target substrates. Our study was focused on analyzing how the processing conditions of the microparticles can affect the bonding dynamics by the formation of an oxide/hydroxide layer. The bonding dynamics was quantified in the form of critical bonding velocity profiles. This study highlights the critical velocity profiles of high purity aluminum microparticles that have undergone processing under elevated temperatures in dry air and humidity. The critical velocity profiles in this study are obtained through a laser induced projectile impact test that can accelerate the microparticles to extreme strain rates similar to that in a cold spray process. This study concluded that there was negligible effects of the treatment of the microparticles to elevated temperatures at dry air conditions. Furthermore, our results also revealed that the exposure of the microparticles to elevated humidity levels can increase the critical bonding velocity. This was attributed to the formation of oxide/hydroxide layers in the microparticles that can act as a barrier for bonding.

Introduction

Cold spray coating process is a subset of thermal spray techniques[1]. But unlike other thermal spray techniques, instead of melting and re-solidification, cold spray utilizes the kinetic energy of the accelerated microparticles to create plastic deformation at the interface which ultimately leads to the adhesion of the microparticles[2], [3]. Cold spray additive manufacturing process is currently defined as a coating process, in which a stream of microparticles (µPs) are accelerated to high speeds and subjected to extreme collisions so as to achieve a solid-state consolidation of the µPs[3]. The uniqueness of this process lies in its ability to create a coating without melting of the µPs[3]. Strain rates involved in
this event can be very high in the range of $10^6$ or higher[4]. The coatings created through this process have found a wide range of applications across various industrial sectors[5] ranging from aerospace[6] to medical applications[7]. The applications can be tuned to achieve the desired functionality depending on the need[8], [9]. Although cold spray provides flexibility in material selection[10], there is a particular interest in cold sprayed aluminum coatings. Some of the reasons that contribute to this interest is the easy availability of this metal, low production cost, involvement in a wide range of applications related to repair, wear, and corrosion resistance and because of the ductile behavior and low density of the metal[11].

In the cold spray process, the kinetic energy of the accelerated $\mu$Ps controls the plastic deformation at the interface of the $\mu$Ps and the target substrates[3]. Crossing a critical threshold velocity can ultimately lead to the adhesion of these $\mu$Ps to the target substrates. Several mechanisms have been proposed for the bonding behavior of the $\mu$Ps[4]. Adiabatic shear instability followed by extensive plastic deformation at the interface of both the $\mu$Ps and the target substrates can lead to the bonding behavior[4]. Material ejecta in the form of jets have also been proposed as a precursor to the bonding behavior[12]. Cold spray is a multivariable process in which the bonding dynamics can be affected by several parameters. These parameters can either be the processing conditions or the material properties[3], [13], [14]. One of the material properties that can affect the bonding dynamics is the presence of an oxide layer[15]–[17]. The removal of oxide layer and the exposure of the native metals is of utmost importance for the formation of the metallurgical bonds as the oxide layer can act as a barrier in bonding[18], [19]. During cold spray microscopic collisions, the onset of severe plastic deformation can fracture the oxide layer
thereby exposing the base metals for bonding[20]. Aluminum has an inherent presence of a native oxide layer[21], [22]. It is also prone to surface oxidation and surface hydroxide formation[22], which can increase the oxide/hydroxide layer at the surface. Presence of a thicker oxide/hydroxide layer can require additional energy from the μPs for removal. Several studies have been done to predict the bonding behavior with the presence of additional oxide layers[15]–[17], [23]. Experimental studies have also established the correlation between μP oxygen content and the adherence of the μPs in cold spray process[24]. In the cold spray process, the microparticles can undergo oxidation either during the process such as during gas atomization for creation of the feedstock powders[25], temperature induced oxidation, or under storage conditions etc. Therefore, it is imperative to understand the fundamentals behind the bonding dynamics of the microparticles with an additional oxide/hydroxide layer to optimize the cold spray process. Studies related to the oxide/hydroxide effects mentioned previously have been carried out in the conventional cold spray setup or through simulation studies. Laser Induced Projectile Impact Test (LIPIT)[26] provides the ability to accelerate a single microparticle in controlled environment to supersonic speeds at high strain rates similar to that in the cold spray process. In our study, we inculcated the quantification of the stroboscopic LIPIT images, to create critical bonding velocity profiles for the different types of feedstock powders. Initially, we subject high purity aluminum microparticles to different processing conditions such as elevated temperatures in dry air and humidity and then through microballistic collisions in the LIPIT, we can quantify and correlate individual particles critical velocity and bonding dynamics to that of the processing conditions.
Materials and Methods

Gas atomized high purity aluminum microparticles (Dia ~10µm) subjected to different processing conditions were procured from UTRC (East Hartford, CT). These microparticles had undergone different processing treatments. Our study focused on seven batches of microparticles. Processing conditions were introduced to these microparticles so as to introduce an oxide/hydroxide layer. The control sample “As received” was devoid of any treatments. Table 1 summarizes the different treatments undertaken by the high purity aluminum µPs prior to any single particle impacts. Fig. 5.1 represents the schematics of the fluidized bed reactors for treatment of the µPs at elevated temperatures and humidity to introduce oxide/hydroxide layers.

The launching pads for the micro-ballistic experiments were created by spin coating a silicone elastomer (Sylgard 184, Dow Chemical, 1:10 ratio) on a glass substrate (Fisherbrand™ Cover Glasses No. 2) and then crosslinking it at 200 °C for 1 h. Prior to the spin coating of the elastomer, the cover slip was sputter coated with gold (~ 80 nm thick). The cured launch pad is cut into 5mm wide strips through a diamond tip scriber. The µPs are then spread on the launch pad. For micro-ballistic experiments through LIPIT, individual µPs are selected and targeted at the focal point of the ablation laser. The ablation creates an expansion of the elastomer film. The rapid expansion of the elastomer leads to the acceleration of the µPs towards the target substrate. Through the temporal and spatial calibration of the stroboscopic images, we can obtain the velocity profiles of the accelerated µPs. This will be analyzed to quantify the critical velocity profiles of the treated and untreated µPs. This process has been described in detail elsewhere.[26], [28], [29].
Figure 5.1 Schematic illustration of the fluidized bed reactors for treatments of the μPs[27]

High purity aluminum (99.99%, Sigma-Aldrich) was selected as the target substrates for single particle experiments. Electrochemical polishing was done using an in-house setup (Fig. 5.2). The electrochemical polishing was done with an electrolyte solution of
perchloric acid (70%, A.C.S. Reagent, Sigma-Aldrich) and ethanol (Pharmco Products Inc) mixture at a current density of 5 A/mm² and at a temperature of 10°C for 30s. After electrochemical polishing, these target substrates were rinsed with deionized water to remove any extra electrolyte on the surface and then air dried.

Figure 5.2 Schematic illustration of the in-house electrochemical polishing setup for polishing of the aluminum substrates.

For SEM micrographs, a high-resolution scanning electron microscope (FEI Magellan 400) was used. The samples prior to imaging were sputter coated with a thin layer of Au (~2 – 5 nm).

Results and Discussion
The gas atomized high purity aluminum μPs were subjected to different processing conditions as shown in Table 1. Studies have shown the growth of thermally induced oxide layer when aluminum is subjected to elevated temperatures under dry air conditions[30].
In this study, it was observed that at temperatures below 300°C, the rate of oxide growth was very fast, but it plateaued at a value for thickness. However, with temperatures exceeding 300°C, the growth of oxide layer slowed down but there was not any limiting effects on the growth of thickness of the oxide layer. Therefore, for our studies, the processing conditions were limited to an upper limit of 300°C. By exposing the µPs to an elevated temperature in dry air conditions, it was hypothesized that, an oxide layer will form on the µPs. As the oxide layer acts as a barrier for bonding, therefore it will directly affect the bonding dynamics and the $v_{cr}$ of the treated µPs. The quantification of this results can be done in terms of critical velocity profiles for each batch of the µPs.

Table 5.1 Processing conditions of the high-purity aluminum µPs

<table>
<thead>
<tr>
<th>Nomenclature of the µPs</th>
<th>Processing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Received</td>
<td>No processing</td>
</tr>
<tr>
<td>HT-Baseline</td>
<td>Exposure Times to Dry Air at 300°C 0 minutes</td>
</tr>
<tr>
<td>HT-30</td>
<td>Exposure Times to Dry Air at 300°C 30 minutes</td>
</tr>
<tr>
<td>HT-60</td>
<td>Exposure Times to Dry Air at 300°C 60 minutes</td>
</tr>
<tr>
<td>HT-240</td>
<td>Exposure Times to Dry Air at 300°C 240 minutes</td>
</tr>
<tr>
<td>RH 50%</td>
<td>50% RH / 29°C for 4 days</td>
</tr>
<tr>
<td>RH 95%</td>
<td>95% RH / 29°C for 4 days</td>
</tr>
</tbody>
</table>
For several applications like energy conversion[31], the feedstock aluminum powders require the presence of an oxide layer. However, during the production of these powders through gas atomization, the aluminum can form hydroxides with/without the oxide layers. During the cold spray process, if the humidity conditions are elevated (>50%), along with presence of high temperatures, the aluminum can also form oxide-hydroxide layers[25]. These can affect the adhesion of the µPs. Therefore, it is imperative that we quantify and understand the bonding behavior of the µPs that have been also exposed to humidity. This will help in optimizing the cold spray process altogether.

