MICROSTRUCTURAL EVOLUTION IN COLD SPRAYED
AND HEAT TREATED AUSTENITIC STAINLESS STEEL
304L

by

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A DISSERTATION

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ABSTRACT

The US Department of Energy (DOE) has identified stress corrosion cracking (SCC) in nuclear dry cask storage system (DCS) as a critical issue that needs to be addressed for the continued safe storage of spent nuclear fuel. Cold spray (CS) has been proposed as a possible solution to repair the damage caused by SCC due to its low thermal input and lack of melting. However, it was shown that cold sprayed material in the as-sprayed condition exhibits poor corrosion performance. In this work, the use of in-situ laser heating known as laser heated cold spray (LHCS), will be discussed as a method to improve the corrosion performance of the cold sprayed material through targeted heat treatment. Furthermore, an in-depth investigation of the properties of cold sprayed and laser-heated cold sprayed SS304L coatings is presented. Using advanced techniques such as neutron diffraction, transmission electron microscopy, and procession electron diffraction, valuable insights into the residual stress, recrystallization kinetics, and strain-induced martensite transformation in these coatings have been uncovered. The key findings of the research have revealed cold sprayed material to exhibit a two-phase recrystallization mechanism, with accelerated kinetics in the prior particle interface regions. Additionally, it has been discovered that cold spray suppresses strain-induced martensite. Finally, the residual stress in cold spray and laser heated cold spray was characterized using neutron diffraction, and the use of analytical models to predict the residual stress in cold spray was investigated. These findings have important implications for the use of cold spray in the repair and maintenance of nuclear dry cask storage containers.
DEDICATION

This dissertation is dedicated to my wife, Brett, who has been my unwavering source of love, support, and encouragement throughout this academic endeavor.

And to my dog, Dolly, and my cat, Lana.
## LIST OF ABBREVIATIONS AND SYMBOLS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CDRX</td>
<td>Continuous Dynamic Recrystallization</td>
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<tr>
<td>CMWP</td>
<td>Convolutional Multiple Whole Profile</td>
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<td>CS</td>
<td>Cold Spray</td>
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<tr>
<td>DCSS</td>
<td>Dry Cask Storage System</td>
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<tr>
<td>DDRX</td>
<td>Discontinuous Dynamic Recrystallization</td>
</tr>
<tr>
<td>DE</td>
<td>Deposition Efficiency</td>
</tr>
<tr>
<td>DOE</td>
<td>Department of Energy</td>
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<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
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<td>EBSD</td>
<td>Electron Backscatter Diffraction</td>
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<tr>
<td>ECAP</td>
<td>Equal Channel Angular Processing</td>
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<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
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<tr>
<td>FWHM</td>
<td>Full Width Half Max</td>
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<tr>
<td>GDRX</td>
<td>Geometric Dynamic Recrystallization</td>
</tr>
<tr>
<td>GOS</td>
<td>Grain Orientation Spread</td>
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<tr>
<td>GROD</td>
<td>Grain Reference Orientation Deviation</td>
</tr>
<tr>
<td>HFIR</td>
<td>High Flux Isotope Reactor</td>
</tr>
<tr>
<td>HIDRA</td>
<td>High Intensity Diffractometer for Residual Stress Analysis</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>IPF</td>
<td>Inverse Pole Figure</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>--------------------------------------------------</td>
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<tr>
<td>LACS</td>
<td>Laser Assisted Cold Spray</td>
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<td>LHCS</td>
<td>Laser Heated Cold Spray</td>
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<tr>
<td>LIPIT</td>
<td>Laser Induced Particle Impact Test</td>
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<tr>
<td>LPBF</td>
<td>Laser Powder Bed Fusion</td>
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<tr>
<td>MWP</td>
<td>Multiple Whole Profile</td>
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<td>PED</td>
<td>Procession Electron Diffraction</td>
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<td>RDRX</td>
<td>Rotational Dynamic Recrystallization</td>
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<tr>
<td>RS</td>
<td>Residual Stress</td>
</tr>
<tr>
<td>SCC</td>
<td>Stress Corrosion Cracking</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SFE</td>
<td>Stacking Fault Energy</td>
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<tr>
<td>SMAT</td>
<td>Surface Mechanical Attrition Treatment</td>
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<tr>
<td>SNS</td>
<td>Spallation Neutron Source</td>
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<tr>
<td>SRV</td>
<td>Static Recovery</td>
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<tr>
<td>SRX</td>
<td>Static Recrystallization</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<tr>
<td>TWIP</td>
<td>Twinning-Induced Plasticity</td>
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<td>WAAM</td>
<td>Wire Arc Additive Manufacturing</td>
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<tr>
<td>XLPA</td>
<td>X-ray Line Profile Analysis</td>
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<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>ρ</td>
<td>Dislocation Density</td>
</tr>
<tr>
<td>&lt;x&gt;</td>
<td>Crystallite Size</td>
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CONTENTS

ABSTRACT ................................................................................................................................. ii
DEDICATION ............................................................................................................................. iii
LIST OF ABBREVIATIONS AND SYMBOLS ........................................................................ iv
ACKNOWLEDGEMENTS ............................................................................................................ vi
LIST OF TABLES ......................................................................................................................... xi
LIST OF FIGURES ..................................................................................................................... xii
CHAPTER 1 : INTRODUCTION ............................................................................................... 1
  1.1.0 Motivation ....................................................................................................................... 1
  1.2.0 Literature Review .......................................................................................................... 5
  1.3.0 Summary of Findings from Literature ......................................................................... 26
  1.4.0 Research Objectives and Dissertation Structure ....................................................... 27
  References ............................................................................................................................... 27

CHAPTER 2 : MARTENSITE FORMATION AND DYNAMIC RECRYSTALLIZATION IN COLD SPRAYED SS304L .......................................................................................... 35
  Abstract ................................................................................................................................. 35
  2.1.0 Introduction ................................................................................................................... 35
  2.2.0 Methods ....................................................................................................................... 38
  2.3.0 Results ......................................................................................................................... 40
  2.4.0 Discussion .................................................................................................................... 46
  2.5.0 Conclusions ............................................................................................................... 57
  Acknowledgments ................................................................................................................ 59
CHAPTER 3 : QUANTIFYING DISLOCATION DENSITY AND RECRYSTALLIZATION KINETICS IN LASER HEATED COLD SPRAY SS304L ..........65

Abstract .................................................................................................................................................. 65

3.1.0 Introduction .................................................................................................................................. 66

3.2.0 Experimental Methods .................................................................................................................. 71

3.3.0 Results .......................................................................................................................................... 76

3.4.0 Discussion ...................................................................................................................................... 90

3.5.0 Conclusion ...................................................................................................................................... 100

Acknowledgements ............................................................................................................................... 100

Reference ............................................................................................................................................... 101

CHAPTER 4 : EFFECTS OF LASER HEATING ON MICROSTRUCTURE AND DEPOSITION PREOPERTIES OF COLD SPRAYED SS304L ................................................................. 106

Abstract ............................................................................................................................................... 106

4.1.0 Introduction ................................................................................................................................... 107

4.2.0 Experimental Methods .................................................................................................................. 109

4.3.0 Results .......................................................................................................................................... 112

4.4.0 Discussion ...................................................................................................................................... 121

4.5.0 Conclusion ...................................................................................................................................... 133

Acknowledgements ............................................................................................................................... 134

Reference ............................................................................................................................................... 134

CHAPTER 5 : RESIDUAL STRESS IN COLD SPRAYED SS304L MEASURED VIA NEUTRON DIFFRACTION AND COMPARISON OF ANALYTICAL MODELS TO PREDICT THE RESIDUAL STRESS ........................................................................................................ 138

Abstract ............................................................................................................................................... 138

5.1.0 Introduction ................................................................................................................................... 138

5.2.0 Experimental Methods .................................................................................................................. 142
LIST OF TABLES

Table 2.1 Measured chemical composition of the 304L stainless steel powder (wt. %)............ 39
Table 2.2 The average measurement of particle dimensions, flattening ratio, and strain for both samples. Given error is the standard deviation for each value of 20 particle impacts........ 48
Table 3.1 Chemical composition of the 304L stainless steel powder (wt. %)....................... 71
Table 3.2 Values used in ABAQUS for modeling laser heating........................................... 76
Table 3.3 Relevant dislocation densities measured via line profile analysis.......................... 93
Table 4.1 Chemical composition of the 304L stainless steel powder (wt. %).......................... 110
Table 4.2 Grain size data obtained from EBSD scans (µm).............................................. 117
Table 5.1 Chemical composition of the 304L stainless steel powder (wt. %)....................... 143
Table 5.2 Spray conditions for manufacturing samples...................................................... 143
Table 5.3 Material constants for residual stress analysis.................................................. 147
Table 5.4 Input Parameters for Models............................................................................. 148
# LIST OF FIGURES

Figure 1.1 Overview of the cold spray process........................................................................... 6

Figure 1.2 Effects of pressure (400 PSI (2.76 MPa), 600 PSI (4.14 MPa), 800 PSI (5.52 MPa))
on cold spray particle velocity in the nozzle (2 mm throat diameter, 6.3 mm exit diameter, 196
mm length, 45 mm converging section) at 350 °C ................................................................. 8

Figure 1.3 Effects of spray gas temperature on cold spray particle velocity in the nozzle (2 mm
throat diameter, 6.3 mm exit diameter, 196 mm length, 45 mm converging section) at 600 PSI
(4.14 MPa) .................................................................................................................................. 9

Figure 1.4 Effect of temperature on the total martensite percentage in tensile test pulled at
engineering strain rates replotted from T. Angel et al. [33]......................................................... 16

Figure 1.5 Overview of the differences between the LACS and LHCS processes................. 19

Figure 1.6 Evolution of residual stresses in cold spray coatings adapted from
V. Luzin et al. [60] .......................................................................................................................... 24

Figure 2.1 EBSD of powder used for deposition........................................................................ 41

Figure 2.2 (A) EBSD phase maps of cold sprayed SS304L using spray gas at 350 °C and
(B) spray gas at 25 °C .................................................................................................................... 42

Figure 2.3 A) Neutron diffraction profiles with peaks labeled for as-received powder, 25 °C
deposition, and 350 °C deposition. B) BCC/martensite phase percentage in cold spray
deposition as a function of depth with the as-received powder content as a reference. .............. 43

Figure 2.4 TEM bright field images of prior particle interfaces showing nanocrystalline
grains in the sample sprayed at 350 °C (A, B) and highly deformed grains / banded
microstructure with a lack of nanocrystalline equiaxed grains in the sample sprayed at
25 °C (C, D) .................................................................................................................................. 44

Figure 2.5 PED results of 350 °C spray at prior particle interface IPF maps are taken with
respect to the impact direction. High-angle grain boundaries (> 15°) are indicated by
the black lines. ............................................................................................................................... 45
Figure 2.6 PED results of 25 °C spray at prior particle interface IPF maps are taken with respect to the impact direction. High-angle grain boundaries (> 15°) are indicated by the black lines. ................................................................. 46

Figure 2.7 Schematic representation of an ideal prior particle interface as observed in the present observations of cold spray coatings for the 350 °C sample. ................................................. 47

Figure 3.1 Experimental setup for measuring dislocation density as a function of position (A) and dislocation density as a function of temperature (B). Adapted from work by An et al. [21] (additional detectors not shown for simplicity)................................................................. 73

Figure 3.2 EBSD IPF maps at the top and bottom of cold sprayed SS304L in the as-sprayed condition and after laser heating to 750 °C and 950 °C. All maps are taken with respect to the sprat direction (top to bottom). ........................................................................ 77

Figure 3.3 GOS maps obtained from EBSD results with the top and bottom of cold sprayed SS304L in the as-sprayed condition and after laser heating to 750 °C and 950 °C.................................... 78

Figure 3.4 TEM bright field images showing A) Overview of the prior particle interface region in cold sprayed SS304L and B) magnified view of the nanocrystalline size grains at the prior particle interface. ........................................................................ 79

Figure 3.5 Dislocation density as a function of depth as measured by CMWP and W-H and the corresponding FWHM for CS samples corresponding to the EBSD maps shown in figure 3.2 .................................................................................. 81

Figure 3.6 Dislocation Character for laser heated samples as a function of depth.......................... 82

Figure 3.7 Dislocation density and crystallite size results from CMWP as a function of temperature in cold sprayed SS304L for temperatures from 25 °C to 1000 °C ......................... 84

Figure 3.8 DSC results for cold sprayed SS304L ........................................................................ 85

Figure 3.9 Dislocation density calculated with Williamson-Hall analysis in the as-sprayed condition and at a position correlating to 0.8 mm into the 750 °C deposit. ............................... 87

Figure 3.10 Comparison of temperature measured with thermocouples and that simulated with ABAQUS for a calibration test sample with dimensions 2” x 4” x ½”................................. 88

Figure 3.11 Maximum temperature plotted as a function of depth for both the 750 °C and 950 °C samples as well as the temperature vs time profiles for the surface and interface of both samples showing how the maximum temperature reach is extremely short. Particularly at the surface of the coating. .................................................................................. 89
Figure 3.12 Example of the effects of a bimodal grain structure on peak fitting. It can be seen that the peak is made up of two peaks with different strengths. It should be noted that deconvoluting these effects is not as simple as fitting each apparent peak. 93

Figure 3.13 DSC results from SS304L, EBSD at key inflection points in the DSC results (indicated by vertical lines), and comparison of the data to the derivative of the properties measured from neutron diffraction. 99

Figure 4.1 Laser geometry with respect to the sample and spray nozzle. 110

Figure 4.2 Inverse pole figure (IPF) maps (A) and phase map (B) taken from EBSD data of typical powder particles. High-angle grain boundaries (>15°) shown as black lines. 113

Figure 4.3 SEM backscatter images of deposition near the surface (A, B and C) and near the interface of the substrate and deposition (D, E and F). Examples of prior-particle interfaces denoted with black arrows. 114

Figure 4.4 Hardness depth profile of deposition. The substrate is not included in this graph. The hardness of the substrate material was 175 HV0.1. Error bars in data were taken as one standard deviation of 10 random points taken on rolled SS304L. 115

Figure 4.5 IPF orientation maps with respect to z direction (sample normal and direction of spray gun translation) of samples, with top row taken within 200 µm of surface (A, B and C) and bottom taken within 200 µm of baseplate (D, E and F). 116