As the objective of the study was to quantify the critical velocity profiles of the treated µPs, therefore as a control the critical velocity profiles of unprocessed µPs (As- received) were also obtained for comparison. The high strain rate single particle impacts were recorded by an ultra-fast stroboscopic image. The measured impact and rebound velocity profiles of the µPs from the spatial and temporal calibration of these stroboscopic images gave us the critical velocity profiles for all the feedstock µPs. The $v_i - v_r$ spectra have been plotted for different feedstock µPs. From the $v_i - v_r$ spectra of the µPs subjected to elevated temperatures in dry air (Fig. 5.3), we can observe that the critical velocities ($v_{cr}$) was almost similar for all the cases. The $v_{cr}$ for HT-Baseline µPs, HT-30 µPs, HT-60 µPs and HT-240 µPs were 817m/s, 822 m/s, 817 m/s and 822 m/s respectively. The $v_{cr}$ of the control batch (As-Received) was 816m/s. No significant difference was also observed in the rebound velocities for the high temperature exposed in dry air µPs to that of the high purity aluminum µPs subjected to no processing conditions. This was in contrast to what was hypothesized previously based on literature, that exposure to elevated temperatures
might induce an oxide layer thereby affecting the adhesion inversely. Quantification of the oxide layer thickness for similar μPs have been done elsewhere[32].

Figure 5.3 Velocity profiles of the high temperature exposed to dry air aluminum μPs:

Measured $v_l - v_r$ spectra for an aluminum μP impacting an aluminum target substrate.
The aluminum target substrate was electrochemically polished prior to the single-particle experiments. The plots have been color scaled to the diameter dependence of the μPs.

**Figure 5.4 Velocity profiles of the aluminum μPs subjected to humidity:** Measured $v_i - v_r$ spectra for an aluminum μP impacting an aluminum target substrate. The aluminum target substrate was electrochemically polished prior to the single-particle experiments. The plots have been color scaled to the diameter dependence of the μPs.
From the measurements through TEM and XPS, the oxide layer thickness for similar µPs was quantified in a different study[32]. Their results did not show any significant difference in the thickness of the oxide layers for all the µPs exposed to elevated temperatures under different processing conditions in dry air. Their measurements provided a value of ~5-6nm of oxide layer thickness. Aluminum at room temperature also has a native thickness in the magnitude of ~5nm[33]. Therefore, the control µPs (As-received) should also have similar oxide layer thickness. This was also verified by the study carried out earlier by Lienhard et al.[32]. Therefore, the insignificant difference in the \( v_{cr} \) profiles of the HT-Baseline, HT-30, HT-60, HT-240 and As-Received µPs can be attributed to this. All the above mentioned µPs have similar thickness of oxide layer. So, they can be treated as identical in terms of oxide layer thickness. Therefore, the \( v_{cr} \) should also be in the similar range for all the µPs exposed to elevated temperatures in dry air. The energy required to overcome the oxide layer barrier will be similar, which will also make the \( v_{cr} \) similar to each other.

However, from our studies we can observe a significant difference in the \( v_{cr} \) of the µPs exposed to higher levels of humidity (RH-95) as compared to RH-50 and the control batch (Fig. 5.4). The \( v_{cr} \) for RH-50 µPs and RH-95 µPs were 800m/s and 881 m/s respectively. As hypothesized before, the exposure of µPs to humid environments can change the surface morphology of the µPs and might introduce oxide/hydroxide layer. The increase of the \( v_{cr} \) from our studies for the µPs exposed to humidity can be attributed to this. TEM and XPS studies by Lienhard et al.[32] for similar µPs, also gave us a quantification of the oxide/hydroxide layer thickness. Their results showed that for RH-50 µPs, the oxide/hydroxide layer was similar to that of the control µPs. This is in agreement with our
$v_{cr}$ measurements. However, for RH-95 $\mu$Ps, there was an increase in the oxide/hydroxide layer thickness (~8nm). This also is in agreement with our $v_{cr}$ profiles for the RH-95 $\mu$Ps. Together we can attribute the increase in the $v_{cr}$ of the RH-95 $\mu$Ps, to that of an increase in the oxide/hydroxide layer thickness. The presence of the additional oxide/hydroxide layer might be contributing to the increase in $v_{cr}$. Additional energy is required by the collision to overcome this barrier, which thereby drives an increase in the $v_{cr}$[34]. The FTIR studies by Lienhard et al.[32] for similar group of $\mu$Ps also confirmed the presence of hydroxide layer for RH-95 $\mu$Ps.

![Graphs illustrating $v_{cr}$ profiles](image)

Figure 5.5 Observance of scatter in the $v_i - v_r$ spectra for heat-treated and control group $\mu$Ps. Surface morphology changes are denoted in terms of scatter in the $v_{cr}$ profiles of the $\mu$Ps. The plots have been color scaled to the diameter dependence of the $\mu$Ps.
As the feedstock μPs were subjected to different processing conditions, therefore the surface morphology of the μPs will have different profiles. There might be differences in the uniformity of surface morphology the μPs. There can also be a difference in the oxide layer thickness within the same μP. This can give rise to differences in their characteristic speeds for the same diameter of the μPs. For our experiments, the μPs selected had an average diameter of ~10μm. Due to the above reason, the adherence of the μPs can also vary which can also affect the resultant critical velocity profiles. Thus, we have considered two characteristic velocities for the bonding of the μPs to occur. One is low impact speed

![Graphs showing scatter in critical velocity spectra](image)

**Figure 5.6** Observance of scatter in the $v_l - v_r$ spectra for humidity-treated and control group μPs. Surface morphology changes are denoted in terms of scatter in the $v_{cr}$
profiles of the µPs. The plots have been color scaled to the diameter dependence of the µPs.

of bonding µPs (LSBP) and the other being the high impact speed of rebounding µPs (HSUP). Our studies revealed LSBP to be higher than the HSUP for the As-received µPs (Fig. 5.5-5.6). This result was expected due to the absence of any processing conditions for this batch of µPs. However, the difference in LSBP and HSUP was significant for all the cases of HT µPs with a difference of <50m/s. This might suggest surface modification to a certain extent. However, for µPs exposed to humid environment, we can see the difference between the LSBP and HSUP in RH-95 to significantly rise to ~140m/s (Fig. 5.7). This might suggest extensive unevenness in the uniformity of the oxide/hydroxide layer or even

![Figure 5.7 Trends of LSBP and HSUP for the heat treated and humidity treated µPs](image-url)
crystallinity of the oxide/hydroxide layer. The LSBP and HSUP for all the μPs have been summarized in the plot (Fig. 5.7).

The differences in the observed critical $v_{cr}$ in between the as-received μPs the RH-50 and RH-95 μPs led to the assumption of the presence of a significant thickness of oxide/hydroxide layer that could act as a barrier for metallurgical bonding. This was later confirmed by oxide/hydroxide thickness measurements by Lienhard et al.[32] In Chapter 3, additional oxide layers were introduced on the target substrate and the deformation features post collision were observed through SEM micrographs. The SEM micrographs in that study had revealed fracture of the oxide layers and presence of jetting remnants. Similarly in this study the deformation behavior post collision was studied through SEM micrographs (Fig. 5.8). Our studies reveal the presence of jets (white arrows). In contrast to the previous study, the jet formation is quite pronounced for all the cases of bonded μPs. In the previous study, the target substrate was Al6061 which has a higher magnitude of hardness. As high purity aluminum is a relatively softer target material, therefore the impact energy required to plastically deform a softer material is lower and it can exhibit higher flowability for the same impact energy as compared to that of Al6061.
Figure 5.8 Post impact features of the bonded µP: Top view scanning electron micrographs of a bonded µP with (or without) different processing conditions. Arrow marks (white) indicate the presence of jet at the interface of the bonded µP and the target substrate.

Conclusion

In summary, high purity microparticles (µPs) were subjected to several processing conditions in terms of heat treatment in dry air and humid environments. Their collision dynamics by LIPT impacts were quantified so as to create the critical velocity profiles. From our studies it was observed that the heat treatment in dry air had minimal effects on
the bonding dynamics of the µPs whereas the µPs exposed to humid environment had a large deviation in their critical velocities in comparison to that of the control group. There was a significant increase of the critical velocities for µPs exposed to humid environment at 95% relative humidity. This behavior was attributed to the growth and presence of a significant oxide/hydroxide layer in the µPs. Pronounced jets were also observed on the interface of the bonded µPs through electron micrographs. This study can help us in identifying the critical velocity trends of the µPs subjected to heat treatments or exposed to humid environments. Overall, this can help us in gaining a better understanding of the cold spray process, together with expanding our understanding of the storage and handling conditions of the µPs. As exposure of the µPs to the environment through storage and handling together with processing conditions can introduce additional oxide/hydroxide layers or contaminants on the surface of the µPs, therefore careful controlled process and storage/handling parameters should be considered to minimize these effects.

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Supporting Information

Figure 5. S1 Plot showing the distribution of the µP diameters as quantified from the optical micrographs.
References


CHAPTER 6

COMPARISON STUDY OF QUASI-STATIC AND SUPersonic
IMPACT HARDNESS OF ALUMINUM AND COPPER AT THE
MICROSCALE

This chapter focuses on rate-dependent mechanisms like ultra-high strain rate plastic
deformation processes and the strength of metals at both the quasi-static and high strain
rate regimes. This is a manuscript in preparation.