Figure 4.6 GOS (grain orientation spread) map of samples with top row being taken within 200 µm of surface (A, B and C) and bottom taken within 200 µm of baseplate (D, E and F). Columns correspond to laser temperatures at surface. 118

Figure 4.7 Phase map of samples with top row being taken within 200 µm of surface (A, B and C) and bottom taken within 200 µm of baseplate (D, E and F). Columns correspond to laser temperatures at surface. 119

Figure 4.8 The X-ray diffraction pattern in logarithmic intensity scale for the top of the CS deposit. The open circles and the solid line represent the measured and the fitted X-ray diffraction patterns, respectively. A part of the pattern is presented in the inset with linear intensity scale. The difference between the measured and the fitted patterns is also shown at the bottom of the inset. 120

Figure 4.9 XLPA results showing A) the dislocation density and B) the diffraction domain size in the CS and LHCS with 750 °C samples. 121
Figure 4.10 A) Hall-Petch relationship between calculated grain size and hardness, error bars in y axis correspond to one standard deviation in the data collected and error bars in x axis correspond to minimum and maximum achievable values by varying undetected grain size values B) Taylor relationship between the measured hardness of the cold spray deposit and the dislocation density as measured by XLP A.......................................................... 129

Figure 5.1 Overview of the heating profile used for LHCS sample.............................................. 144

Figure 5.2 Neutron Diffraction was used for residual stress measurements showing the gauge volume size and direction in the cold spray material for each residual stress measurement........................................................................................................... 146

Figure 5.3 SEM SE image of CS powder used in the depositions.................................................. 149

Figure 5.4 Stress-Strain Curves for plate used as substrate here. A yield point of 270 MPa was used to determine max residual stress possible in Figure 5.9.......................................................... 150

Figure 5.5 Hardness results for various conditions show how laser heating softened the material at the deposit's surface (1 mm) but did not bring the hardness back down to that of wrought, likely due to the relatively still fine grain size in the fully recrystallized material........................................................................................................................................ 151

Figure 5.6 Inverse pole figure (IPF) maps from EBSD taken with respect to the spray direction (top to bottom) showing A) the cold spray microstructure near the bottom of the LHCS deposit, which exhibits an as-sprayed microstructure and B) the fully recrystallized microstructure from near the surface of the laser heated sample................................................. 152

Figure 5.7 Residual strain as a function of depth for the LD and TD in the 18-pass as-sprayed material. This data shows that an assumption of biaxial symmetry for strain in the sample is reasonable. ..................................................................................................................... 153

Figure 5.8 Example of the peak broadening in the cold spray material due to type II and type III microstresses. Representative peaks are for the 6-pass BD and the collection time was the same for both peaks. .................................................................................................................. 154

Figure 5.9 Residual Stress measurements for cold spray and 750 °C LHCS coatings. The data indicated in red was analyzed using the method by Luzin et al., while the data highlighted in black was analyzed using a more traditional Hooke’s law approach................. 156

Figure 5.10 Fitting of the Tsui and Clyne and Boruah Model to Experimental Data. Hatched grey areas indicate the areas beyond the yield stress measured for the cold-rolled SS304L used in these experiments. ........................................................................................................ 157
Figure 5.11 Graphic of residual stress evolution in Cold Spray coatings, adapted from work by V. Luzin [60]. A ratio of peening and quenching stress is generated during the cold spray deposition process. After deposition, the residual stress from thermal coefficient mismatch is added, if any, as well as a stress due to a temperature gradient. Finally, these stresses are added up to produce the final stress state.

Figure 6.1 Graph of strain induced martensite percentage at various temperatures as a function of strain. Replotted from the work of Angel et al.

Figure 6.2 Generation of residual stress in cold spray coatings. Adapted and modified from work by V. Luzin.
CHAPTER 1: INTRODUCTION

1.1.0 Motivation

The ability to cold spray SS304L is desired to repair corrosion damage, specifically stress corrosion cracking, in spent nuclear fuel dry cask storage systems (DCSS). Cold spray is preferred due to its portability and low heat input, particularly when compared to traditional repair processes such as welding. The U.S. Department of Energy (DOE) has identified the repair of stress corrosion cracking (SCC) on these DCSSs as a critical task for the continued safe storage of spent nuclear fuel and, as such, has funded research projects in cold spray and other additive manufacturing repair processes for this purpose. DCSSs were created to fulfill the need for a short-term storage solution for spent nuclear fuel created as a byproduct of energy production. This interim solution is projected to be the primary storage source for spent fuel rods for the next 60 years [1]. These dry cask storage containers are manufactured using traditional fusion-based welding techniques. Due to a combination of these traditional welding techniques and the fact that these canisters are often located in corrosive coastal environments, they can be highly susceptible to stress corrosion cracking. Cold spray is a possible repair technique for corrosion in these situations where both portability and low heat input are desired.

Austenitic stainless steels, specifically SS304L, are commonly used in the nuclear industry due to their resistance to radiation damage, good corrosion resistance, strength, and stability at extreme temperatures [2]. In addition, austenitic stainless steels have excellent corrosion resistance and a minimal price premium compared to other structural steels with poor corrosion resistance. This combination of attributes often makes them desirable for applications
where the steel is intended for a long-term application, as the small price premium becomes negligible compared to the repair and maintenance cost due to corrosion. Austenitic stainless steel is one of five classes of stainless steel. It has a face-centered cubic (FCC) structure due to the addition of a significant nickel content (8-12%), is not magnetic and is known for its good formability at low temperatures due to its high ductility. Additionally, the high chrome content make it resistant to corrosion.

Intergranular stress corrosion cracking (IGSCC) is a phenomenon that can occur in 304L stainless steel, particularly when the material is exposed to a corrosive environment and experiences tensile stress. A combination of factors, including the presence of chlorides, high temperatures, and mechanical stresses, can cause IGSCC. When these factors are present, IGSCC can lead to rapid and catastrophic failure of the material. IGSCC can be prevented through proper material selection, design, and maintenance. In cases where IGSCC is a concern, it is crucial to carefully monitor the environment and the mechanical stresses to which the material is exposed.

Sensitization is a particular issue with 304L stainless steel, particularly in welded components. Sensitization occurs when the material is heated to a temperature range between 425 and 815 degrees Celsius, causing the formation of chromium carbide at the grain boundaries in a process termed grain boundary sensitization. This segregation of chromium to the grain boundaries reduces the amount of chromium available to form the passive layer that protects the steel from corrosion, making the material susceptible to intergranular corrosion. Sensitization can be prevented through careful control of the heat treatment process and by reducing the carbon content in the steel. SS304L is a low carbon content variant of the SS304 alloy which increases the time that needs to be spent in the sensitization region from seconds to almost 10
hours. If 304 with a higher carbon content is used over 304L, welding and heat treatment time can lead to grain boundary sensitization; for this reason, 304L is most commonly used as the price premium is minimal.

For the repair of DSCC’s low heat input is critical. Cold spray is a low heat input, solid-state additive manufacturing process by which metal particles are accelerated to supersonic velocities so that they plastically deform upon impact, creating a fully dense solid coating or deposit. It provides many benefits for coating applications over traditional fusion-based additive processes. While cold spray does not provide the spatial resolution of fusion-based processes such as powder bed additive or directed energy deposition, the minimal heat input of cold spray and lack of solidification effects are often desired. Additionally, the cold spray process is highly portable compared to many additive techniques, with commercially available cold spray systems being available that can be moved and even sprayed by hand, similar to a bead blasting process.

Cold spray of austenitic stainless steels presents unique challenges due to the high thermal expansion coefficient and low thermal conductivity, which can lead to the generation of significant residual stresses, and its tendency to form martensite when plastically deformed, which can lead to poor mechanical performance and corrosion properties. In addition, the work hardening of austenitic stainless steels during cold spray causes poor ductility in the material that can cause issues with the longevity of the repair and its ability to withstand thermal cycles. Ex-situ furnace heat treatment has shown the ability to restore ductility in cold sprayed austenitic stainless steels and to eliminate any martensite phase in the deposit [3-7]. However, ex-situ heat treatments negate the portability of cold spray and are often not practical for large parts or parts that cannot be heated to high temperatures in a furnace, such as DCSSs.
Considering these challenges associated with cold spray of austenitic stainless steels, the use of in situ laser heating to recrystallize the material and restore ductility is proposed. Laser systems can bring targeted heat treatment to cold spray coatings, maintaining the system's portability and localizing the heat to the repair area. In addition, laser heating allows the material's ductility to be restored by recrystallizing the material after cold spray deposition. In this application, the low thermal conductivity of austenitic stainless steels can be a benefit as it allows the heat from the laser to stay concentrated in the area of repair and not spread out to the rest of the material.

A major concern that needs to be investigated concerning laser heating is residual stress. Residual stresses are typically seen as beneficial with respect to cold spray since the peening effect caused by cold spray creates compressive stresses, which are thought to suppress crack growth in the coatings. While this can be true, these residual stresses in the as-sprayed condition can lead to adhesion issues with the substrate. Using laser heating with austenitic stainless steels creates an additional issue with residual stresses related to these steels' high thermal expansion coefficient. Thermal expansion combined with heat gradients brought on by the low thermal conductivity can create tensile stresses in the material, potentially creating cracks and causing additional problems with the adhesion of the coatings. The concentrated heat source of laser heating can create large thermal strains and residual stresses that may promote the crack formation and cause debonding. This dissertation seeks to evaluate the positive potential of in situ heating on the microstructure and mechanical properties of cold sprayed 304SS, while understanding and mitigating possible negative-side effects.
1.2.0 Literature Review

A review of the literature most relevant to this dissertation is discussed below. These topics cover the fundamentals of cold spray, the laser heating processes, and the analysis techniques used to quantify the effectiveness of the laser heating process for cold spray repairs of austenitic stainless steel materials.

1.2.1 Overview of the cold spray process

Cold spray is a solid-state additive manufacturing process that works by accelerating powder particles (typically 15-45 microns) through a DeLaval converging-diverging nozzle to speeds such that they plastically deform and create a fully dense coating upon impact with a substrate (500-2000 m/s) [8]. The number of processing parameters that can be altered during cold spray is numerous. A few, key parameters have more pronounced effects on the cold spray deposition: the spray gas, temperature, and pressure. To understand these parameters that most affect the success of the cold spray process, it is necessary to understand the fluid dynamics of the gas flow and powder particles in the gas flow, the impact physics that control the deformation of the powder particles, and the processing-microstructure-properties relationship between these parameters and the final cold spray product.
1.2.2 Fluid mechanics

Fluid Dynamics plays an important role in the cold spray process, as it directly controls a powder particle's velocity upon impact in cold spray. Cold spray systems use a high-pressure gas to accelerate the powder particles through a De-Laval converging-diverging nozzle to the speeds necessary for cold spray. The speed of the gas exiting the nozzle is affected by the temperature, pressure, and geometry of the nozzle. According to the work from V.K. Champagne [9], the velocity of the gas in the cold spray nozzle is described as follows:

\[ U_g = \sqrt{2 \frac{k}{k-1} RT_i \left[ 1 - \left( \frac{P}{P_i} \right)^{\frac{k-1}{k}} \right]} + U_{gi}^2 \]

Equation 1.1

where \( U_g \) is the gas velocity, \( k \) is the gas-specific heat ratio, \( T_i \) is the initial gas temperature, \( P \) is the gas pressure, \( P_i \) is the initial gas pressure, and \( U_{gi} \) is the initial gas velocity. The dependence of the gas temperature on the pressure is:
\[ T_g = T_{gi} \left( \frac{P}{P_i} \right)^{(k-1)/k} \]

Equation 1.2

Where \( T_g \) is the gas temperature and \( T_{gi} \) is the initial gas temperature.

This can be rearranged as follows:

\[ P = P_i \left( \frac{T_g}{T_{gi}} \right)^{k/(k-1)} \]

Equation 1.3

Substituting this into equation 1 results in:

\[ U_g = \sqrt{2 \frac{k}{k-1} RT_i \left[ 1 - \frac{T_g}{T_{gi}} \right] + U_{gi}^2} \]

Equation 1.4

After substitution, it is apparent from equation 1 and equation 4 that as the gas's temperature or pressure increases, the gas's velocity will also increase in the cold spray nozzle. This can be related to the particle velocity by accounting for the drag of the particle in the gas using the equation:

\[ \frac{dU_p}{dt} = \frac{3 C_d \rho_g}{4 D_p \rho_p} (U_g - U_p) |U_g - U_p| \]

Equation 1.5

where \( U_p \) is the particle velocity, \( t \) is the time, \( C_d \) is the drag coefficient, \( D_p \) is the particle diameter, \( \rho_g \) is the gas density, and \( \rho_p \) is the particle density.

Figures 1.2 and 1.3 show the effects of temperature and pressure on the powder particle velocity in the cold spray nozzle and the particle's speed on exit from the nozzle. While the pressure and temperature of the spray gas control the particle velocity, this does not tell us the particle
velocity necessary for a successful deposition. The range of appropriate particle velocities is the velocities that fall between the critical velocity and the erosion velocity.

Figure 1.2 Effects of pressure (400 PSI (2.76 MPa), 600 PSI (4.14 MPa), 800 PSI (5.52 MPa)) on cold spray particle velocity in the nozzle (2 mm throat diameter, 6.3 mm exit diameter, 196 mm length, 45 mm converging section) at 350 °C
Figure 1.3 Effects of spray gas temperature on cold spray particle velocity in the nozzle (2 mm throat diameter, 6.3 mm exit diameter, 196 mm length, 45 mm converging section) at 600 PSI (4.14 MPa)

1.2.3 Current state of cold spray of SS304L

Significant work has been done looking at both the feasibility of cold spray of austenitic stainless steels and these coatings' microstructure and mechanical properties. This work primarily focuses on SS304 and SS316 stainless steel cold spray. For this section, we will consider both of these materials as they behave very similarly and have minimal composition differences, with the most notable change being that 316 has an addition of 2% molybdenum to help with its corrosion resistance to chlorides. The first work that shows the successful deposition of austenitic stainless steels with cold spray was done by T. Schmidt et al. as part of
their work to develop a generalized parameter window for cold spray deposition. It was shown that helium gas is needed for a good deposition and that −45±15 µm particle size distribution leads to the best quality depositions [10, 11]. Subsequent work by Borchers et al. looked at the microstructures that developed in cold sprayed SS316 due to the high strain rate of cold spray [12]. These sprays were done at 30 bar (435 PSI) and 400 °C and showed that the microstructure was heavily deformed with a high dislocation density but that the microstructure was uniform compared to other cold spray material. It was claimed that this is due to the low thermal conductivity of SS316, which makes that response more sensitive to global temperature than adiabatic heating and allows for the heat to dissipate more slowly allowing for a more uniform microstructure in the material.

Subsequent work on the cold spray of austenitic stainless steel has looked at the following categories: ex-situ heat treatment of deposits to restore mechanical properties, optimization of deposition parameters, particle size and variability, fracture behavior and mechanical properties of as-sprayed material, and corrosion resistance.

Optimizing the spray gas temperature, pressure, and type provides the most significant overall improvement in the quality of cold spray deposits. Literature shows that higher gas temperatures and pressure lead to better deposition for austenitic stainless steels [13-17], with some literature using pressures and temperatures as high as 1015 psi and 900 °C [18]. However, these high pressures and temperatures can lead to nozzle clogging and fouling, reducing the lifespan of the cold spray system. Literature by Spencer et al. also shows that single-size smaller particle sizes (-10 µm) lead to better deposition but can cause nozzle fouling and powder feed issues that are remedied by using mixed particle sizes [19]. Adachi et al. successfully produced
cold spray coatings using nitrogen at a pressure of 3.5 MPa (407 PSI), 800 °C, 5-20 µm powder particles, and a 40 mm standoff distance [20].

Cold spray material typically exhibits a higher hardness, and little to no ductility compared to wrought material's fracture and mechanical properties [21-23]. The low ductility of cold sprayed 304 and 316 stainless steels is especially notable since these materials have high ductility in the wrought conditions of 50-90% [24]. Heat treatment has been shown to improve the mechanical properties of cold sprayed SS304L by decreasing the hardness and increasing both the elastic modulus and ultimate tensile strength [3-5, 25, 26]. This improvement in mechanical properties is true for all heat treatments starting at temperatures above 200 °C with rapid transitions in material properties around 700 °C and slowing effectiveness at heat treatments above 1100 °C [27]. Work by Al-Mangour et al. showed the ability to achieve 25% elongation to failure with an 1100 °C heat treatment [28]. Work by Massar et al. showed improvement in the density of stainless steel after heat treatment of powders and an indication of strain-induced martensite [29]. Multiple groups have also shown a reduction or elimination of any bcc phase with heat treatment and improved corrosion performance.

The corrosion performance of cold sprayed austenitic stainless steels is important as austenitic stainless steel is often chosen for its mechanical properties and corrosion performance. Research shows that the corrosion performance of as-deposited austenitic stainless steels is worse than that of wrought [30] but can extend the life of the underlying material, and the peening effect can reduce stress corrosion cracking in welds [31]. However, good performance of the cold spray coating is also desired and heat treatments are shown to improve the corrosion performance of this material close to that of wrought material [6]. Since cold spray is desired due
to its portability the use of a portable heat source is desired, for that purpose a laser is implemented for heating in a process known as LHCS.

1.2.4 Strain-Induced Martensite Formation in SS304L

The discovery of metastable strain-induced martensite in austenitic stainless steels such as SS304(L) and SS316(L) was initially documented by Erich Scheil in 1932 [32]. T. Angel's subsequent research in 1954 greatly contributed to the understanding of this transformation [33]. Venables' investigations [34], followed by Lagneborgj's [35], revealed that ε, an hcp phase often called ε-martensite, can act as a precursor to strain-induced martensite (α'), initiating the formation of strain-induced martensite embryos in austenitic stainless steels. In 1970, P. Mangonon et al. conducted further studies demonstrating that strain-induced martensite is formed through the sequence of γ→ε→α', where γ represents the austenite phase, ε is an hcp phase, and α' is the strain-induced body-centered tetragonal (BCT) phase [36]. Mangonon et al. also demonstrated that the nucleation of α' can occur heterogeneously at intersections of ε bands or where ε bands meet twin or grain boundaries. Both Lagneborgj and Goodchild et al. later indicated that while the ε phase is frequently observed at these shear band intersections, it is not essential for the formation of α'. Furthermore, α' can be generated in grains oriented correctly relative to the axis of tensile straining, albeit less frequently [37]. The formation of ε can be increased at cryogenic temperatures but traditionally very little is seen at room temperature meaning that it is traditionally not seen [38]. Additionally, the α' that forms a BCT phase can be approximated as a BCC phase due to the interstitial carbon in the phase making the BCT phase close to BCC with A=B and C being increased by approximately 0.1Å [39].

The reporting of the formation of strain-induced martensite in austenitic stainless steel cold spray literature varies, with some literature suggesting that it does form and some
suggesting that it does not. Notably, Borchers et al. show a reduction in martensite after cold spray [12]. However, when this literature is looked at holistically, a pattern emerges. Most literature does not show martensite in the deposition, and this same literature also reports using a single-phase powder [4, 17, 23, 40], with the opposite being true for sprays that do see martensite in the deposition [3, 41, 42]. Additionally, the work by Borchers et al. used a much higher deposition temperature which likely led to the reduction in martensite [12]. It should be noted that the martensite and ferrite phases cannot be distinguished with any of the methods used as both are BCC. Considering all that literature shows, it is likely that the BCC phase fraction seen in some cold spray literature is a retained phase from the powder used to spray. It should also be noted that when investigating the literature on 304L stainless steel, 304 is also considered as the maximum carbon content is the only difference between the two. Recent literature shows that the carbon can act as an austenitic stabilizer and that the reduction of carbon can promote the formation of strain induced martensite, however, the limited carbon difference in 304 vs. 304L would likely make a minimal difference [43, 44].

The possibility of strain-induced martensite formation in cold spray literature is an interesting scientific question worth investigating, as strain-induced martensite exhibits poor corrosion performance compared to the austenitic phase. The formation of strain-induced martensite in austenitic stainless steels is a well-known phenomenon [24, 45-49]. Furthermore, literature shows that as much as 90% phase fraction of martensite can form in SS304L under deformation [33]. The possibility of strain-induced martensite formation in cold sprayed SS304L raises concerns due to its negative impact on the mechanical properties and corrosion performance of austenitic stainless steels. Martensite formation results in a transformation from the desired austenitic phase to the less desirable martensitic phase, leading to reduced ductility,
toughness, and increased hardness. These changes can increase the susceptibility to cracking and compromise the mechanical integrity of the material. Furthermore, martensite makes them more vulnerable to corrosion attacks, including localized corrosion, pitting, and stress corrosion cracking. Careful monitoring and control of strain induced martensite formation through optimized process parameters and thermal treatment are essential to maintain the desired mechanical properties and corrosion resistance in cold sprayed SS304L coatings.

While cold spray has high total strains that can exceed 100 % at the prior particle interface, it also has high strain rates ($10^6$ – $10^9$ S$^{-1}$) that may inhibit strain-induced martensite formation in cold spray material. Literature shows that both heat and high strain rates can impede the strain-induced martensite transformation [37-40], but no literature looks at the extreme strain rates and conditions in cold spray deposition. Instead, multiple papers individually examine each factor that must be considered when evaluating strain-induced martensite in cold spray. The characteristics of cold spray that are the most important to consider when evaluating strain-induced martensite formation are the compressive stresses, high strain rate, elevated gas temperature, and total strains. Many papers in literature look at the effects of each of these factors independently, and some combine multiple, but not all, of these factors, such as shock loading and surface mechanical attrition treatment, which both combine the high strain rate and compressive strains of cold spray but do not fully cover the extent of total strain or the elevated temperature of cold spray. Additionally, literature often shows that compressive strain suppresses the strain-induced martensite transformation compared to tensile strains of the same magnitude. In literature, the average strain seen in a cold spray particle is somewhere around 0.4 to 0.8 [8]. Hence, based on literature examining compressive strains, it can be anticipated that the material
would contain approximately 80 to 90% martensite if subjected to room temperature and engineering strain rates of $10^{-3}$ S$^{-1}$.

Perhaps the most critical factor to consider in cold spray concerning strain-induced martensite is the temperature of the material. Literature shows that elevated temperatures can drastically reduce the amount of strain-induced martensite, as can be seen in work by T. Angel et al., where at equal plastic strains of 0.6, either 90% or 4% strain-induced martensite can be formed depending on if the temperature is –188 °C or 80 °C respectively [33]. With a spray gas temperature in literature ranging from 300 °C to over 1000 °C for austenitic stainless steels, and the cold spray deposit experiencing temperatures similar to that of the spray gas, most literature takes place well above the temperatures investigated in this work. Additionally, significant literature cites high strain rates as impeding martensite formation in austenitic stainless steels due to the temperature rise from adiabatic heating. Likely, both the adiabatic heating and the heat transfer from the spray gas are sufficient enough in cold spray to suppress the strain-induced martensite transformation.
1.2.5 Dislocation Density/Structures in cold spray

The high impact velocity and large total strains in cold spray generate a dense dislocation network in the deposit. Often literature points to this high dislocation density as the driving force for many of the properties of cold spray, such as its high hardness and lack of ductility. Borchers et al. looked at the formation of dislocation loops in cold spray copper coatings due to the “ultra-high strain rates” in cold spray coatings [50]. It was seen that a large number of intrinsic and extrinsic dislocation loops were formed, with the most probable formation mechanism for these loops being the agglomeration of point defects generated by dislocation climb during or immediately after deformation, leading to the annihilation of the latter. Additionally, the work showed that these dislocation loops persisted up to 600 °C, leading to over double the hardness in cold sprayed material compared to that of cold rolled and annealed bulk copper. Liu et al. quantified the dislocation density in aluminum copper cold spray coatings using neutron
diffraction and the Williamson-Hall method. This work showed a dislocation density of $10^{14}$ m$^{-2}$ for these coatings [51]. Additionally, work by Azarmi has shown the dislocation density to be $10^{17}$ m$^{-2}$ at the prior particle interface, as measured using a TEM [52].

The measurement of dislocation density in cold spray coatings has significant practical applications. It allows for exploring the kinetics and microstructural evolution of cold spray coatings. The convolutional multiple whole profile (CMWP) method provides valuable parameters for cold spray simulations, including dislocation density, crystallite size, and dislocation character. In a study by Msolli et al., the microstructural evolution in cold sprayed coatings was simulated using a computational framework based on geometrically necessary dislocation density [53]. The findings revealed that dislocation evolution in cold spray could explain various microstructural features, such as highly refined prior particle interfaces. The study also investigated the effects of different processing parameters on the dislocation density evolution in the coatings. Such research has the potential to accelerate our understanding of the kinetics and microstructural evolution of cold spray upon heating, enabling the customization of cold spray coating properties for specific applications.

**1.2.6 Laser Heated Cold Spray and Laser Assisted Cold Spray**

The use of in situ laser heating with cold spray deposition is currently divided into two main categories, laser assisted cold spray (LACS) and laser heated cold spray (LHCS). The motivation behind the development of LACS and LHCS is driven by the desire for increased deposition efficiency, the ability to successfully produce fully dense coatings from steels and higher strength materials, and enhanced microstructures closer to that of wrought material from cold spray. LHCS and LACS have been shown to improve both the mechanical properties and the adhesion strength of cold spray coatings [54-57]. These forms of laser heating are considered
in-situ laser heating in that they both are without the need to remove or rearrange the sample or
spray system. LACS is done by running the laser simultaneously during the cold spray process,
while LHCS decouples this process by spraying and then laser heating the deposit over the
deposit's surface. LHCS provides the benefit of decoupling the laser heating process from the
cold spray process allowing for the examination of both the microstructure after deposition and
the microstructure after laser heating. Decoupling these processes simplifies much of the analysis
since material is not being added during the heating process, no deformation is occurring, and the
effect of the spray gas temperature does not need to be accounted for in any thermal analysis.
Decoupling the spray process and heating process in this way does not allow for the study of
laser heating on the adhesion and porosity of the deposits but allows for a closer examination of
the recrystallization kinetics in cold sprayed materials.
Figure 1.5 Overview of the differences between the LACS and LHCS processes

Work on laser assisted cold spray has taken three main shapes in literature, including using the laser co-axially aligned with the cold spray deposition, off-axis alignment with the laser spot coincident with the deposition center, and off-axis alignment with the laser spot...
leading the cold spray deposition. Laser assisted cold spray (LACS) has been shown to improve the deposition efficiency and increase the thickness of deposited material compared to conventional cold spray [55, 58-63], such as the case of titanium where Bray et al. showed a doubling in the build rate using the LACS process over traditional CS [54, 64]. The LACS process also leads to significant changes in microstructure, including recrystallization and grain growth, which can result in increased ductility and decreased hardness [63, 65]. However, measurements of ductility for LACS deposited material are scant in the current scientific literature. Recent results on LACS of AA7075 powders demonstrate increases in ductility, indicating the potential for LACS to produce materials with improved mechanical properties [65].

While most work involving laser heating has focused on the use of LACS to improve the deposition properties and allow for the deposition of higher-strength materials with cold spray, increasing work has been done on LHCS to look at its ability to anneal the cold spray coating and in some cases provide surface remelting of cold spray coatings [66-71]. The aim of laser heating of cold spray deposits at temperatures below the melting temp is mostly the same as furnace heat treatments of cold sprayed deposits, to recrystallize the microstructure and improve the mechanical properties of the coating. Using a laser for this purpose has the advantage of keeping the cold spray system portable and allowing for the heat treatment of coating applied to parts far too large for a furnace. However, using a laser for heat treatment has the added hurdle of high temperature gradients due to the localized and rapid heating caused by a laser not seen with furnace heat treatments [64].

Previous work has reported the benefits of LHCS for an increasing number of cold sprayed alloys, including aluminum alloys, Cu, stainless steel, Inconel, and Titanium alloys, to
alter the microstructure of the cold spray deposits beneficially\cite{66, 67, 69, 70, 72-75}. LHCS has shown reduced hardness for stainless steel, aluminum alloys, and Cu. The laser power needed to reduce hardness for Al 6061 and Cu is as low as 95 W using a 6 mm diameter laser spot size \cite{71}. Laser heating of cold spray can introduce additional stresses in the cold spray material, which can result in cracking or delamination of the deposit; however, with laser process optimization, the recrystallization of material can be achieved without damage to the coatings \cite{69, 70}. Recent work by Razavipour et al. has looked at artificial neural networks for the hardness prediction and optimization of laser heating parameters to optimize cold spray copper coating's mechanical properties \cite{76}. In this work by Razavipour et al., it was found that the neural network could predict the hardness of the cold spray coating based on the local thermal history in the coating resulting from the laser heat treatment process. Research in laser heated cold spray shows that further applications or the localized optimization of cold spray material properties using a laser model to predict and optimize the coating properties and laser heating parameters will become more critical.