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Abstract

Material properties and deformation dynamics are strain-rate-dependent. Thus, an
understanding of material characteristics at a range of strain rates can extend our
knowledge of the rate-dependent mechanisms contributing to plastic deformation
processes and the strength of metals at both low strain rates (LSR) and at high strain rates
(HSR). At LSR, flow stress and dislocation kinetics, leading to low strain rate deformation
and failure mechanisms, can be potentially different from those at HSR. Although LSR
hardness (including quasi-static) and the material’s fundamental mechanical
characteristics, such as plastic flow behavior, have been studied extensively using instrumented microscopic indentation methods, very few studies can be found about ultra-HSR hardness (via supersonic impact) due to limited instrument capability.

The hardness of a material is a multi-variable physical property that can be determined by various types of indentation tests. Typically, hardness is defined by an applied force and plastically deformed surface area. However, in this work, quasi-static hardness was determined via the energy dissipation from the load-depth profile of a spherical indenter (~20 μm diameter). The ultra-HSR impact hardness of a specimen was determined through micro-ballistic collisions. The impact behavior of the single microsphere of alumina (~20 μm diameter) was quantified using the advanced laser-induced projectile impact test (α-LIPIT). The impact and rebound speeds of the microspheres after impact on a target substrate (pure aluminum and copper) were measured. As the amount of energy dissipation during the collision depends on the volume of the plastic deformation, the impact hardness was calculated using the post-impact residual volume measured by an optical profilometer. This study showed a significant strain rate hardening effect on both aluminum and copper as the ultra-HSR impact hardness was found to be greater than LSR hardness. A quantitative relationship between the strain rate and the material impact response was also established by numerical simulations of the micro-ballistic collisions and spherical indentations. The demonstrated approach will provide a new method of non-destructive HSR characterization.
Keywords

Impact hardness, advanced laser induced projectile impact test (α-LIPIT), nano-indentation, numerical simulations, impression profiles, strain rate dependent plasticity, strain rate hardening.

Introduction

Extensive investigations have been conducted into the mechanical behavior of materials under deformation in order to understand the underlying failure mechanism associated with it[1]. It has been established in the literature that material response is strain rate dependent[2]. Strain rate-dependent mechanical response of materials includes material strength[3]. Metals have been generally used in a wide variety of applications due to their enhanced mechanical strength in comparison to certain other material systems. In pertinence to our previous investigations in other chapters of this work, cold spray applications have majorly focused on metallic systems[4]. The strain rate regimes in the CS process are in the order of $10^6 \text{ s}^{-1}$[5]. However, for several different applications, studies on the mechanical behavior of metals have been focused to the quasi-static regime[6], [7]. In order to analyze and optimize the mechanical properties of the CS coatings, micromechanical studies such as indentation hardness have also been performed[8]. Depending on the aim and application, low strain rate (LSR) and high strain rate (HSR) studies can be performed to examine the material response of the metal at different strain rate regimes.

Instrumented microscopic indentation methods are now common in studying a material’s fundamental mechanical characteristics, such as plastic flow behavior at low strain rates[9].
At a low strain rate, flow stress, and dislocation kinetics, leading to low strain rate, deformation and failure mechanisms can be potentially different from those at high strain rates[10]. At HSR, inertia effects might become relevant for the determination of dynamic material properties and microstructural evolutions[11]. Furthermore, in metallic systems, strain rate hardening and softening behavior has also been observed [12]–[14]. In this aspect, studying the microscopic hardness of materials under both low strain rates and ultra-high strain rates can extend our knowledge of the rate-dependent mechanisms contributing to plastic deformation processes and ultra-high strain rate strength of metals.

Unlike in BCC metals, where the strain rate effects are controlled by the dislocation core properties, the phonon drag has been attributed to the strain rate properties in FCC metals[10], [15]–[17]. Although low strain rate hardness (including quasistatic) has been studied extensively in the literature[18], [19] very few studies can be found on the subject of ultra-high strain rate hardness (impact) due to limited instrument capability.

Thus, this study is done to characterize the quasi-static and dynamic hardness of metals so as to study the strain rate sensitivity of hardness for metals at low strain rates and ultra-high strain rates. Material hardness can be measured by indentation[20], [21]. Typically, hardness is defined by an applied force and plastically deformed surface area[22]. Work done by the authors [23]–[25] established that energy dissipated, or work done during indentation, can also be used to describe the hardness. This study aims to define hardness in terms of energy dissipation and then measure the quasi-static and dynamic hardness of metals as a comparative model.

In this work, quasi static hardness was determined via the energy dissipation from the load-depth profile of a spherical nano-indenter. The ultra-HSR impact hardness of a specimen
was determined through micro-ballistic collisions. The impact behavior of the single microsphere was quantified using the advanced laser induced projectile impact test (α-LIPIT). The impact and rebound speeds of alumina microspheres after impact on a target substrate (pure aluminum and copper) were measured. As the energy dissipation during the collision depends on the volume of the plastic deformation, the impact hardness was calculated using the post impact volume measurements measured from a laser profilometer. Numerical simulations were performed using JC parameters as described in the later section to validate the experimental results at both the strain rate regimes. A quantitative relationship between the material response as a function of strain rate was established through experimental results which were simultaneously verified by numerical simulation analysis. This can extend our knowledge of the rate dependent material response of metals.

**Materials**

For this study, commercially available high purity aluminum plates, (99.999% purity, 0.25 mm thick) and pure copper plates (99.98% purity, 0.5mm thick) were procured from Sigma-Aldrich. These metals were selected as target substrates based on their plasticity and strain rate sensitivity. The procured aluminum and copper plates were cut into 5 mm x 5 mm areas prior to polishing. In order to obtain an adequately smooth surface at the micron scale, these metals were electrochemically polished. Electrochemical polishing for aluminum was done with an electrolyte solution of perchloric acid (70%, A.C.S. Reagent, Sigma-Aldrich) and ethanol (Pharmco Products Inc) mixture at a current density of 5 A/mm² and at a temperature of 10°C for 30s. Electrochemical polishing for copper was done with an electrolyte solution of phosphoric acid (99.999%, Sigma-Aldrich) and ethanol
(Pharmco Products Inc) mixture at a current density of 5 A/mm² and at a temperature of 10ºC for 2 minutes. After electrochemical polishing, these target substrates were rinsed with deionized water to remove any extra electrolyte on the surface and then air dried. These samples were then taken for both quasi static and ultra-high strain rate experimental analysis to obtain comparable results. Native oxide layers developed during the experimentation have been neglected so as not to influence the results of this study.

Methods

**Low strain rate characterization through spherical nano-indentation (University of Connecticut group)**

Low strain rate characterization was performed in an iNano™ system (KLA, TN, USA) nano indenter by using a 20 μm diameter conospherical diamond indenter with a maximum load of 45 mN at room temperature. The displacement rate is approximately 50 nm/s, which corresponds to a strain rate of $\varepsilon \sim 10^{-2} \text{s}^{-1}$. A total of 25 indents were done on each aluminum and copper sample and the corresponding loading unloading curve was obtained for further analysis. Nano indentation hardness was found out from the area under the loading unloading curve as based on the Oliver-Pharr[26] and Tabor method[20]. It has been described later in the results and discussion section.

**Ultra-high strain rate characterization through advanced laser induced projectile impact test (University of Massachusetts-Amherst group)**

Ultra-high strain rate characterization was performed through an advanced laser induced projectile impact test (LIPIT), as described elsewhere[27]–[29]. The launch pad for this
experiment was prepared by spin coating silicone elastomer (Sylgard 184, Dow Chemical) on an ~80 nm thick gold-coated glass substrate (Fisherbrand™ Cover Glasses No. 2) at 1000 RPM for 30s and then crosslinking it at 200 °C for 1 h.

Alumina microspheres (~ 20 μm diameter, Pace Technology) were placed on this launch pad and individual microspheres were aimed and subsequently accelerated through ablation and expansion of the elastomer layer of the launch pad to impact velocities in the range 50 m/s <\(v_i\) < 800 m/s. The impact and rebound velocities of the alumina microspheres post impact on the target (high purity aluminum or pure copper) substrate were measured through the spatial calibration of the stroboscopic images acquired and the controlled inter pulse time of ultrafast white light laser pulses as described elsewhere.

Strain rates are in the order of \(\varepsilon \sim 10^8 s^{-1}\) for micro-ballistic indentation through \(\alpha\)-LIPIT. Energy dissipation was calculated from the difference in particle impact and rebound velocities, which relate to a change in the particle’s kinetic energy. The impact hardness of the ultra-high strain rate indents was defined through the energy dissipation of the impact and the impression profile of the indents to calculate the plastically deformed volume, as described later in the results and discussion section.