LACS can provide some benefits over LHCS by delivering heat to the cold spray deposit during the deposition of each layer, delivering more even heating to the deposit, and reducing the temperature gradient. Additionally, this additional heat input can help to soften the substrate prior to particle impact, improving the bonding of particles or enabling the ability to cold spray materials that would otherwise not adhere.

In summary, LHCS has shown a reduction in coating hardness produced with cold spray and could be used to reduce the effects of work hardening during cold spray deposits. LHCS allows us to more closely study the effects of laser heating on the microstructure in cold spray deposits apart from the cold spray process itself and, for this reason, may provide benefits for
research applications. Additionally, LHCS can provide less heat input than LACS or furnace heat treatment methods which is beneficial for heat sensitive applications. More work needs to be done on LHCS to fully understand how it affects the microstructure of the deposited coating and the residual stress in the coatings.

1.2.7 Rapid recrystallization and grain growth in highly deformed materials

One of the main goals that is hoped to be achieved through the laser heating of cold spray material is the recrystallization of cold spray material. For a material such as cold spray where large amounts of plastic deformation are taking place and ultimately result in a highly deformed bimodal microstructure understanding the effects the heating has on the recrystallization kinetics in the material is of interest. Gaining a comprehensive understanding of these kinetics enables the reduction of heat input during laser heating and the fine-tuning of heating profiles to avoid undesirable microstructures.

Literature shows that deformation and cold work can increase the kinetics of recrystallization in metals. The increase of kinetics in highly deformed materials is a well-known phenomenon caused by the decrease in grain size and increase in plastic strain [27, 77]. The effects of these parameters on the recrystallization time can be best seen through the Arrhenius equation [78]:

\[
t_{0.5} = Ad_0^m \dot{\varepsilon}_p \dot{\varepsilon}_q \exp \left( -\frac{Q_{st}}{RT} \right)
\]

Equation 1.6

where \(d_0^m\), \(\dot{\varepsilon}_p\), and \(\dot{\varepsilon}_q\) represent the initial grain size, effective plastic strain, and mean strain rate. Work by Smith et al. characterized the deformation and annealing of 304 stainless steels and showed a decrease in recrystallization time with cold working of 304 stainless steel [7].
The strain rates ($10^7$ to $10^9$ S$^{-1}$) and deformation levels seen in cold spray are typically only matched by ballistic impact tests [19, 79, 80]. Since recrystallization due to heating is not often studied in these cases, the speed and mechanisms that control recrystallization in these highly deformed materials are not often investigated. Understanding these mechanisms may help to understand cold spray better and can assist with understanding how cold spray behaves with heating so that its properties can be tailored best for its intended use case.

1.2.8 Residual stress in cold spray

Cold spray provides many advantages over thermal spray and traditional fusion-based additive manufacturing processes; one of these advantages is that the residual stresses in cold spray are typically compressive, compared to tensile in fusion based processes, which can be beneficial to prevent stress corrosion cracking [81-92]. However, it is still necessary to understand these residual stresses and the formation of the stresses as excessive compressive residual stresses can cause issues with adhesion and warping of the cold spray coating. The primary components of cold spray coating include both intrinsic stresses that occur during the cold spray deposition, such as a peening stress, and cooling stresses that occur after deposition during the cooling of the cold spray coating back to room temperature [92].

The peening stress is the primary intrinsic stress during cold spray, which is created by the subsequent impact of a particle on previously deposited material that acts as additional shot peening on the workpiece. This peening stress is the main driving force of the compressive stress typically observed in the surfaces of cold sprayed material. The thermal coefficient mismatch stress and cooling stresses occur during cooling of the deposit and substrate. The thermal coefficient mismatch stress is due to the difference in the coefficient of thermal expansion in the substrate and the deposited material and creates either a tensile or compressive stress in the
coating depending on which material has the larger coefficient. The second residual stress that will be created during material cooling is one due to the thermal gradient after the deposition ends. The residual stress due to this thermal gradient will be tensile on the side of the material which is hotter and compressive on the cooler side during deposition, creating a tensile stress at the deposition surface during most cold sprays. The effects of this stress due to temperature gradients have been shown in work by Marzbanard et al., where the heat transfer rate from the coating substrate could affect the residual stress in the coating [93]. The magnitude of these cooling stresses was also found to depend both on the substrate temperature and the spray gas temperature.

Figure 1.6 Evolution of residual stresses in cold spray coatings adapted from V. Luzin et al. [60]

Limited work exists that measures the residual stress in cold sprayed material due to the difficulty of taking these measurements. Taking these measurements is difficult due to the cost of the required equipment and an upper limit to coating thickness before cracking and adhesion issues become a problem. Most work in the literature focuses on measuring residual stress in
cold spray coatings after deposition though some work has looked at residual stress formation during deposition, which can provide valuable insight [94]. Post deposition measurement techniques used to measure residual stress in cold spray coatings include curvature, crack compliance, incremental hole drill, X-ray diffraction, synchrotron X-ray diffraction, and neutron diffraction [92, 95]. Each technique has its advantages and limitations, outlined in detail by V. Luzin in the review “Advanced Residual Stress Analysis in Thermal Spray and Cold Spray Processes” [92]. This work uses neutron diffraction due to its accuracy, resolution, and penetrating depth.

1.2.9 Neutron diffraction for measurement of residual stresses

Neutron diffraction is one of the most accurate and precise, nondestructive ways to measure residual stresses in crystalline materials. For example, elastic strains in crystalline materials can be determined by measuring the interplanar atomic spacing in the materials. Neutrons can be used to map this elastic strain in the material due to the high penetrating power of neutrons. The 3-D volume from which the measurement is taken for each data point is set by the cross section of the beam size, and the detector and high resolutions can be achieved with sufficient measurement time.

Previous work on measuring residual stresses in cold spray coatings using neutron diffraction has been strongly influenced by the work of V. Luzin et al. [96]. Work by Vladimir Luzin developed a set of assumptions and techniques to simplify and more successfully analyze cold spray coatings with a flat geometry. These main assumptions and the implications of these assumptions can be read about more fully in his work but are summarized below:

1. For a flat geometry, a zero-plane stress state can be assumed with a stress component normal to the cold spray coating to be zero.
2. Coating properties are uniform in the in-plane direction near the center of the coating. However, this will break down at the edge of the coatings and cannot be assumed to be uniform.

3. The biaxial stress profile allows the in-plane stress component to describe the stress state in cold spray coating. In addition, this means that the stress state can be fully described by measuring just the strain in an in-plane and out-of-plane direction.

4. The assumptions in 1-3 allow for the determination of $d_0$ using Hooke's law.

1.3.0 Summary of Findings from Literature

- Austenitic stainless steels can be successfully sprayed using cold spray but have little to no ductility and often show a significant martensite phase.

- Ex situ heat treatment has been shown to restore ductility in cold spray austenitic stainless steels and eliminate the strain induced martensite.

- Mechanical work, which increases the dislocation density in material, can significantly increase the kinetics of recrystallization in a material.

- The CMWP analysis method can be used to determine material properties and dislocation density from diffraction data.

- Significant compressive residual stresses can be generated in cold spray, which are typically seen as beneficial. However, it is traditionally hard to measure and hard to simulate these residual stresses. An analytical model may help to predict the residual stress more easily in cold spray.
1.4.0 Research Objectives and Dissertation Structure

Considering the findings from literature, the following topics will be investigated:

1. Investigate the formation of strain induced martensite during the cold spray deposition of austenitic stainless steel.

2. Quantify the changes in dislocation density in CS and LHCS deposits as a function of position and temperature in the deposit.

3. Use LHCS to modify the microstructure and mechanical properties of LHCS through recrystallization.

4. Measure the residual strain and stresses in cold sprayed and laser heat treated, cold sprayed 304 stainless steel.

This research is presented in a paper-style format. Following the introduction, chapters 2-5 address the four technical objectives in the order listed above. These chapters are followed by a conclusion and recommendations for future research in chapter 6.

References


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CHAPTER 2: MARTENSITE FORMATION AND DYNAMIC RECRYSTALLIZATION IN COLD SPRAYED SS304L

Abstract

In this study, a comprehensive set of characterization techniques are employed to demonstrate that the cold spray deposition process can result in a significant increase of martensite in austenitic stainless steel. The lack of consensus in the literature on the formation of strain-induced martensite in cold spray can be attributed to the diverse processing conditions and measurement techniques used in different studies. In this work EBSD, neutron diffraction, TEM imaging, and precession electron diffraction were used in combination to examine whether strain-induced martensite is formed during cold spray deposition of 304L stainless steel powder and to give further insight into possible mechanisms controlling this phenomenon. Cold spray was performed at both 350 °C and room temperature (25 °C) to investigate the effects of spray temperature on the martensite transformation. It is shown that the strain-induced martensite formation is significantly suppressed compared to that which would be expected for comparable levels of plastic strain at quasi-static strain rates. Additionally, the spray gas temperature is shown to directly impact the microstructure formed at the prior particle interface and the formation of dynamically recrystallized regions.

2.1.0 Introduction

Cold gas dynamic spray, or cold spray (CS), is a solid-state additive manufacturing technique that uses high-pressure gas to accelerate particles (typically 15-45 µm in diameter) to a
high velocity (typically 300-2500 m/s) through a DeLaval converging-diverging nozzle [1]. This rapid velocity results in plastic deformation of the particles upon impact, resulting in bonding and a dense deposition with minimal porosity. After cold spray deposition, spherical particles experience an average plastic strain of 50-90% [2]. As this plastic strain is experienced by small particles moving at high velocities, the average strains or strain rates during particle impact are not uniform over the impacting particle. Literature reports strain rates in the prior particle interiors of $10^4$ to $10^5$ s$^{-1}$ [3] and $10^7$ s$^{-1}$ to $10^9$ s$^{-1}$ in the adiabatic shear zones at the prior particle interface [3-5].

Due to both the extent of plastic strain during cold spray and the tendency of austenitic stainless steels to form strain-induced martensite under deformation, the question of whether CS promotes deformation-induced martensite in austenitic stainless steel has arisen in cold spray literature. The strain-induced martensite transformation in austenitic stainless steels is a well-known phenomenon that is comprehensively reported in literature [6-11]. The literature on cold spray of austenitic stainless steels consists of two categories, one consists of those that report a secondary BCC phase in the deposit which is attributed to the initial powder feedstock microstructure [12-14], and a second category that consists of those that show no formation of martensite in depositions produced using single phase initial feedstock powder [15-18]. Notably, work by Borchers et. Al. showed a reduction in martensite measured by XRD relative to the powder feedstock after cold spray deposition in SS316 [19].

Strain-induced martensite can significantly affect both the mechanical properties and the corrosion behavior of austenitic stainless steels, and for this reason, it has been widely studied since the introduction of these alloys in the early 20th century. The formation of metastable strain-induced martensite in austenitic stainless steels such as SS304(L) and SS316(L) was first...
reported in 1932 by Erich Scheil [20]. Later work by T. Angel in 1954 greatly expanded upon the understanding of this transformation [21]. Work by Venables [22] and later by Lagneborgj [23] showed that ε, an hcp phase, can serve as a precursor to strain-induced martensite (α′) to initiate strain induced martensite embryos in austenitic stainless steels. Further work by P. Mangonon et al. in 1970 showed that strain-induced martensite is formed by the sequence of γ → ε → α′, where γ is the austenite phase, ε is an hcp phase, and α′ is the strain induced body centered tetragonal (BCT) phase [24]. Additionally, this work by Mangonon et al. shows that the nucleation of α′ can occur heterogeneously at intersections of ε bands or where ε bands abut twin or grain boundaries. Both Lagneborgj and Goodchild et al. later show that while the ε phase is often formed at these shear band intersections, it is not necessary for the formation of α′ and that, while less common, α′ can be generated in grains that are oriented in the correct orientation relative to the tensile straining axis [25].

The strain-induced martensite transformation, as it applies to high strain rate transformations, has been more thoroughly researched outside of the context of cold spray deposition. A series of works by Olson et al. proposes that at low strain levels, α′ forms more readily during high strain rate tension than low-rate tension, in an idea known as the Olson-Cohen analysis [26-30]. However, studies of stress amplitude and strain rate on the martensitic phase transformation performed by Murr et al., Hecker et al., and Staudhammer et al. demonstrated that at larger total strains (above 0.25), adiabatic heating due to straining begins to play a significant role reducing the driving force for the γ → α′ transformation [31-34]. Furthermore, Murr et al. propose that α′ only occurs at shear band intersections where the definition of shear bands consists of bundles of faults, twins, and the ε phase. They postulate that
the “growth” of the $\alpha'$ phase is not growth but the coalescence of the $\alpha'$ embryos. At high strain rates this coalescence is also inhibited, further restricting the $\alpha'$ product.

The objective of this current study is to investigate the presence of martensite in cold sprayed SS304L deposits and to evaluate whether additional strain-induced martensite is formed during the cold spray process due to the plastic deformation upon initial impact as well as the subsequent peening effect. Cold spray provides a unique set of conditions, such as high strain rates, elevated temperatures, repeated peening effects, and small grain sizes, which are not easily replicated in other metal forming processes. Due to this unique set of circumstances, investigating the strain-induced martensite transformation in cold sprayed austenitic stainless steel is worthwhile. The mechanisms that promote or inhibit the strain-induced martensite phase transformation in cold sprayed material are investigated using a combination of neutron diffraction, electron backscatter diffraction (EBSD), transmission electron microscopy (TEM), and precession electron diffraction (PED).

2.2.0 Methods

In this study, SS304L was deposited via cold spray onto a 1/8” SS304L substrate using a VRC GEN III high pressure cold spray system (VRC Metal Systems, Rapid City, SD). Nitrogen gas atomized powder from Sandvik Osprey Ltd. with a nominal particle size of 15-45 $\mu$m was used (see composition in Table 2.1). Sieve analysis showed the particle size to be 99.8% -45+15 $\mu$m with 0.2% being +45 $\mu$m, while laser diffraction analysis showed the d10, d50, and d90 to be 28.7 $\mu$m, 40.5 $\mu$m, and 55.5 $\mu$m respectively. The powders were used in the as-atomized condition and no additional heat treatment was done to the powders. A DeLaval converging-diverging nozzle was used with a throat size of 2.00 mm and a length of 196 mm. Helium gas was used as the spray gas with a pressure of 600 psi (4.14 MPa) and temperature of 350 °C and
25 °C, respectively. Four layers were deposited, each with a layer thickness of 0.5 mm for a nominal coating thickness of 2 mm for each sample and an overall size for the depositions of 25x25x2 mm. The gun velocity during deposition was 100 mm/s.