**Numerical simulations (Northeastern University group)**

Finite element software ABAQUS® (Dassault Système, USA)[30], was used to simulate both the low strain rate and ultra-high strain rate impact hardness based on the energy dissipation model as described later in the results and discussion section. Johnson-Cook plasticity model[31] (Eq. 6.1) was used to model the impact hardness at a range of strain rates and then verify the experimental results through parameter fitting of the experimental results.
\[ \sigma = (A + B \varepsilon_p^n) \left[ 1 + C \ln \left( \frac{\dot{\varepsilon}_p}{\dot{\varepsilon}_0} \right) \right] \left[ 1 - \left( \frac{T - T_R}{T_m - T_R} \right)^m \right] \]  

(6.1)

where \( \sigma \) is the flow stress, \( \dot{\varepsilon}_p \) and \( \dot{\varepsilon}_0 \) are the strain rate and the reference strain rate, \( T_m \) is the melting temperature, \( T_R \) is the reference temperature, \( m \) is the temperature exponent, \( A, B, C \) and \( n \) are the strain-hardening model parameters. The data for the material properties of aluminum and copper for the modelling have been taken as used in the literature [31], [32] and the MPDB software database[33]. This model integrated 3D continuum mechanics with non-linear contact interaction (general contact algorithm) between the indenter and target substrate along with plasticity and large-scale deformation mechanics.

**Table 6.1** Original values of bilinear Johnson-Cook plasticity model parameters[31]–[33].

<table>
<thead>
<tr>
<th></th>
<th>OFHC Copper</th>
<th>Pure aluminum</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>90</td>
<td>8</td>
</tr>
<tr>
<td>B</td>
<td>292</td>
<td>90</td>
</tr>
<tr>
<td>C</td>
<td>0.025</td>
<td>0.2</td>
</tr>
<tr>
<td>( n )</td>
<td>0.31</td>
<td>0.35</td>
</tr>
<tr>
<td>( m )</td>
<td>1.09</td>
<td>0.7</td>
</tr>
<tr>
<td>( T_m(K) )</td>
<td>1356</td>
<td>933</td>
</tr>
<tr>
<td>( T_R(K) )</td>
<td>293</td>
<td>293</td>
</tr>
</tbody>
</table>

**Impression profile measurements**

Both the indentation methods (nano indentation and LIPIT) will leave a deformation on the surface of the specimen post indentation/impact. The impression profile for all the post
impact indents at low strain rate and ultra-high strain rate was mapped through laser profilometry (Zygo Nexview Optical Profilometer). Observational analysis of the impression profiles was also done through optical microscope images and scanning electron microscopy (FEI Magellan 400).

Results and Discussion

The underpinning idea of energy dissipation-based hardness measurement at ultra-high strain rates has been obtained from [23], [24], [34], where the authors describe the hardness

\[ H_{HSR} = \frac{\text{Energy dissipated}}{\text{Volume of plastic deformation}} = \frac{\Delta E}{V_p} \]  

(6.2)

\[ \Delta E = \frac{1}{2} \left( \rho \frac{4\pi}{3} R^3 \right) \left( v_i^2 - v_r^2 \right) \]  

(6.3)

as high strain rates as a ratio of loss of kinetic energy to that of the indentation volume. Extending this idea to the ultra-high strain regime, we define the hardness at ultra-high strain rates, \( H_{HSR} \) as

where the energy dissipation by plastic deformation, \( \Delta E \) is calculated as a function of impact \( v_i \) and rebound velocities \( v_r \) of the impactor of mass \( m \), density \( \rho \) and radius \( R \). Plastically deformed volume, \( V_p \) is calculated from the laser profilometry measurements of the residual deformation depth.

For accurately measuring the dynamic material deformation, plastic waves generated must be the dominant source of wave propagation or energy dissipation[35]. This can also validate our ballistic hardness measurement method. In the case of nanoindentation, plastic deformation is the dominant means of energy dissipation[36]. However, for micro-ballistic
impacts through LIPIT, due to the large strain rates involved, the pre-dominant energy
dissipation mechanism is less defined. One dissipation mechanism could be the plastic
deformation through the impacting alumina µP or the impactor itself. However, any plastic
deformation of the impacting alumina µP would be accompanied by fracture. Since,
through the stroboscopic LIPIT images, any fracture of the impacting alumina µP couldn’t
be observed therefore, we can assume that there was negligible plastic deformation of the
impacting alumina µP, and therefore no energy dissipated by the µP. The particle may
deform upon impact, but this deformation will be recovered elastically and will be
accounted for in the measurement of \( v_r \). Another energy dissipation mechanism could be
vibration of the specimen surface in the form of Rayleigh waves. However, in a plastic
impact, the fraction of the kinetic energy dissipated through elastic waves is negligible (\(< 3\% \) of energy dissipation), according to the literature[37]. The contribution of inertia
effects from the specimen (Al 7075 at 300-1300 m/s) has been shown to be negligible
according to the projectile’s penetration resistance equation in literature[38]. Therefore, we
can establish the validity of our micro-ballistic method for the determination of the high-
strain rate hardness through energy dissipation method along with an assumption that
inertia effects have been insignificant for micro-ballistic experiments. Fig. 6.1 shows a
comparative schematic illustration of the methods and the parameters that have been
selected for our experiments.
Figure 6.1 Schematic illustration for (a) nanoindentation and (b) micro ballistic impact.

Table 6.2 Parameters associated with the experimental setups of nano indentation and microballistic impact.

<table>
<thead>
<tr>
<th></th>
<th>Nano indentation</th>
<th>Microballistic impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indenter</td>
<td>Conospherical diamond R~ 10µm</td>
<td>Spherical alumina R~ 10µm</td>
</tr>
<tr>
<td>Indentation speed (m/s)</td>
<td>~ 10^{-8}</td>
<td>~ 10^3</td>
</tr>
<tr>
<td>Nomional strain rate, $\nu_i/h_{max}$ (s^{-1})</td>
<td>~ 10^{-2}</td>
<td>~ 10^8</td>
</tr>
<tr>
<td>Measured quantities</td>
<td>Load-displacement curve</td>
<td>$\nu_i$ and $\nu_r$</td>
</tr>
</tbody>
</table>
The quasi-static hardness was defined through typical loading-unloading curves obtained in a nano-indenter[39] by the University of Connecticut group. The energy dissipated by plastic deformation for this case, $\Delta E$ is defined by the area enclosed by the loading-unloading curves. Through the loading-unloading plot, by measuring the residual deformation depth ($h_p$), we can use a simple geometric equation to determine the plastically deformed volume remaining after indentation (Eq. 6.3). As we have selected a spherical geometry of the nano-indenter tip and assuming the residual impression to be in the form of a spherical cap, we can define the quasi-static of LSR hardness ($H_{LSR}$) as,

$$H_{LSR} = \frac{\text{Energy dissipated}}{\text{Volume of plastic deformation}} = \frac{\Delta E}{V_p}$$  \hspace{1cm} (6.4)

$$V_p = \frac{\pi h_p^2}{3} (3R - h_p)$$  \hspace{1cm} (6.5)

The contact area at a particular depth of indentation depends on two parameters, shape of the indenter and elastic–plastic response of the material being indented[39]. In this current experiment, the pile-up and sink-in effects from the contact response of the indenter on the material have not been taken into consideration. From the loading-unloading curves in Fig. 6.2, we can observe small elastic recovery of both pure Cu and high purity Al samples, indicating the major deformation to take place plastically. Also, from the slope we can see that there is less elastic recovery of Cu as compared to Al. There was an increase in maximum depth for the same load values of Al as compared to Cu indicating Al to be a softer material. The quasi static (LSR) hardness from nanoindentation for pure Cu was measured to be $0.60 \pm 0.13$ GPa whereas for high purity Al it was $1.68 \pm 0.16$ GPa. Thus,
our studies revealed that, at a strain rate of $10^{-2}$ per second, pure copper is almost 3 times harder than that of high-purity aluminum.

![Graph and Optical Micrographs](image)

**Figure 6.2** (a) Loading-unloading curves obtained from the LSR spherical nanoindentation. (b) Optical micrographs showing the residual impression from the LSR spherical nanoindentation for aluminum and copper.

In the preceding sections, we had validated micro-ballistic hardness through energy dissipation method. For the micro-ballistic experiments by the University of Massachusetts-Amherst group (Fig. 6.3), the average diameter of the alumina µP were $20.0 \pm 0.22 \, \mu m$ for high-purity Al impacts and $20.8 \pm 0.23 \, \mu m$ for pure Cu impacts. The particle impact velocity ($v_i$) ranged from $\sim 50-800 \, m/s$ for Al impacts and $\sim 100-700 \, m/s$ for Cu impacts. A maximum penetration of $16.9 \, \mu m$ for Al and $14.3 \, \mu m$ for Cu was
observed. $\Delta E$ is a measure of how efficiently the material can dissipate kinetic energy from impact. The slope values were obtained by fitting the linear portion of the $\Delta E$ curves.

**Figure 6.3** (a) Micrograph showing impact and rebound of alumina microparticle (b) SEM micrograph showing the residual impression on Cu target substrate after alumina impact (c) Profile map of residual impression after alumina impact on Cu substrate with $h_{\text{max}}=6.7\mu m$
Figure 6.4  Energy dissipation as a function of indentation volume for high purity aluminum and pure copper at LSR and HSR regime for a range of $v_i$. The slopes were obtained by fitting the linear portion of the $\Delta E$ curves.