Table 2.1 Measured chemical composition of the 304L stainless steel powder (wt. %).

<table>
<thead>
<tr>
<th>C</th>
<th>N</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.14</td>
<td>1.5</td>
<td>0.023</td>
<td>0.006</td>
<td>0.73</td>
<td>18.7</td>
<td>8.3</td>
<td>Balance</td>
</tr>
</tbody>
</table>

The cold spray specimen was prepared for neutron diffraction measurements by using electrical discharge machining (EDM) to section a square from the center of the deposition 20x25 mm in size. Two powders were also prepared for neutron diffraction, one was an as-received powder, and another was heat treated at 750 °C for 1 hour in a furnace to ensure complete recrystallization. A vanadium canister was used for measurements of the metal powders. A gauge volume of 0.3x17x6 mm and a 30 Hz chopper were used, resulting in a wavelength of 2.88 Å with a collection time of 15 minutes per data point. Each of the powder samples used a 5 mm beam with a collection time of 5 min. Phase fraction from the neutron diffraction results was calculated using the VDRIVEX and GSAS software. EBSD was performed on a JEOL 700 FE SEM using an accelerating voltage of 20 kV and a step size of 0.125 µm from leftover material used to make the same samples for neutron diffraction. Samples for TEM and PED were made using a Tescan FIB from the same material used for EBSD.

While EBSD gives us an excellent look at the cold spray microstructure and the overall phase distribution in the material, the reliability of pattern indexing at the prior particle interfaces is lacking due to the high amount of deformation at the prior particle interfaces and small grain size. For this purpose, TEM imaging and procession electron diffraction (PED) were performed to look at these areas to investigate both the grain structure as well as the phase fraction distribution at the prior particle interfaces. The prior particle interface was lightly etched with Kalling’s No. 2 etchant prior to FIB lift out to identify the prior particle interfaces. An FEI
Tecnai F-20 operating at 200 keV was used for TEM imaging, and PED was performed using the Topspin software on the Nanomegas ASTAR system. The PED scans were done using a 30-micron condenser aperture with a 3 nm step size, a precession angle of 0.5 degrees, with ten precessions per frame. Grain orientation spread (GOS) maps were used to look for the possibility of dynamically recrystallized grains. GOS maps assign a single color to each grain based on the total average spread from the median orientation angle for all points in a grain. This means that recrystallized grains with a low defect density and, therefore, a lower spread will have a smaller value, while highly deformed grains with a large defect density will have a much larger value.

2.3.0 Results

EBSD mapping of the as-received powder (Figure 2.1) and the cold sprayed austenitic stainless steel (Figure 2.2) shows the presence of a second phase. This phase is either the ferrite BCC phase or the martensitic BCT phase; in this paper, this phase will be referred to as the BCC phase for simplicity. It should be noted that standard, Hough-based indexing routines in EBSD cannot differentiate between the BCC and BCT phases in steel. The BCC phase in the as-received powder is evenly distributed throughout the powder particle, and the BCC grains are approximately 1-5 µm in size. In the cold spray deposition, the BCC phase also appears to be evenly distributed throughout the deposition and ranges from 1-5 µm in size.
Figure 2.1 EBSD of powder used for deposition.

EBSD of the cold spray deposited at 350 °C (Figure 2.2a) shows considerably less BCC phase fraction (2.3%) than that deposited at 25 °C (30.5%) (Figure 2.2b). The BCC phase fraction in both samples is evenly dispersed over the sample and does not appear to be segregated to any region of the particle after impact. The prior particle interface area in the 25 °C sample provided better indexing than the 350 °C sample.
GSAS-II was used to determine the BCC phase fraction for the as-received powder, the 350 °C cold spray deposition, and the 25 °C cold spray deposit using neutron diffraction (Figure 2.3). The 350 °C cold spray deposition shows an average BCC phase fraction of 2.5 % while the as-received powder shows a BCC phase fraction of 2.2%. Reducing the maximum spray temperature to 25 °C increased the BCC phase fraction to 30.2%. The 350 °C cold spray deposit reports a slightly higher percentage of BCC than the as-received powder, while the 25 °C deposit reports a significant increase in the BCC phase fraction. No other phases were seen in the neutron diffraction patterns. This result raises the question of whether this phase fraction increase is evenly distributed over the cold spray deposit or localized to the prior particle interface. Localization to the prior particle interface could cause issues for corrosion by sensitizing the prior particle interfaces.
Figure 2.3 A) Neutron diffraction profiles with peaks labeled for as-received powder, 25 °C deposition, and 350 °C deposition. B) BCC/martensite phase percentage in cold spray deposition as a function of depth with the as-received powder content as a reference.

TEM of the prior particle interfaces shows a highly deformed microstructure (Figure 2.4). TEM of the 350 °C sample shows a band of dynamically recrystallized grains at each prior particle interface, while that at 25 °C shows does not show any clear presence of the equiaxed grains at the prior particle interface. The 25 °C samples show some banded features that are not well described in the literature.
Figure 2.4 TEM bright field images of prior particle interfaces showing nanocrystalline grains in the sample sprayed at 350 °C (A, B) and highly deformed grains / banded microstructure with a lack of nanocrystalline equiaxed grains in the sample sprayed at 25 °C (C, D).

PED maps at the prior particle interfaces show a highly refined microstructure at the prior particle interface with the GOS map indicating dynamically recrystallized grain in this region for the case of the sample sprayed at 350 °C (Figure 2.5). Below the prior particle interface, in the material that was impacted from the secondary impact, a refined microstructure with a large
grain orientation spread is present in both conditions. For the sample sprayed at room temperature (25 °C) (Figure 2.6), a heavily deformed microstructure can be seen with many more elongated, flattened grains than can be seen in the sample sprayed at 350 °C. Additionally, while some nano-size grains can be seen in band contrast maps for the 25 °C sample, there is not a clear band of nanocrystalline grains as seen in the 350 °C sample. The percentage and distribution of the ferrite phase are similar for both samples, with no clear segregation of the phase to any region. This indicated that the strain-induced martensite phase is not preferentially formed in any specific region in the deposit. For both samples, twins were looked for with a twin recrystallization twin definition of 60° about <111> and a deformation twin of 60° about <112>. Neither sample showed a clear presence of twins. Some “twins” appeared in both samples but aligned with ambiguities from the PED indexing process that resulted from crystallographic symmetry in the diffraction patterns. This is a known issue that can arise from PED.

Figure 2.5 PED results of 350 °C spray at prior particle interface IPF maps are taken with respect to the impact direction. High-angle grain boundaries (> 15°) are indicated by the black lines.
Figure 2.6 PED results of 25 °C spray at prior particle interface IPF maps are taken with respect to the impact direction. High-angle grain boundaries (> 15°) are indicated by the black lines.

2.4.0 Discussion

The work in this paper shows that cold spray of austenitic stainless steels can form strain-induced martensite and that the extent of this formation is mainly dependent on the spray gas temperature. It is well reported in literature that deformation of austenitic stainless steels, including SS304L, can cause the formation of strain-induced martensite [6-11], with the phase fraction of martensite reaching as high as 40% in tension and 85% in cold rolled material at room temperature [6, 21]. Additionally, in uniaxial and biaxial tension, both elevated temperatures and high strain rates have been shown to suppress the strain-induced martensite formation, both of which are seen in cold spray [21, 33]. Neutron diffraction of the cold spray deposit shows an increase of 0.4% in the bulk phase fraction of BCC/martensite after deposition at 350 °C and an increase of 28.1% after deposition at room temperature as measured. Examination of the prior particle interface with PED showed a BCC phase at the prior particle interface in both samples,
though the formation was much more pronounced in the samples sprayed at 25 °C. Notably, a clear band of equiaxed grains devoid of BCC is seen in the samples sprayed at 350 °C, while material sprayed at room temperature shows no evidence of a BCC-free area at the prior particle interface. Work by Zou et al. showed three distinct regions to exist at the prior particle interface for cold sprayed samples. These three regions provide a valuable framework to discuss the effects seen at the prior particle interface during cold spray deposition as similar results are seen here; these regions are as follows (Figure 2.7) [35]:

1. The prior particle interior
2. The transition region between the interface and interior
3. The prior particle interface

![Figure 2.7 Schematic representation of an ideal prior particle interface as observed in the present observations of cold spray coatings for the 350 °C sample.](image)

**2.4.1 Conditions in Cold Spray Particles During Impact**

It is necessary to understand the strains, strain rates, and temperatures associated with each region in the cold spray particle to understand the deformation mechanisms seen in each
region. For the prior particle interior, the total strain can be reasonably estimated by looking at
the shape of the particle after deposition. The total average plastic strain in cold sprayed material
can be estimated by measuring the width and height of the particle after impact [36]:

$$ f_r = \frac{w}{d_0} $$
Equation 2.1

where $w$ is the width after impact and $d_0$ is the initial particle diameter. $d_0$ can be calculated as:

$$ d_0 = \frac{\sqrt[3]{wh}}{2} $$
Equation 2.2

From this, the average strain $\varepsilon$ can be solved as:

$$ \varepsilon = \ln \left( \frac{d_0}{h} \right) $$
Equation 2.3

Twenty grains were measured for each sample to give an average flattening ratio after deposition
of 1.36 for the material sprayed at 350 °C and 1.29 for the material sprayed at 25 °C resulting in
a total average plastic strain of 60.8% for the 350 °C material and 50.5% for the material sprayed
at 25 °C (Table 2.2).

Table 2.2 The average measurement of particle dimensions, flattening ratio, and strain for both
samples. Given error is the standard deviation for each value of 20 particle impacts.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$w$, µm</th>
<th>$h$, µm</th>
<th>$d_0$, µm</th>
<th>$f_r$</th>
<th>$\varepsilon$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>350 °C</td>
<td>45.3 ± 10.9</td>
<td>18.3 ± 5.45</td>
<td>33.3 ± 7.2</td>
<td>1.36 ± 0.16</td>
<td>60.8 ± 22.7</td>
</tr>
<tr>
<td>25 °C</td>
<td>42.5 ± 9.1</td>
<td>19.96 ± 4.7</td>
<td>32.7 ± 5.8</td>
<td>1.29 ± 0.14</td>
<td>50.5 ± 21.2</td>
</tr>
</tbody>
</table>

The average temperature for the prior particle interior can be estimated using numerical
simulations of the spray gas speed, temperature, and powder thermal conductivity. The
temperature of the powder particles prior to impact can be estimated from simulations to be 120
°C for 15 μm particles and 240 °C for 45 μm particles. These estimates are made using numerical simulations from K. Sakaki [37]:

\[
\frac{dT_p}{dt} = (T_g - T_p) \frac{6h}{c_p \rho_p D_p}
\]

Equation 2.4

where \( T_p \) is the particle temperature, \( h \) is the heat transfer coefficient, and \( c_p \) is the specific heat of the particle, and \( T_g \) is calculated as:

\[
T_g = T_{gi} \left( \frac{P}{P_i} \right)^{(k-1)/k}
\]

Equation 2.5

where \( T_g \) is the gas temperature, \( T_{gi} \) is the initial gas temperature, \( k \) is the gas-specific heat ratio, \( P \) is the gas pressure, and \( P_i \) is the initial gas pressure. It should be noted that the temperature of the powder particles is likely higher than this number due to frictional heating.

Values such as the strain rates in the material and the temperatures and strains at the prior particle interface are helpful when comparing the microstructures seen in the particle impacts to that seen in literature. While no method exists to measure these values at the current moment, many simulations have been made in literature that can provide some insight into these values. For example, work by T. Schmidt et al. looked at the temperature distribution in a cold sprayed particle due to adiabatic heating using simulations and estimated temperature increases at the prior particle interface in copper in excess of 750 °C [38]. In addition, in work by Talonen et al. [39], it was shown that strain rates of only \( 10^1 \) s\(^{-1} \) in tensile testing could cause adiabatic heating, raising the temperature of the material above 80 °C in 301LN stainless steel.
Cold spray literature on the deformation of cold spray particles commonly reports strain rates of $10^7 \text{s}^{-1}$ to $10^9 \text{s}^{-1}$ in the adiabatic shear zones [3-5, 40-48]. The strain rate in the prior particle interior is harder to estimate, but some literature suggests that the strain rate in this area is likely $10^4$ to $10^5 \text{s}^{-1}$ [3]. Based on the literature on the strain-induced martensite transformation at high strain rates, a strain rate of $10^4$ to $10^5 \text{s}^{-1}$ in the prior particle interior still exceeds the strain rate seen in most literature to impede strain-induced martensite formation significantly. While information on the total strain at the prior particle interface is lacking, it is safe to assume that the strain in this area is well above 100 % [40, 44, 49-52].

2.4.2 Formation of Strain-induced Martensite in Cold Sprayed SS304L

The extent of the strain-induced martensite transformation in both samples is less than what would be expected at room temperature and quasi-static strain rates. Many authors have shown the formation of strain-induced martensite to have a direct relationship to the total strain experienced during plastic deformation [20, 21, 25, 32]. T. Angel demonstrated this relationship at various formation temperatures, showing approximately 20% strain-induced martensite formation at 50% applied strain and nearly 40% strain-induced martensite at 75% applied strain [21]. Similarly, work by Shintani et al. showed 70% strain-induced martensite after cold rolling to 50% strain which is considerably more than the 30% seen in the room-temperature cold spray specimen [6]. From these observations, it is clear that the conditions of cold spray are suppressing the strain-induced martensite transformation.