In Fig. 6.4, the impacting events are plotted in black triangles for nanoindentation and in color for the micro-ballistic method. The different colors represent the $v_i$ dependency of the micro-ballistic impacts. The slope of these log-log plots represents the measured hardness since it is defined as the ratio of energy dissipation and indentation volume. For both materials, nanoindentation and micro-ballistic collisions produce different hardness measurements. We can observe a non-linear increase in the hardness values with an increase in strain rates. This has been postulated in literature[34]. This is because of the difference in the strain rates of the techniques. While the range of impact velocities that we
tested is broad, from ~50m/s to ~800m/s, all velocities in this range correspond to strain rates on the order of $10^7$. Thus, the points all correspond to a similar measurement of hardness. The ultra-high strain rate hardness was measured to be $1.7\pm0.56$ GPa for Al whereas for Cu it was $2.5\pm1.08$ GPa. Comparing the plots for Al and Cu, we can see that the increase in material hardness from LSR to HSR is more pronounced for Al than it is for Cu. This means that Al is intrinsically more sensitive to strain rate than Cu. The variation in strain rate hardening in FCC metals can be correlated to the movement of dislocations and the yield strengths of the metals [40]. The enhancement effect resulting from the strain rate increase is greater for Al. When the strain rate is increased, from LSR to HSR, the hardness of Al is almost tripled, while the hardness of Cu is not even doubled. The melting point of Cu is higher than Al, therefore the thermal softening effects can be more pronounced in Al as that in Cu. Together, at same impact conditions, the heat generation is same in both the metallic systems. However, as Cu is a better thermal conductor than that of Al, therefore the local temperature rise in Cu substrates will be lower. This can suppress the thermal softening behavior in Cu substrates. Thus, Al will show a higher strain rate sensitivity as that of Cu at higher strain rate regimes. We can also observe from the slopes of the measured hardness from LSR and HSR that there is a linear trend with lower offset in Cu substrates but for Al the offset in hardness values in between LSR and HSR is significant. This observation might mean that the density difference in both the materials can be contributing to inertia effects for the higher density material.

The current study was extended to carry FEA simulation (Northeastern University group) using the experimental data at both LSR and HSR, in order to validate the experimental
results. Both the static indentation and dynamic impacts were simulated with a non-linear static/dynamic analysis as described earlier. The hardness values were calculated based on the energy method (Eq. 6.2-6.5). In the FEA models, the total energy is typically defined as,

\[ E_{\text{total}} = E_I + E_V + E_{FD} + E_{KE} - E_w \]  
\[ E_I = E_E + E_P + E_A \]  

where \( E_I \) is the internal energy of the system which is the sum of recoverable elastic strain energy \( E_E \), plastic dissipation energy \( E_P \) and artificial energy \( E_A \) for controlling hourglassing deformation; \( E_V \) 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. Based on the energy balance, the sum of these energies \( (E_{\text{total}}) \) should be constant. In the nano-indentation process, the \( E_{\text{total}} \) before the indentation is zero. \( E_V \) and \( E_{KE} \) are also zero due to the quasi-static feature of the nano-indentation. While in the impact-indentation process, the \( E_{\text{total}} \) before the impact is the initial particle kinetic energy \( (E_{KE}^{\text{initial}}) \). The external work \( E_w \) is zero. In both nano- and impact indentation process, \( E_{FD} \) and \( E_A \) are negligible comparing to the internal and kinetic energy. Thus, the total energy for nano- and impact indentation can be rewritten as,

\[ E^{\text{nano}}_{\text{total}} = 0 = E_I - E_w = E_E + E_P - E_w \]  
\[ E^{\text{impact}}_{\text{total}} = E_{KE}^{\text{initial}} = E_I + E_V + E_{KE} = E_E + E_P + E_V + E_{KE}^{\text{particle}} + E_{KE}^{\text{substrate}} \]  

Comparing \( E^{\text{nano}}_{\text{total}} \) and \( E^{\text{impact}}_{\text{total}} \) with Eq. 6.6-6.9, the dissipation energy in FE simulations for nano- and impact indentation was described as
\[ E_{\text{diss}}^{\text{static}} = E_W = E_E + E_P \quad (6.10) \]
\[ E_{\text{diss}}^{\text{dynamic}} = E_{KE}^{\text{initial}} - E_{KE}^{\text{particle}} = E_E + E_P + E_V + E_{KE}^{\text{substrate}} \quad (6.11) \]

**Figure 6.5** Energy dissipation profiles during (a) nano-indentation and (b) impact-indentation (micro-ballistic impacts) in FE simulation. The loading-unloading stages in nano-indentation and the particle impact-rebound stage in HSR impacts are separated by the dashed lines (black).
Fig. 6.5 shows the typical time histories of the energy components in Eq. 6.10-6.11 for copper substrate in nano-indentation and micro-ballistic impact simulations. The maximum indentation depth achieved in both simulations is the same with $h_{\text{max}} = 0.566\mu\text{m}$. However, $E_{\text{diss}}^{\text{dynamic}}$ is found to be slightly higher than $E_{\text{diss}}^{\text{static}}$ under this same $h_{\text{max}}$ condition. In Fig. 6.5, it is seen that the energy is mainly dissipated through plastic deformation for both simulations. Though there is still small amount of $E_E$ stored in the system, most of them is recovered during the unloading process in nano-indentation (Fig. 6.5a) and the particle rebounding process in micro-ballistic impacts (Fig. 6.5b). The $E_{FD}$ is confirmed negligible in both simulations. The viscous dissipation energy $E_V$ is observed to have a relatively large value at the end of impact simulation. However, it is noted that $E_V$ is mainly generated after the particle rebounding (Fig. 6.5b). Thus, $E_V$ only affects $E_E$ and the kinetic energy in the substrate $E_{KE}^{\text{substrate}}$. Its contribution to the μP rebound kinetic energy $E_{KE}^{\text{particle}}$ (and then $E_{\text{diss}}^{\text{dynamic}}$) can be negligible. Therefore, the slightly higher $E_{\text{diss}}^{\text{dynamic}}$ than $E_{\text{diss}}^{\text{static}}$ (or slightly higher dynamic hardness than static hardness) at the same $h_{\text{max}}$ is mainly due to the larger $E_P$ in micro-ballistic indentations, which is caused by the additional strain-rate effect during μP impact. The validity of the hardness model by energy dissipation method at the quasi static and HSR regimes has been plotted in Fig. 6.6. An agreement between the simulated and the experimental values of hardness at LSR and HSR was observed from this study.
Figure 6.6 Comparative energy dissipation profiles during LSR indentations and HSR through experiments and simulation for both pure Cu and high-purity aluminum.

Conclusions

With greater advancement and understanding of nanoindentation processes, it is being widely used as a non-destructive characterization method for understanding material behavior from macro to nano scales. In metals, the material properties are strain rate dependent. Thus, understanding the underlying material science at different strain rates can extend our knowledge of the rate-dependent mechanisms contributing to plastic deformation processes at micro scales. Thus, in this study the quasi static and the dynamic behavior of high purity aluminum and pure copper was quantified by a nano indenter (low strain rate) and by using an advanced laser induced projectile impact test (LIPIT) for ultra-
high strain rate respectively. Through these quantifications of material response, one of the important material parameters, i.e., hardness was quantified by energy dissipation method. The results indicated a strain rate sensitivity of hardness for both the metals. The low strain rate hardness was lower than ultra-high strain rate hardness for pure Al and pure Cu. This was attributed to strain rate hardening effect induced by increase in strain rates. Al was found to be intrinsically more sensitive to strain rates as compared to that of Cu in terms of hardness. This approach can be useful in modelling and determining the material hardness at different strain rates.

**Acknowledgments**

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References


CHAPTER 7

COLLISION DYNAMICS OF TANTALUM MICROPARTICLES AT ULTRA-HIGH STRAIN RATES

This chapter focuses on the dynamic response and the deformation behavior of tantalum µPs under extreme collision events for cold spray applications.

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Introduction

Refractory materials such as tantalum show very limited material degradations even at high temperatures and under corrosive environments thus making it an attractive advanced material for different industries[1]–[3]. Even at elevated temperatures, Ta shows excellent resistance against corrosion by various acids, salts and organic chemicals[2], due to the formation of a passive oxide film. Cold-spray process in recent years has employed different material systems including deposition of refractory materials[4]. Amongst other refractory materials, tantalum demonstrates excellent ductility[5]. Deposition coating of refractory metals such as tantalum has been challenging due to the high melting temperatures involved. However, through cold spray additive manufacturing process, tantalum coating depositions have been made possible[6]. Cold spray solid consolidation deposition process does not require the globalized melting of the feedstock powder as it can create a coating by plastic deformation below the melting temperatures of the
powders[7]–[9]. Although literature shows few studies on the bulk deposited tantalum coatings[10], [11], there has not been any study so far on the single particle characterization of the Ta coatings by cold spray process at ultra-high strain rates. Thus, this study was carried out to understand the collision dynamics of Ta through single particle micro-ballistic collisions and observe the post impact microscale morphologies of tantalum microspheres at ultra-high strain rates. This can help us in understanding the deformation behavior of the tantalum coating at these ultra-high strain rates.

**Materials and methods**

To investigate the high strain rate plasticity of Ta particles, GAM AM 325 particles were impacted with sapphire and tantalum substrates (Sigma-Aldrich) through the Laser-Induced Projectile Impact Test (LIPIT). The LIPIT experimental method has been described in detail elsewhere[12], [13]. Due to the high density of tantalum (density=16.6 g/cm³), it was a challenge to accelerate the Ta µPs above 300 m/s. In order to resolve this, a new design of the launching pad was made for accelerating heavy µPs such as Ta. The new launch pad was developed for LIPIT characterization using high-modulus polyimide film (1/3 mil, Ted Pella) and a new ablation material (laser absorbing dye + polystyrene). LIPIT, uses an ablation laser of wavelength 1064nm. IR 165 dye was procured from Luxottica Exciton. IR 165, Polystyrene (MW 35 kDa, Sigma-Aldrich) and Cyclopentanone, 99% (Alfa Aesar) were mixed in weight ratio of 1:10:50. IR165 dye has maximum absorption around this wavelength, thus providing a better efficiency in energy absorption from the ablation laser. The resultant mixture was spin coated on a glass substrate (Fisherbrand™ Cover Glasses No. 2) to create a thin layer. Then Au was sputter
coated on top of this IR165 coated cover glass. After that a polyimide film (1/3 mil, Ted Pella), is placed on top of the IR165/Au coated glass substrate to create the new bilayer launch pad. The new launch pad was able to accelerate Ta particles up to 525 m/s for ~10\(\mu\)m particles. The \(\mu\)Ps post impact with the sapphire substrates were captured by a steel pin hole as described in Appendix B.

**Figure 7.1** Schematic illustration of the new bilayer polymer launch pad for accelerating heavy microparticles.

For SEM micrographs, a high-resolution scanning electron microscope (FEI Magellan 400) was used. The samples prior to imaging were sputter coated with a thin layer of Au (~2 – 5 nm). The electron back scatter diffraction maps (EBSD) were recorded by Verios 460L SEM and the FIB characterization was done by Helios 460F1 Dual Beam at UConn Thermo Fisher Scientific Center for Advanced Microscopy and Materials Analysis (CAMMA).
Results and Discussion

The dynamic response of Ta µPs to Ta and sapphire substrates have been shown in Fig. 7.2-7.3. Micro-ballistic impact of Ta on sapphire substrate is conducted to produce most of the plastic deformation on the particle side. In Ta-Sapphire impacts, the Ta particles demonstrated highly inelastic deformation at a relatively low impact velocity ($v_i$) range (100-300 m/s) due to the ductility and the high density of the Ta µPs. To observe the high strain rate coupled ductility effects, the target substrate was replaced with ductile Ta substrate. From the rebound velocities spectra (Fig. 7.3), for impact speeds up to 300m/s, a higher elastic recovery is evident as compared to the results from impacts with sapphire. The critical velocity ($v_{cr}$) was found to be 464 m/s for Ta µPs- Ta substrate impacts whereas for Ta µPs-sapphire impacts, the $v_{cr}$ was found to be 406 m/s. This correlated well with the theoretical literature values of the critical velocities of tantalum in the bulk cold spray process[14]. The lower critical velocities of the tantalum µPs could be related to the higher elastic and shear modulus of Ta[15]. Through the work established by Assadi et al.[16], the bonding mechanism of the µPs were attributed to adiabatic shear instability. The same study also established a relationship between the critical velocity of µPs to the density of the µPs. With the increase in the density of the metal, the critical velocity decreased significantly[16].
Figure 7.2 CoR spectra of micro-ballistic impacts for Ta μPs to that of Ta and sapphire substrate.

Capture of rebounding Ta μPs for dynamic plasticity model studies: Furthermore, in order to understand the deformation behavior of the bonded μPs, the μPs were subjected to microscopic collisions against a rigid substrate (sapphire) and captured post impact by a steel pin hole. Post impact morphological and microstructural studies were done on the μPs as a function of impact velocities. These observations can demonstrate the high strain rate induced deformations in the metallic system.
Figure 7.3 $v_i - v_r$ spectra of micro-ballistic impacts for Ta $\mu$Ps to that of Ta and sapphire substrate. The graphs have been color scaled to represent the diameter dependance of the high strain rate impacts.

Ta $\mu$Ps were accelerated over a range of impact velocities with a direction normal to the surface of the rigid target substrate (sapphire). The particles undergo plastic deformation during impact with the rigid substrate and lose their initial spherical shape. Ta $\mu$Ps post collision with sapphire substrates at a broad impact velocity ($v_i$) range from 50m/s<$v_i<$450m/s(bonded) were captured and re-oriented to study the impact velocity dependent microstructural behavior (Fig. 7.4). The shape of the deformed Ta $\mu$Ps can be used to improve the HSR dynamic contact impact velocity dependent plasticity models of the Ta $\mu$Ps. From our studies (Fig. 7.4) we could observe a $v_i$-dependent plastic deformation, with the deformation increasing as a function of $v_i$. Through visual observation studies of the
SEM micrographs of the captured µPs, it is determined that Ta µPs impacting below \( v_i < 150 \text{ m/s} \) tend to maintain their initial spherical shape, but with increasing impact velocity \( (v_i > 150 \text{ m/s}) \), the Ta µPs display a flattened shape. Near the \( v_{cr} \), \( v_i > 400 \text{ m/s} \), extensive plastic deformation is observed. As the deformation behavior is dictated by dislocations therefore, it is inferred that at high impact velocities, coupled with extreme strain rates might be contributing to the extreme plastic deformation by twinning. Twinning was observed on the surface of the captured Ta µPs (Fig. 7.4).

![Fig. 7.4](image)

**Figure 7.4** Captured Ta particles post collision with a sapphire substrate show \( v_i \)-dependent plastic deformation.

Post-impact cross-sectional study of Ta µPs:

Focused ion beam milling of bonded Ta µPs to a Ta substrate was performed to observe the post-impact microstructural deformation. The EBSD mapping showed the presence of deformed grains across the µP with certain regions showing elongated grains with
nanometer length scale. Dynamic recrystallization at ultra-high strain rates can contribute to the non-uniformity of grain sizes[17]. At high strain rates, plastic deformation through twinning has been reported as the major deformation mechanism in tantalum[18]. Our results from the EBSD mapping analysis also indicate the presence of slip bands and twinning at the Ta µPs side (Fig. 7.5). At high strain rates, the stress concentrations through dislocation pile up at the grain boundaries leads to the twinning behavior.

Figure 7.5 Top view SEM and cross sectional EBSD map of Ta µP bonded to a Ta substrate at \( v_1 = 498 \) m/s. The analysis shows the presence of slip bands and twinning.
Conclusion

In summary, laser induced projectile impact tests (LIPIT) were used to study the ultra-high strain rate dynamic deformation behavior of refractory material, tantalum. As cold spray coating process involve strain rates comparable to LIPIT impacts, therefore Ta μPs were accelerated using this system with controlled process parameters. From these single particle impact study, the critical velocities of the μPs were found to be in agreement with the theoretical values. A higher elastic recovery was observed for μPs subjected to collisions with Ta substrates as compared to a rigid sapphire substrate. The morphological and microstructural studies of the μPs post impact demonstrated plastic deformation by twinning in the μPs. We could also observe a $v_i$-dependent plastic deformation, with the deformation increasing as a function of $v_i$. 
References


In recent years, applications of cold spray (CS) additive manufacturing process has been extended to a wide variety of fields ranging from aerospace to biomedical. Fundamental understanding of the material science aspect of this process can help us in optimizing it even further.

The current work investigated the extreme dynamic behavior of metallic systems through micro-ballistic single-particle collisions. The micro-ballistic collisions of the microparticles at these extreme strain rates were achieved by the advanced laser-induced projectile impact test (α-LIPIT). This study focused on investigating the high strain rate non-linear dynamic response of the materials as a function of material and process parameters influencing the CS process.

In Chapter 3, our studies quantified the effects of oxide layer on the critical velocity through single particle micro-ballistic studies of Al6061 μPs on Al6061 target substrates, with systematically increasing substrate oxide thickness. Our results indicated two transition velocities, originating from the onset of oxide layer fractures and shear instability. For lower impact velocities, a common trend of \(2v_i^{-1/2} \) in the CoR was observed irrespective of the substrate oxide layer thickness. However, a deviation was observed from this behavior with the onset of oxide layer fracture at higher impact velocities. Deviation from this trend at higher impact velocities was attributed to severe plastic deformation resulting in partial interfacial bonding followed by shear instability. This overall trend was explained
by a semi-empirical fitting function. Morphological studies revealed impact induced fracture at the interface, together with evidence of jetting remnants. Overall, this study provided a systematic quantification of the substrate oxide layer as a barrier to bonding.

In Chapter 4, our studies quantified the effects of elevated temperatures on the bonding dynamics of the µPs to that of the substrate. In this study, as a model system, Al6061 µPs were subjected to microscopic collisions against the Al6061 and a rigid sapphire target substrate. We observed a non-linear lowering of the critical velocities at elevated temperatures which was attributed to the onset of an internal viscous flow and thermal softening at the elevated temperatures. Furthermore, through the quantification of deformation behavior of the µPs against a rigid substrate, we observed a linear increase in the deformation of the µPs with increasing temperatures and also with an increase in the impacting velocities. The results also indicated material loss and presence of extensive radial cracks in the deformed µPs. Together, this study demonstrated and quantified the coupling effects of elevated temperatures and impact velocities on the deformation dynamics of the µPs/substrate.