The temperature of the spray gas is shown to significantly suppress the amount of strain-induced martensite formed during the cold spray deposition process. The deformed material's temperature arguably has the most significant overall effect on suppressing the amount of strain-induced martensite formed. Cooling samples during deformation to -188 °C can cause as much
as 85% martensite to be formed, while heating to 80 °C results in as little as 4% martensite when pulled in tension [21]. Work by Mukarati et al. simulating the martensite transformation in 301LN stainless steel showed the volume percentage at various total strains to approach 0% at all temperatures above 120 °C [53]. While little work exists looking at the martensite percentage formed at temperatures much above 100 °C, it can be assumed that limited martensite can be formed at temperatures above 100 °C. Tensile test experiments by Huang et al. [54] show that at low temperatures, martensite formation dominates, and the strain rate sensitivity is proportional to the transformation rate. At higher temperatures, slip dominates, and the strain rate sensitivity decreases with an increase in strain, an observation that is consistent with most microstructurally stable metal systems. The lack of strain-induced martensite in the samples sprayed at elevated temperatures is consistent with the literature. Many authors show that increasing the temperature of the work material will limit the strain-induced martensite transformation considerably at all strain rates. The heating of the particles as they travel through the cold spray system and the adiabatic heating caused by deformation likely causes a temperature rise to the point where strain-induced martensite is not formed in the prior particle interior after cold spray. These findings are also consistent with the present literature on the cold spray of austenitic stainless steels, as all current literature uses spray temperatures above 100 °C.

The cold spray sample sprayed at 25 °C shows a reduction in the amount of strain-induced martensite expected compared to quasi-static strain rates at 25 °C, which can be explained by the higher strain rate in cold spray. Literature shows that the strain rate can play a significant role in suppressing the strain-induced martensite phase transformation. Research shows that high strain rates can inhibit strain-induced martensite formation, pointing to both adiabatic heating due to plastic deformation and twinning being responsible for a deviation from
the expected strain-induced martensite formation[32-34, 55]. These strain rates are not easily achievable in other metal deformation techniques, with the highest strain rates reported in literature being approximately \(10^5\) s\(^{-1}\). However, shock loading experiments such as the work by Staudhammer et al. may approach the strain rates seen in cold spray as these experiments have a strain rate in excess of \(10^4\) s\(^{-1}\). These shock loading experiments show approximately 1% to 4% martensite formed depending on temperature and shock pressure, with the stress state and temperature rise during shock loading suppressing the strain-induced martensite. Additionally, work by Staudhammer et al. showed that the \(\alpha’\) phase in shock loading experiments formed at shear bands only. Work by Chen et al. shows that at high strain rates (\(10^5\) s\(^{-1}\)), created using surface mechanical attrition treatment (SMAT), the formation of strain-induced martensite is impeded due to a change in deformation mechanism from glide-based plasticity to deformation twinning, resulting in the formation of ultra-fine grains and dislocation pileup as observed in the TEM [55]. Chen et al.'s work indicate that when strain rates are low, dislocation-based activities such as accumulation, interaction, tangling, and spatial rearrangement, as well as the austenite to martensite transformation, are the primary deformation mechanisms. However, at higher strain rates, deformation twinning becomes the dominant mechanism. In the present work, a clear presence of twins is not observed in either deposit. Additionally, it is worth noting that the twins seen in the work by Chen et al. are much finer than any of the features seen in TEM or PED in either of the samples in this paper.

Many authors attribute the lack of strain-induced martensite at high strain rates to be predominantly due to adiabatic heating in the high strain rate regions. Work by Sunil et al. looked at the formation of strain-induced martensite in high strain rate compression tests using a split-Hopkinson bar setup [56]. This work also looked at the effect of strain rate in compression
on strain-induced martensite in which a 1-D heat transfer equation was used to determine that the maximum temperature due to adiabatic heating was 120 °C and that this significantly elevated temperature impeded the strain-induced martensite transformation for SS304L. Furthermore, this work by Sunil et al. found that the formation of strain-induced martensite decreased with strain rate for all strains above 0.15. At a strain rate of $10^3$ s$^{-1}$ and strain of 50% slightly less than 20%, strain-induced martensite was formed. This amount is considerably less than the 30% seen here for cold spray at room temperature. This comparison means more strain-induced martensite is formed in the cold spray at the calculated average strain and expected strain rate of cold spray than in non-cold spray literature. The amount of strain-induced martensite seen in the cold spray produced at room temperature is equal to that seen in the work by Sunil et al. at a strain rate of 1 s$^{-1}$ and strain of 0.8. This difference could be due to the peening effects seen by the cold spray material by the subsequent impact of powder particles, or it could be due to the more complex strain field seen in a particle impact that will not be entirely compressive in nature. In work by Chen et al., the SMAT process, which creates a peening force, was shown to produce approximately 22% strain-induced martensite near the peened surface, which had a strain rate of $9 \times 10^4$ s$^{-1}$ which is in reasonable agreement with the amount of strain-induced martensite seen in the room temperature sample.

2.4.3 Effect of Spray Temperature on the Microstructure at the Prior Particle Interfaces

It is worth noting that in the samples produced at 25 °C, a band of dynamically recrystallized grains is not clearly seen as it is in the sample produced at 350 °C. The presence of ultrafine grains at prior particle interfaces has been reported in literature many times and is believed to be caused by the ultra-high strain rate deformation at the prior particle interfaces [2, 4, 35, 41, 42, 57]. It is usually described in literature that these grains are the result of “dynamic
recrystallization”, though many mechanisms have been proposed that could cause this effect. These mechanisms are outlined in work by Rokni et al. and Liu et al. and include continuous dynamic recrystallization (CDRX), geometric dynamic recrystallization (GDRX), rotational dynamic recrystallization (RDRX), progressive subgrain misorientation recrystallization (PriSM), static recovery (SRV), and static recrystallization (SRX) [2, 58]. The GDRX and RDRX are all forms of the broader CDRX umbrella, which include the continuous recrystallization of grains during deformation through the means of diffusion. SRV and SRX are forms of recrystallization that are proposed to form due to residual heat and peening stresses due to subsequent impacts, which also require diffusion. The PriSM mechanism models mechanically driven lattice rotations within an adiabatic shear band that result in recrystallization, which, unlike the other proposed mechanisms, does not rely on diffusion, which is argued to be too slow for recrystallization in high strain rates such as that seen in cold spray. This paper’s data is insufficient to support any of the proposed dynamic recrystallization models for cold spray. However, the following is intended to add to the discussion currently in literature and highlight how the observed microstructure and the effect of temperature on the microstructure at the prior particle interface can be interpreted in the light of each proposed mechanism.

While SRX and SRV have both been shown in CS materials, the low stacking fault energy of SS304L would support SRX. SRX is more likely than SRV in low stacking fault energy materials because the activation energy is lower for recovery than recrystallization. Additionally, literature has shown the presence of CDRX in cold rolled SS304L. While SS304L typically prefers discontinuous dynamic recrystallization (DDRX) due to its low stacking fault energy, literature has shown that decreasing the grain size in 304L from 35 to 8 μm can shift the
recrystallization mechanism to CDRX. The average grain size in the as-atomized powders is less than 10 μm which would support the formation of CDRX [59]. Additionally, it has been shown that the formation of CDRX can occur in type 304 stainless steel at elevated temperatures of 800 to 1000 °C during cold rolling of heat treated material with an initial grain size of 7 μm and could result in grain sizes as small as 1 μm [60]. It is worth noting that DDRX has been shown in simulations of type 304 stainless steel for an initial grain size of 35 μm at 1000 °C, where at a strain of 3.0 100% recrystallization had occurred, resulting in a predicted grain size of 6 microns. This predicted grain size is an order of magnitude larger than the measured grain size seen in TEM of cold sprayed material [61].

Dynamic recrystallization through diffusion-based means has been previously reported in cold sprayed materials, with the most reported method for recrystallization being a diffusion-based rotational dynamic recrystallization mechanism. This method was first described by Meyers et al. for high strain rate deformation of 304 stainless steel using a Hopkinson bar where the argument is made that at high strain rates ($10^4$ s$^{-1}$) diffusion at the grain boundaries, which is much faster than bulk allows for grain boundary reorientation and dynamically recrystallized grains [62]. This same method was proposed for dynamic recrystallization in cold spray in work by Zou et al. for cold sprayed nickel [35]. Dynamic recrystallization, as described by Zou et al., begins with the formation of elongated subgrains at the prior particle interface due to the high dislocation density formed during cold spray; these subgrains continue to evolve and form further subgrains due to additional dislocation formation as the strain at the particle interface increases. At this point, small, refined subgrains exist at the prior particle interface separated by low-angle grain boundaries. As more strain occurs, the misorientations between these subgrains increase to accommodate this deformation by rotating. This rotation forms small, dynamically
formed recrystallized grains separated by high-angle grain boundaries [63]. The approximate grain size caused by dynamics recrystallization via this method can be approximated using the relationship [64]:

$$\left( \frac{\sigma}{G} \right) \left( \frac{D_r}{b} \right)^n = k$$

Equation 2.6

Where n and K are constants (0.8 and 15 respectively), b is the burger vector, $D_r$ is the dynamically recrystallized grain size, $G$ is the shear modulus, and $\sigma$ is the applied stress. For cold spray $\sigma$ can be described by the mean pressure during impact approximated as $\sigma = 0.5 \rho u^2$ where $\rho$ is the density of the material and $u$ is the velocity. This material gives a grain size of 50-125 nm, which is within the range seen in the PED results.

The PriSM mechanism for dynamic recrystallization provides an intriguing theory of dynamic recrystallization in high-strain rate materials [65]. The PriSM mechanism asserts that other models do not sufficiently describe the observed dynamic recrystallization grain size in high strain rate materials and proposes that mechanical rotation of subgrains during deformation and boundary refinement via diffusion during cooling occur at shear bands to explain much smaller grain sizes. This mechanism is consistent with the findings of fine dynamically recrystallized grains on the order of 100 nm (0.1 μm) in this paper. Work by Rojas et al. provides more evidence for dynamic recrystallization in cold spray materials being possible without the need for diffusion [66]. In Rojas's work, both experiments and simulations show the formation of dynamically recrystallized grains in silver nanocube high-velocity impacts. The paper proposed that the large shock wave stress and high dislocation density in the nanocubes were not sufficient for recrystallization alone. Instead, the pathway for recrystallization was hypothesized to be that
the shock loads during impact produced a considerable amount of boundaries, such as grain boundaries and twins, and that once these are developed, the lattice rotates within these boundaries through the large shear stresses caused by the shock wave. This occurs without the need for dislocation diffusion and accounts for the gradient in properties seen in cold spray particle impacts due to the decreasing shockwave pressure away from the impact surface. The exact mechanism for dynamic recrystallization in cold spray is still unclear and needs further investigation though the lack of these grains in lower-temperature sprays provides some additional context to the proposed mechanisms.

2.5.0 Conclusions

In conclusion, it has been shown that cold spray can produce strain-induced martensite and that the extent of this transformation is mainly dependent on the spray gas temperature. Additionally, the reduction of the spray gas temperature was seen to influence the microstructure at the prior particle interface region. While EBSD results cannot definitively show the phase fraction of martensite in cold spray due to the limited sample area and difficulty in indexing the prior particle interface regions, neutron diffraction data clearly shows a slight increase in the BCC/BCT phase from the as-received powder in cold spray material produced at a spray temperature of 350 °C and a much more significant increase of 30% in that produced at 25 °C. The literature gives compelling evidence to believe that the conditions that exist in cold spray at elevated temperatures significantly reduce the amount of strain-induced martensite formed. If spray temperatures can be increased further without clogging the cold spray nozzles, cold spray could reduce the formation of strain-induced martensite in-situ without needing post-heat treatments on the material. The likely cause of the BCC/BCT phases in the as-received powder is the high cooling rate seen by the powder during inert gas atomization. Ferrite is a metastable
BCC phase that can form when liquid steel cools rapidly from a molten state so that the stable austenitic room temperature phases cannot form. This is distinctly different from the formation of strain-induced martensite, and it is not clear if some fraction of this initial BCC phase in the powder is retained in the deposits or if elevated spray temperatures would work to reduce this phase or only limit the formation of new strain-induced martensite. These conclusions are consistent with that seen in literature in which deposits made from powder with no initial BCC phase fraction showed no BCC phase fraction when measured via XRD or EBSD, and those with BCC in the powder showed BCC in the deposit as well as finding which suggest that cold spray did indeed result in the reduction of the BCC phase fraction in cold sprayed material from that in the as-received powder. A summary of the findings is given below:

- Neutron diffraction showed a 0.4% increase in BCC phase/martensite after cold spray of the powder particles at 350 °C and an increase of 28.1% when sprayed at 25 °C showing that the strain-induced martensite transformation can occur in cold spray and that a correlation between spray temperature and the strain induced martensite transformation exists.

- These findings suggest that adiabatic heating due to the high strain rates, large total strains, and the heat input from the spray gas work together to suppress the strain-induced martensite transformation throughout the cold spray deposit.

- A more substantial presence of ultrafine grains, possibly due to dynamic recrystallization, was seen at the prior particle interface in the samples sprayed at 350 °C when compared to that sprayed at 25 °C indicating that the spray temperature plays a role in the ability for these recrystallized grains to form at the prior particle interfaces.
• This work suggests that the strain-induced martensite transformation can be suppressed or eliminated with sufficiently high spray gas temperature if nozzle fouling can be controlled at elevated temperatures.

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References


CHAPTER 3: QUANTIFYING DISLOCATION DENSITY AND RECRYSTALLIZATION KINETICS IN LASER HEATED COLD SPRAY SS304L

Abstract

This paper investigates the dislocation density and recrystallization kinetics in cold sprayed and laser heated cold spray SS304L via neutron diffraction, the convolutional multiple whole profile (CMWP) method, differential scanning calorimetry (DSC), and electron diffraction. These results were then coupled with thermal simulations to provide a more complete picture of the rapid recrystallization process in laser heated cold spray SS304L. It was found that the cold spray process resulted in a uniform dislocation density throughout the material. Additionally, laser heating showed rapid recrystallization in the samples, resulting in reduced dislocation density. Furthermore, it was found that at lower heating rates, the cold sprayed material exhibited distinct recovery and recrystallization temperatures. At high heating rates, the more rapid kinetics of recrystallization at the prior particle interface regions become more pronounced than those at the prior particle interior, leading to the necklacing of recrystallized grain at the prior particle interface around the prior particle interior under certain heating conditions. Comparison of these results with thermal simulations and the in-situ dislocation density as a function of temperature shows that the resulting microstructure and degree of recrystallization can be approximated by the maximum temperature reached at any location. This allows the optimization of coating properties and tool path geometry using thermal simulations.
3.1.0 Introduction

High pressure cold spray, or cold spray (CS), is a solid-state additive manufacturing technique in which particles (typically 15-45 µm) are accelerated using high-pressure gas through a converging-diverging nozzle to supersonic velocities (typically 1000-2500 m/s) [1]. The high-speed particles carry enough velocity to plastically deform upon impact with the substrate, forming a fully dense coating with minimal heat input. However, the extreme deformation at low temperatures in the cold spray process results in distinctive microstructures, unique deformation mechanisms, and high dislocation densities that can lead to undesirable material properties [2]. Laser heated cold spray (LHCS) builds upon the cold spray process by using a laser rastered over the material's surface after deposition to alter the microstructural and mechanical properties of the deposition. For example, it has been previously shown that laser heating SS304L can result in rapid recrystallization, grain growth, and a corresponding decrease in deposit hardness [3]. Since cold spray is often a desired technique due to its portability and flexibility, it is desired to use a laser to improve the mechanical properties. As such, it is necessary to understand the dislocation density and recrystallization kinetics during laser heating to optimize the laser heating profiles for optimal material properties at minimal heat input.

In the case of cold spray (CS) deposition, which is controlled by the low-temperature deformation of powder particles, dislocation density plays a crucial role in determining the behavior and properties of the deposited material. The presence of a high dislocation density can result in an increase in hardness, as well as a decrease in ductility, in the material. This process of dislocation buildup can be reversed through recovery, recrystallization, and grain growth. Literature has well-documented the phenomenon of severe plastic deformation and the resulting increase in dislocation density in the CS process. Studies such as those conducted by Rokni et al.
have revealed the microstructural evolution of dislocations in AA7075 heated in-situ using Transmission Electron Microscopy (TEM) and have demonstrated that the CS process accelerates the precipitation kinetics of the annealing process [4]. Wang et al. showed in TEM images of cold spray splats that the severe plastic deformation undergone during the cold spray process leads to refined microstructure along the exterior of prior particles resulting in dislocation tangles and dislocation walls [5]. Furthermore, research by Borchers et al. has investigated the annealing of cold sprayed copper and found that while recrystallization and an associated reduction in hardness are observed, the hardness of annealed cold sprayed material is still almost twice that of cold rolled and annealed copper, due to the formation of dislocation loops in CS material that was not annihilated during annealing. [6]. Additionally, this plastic deformation has been shown to result in microstructural phase changes in cold sprayed material. Previous work by Tian et al. [7] quantified the dislocation density in Al-Cu cold sprayed coatings and found the cold spray process to increase the dislocation density in cold sprayed Al-Cu by three to ten times resulting in a dislocation density on the order of $10^{14} \text{ m}^{-2}$.

Laser heating can be used to induce recrystallization and modify dislocation density, improving the material properties; therefore, it is crucial to comprehend the dislocation density evolution and recrystallization kinetics during laser heating to better control and understand this process. Various studies have been done looking at the effects of isothermal heat treatments on SS316L and SS304L [8-16]. The only previous work to look at rapid heating profiles on cold spray was done by Brassart et al., who looked at the recrystallization behavior of SS316L at various heating profiles using a Gleeble system [17]. This work showed the prior particle interface regions and prior particle interior regions to have separate recrystallization and evolution mechanisms. Understanding of these increased mechanisms can be gained through
methods such as the Williamson-Hall (W-H) or convolutional multiple whole profile (CMWP) method [18, 19].

Diffraction-based line profile analysis techniques, such as the Williamson-Hall (W-H) and the convolutional multiple whole profile method (CMWP), can provide the quantitative data needed to understand the kinetics of cold spray by offering greater versatility in materials characterization, by allowing for the simultaneous measurement of key properties such as dislocation density and crystallite size as a function of both position and time. This capability is particularly valuable in understanding the dynamic behavior of materials under changing conditions, and can provide insights into important phenomena such as phase transformations, deformation mechanisms, and thermal stability. Many methods exist to determine dislocation density, including direct observation using TEM and many diffraction-based indirect observation methods. Direct observation and measurement of dislocation density in the TEM is not preferred due to the being time and labor consuming, the small sample size of TEM samples, and the challenges of identifying individual defects in highly deformed material among others. Additionally, direct observation in the TEM does not allow for the measurement of these values as a function of temperature. The CMWP and W-H methods are two diffraction-based indirect methods that are used in this work [18, 19].

The Williamson-Hall method is one of the most basic ways to deconvolute the effects of the dislocation density and crystallite size on peak broadening and is a peak-breath-based form of X-ray line profile analysis (XLPA). The effects of particle size of crystallite size and lattice strain can be deconvoluted because the kinematic theory of x-ray scattering shows that the particle size effect is diffraction order independent and lattice distortion which is directly related to the dislocation density is diffraction order dependent [20]. The W-H method has the advantage
of being both a simple analysis as well as having decades of use in literature. In addition, the W-H method has many modified versions that help to address its use with other forms of scattering, such as neutron diffraction and the effects of lattice strain on the material. The Williamson-Hall method works by plotting the peak broadening as a function of the lattice spacing for various peaks to deconvolute the effects of dislocation density and lattice size on peak broadening.

The main advantage that CMWP has over the W-H method is that it factors more complex lattice strain effects than just the dislocation density, dislocation character, and crystallite size. The CMWP process, which is a method of X-ray line profile analysis (XLPA), was developed by Gábor Ribárik and Tamás Ungár. The CMWP method is a Fourier-based method that uses models of various physical properties and the effect that they each have on the diffraction pattern in a crystalline material to compute a theoretical diffraction profile and then iterate these parameters to find the best fit for each diffraction peak. Methods like the CMWP method differ from methods such as Rietveld refinement or the Williamson-Hall method as CMWP is a bottom-up method meaning that the physical profiles that are fitted are developed using the physical properties of various types of lattice defects. Rietveld refinement or the Williamson-Hall are top-down methods where profiles such as Gaussian, Lorentzian, pseudo-Voight, or Pearson-VII are fitted to the peak shape first. This can make it hard to extract specific data and make a correlation between the parameters that control these peak fits and the physical properties of the material being measured. In CMWP various physical models for lattice defects and how these defects effect peak broadening from an idea case are modeled and the Levenberg–Marquardt and the Monte Carlo methods are applied consecutively to provide the global optimum values of the physical parameters characterizing microstructures [18].
Neutron diffraction has some key advantages for measuring the dislocation density in cold spray, by selecting neutron diffraction over X-ray diffraction or synchrotron diffraction as the preferred diffraction technique material properties can be analyzed without mechanical preparation, which could affect the physical attributes being measured. Additionally, neutron diffraction allows bulk material properties to be examined during in-situ heating experiments due to the penetrating distance of neutrons in metals. While work has been done to compare the Williamson-Hall and CMWP methods across material types and compare the use of both neutron and X-ray measurements this is still an area that needs significant work to ensure that these comparisons can be performed.

In this paper, a variety of approaches are employed to quantitatively characterize the dislocation character and density in cold spray. To achieve this goal neutron diffraction is used in conjunction with the line profile analysis technique, CMWP, to measure the dislocation density and crystallite size as a function of position and time, both after laser heating and during induction heating of the material, providing valuable insight into the increased recrystallization kinetics in cold-sprayed material. The dislocation density is measured as a function of position via neutron diffraction in LHCS. Additionally, the dislocation evolution in cold spray as a function of temperature is investigated using in-situ neutron diffraction measurement during heating of freestanding cold sprayed material. The VULCAN beam line at the spallation Neutron Source (SNS) at Oak Ridge National Lab (ORNL) was used to perform neutron diffraction, and the dislocation density and texture of LHCS SS304L was analyzed at a spatial resolution of 0.2 mm. Differential scanning calorimetry (DSC) was performed on the cold spray specimens so that it could be used to verify the results found through neutron diffraction. The results were then coupled with thermal simulations to provide a more complete picture of the recrystallization
kinetics in LHCS. Furthermore, these results can present a characterization of the increased kinetics of recrystallization in cold sprayed material. Finally, the neutron diffraction data is then coupled with thermal simulations, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) to provide a complete picture of the recrystallization mechanism for understanding the recrystallization mechanisms behind the LHCS process.

3.2.0 Experimental Methods

Stainless steel 304L coatings were produced using a VRC Gen III high pressure cold spray system (VRC Metal Systems, Rapid City, SD). SS304L powder from Sandvik Osprey Ltd. with a nominal powder size of 15-45 µm (see compositions in Table 3.1) was used. The depositions were made using a DeLaval converging-diverging nozzle with a 2.0 mm throat and 197 mm length. Helium gas was used with a pressure of 600 psi with a temperature of 350 °C. A total of 4 passes was made with a y spacing of 0.5 mm so that a deposit with size 25x25x2 mm was created. A total of four samples were made, and after deposition an LDM-4000-100 variable power 940 nm wavelength diode laser (Laserline, Mülheim-Kärlich, Germany) was used to laser heat the samples. The laser was overfocused to create a 6mm x 4mm ellipse with a powder density function that can be approximated by a top hat function. One sample was left as deposited, one was heated to 750 °C, and one was heated to 950 °C. The laser was moved at a speed of 10 mm/s so that each laser heated sample was exposed to the laser for a total time of 62.5 s. Two additional samples of 4mm and 2 mm thickness were made for the in-situ neutron heating experiments and DSC experiments, respectively.

Table 3.1 Chemical composition of the 304L stainless steel powder (wt. %).

<table>
<thead>
<tr>
<th>C</th>
<th>N</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.14</td>
<td>1.5</td>
<td>0.023</td>
<td>0.006</td>
<td>0.73</td>
<td>18.7</td>
<td>8.3</td>
<td>Balance</td>
</tr>
</tbody>
</table>

3.2.1 Neutron Diffraction of Cold Spray Coatings
For each of the three samples used for position-dependent measurements, a section of the 25 mm deposition was cut from the center with dimensions of 25 x 20 mm using a wire EDM. This allowed for a consistent cross section during measurements. The samples were aligned edge on to the beam with an incident angle of 0 degrees (Figure 2.1a). The neutron beam was shaped to a size of 0.3 x 17 mm so that the shorter dimension was through the thickness of the sample. 5 mm collimators were used on the detector side of the sample. The sample was then swept through the beam with a step size of 0.3 mm with a collection time of 15 minutes per data point. A 30 Hz chopper setting was used. Additionally, five powder samples were measured with neutron diffraction. One was as-received from Sandvik, and four were heated at 650, 750, 850, and 950 °C for 1 hour in a furnace, respectively. The sample heated to 750 °C was seen to have the least peak broadening and was used as a reference sample for instrumental peak broadening.

For the sample measured as a function of temperature, cubes 17 x 17 x 6 mm were manufactured of freestanding cold sprayed material. The samples were aligned 45 degrees to the incident beam and held on either side with a ceramic grip (Figure 3.1b). The samples were heated using an induction coil to a temperature of 1000 °C at a rate of 1 °C/s. Data was collected continuously and chopped into 5-second intervals after collection for analysis.
3.2.2 CMWP analysis

The CMWP process was used to extract data about the dislocation density, crystallite size, and dislocation character from the neutron diffraction data. Instrumental broadening profiles were created for the CMWP process from the feedstock powders heat treated at 750 °C for two hours. In order to minimize the variability in the CMWP results that result from uncertainty in creating the background spline file, all background and peak index files were created systematically using MATLAB. The mean diffraction domain size \(<x>_{\text{area}}\) is calculated as \(<x>_{\text{area}} = m \exp(2.5\sigma^2)\), where \(m\) is the median and \(\sigma^2\) is the log-normal variance of the diffraction domain size distribution. The burgers vector of 0.2539 nm, a dislocation contract factor \((\vec{C}_{h00})\) of 0.29, and a lattice parameter \((a)\) of 0.359 nm was used. The software ANIZC was used to calculate both \(\vec{C}_{h00}\) and \(q\) using the anisotropic elastic constants for SS304L [22-24]. The
values of q were calculated for pure edge and pure screw dislocations as 1.59 and 2.38, respectively.

3.2.4 Williamson-Hall Analysis

In addition to the CMWP approach, the W-H method was used to obtain the dislocation density and crystallite size at select data points for comparison to the CMWP method. The four highest order peaks (111, 200, 220, 311) were used for the Williamson-Hall analysis. A modified Williamson-Hall analysis as used in Woo et al., was used to determine the dislocation density and provide an additional data point for verifying the accuracy of the CMWP on neutron diffraction data [25]. The Williamson-Hall method is one of the earliest methods created that attempts to separate the effects of grain size and dislocation density to the overall peak broadening in diffraction so that both of the values can be resolved. VDrive was used to perform single peak fitting of seven unique peaks (200, 311, 112, 111, 420, 220, 133, and 135) for each data point [26]. The modified Williamson-hall method asserts that the total peak broadening (ΔK) for diffraction is a combination of both its grain size, D, and lattice strain effects, ΔK^D. (ΔK^D)^2 is defined as (ΔK^D)^2 = (πA^2b^2/2)ρ(K^2C) + O(K^2C)^2 which leads to the modified Williamson-Hall equation:

\[ ΔK^2 = \left(\frac{0.9}{D}\right)^2 + \frac{πA^2b^2}{2}ρ(K^2C) + O(K^2C)^2 \]

Equation 3.1

Where A is a constant the effective outer cutoff radius, b is the burgers vector, K=1/d, where d is the d-spacing, D is the average sub grain size, C is the average contrast factor, ρ is the dislocation density, and O represents noninterpreted, higher order terms. Based on the following equation (ΔK)^2 vs. K^2C can be plotted and a second order polynomial can be fitted to the data to solve for both the dislocation density and average crystallite subgrain size.
3.2.5 Differential Scanning Calorimetry – DSC

Differential Scanning Calorimetry (DSC) was performed using a Setaram Labsys Evo. DSC was performed up to 1000 °C using a heating rate of 20 °C/s and a sample mass of 54 mg. Two runs were performed back-to-back and the second run was subtracted from the first to isolate the heat flow due to recrystallization. Three additional DSC runs were ran using a heating rate of 20 °C/s and a maximum heat of 490, 650, and 850 °C for EBSD analysis with a nominal weight of 50 mg each.

3.2.6 Microstructural Analysis - EBSD

Part of the remaining sample after cross sectioning was hot mounted using Struers PolyFast mounting compound and polished to 0.05 μm using a vibratory polisher. EBSD maps were obtained on a JEOL 7000 SEM using an Oxford Aztec EBSD system. All EBSD maps were taken with an accelerating voltage of 20 keV, specimen tilt of 70°, and a step size of 0.125 μm for the maps. Low-angle grain boundaries were identified in the software as those ≤ 10° but >2° while high-angle grain boundaries were marked as those with a misorientation angle >10°. Grain orientation spread (GOS) maps were generated using the Channel 5-Tango software with a set scale of 0° to 15° for all maps.