In Chapter 5, our studies quantified the effects of CS process parameters that could induce an oxide or hydroxide layer on the µP side, and their resulting effects on the critical velocity profiles. From our studies it was observed that the heat treatment in dry air had minimal effects on the bonding dynamics of the µPs whereas the µPs exposed to humid environment had a large deviation in their critical velocities in comparison to that of the control group. There was a significant increase of the critical velocities for µPs exposed to humid environment at 95% relative humidity. This behavior was attributed to the growth and presence of a significant oxide/hydroxide layer in the µPs. Pronounced jets were also
observed on the interface of the bonded µPs through electron micrographs. This study revealed that the presence of significant oxide/hydroxide layer can influence the bonding dynamics. Hydroxide/Oxide layer can be introduced through the environment. Therefore, it is imperative to properly store and handle the µPs, so as to minimize the effects arising from the environment including development of oxide/hydroxide layers. The processing conditions can also induce the development of oxide/hydroxide layers and/or introduce contaminants which can in turn significantly affect the critical velocities of the µPs. Therefore, careful controlled process and storage/handling parameters should be considered to minimize these effects.

As, literature has shown that material properties and deformation dynamics are strain rate dependent therefore in Chapter 6, our studies were extended to the material science occurring at the interface of the µPs and the substrate at both low strain rates and ultra-high strain rates. Through this study, the physical property of material hardness was defined by the energy dissipation method at a range of strain rates. For low strain rate characterizations, a spherical nano-indenter was used to measure the quasi-static hardness. The ultra-HSR impact hardness of a specimen was determined through micro-ballistic collisions. The material hardness was defined as a function of the energy dissipated during the collision and the volume of plastic deformation for HSR studies, and it was defined in terms of energy dissipation from the load-depth profile of the nano-indenter and the residual volume of impression. A significant strain rate hardening effect was observed on both the metal systems included in this study (high purity Al and pure Cu). Al was intrinsically found to be more strain rate sensitive as compared to that of Cu. Analysis through numerical simulations of the two methods also established a quantitative
relationship between the material response at both these strain rates. In Chapter 7, our studies investigated the dynamic response and the deformation behavior of tantalum µPs under extreme collision events for cold spray applications. From these single particle impact study, the critical velocities of the µPs were measured and found to be in agreement with the theoretical values.

To conclude, all our results quantified the dynamic behavior of metallic systems at extreme strain rates as a function of certain material and process parameters targeted for CS studies. Furthermore, our investigations were also extended to the study of rate dependent mechanical behavior of metals at both quasi-static and high strain rate regimes in terms of strength of metals, together with understanding the high strain rate plastic deformation process.

Although our studies have shed light on a few aspects influencing the complex CS process, several other areas needs further investigation. Some of the suggested future directions that can be investigated further are:

1. Extension of the current study to a range of materials: Fundamental CS studies have been mainly focused on metallic systems. Recent CS developments have extended themselves into deposition of polymer, ceramic, intermixed coatings etc. As LIPIT presents itself as a unique characterization tool with capabilities to accelerate other material systems including polymers, ceramics etc., therefore the current investigation can be extended to characterize bonding and collision dynamics of other material systems.

2. Extension of the current study to different process variables: In our current study, we have quantified certain parameters such as oxide layer thickness both at the
target substrate side and the µP side, effects of elevated temperatures and material behavior at quasi static and ultra-high strain rates. Yet, through conventional CS and simulated CS studies in the literature, we have seen that CS is a multivariable complex process and other parameters such as angle of the impacts, different geometries of the µPs etc. can also influence the collision and bonding dynamics at the interface and the CS process in its entirety. For example, further exploration of µPs with different incident angles can provide us a measure of the tribological response at the contact interface.

3. Real time measurements: Although through the stroboscopic images, we can quantify certain event parameters such as the flight path of the µPs, the velocities associated, yet real time monitoring of certain other aspects of the µPs needs improvement. For example, as in our studies we have observed that elevated temperatures can influence the bonding dynamics in CS, therefore studies quantifying the exact temperature measurements through optical pyrometry can give us a better understanding of the fundamentals as a function of associated temperature and velocities.
APPENDIX A

ULTRA-HIGH STRAIN RATE CHARACTERIZATION OF CONVENTIONAL AND NANOMATERIAL COPPER COLD SPRAY COATINGS

This chapter focuses on the impact and bonding dynamics of conventional and nanomaterial copper microspheres when subjected to ultra-high strain rate microscopic collisions to copper substrates. This study was done to understand the comparative performance of both types of microspheres for contact related biological applications. This paper has been published in Kristin Sundberg, Caitlin Walde, Bryer Sousa, Swetaparna Mohanty, Jae-Hwang Lee, Victor Champagne, Richard Sisson and Danielle Cote. “Journal of Biotechnology & Biomaterials Volume 10, Issue 4 (2020)”.

Figure A1 SEM micrographs of bonded µP post micro-ballistic impacts using LIPIT system: (a) conventional copper µP accelerated at 700 m/s (b) nano-agglomerate copper µP accelerated at 885 m/s.
Figure A2 Cross-sectional FIB micrographs of bonded μP post micro-ballistic impacts using LIPIT system: (a) conventional copper μP accelerated at 700 m/s (b) nano-agglomerate copper μP accelerated at 885 m/s.

Figure A3 Ultra-high strain rate LIPIT characterization of conventional copper μPs: Representative spectra color scaled with diameter (μm) (a) $v_i - v_r$ (b) CoR.
Figure A4 Ultra-high strain rate LIPIT characterization of nano-agglomerate copper

**µPs**: Representative spectra color scaled with diameter (µm) (a) $\nu_i - \nu_f$ (b) CoE.
APPENDIX B

MATERIALS AND EXPERIMENTAL PROCEDURE

This chapter describes the materials and experimental methods that were used for performing the ultra-high strain rate experiments. The Laser Induced Projectile Impact Test[1]–[3] setup has been described earlier in Chapter 2.

1. Microparticle surface morphology

For microparticle surface morphology, a high-resolution scanning electron microscope (FEI Magellan 400) was used. The samples prior to imaging were sputter coated with a thin layer of Au (~2 – 5 nm). The SEM micrographs of the µPs are as shown below:

Al6061

![SEM micrograph of Al6061 µPs](Image)

**Figure B1** SEM micrograph of Al6061 µPs
Alumina

Figure B2 SEM micrograph of Alumina µPs

Tantalum

Figure B3 SEM micrograph of Tantalum µPs

As received HP Aluminum

Figure B4 SEM micrograph of “As received” HP Aluminum µPs
RH 50% HP Aluminum

Figure B5 SEM micrograph of RH 50% HP Aluminum

RH 95% HP Aluminum

Figure B6 SEM micrograph of RH 95% HP Aluminum

HT Baseline HP Aluminum

Figure B7 SEM micrograph of HT Baseline HP Aluminum
2. Launch pad preparation for microscopic collision experiments

To create a launching pad, silicone elastomer (Sylgard 184, Dow Chemical, 1:10 ratio) is spin-coated on a glass substrate (Fisherbrand™ Cover Glasses No. 2) and then crosslinked at 200 °C for 1 h. Prior to the spin coating of the elastomer, the coverslip was sputter coated with gold (~ 80 nm thick). The cured launch pad is cut into 5mm wide strips through a diamond tip scribe. The \( v_i \) range for this launch pad is \( 50 \text{ m/s} < v_i < 1000 \text{m/s} \). At higher speed range and power, the PDMS film ruptures.

To create a launch pad for \( 0 \text{m/s} < v_i < 50 \text{m/s} \), silicone elastomer (Sylgard 184, Dow Chemical, 1:10 ratio) is spin-coated on a glass substrate at 6000RPM for 60 s (Fisherbrand™ Cover Glasses No. 2) and then crosslinked at 200 °C for 1 h. Prior to the spin coating of the elastomer, the coverslip was sputter coated with gold (~ 80 nm thick). After that, a polyimide tape (Ted Pella, Prod No. 16089-2, TED PELLA) is placed on top of the PDMS launch pad. The PI tape can be layered on top of each other to achieve the necessary velocity. The velocity decreases with an increase in the thickness of the layers of tape up to an extent.

To create a launch pad for \( 1000 \text{m/s} < v_i < 1200 \text{m/s} \), silicone elastomer (Sylgard 184, Dow Chemical, 1:10 ratio) is spin-coated on a glass substrate (Fisherbrand™ Cover Glasses No. 2) at 6000RPM for 60 s. Prior to the spin coating of the elastomer, the coverslip was sputter coated with gold (~ 80 nm thick). After that, a polyimide film (1/3 mil, Ted Pella), is placed on top of the PDMS launch pad. The entire system is left for curing at room temperature for 48h.
After the preparation of the launch pads, the μPs are dispersed on top of the launch pad using a brush. Dispersion of the μPs through any organic solvents is avoided to prevent any oxide/hydroxide layer formation on the surface of the μPs.

3. High-speed bilayer launch pad preparation for Ta micro-ballistic experiments

![Diagram of the new bilayer polymer launch pad for accelerating heavy microparticles](image)

**Figure B8** Schematic illustration of the new bilayer polymer launch pad for accelerating heavy microparticles.

Due to the high density of tantalum (density=16.6g/cm³), it was a challenge to accelerate the Ta μPs above 300m/s. In order to resolve this, a new design of the launching pad was made for accelerating heavy μPs such as Ta. The new launch pad was developed for LIPIT characterization using high-modulus polyimide film (1/3 mil, Ted Pella) and a new ablation material (laser-absorbing dye + polystyrene). The α-LIPIT uses an ablation laser of wavelength 1064nm. IR 165 dye was procured from Luxottica Exciton. IR 165, Polystyrene (MW 35,000 Sigma-Aldrich), and cyclopentanone, 99% (Alfa Aesar) were
mixed in a weight ratio of 1:10:50. IR165 dye has maximum absorption around this wavelength, thus providing a better efficiency in energy absorption from the ablation laser. The resultant mixture was spin-coated on a glass substrate (Fisherbrand™ Cover Glasses No. 2) to create a thin layer. Then Au was sputter coated on top of this IR165-coated cover glass. After that, a polyimide film (1/3 mil, Ted Pella), is placed on top of the IR165/Au coated glass substrate to create the new bilayer launch pad. The new launch pad was able to accelerate Ta particles up to 525 m/s for ~10μm particles.

4. Scanning Electron Microscopy Micrographs
For SEM micrographs, a high-resolution scanning electron microscope (FEI Magellan 400) was used. The samples prior to imaging were sputter coated with a thin layer of Au (~2 – 5 nm).

5. Focused Ion Beam Micrographs and EBSD Mapping
The electron backscatter diffraction maps (EBSD) were recorded by Verios 460L SEM, and the FIB characterization was done by Helios 460F1 Dual Beam at UConn Thermo Fisher Scientific Center for Advanced Microscopy and Materials Analysis (CAMMA).

6. Capture of Rebounded Al6061 µPs
For capturing the Al6061 µPs, a conical-shaped aluminum foil is placed over the target substrate impact area with the opening hole in line with the focal point of the ablation laser. Al6061 µPs travels through the hole and impacts the sapphire substrate; the impact velocity is measured before entering the cover through the spatial and temporal calibration of the stroboscopic images. The captured particles post-collision were then recovered from the target substrate surface with an elastomer for further studies.
7. Calculation of flattening ratio

$D_0$ is defined as the initial diameter of the $\mu$Ps prior to any impacts. Through optical microscopy and through the LIPIT system, the initial shape of the $\mu$Ps were visually investigated and the $D_0$ and the height of the captured particle post-collision were measured. The specific diameter change was quantified in the form of the flattening ratio ($\Delta D / D_0$), which can provide a measure of the plastic deformation occurring in the microparticle w.r.t the impact velocity and temperature. It should be noted that diameter change calculations are accompanied with an error as the SEM micrographs (side view images) cannot represent the entire volume of the captured $\mu$Ps. Therefore, any non-uniformity in the flattening of the surfaces can give rise to errors in measurement.

Flattening ratio $= \left( \frac{\Delta D}{D_0} \right)$
8. Capture of Rebounded tantalum µPs

![Stroboscopic image showing capture of tantalum microsphere by a steel pinhole.](image)

**Figure B11**  Stroboscopic image showing capture of tantalum microsphere by a steel pinhole.

For capturing the Ta µPs, a steel pin hole is placed over the target substrate impact area with the opening hole in line with the focal point of the ablation laser. Here the Al foil is replaced with the steel pinhole due to the higher density of the Ta µPs. Otherwise the Ta µPs could escape or rupture the Al foil at very high impact velocities. Ta µPs travels through the hole and impact the sapphire substrate; the impact velocity is measured before entering the cover through the spatial and temporal calibration of the stroboscopic images. The captured particles post collision were then recovered from the target substrate surface with an elastomer for further studies.

9. Atomic Layer Deposition

Oxide layers of different thicknesses ($h_{\text{ALD}}$) were deposited on the Al6061 target substrates with native oxide layers by using the atomic layer deposition process (Savannah–Thermal
The Al6061 target substrates (McMaster-Carr) were first cut into 5 mm × 5 mm areas. On the Al6061 target substrates, the additional oxide layers were grown by using trimethylaluminum (TMA, Al(CH)₃) and water as precursors. TMA and water were alternately introduced for deposition by using N₂ as the carrier gas flow. One total deposition cycle was defined by a 15 ms H₂O injection, 8 s reaction, 15 ms TMA injection, and an 8 s reaction at 200 °C. The flow rate of the precursors was maintained at 20 sccm in the carrier gas. To achieve a 5 nm thick oxide layer, 50 cycles of the reaction process were completed at a growth rate of 1.06 Å/cycle. The final oxide layer thickness achieved were 10nm and 20nm on top of the native oxide layer.

10. Elevated temperature Experiments with incorporated temperature chamber

Additional modification was done by introducing a temperature chamber to the LIPIT system, to expose both the µPs and target substrate to elevated temperatures. The temperature chamber was constructed of Al6061, allowing temperatures within the chambers to reach elevated levels. The chamber surrounded the site of collision without interfering with the normal functionality of the LIPIT system. Four-heaters were mounted on the inner walls of the temperature chamber and the temperature within the chamber was controlled by a positive feedback loop from the thermocouple attached to the inner wall of the chamber. The ablation stage and the target stage were equipped with two additional thermocouples. The temperature of the experiment was taken to be the average temperature between the thermocouple readings of the ablation and target stage as the flight path of the µPs was directly in between the two stages.
Figure B12  Schematic illustration showing the incorporated temperature chamber with the 4 heaters mounted. This addition does not affect the normal functioning of the LIPIT system.
**Figure B13** Modification of the Laser Induced Projectile Impact Test: 3D Schematic Illustration depicting the incorporation of the temperature chamber to the LIPIT system. The micro-ballistic study of the coupled effects of elevated temperature on both the Al6061 µPs and the target substrate was studied by this system.

### 11. Spherical nano-indentation

Low strain rate characterization was performed in an iNano™ system (KLA, TN, USA) nano indenter by using a 20 µm diameter conospherical diamond indenter with a maximum load of 45 mN at room temperature. The displacement rate is approximately 50 nm/s, which corresponds to a strain rate of $\dot{\varepsilon} \sim 10^{-2}$s$^{-1}$. A total of 25 indents were done on each
aluminum and copper sample and the corresponding loading unloading curve was obtained for further analysis. Nano indentation hardness was found out from the area under the loading unloading curve as described by the Oliver-Pharr method and also through the momentum of impact and the impression profile of the indents as described in the later in the results and discussion section.

Figure B14 Illustration of a spherical nano-indenter and the resultant loading-unloading curve. After complete unloading, the graph shows a residual impression of height $h_c$.

12. Numerical simulations
Finite element software ABAQUS® (Dassault Système, USA)[4], was used to simulate both the low strain rate and ultra-high strain rate impact hardness based on the energy dissipation model as described later in the results and discussion section. Johnson-Cook plasticity model[5] (Eq. B.1) was used to model the impact hardness at a range of strain rates and then verify the experimental results through parameter fitting of the experimental results.

\[
\sigma = (A + B\varepsilon_p^n) \left[1 + C \ln \left( \frac{\dot{\varepsilon}_p}{\varepsilon_0} \right) \left[ 1 - \left( \frac{T-T_R}{T_m-T_R} \right)^m \right] \right]
\]

(B.1)

where \( \sigma \) is the flow stress, \( \dot{\varepsilon}_p \) and \( \dot{\varepsilon}_0 \) are the strain rate and the reference strain rate, \( T_m \) is the melting temperature, \( T_R \) is the reference temperature, \( m \) is the temperature exponent, \( A, B, C \) and \( n \) are the strain-hardening model parameters. The data for the material properties of aluminum and copper for the modelling have been taken as used in the literature [5], [6] and the MPDB software database[7]. This model integrated 3D continuum mechanics with non-linear contact interaction (general contact algorithm) between the indenter and target substrate along with plasticity and large-scale deformation mechanics.

13. Impression profile measurements

Both the indentation methods (nano indentation and LIPIT) will leave a deformation on the surface of the specimen post indentation/impact. The impression profile for all the post impact indents at low strain rate and ultra-high strain rate was mapped through laser profilometry (Zygo Nexview Optical Profilometer).
Figure B15 (a) Optical micrographs of pure Cu and high purity Al showing the nanoindentation indents. (b) SEM micrograph showing the residual impression on Cu target substrate after alumina impact (c) Optical micrograph of a residual impression after alumina impact on a Cu substrate at \( v_i \sim 400m/s \) (d) Profile map obtained through laser profilometry of the residual impression after alumina impact on Cu substrate with \( h_{\text{max}}=6.7\mu m \)

14. Electrochemical polishing

Electrochemical polishing was done using an in-house setup. For aluminum, the electrochemical polishing was done with an electrolyte solution of perchloric acid (70\%, A.C.S. Reagent, Sigma-Aldrich) and ethanol (Pharmco Products Inc) mixture at a current
density of 5 A/mm² and at a temperature of 10°C for 30s. Electrochemical polishing for copper was done with an electrolyte solution of phosphoric acid (99.999%, Sigma-Aldrich) and ethanol (Pharmco Products Inc) mixture at a current density of 5 A/mm² and at a temperature of 10°C for 2 minutes. After electrochemical polishing, these target substrates were rinsed with deionized water to remove any extra electrolyte on the surface and then air dried.

Figure B16 Illustration of an electrochemical polishing setup.
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215


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