3.2.7 ABAQUS Simulations

Simulations of the temperature distribution in the samples was performed using ABAQUS CAE and the USDFLD and DFLUX user subroutines. The USDFLD user subroutine was used to read the maximum temperature on the surface of the plate from the previous iteration and this was fed back into the DFLUX user subroutine in a loop to define the laser heating area on the surface of the plate as well as modulate the flux of the heat input to hold the temperature on the surface of the plate constant. This method models how the temperature is held constant
during the experiments with the use of a pyrometer. The laser was modeled as an overfocused laser with a constant heat input over the area of the laser and having no penetration depth since no material melting occurred. The simulation was set up as a transient heat transfer analysis with DC3D8 elements.

The ABAQUS simulations were verified and calibrated using thermocouple measurements taken from inside a ½” substrate with cold spray deposited on top. The material properties and used for the ABAQUS simulations are given below in table 3.2. These values are specific to the setup used in these experiments. It was found that the temperature was strongly influenced by the thermal conduction into the clamping system and the clamping pressure. As such the values will change greatly for each setup.

Table 3.2 Values used in ABAQUS for modeling laser heating. Constant temperatures of 750 ºC and 950 ºC were modeled to simulate a pyrometer feedback loop by carrying the laser power.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value @ 25 ºC</th>
<th>Value @ 950 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity(k)</td>
<td>W/m/K</td>
<td>14.8</td>
<td>25.0</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>J/kg/K</td>
<td>500</td>
<td>630</td>
</tr>
<tr>
<td>Convection Coefficient</td>
<td>W/m²/K</td>
<td>2</td>
<td>3.3</td>
</tr>
<tr>
<td>Mass Density</td>
<td>Kg/m³</td>
<td>8000</td>
<td>7450</td>
</tr>
<tr>
<td>Emissivity</td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Conductance Sample to Backing Plate</td>
<td>W/m²/K</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Laser Speed</td>
<td>mm/s</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

3.3.0 Results

3.3.1 Microscopy of Cold Spray microstructure

EBSD analysis of the as-sprayed material shows a typical cold spray microstructure with a pancake like microstructure and highly refined grains at the prior particle interfaces. After laser heating the material heated to 950 ºC shows a fully recrystallized microstructure with equiaxed grains that have undergone grain growth near the surface of the deposit with those near the bottom of the 950 ºC deposit showing recrystallization but much less grain growth. Additionally,
traces of the prior particle interfaces can still be seen in the bottom of the 950 °C deposit. In the 750 °C material we see a grain structure where the material at the prior particle interfaces have begun to undergo recrystallization and the material at the bottom closest to the substrate-deposition interface has had little change due to laser heating. Microstructurally this material at the top of the 750 °C deposit is similar to that at the bottom of the 950 °C deposit.

![EBSD IPF maps at the top and bottom of cold sprayed SS304L in the as-sprayed condition and after laser heating to 750 °C and 950 °C. All maps are taken with respect to the spray direction (top to bottom).](image)

Figure 3.2 EBSD IPF maps at the top and bottom of cold sprayed SS304L in the as-sprayed condition and after laser heating to 750 °C and 950 °C. All maps are taken with respect to the spray direction (top to bottom).

Grain orientation spread (GOS) maps provide an additional way to analyze EBSD results by looking at the average lattice orientation deviation from the mean for each grain. In addition, these GOS maps provide a simple way to look for recrystallization, as dislocations will introduce lattice strain and bending, causing a higher orientation spread. These maps clearly show that the
prior particle interface region in the 750 °C recrystallizes first, resulting in fine equiaxed grains “necklacing” the prior particle interior regions. Furthermore, we can see that at the surface of the 950 °C sample, complete recrystallization has occurred and that at the bottom of the 950 °C sample, recrystallization has begun but is not complete.

Figure 3.3 GOS maps obtained from EBSD results with the top and bottom of cold sprayed SS304L in the as-sprayed condition and after laser heating to 750 °C and 950 °C.

TEM shows nanocrystalline grains (<100 nm) at the prior particle interface in the cold sprayed coatings, correlating with the non-indexed regions in EBSD. This region of nanocrystalline grains measures approximately 300 – 500 nm in width. It can also be seen that highly deformed deformation microstructures exist outside of these nanocrystalline regions and show highly deformed and elongated grains due to shear banding. Both these nanocrystalline regions and the shear band region comprise the non-indexed regions from EBSD, which are well
over 1 µm on average. These nanocrystalline grains have been shown previously in work by Roper et al.

Figure 3.4 TEM bright field images showing A) Overview of the prior particle interface region in cold sprayed SS304L and B) magnified view of the nanocrystalline size grains at the prior particle interface.

3.3.2 Quantification of dislocation density as a function of position in LHCS using CMWP

Application of the CMWP process to neutron diffraction data showed a dislocation density of approximately 5 E15 m⁻² in the cold spray coating with no discernable trend in this density as a function of depth through the deposit. It can also be noted that no long-range increase of dislocation density is present in the substrate with a rapid drop-off in FWHM at the deposition/substrate interface. Laser heating of this material showed a rapid decrease in dislocation density with the top 0.2 mm of the sample heated to 750 °C. However, the dislocation in the 750 °C material quickly increases deeper into the deposition returning to a point equal to that of as-sprayed material. For the 950 °C material, a significant portion of the depth of the material has a decreased dislocation density similar to that of the substrate before the dislocation density rises to a point just below that of as-sprayed material. These findings indicate that the
required energy for recrystallization of the coating at the high heating and cooling rates seen due to the laser is close to 750 °C.

Although the analysis of dislocation density in the cold spray specimens using the W-H method exhibits a reasonable correlation with the CMWP results regarding trend, its agreement to the magnitude is limited. It is worth remembering that the value for the outer effective cutoff radius was chosen so that the results had a relative magnitude to those from the CMWP analysis. The W-H results follow the same trend as the CMWP results, albeit with more variability, particularly in the as-sprayed results. It is also notable that while the value of A was chosen to give good agreement with the 950 °C CMWP results and match literature that the increase in dislocation density between the W-H method and CMWP method is not relative with the as-sprayed results showing double the dislocation density as measured by the W-H method to those results obtained from the CMWP method.
Figure 3.5 Dislocation density as a function of depth as measured by CMWP and W-H and the corresponding FWHM for CS samples corresponding to the EBSD maps shown in figure 3.2.

One of the benefits of CMWP over other line profile analysis methods is the ability to extract additional parameters beyond the dislocation density and crystallite size. The measured dislocation character for the three profiles measured in figure 3.4 are shown below. It can be seen that the dislocation character after laser heating to 750 °C was reduced significantly from that in the as spray condition suggesting a shift toward edge dislocations after heating. It can be seen for
the 950 °C sample that only two data points are reported. This is due to the dislocation character trending below 1.59 for these data points. While this suggest a more negative dislocation character these data points were not reported due to them being out of the range of viable parameters.

![Dislocation Character Graph](image)

Figure 3.6 Dislocation Character for laser heated samples as a function of depth

### 3.3.3 Quantification of dislocation density as a function of temperature using CMWP

CMWP analysis of in-situ heating during neutron diffraction elucidates the dislocation density, crystallite size, and secondary phase fraction stability in cold sprayed SS304L and provides transition temperatures for phase transformations and recrystallization. After CMWP analysis, it can be seen that the dislocation density in the cold sprayed material and the crystallite size are both stable from room temperature up to 500 °C. From the range of 500 °C to 700 °C, we see a slight reduction in the dislocation density with very little change in the crystallite size,
indicating that in this range, the dominant mechanism responsible for the decrease in dislocation density may be recovery. In the range of 700 °C to 800 °C, rapid recrystallization and an increase in the crystallite size indicate that complete material recrystallization has occurred. Beyond 800 °C, we see that the dislocation density quickly reaches a minimum to where the CMWP process is no longer effective. We also see evidence of continuing grain growth in this region. It would be expected that, at this point, complete recrystallization has occurred, and that further heating would result in grain growth only. It should be noted that with any diffraction-based deconvolution of material properties a higher confidence exists in the trends in the material properties than the overall magnitude of the material properties. Additionally, the measurement of crystallite grain size has been shown to be accurate at smaller measured crystallite sizes but that the accuracy of the measurements becomes inaccurate with increasing size [27]. Above the range of 150 – 200 nm the crystallite size could become inaccurate.
3.3.4 Measurement of material kinetics during DSC of CS SS304L

The DSC results show two distinct exothermic peaks at 575°C and 725°C, consistent with the recovery and recrystallization processes, respectively. The onset temperature of the first exothermic peak suggests that the material underwent recovery at a relatively low temperature, while the higher temperature for the second peak indicates the occurrence of recrystallization. Additionally, there is a dip between the two peaks, which may be attributed to an endothermic transition associated with the BCC to FCC transformation. This dip suggests that some of the material experienced a phase change during recrystallization. These findings indicate that the material underwent a complex series of structural changes during the heating process, involving both recovery and recrystallization and a phase transformation.
3.3.5 Williamson-Hall analysis of dislocation density in cold sprayed and LHCS material

One of the challenges in applying the Williamson-Hall (W-H) method to neutron diffraction is determining the effective outer cutoff radius (A) to calculate the dislocation density, as opposed to X-ray diffraction, where this value can be easily calculated. However, despite this drawback, the W-H method remains one of the most established and commonly used methods for deconvoluting the effects of dislocation density and crystallite size on peak broadening in diffraction analysis. In this study, the W-H method was used to validate the results of the CMWP analysis. For this work, a value of 0.7 was used for A as it gave a reasonable correlation to the CMWP results and had good agreement with the value 0.63 used by Woo et al. for W-H analysis of neutron diffraction data [25]. It should be noted that for XRD, the value of the effective outer cutoff radius from the CMWP method was 5.22. The average contrast factor

![DSC results for cold sprayed SS304L](image)

Figure 3.8 DSC results for cold sprayed SS304L
was taken as the average contrast factor for edge and screw dislocations for each plane that was fitted, and these numbers were calculated using the ANIZC software developed by Tamás Ungar. The burgers vector is a known value of 2.54 Å for SS304L. The four highest-order peaks (111, 200, 220, 311) were used for each data point, and $\Delta K^2$ vs. $K^2C$ was plotted. A second-order polynomial was fit to these data points, and the constants were used to calculate dislocation density and crystallite size. A select sample of these plots is shown in Figure 3.6. It is worth noting that the dislocation density was determined for each data point, but the crystallite size is not reported because many resulted in a negative number for the intercept, resulting in an error in grain size measurement. An example of this negative intercept is shown in Figure 3.6 for the as-sprayed condition.
3.3.6 Thermal simulation of laser heating process

Performing thermal simulations with ABAQUS enables more precise temperature calculations within the deposit, resulting in a more comprehensive understanding of temperature profiles and how they vary with depth. Two conclusions can be drawn from this data that are relevant to the rapid recrystallization in the cold sprayed material. First the effective heating time for any point in the deposit is much less than the total heating time for the sample. At 950 °C on the surface of the deposit the total time at which the sample spends above 700 °C is only approximately 3 seconds. Second, we can plot the maximum temperature reached as a function of depth against our results for the dislocation density as a function of depth and see that
complete recrystallization is achieved where the temperature in the sample is above 800 °C.

These findings are consistent with the results seen from the in-situ neutron scattering results and DSC.

Figure 3.10 Comparison of temperature measured with thermocouples and that simulated with ABAQUS for a calibration test sample with dimensions 2” x 4” x ½”
Figure 3.11 Maximum temperature plotted as a function of depth for both the 750 °C and 950 °C samples as well as the temperature vs time profiles for the surface and interface of both samples showing how the maximum temperature reach is extremely short. Particularly at the surface of the coating.
3.4.0 Discussion

3.4.1 Quantifying dislocation density in SS304L cold spray

The CMWP process, coupled with neutron diffraction analysis, has proven to be a valuable tool for accurately quantifying various material properties in the cold spray coatings and deconvoluting the kinetics of recrystallization seen in DSC results with recovery and recrystallization seen at 575°C and 725°C respectively. These results were verified using the WH method, and both were found to agree with the observations made relating to the trend in recrystallization with depth from EBSD. The measured dislocation density in the as-sprayed coatings measured via neutron diffraction using the CMWP process is measured as $5.5 \times 10^{15} \text{ m}^{-2}$; these results are comparable to those reported by Tian et al. and Rokni et al. for Al-Cu and AA7075 cold spray coatings [4, 7]. Furthermore, work by Maric et al. measured the dislocation density in cold-rolled SS316L using neutron diffraction and the CMWP process and found a dislocation density of $2.8 \times 10^{15} \text{ m}^{-2}$ at 30% cold-rolling, which is approximately half of what was found to exist for cold spray SS304L [28]. Literature on low strain rate tensile deformation ($10^{-4} \text{ s}^{-1}$) and equal channel angular pressing (ECAP), a severe plastic deformation process, both report dislocation density measurements, as measured by XRD, closest to that seen here for cold sprayed 304 with $4.5 \times 10^{15} \text{ m}^{-2}$ and $6 \times 10^{15} \text{ m}^{-2}$ respectively [29, 30].

Depending on the material, an increase in strain rate can either increase or decrease the formation of dislocation density in materials. Conventionally, FCC metals such as Al, Cu, and Ni show an increase in dislocation density with strain rate by suppressing dislocation annihilation [31, 32]. However, this rule cannot be blanketed across all materials; for example, TWIP austenitic steels have been shown to have a decrease in dislocation density with increasing strain rate [33]. Work by Chen et al. shows that the formation of dislocation density in 304 stainless
Steel is suppressed at higher strain rates in surface mechanical attrition treatment (SMAT) by a factor of 10 [34]. SMAT may provide a closer approximation to cold spray than other high-strain rate deformation processes since it involves a metal ball impinging upon a substrate at high velocities. In the same work that showed similar dislocation densities measured via CMWP to cold spray in low strain rate tensile testing ($10^{-4}$) of 304, it was shown that “high strain rates” ($10^{-2}$) resulted in a significantly lower dislocation density of just $1 \times 10^{15}$ m$^{-2}$ at 60% strain [30]. The strain rate of $10^6 – 10^9$ s$^{-1}$ is typically reported for cold spray material at the prior particle interface, and strain rates around $10^5$ s$^{-1}$ in the prior particle interior. Work by Chen et al. reported the dislocation density as a result of surface mechanical attrition treatment (SMAT) and found dislocation densities of $20 \times 10^{15}$ m$^{-2}$ at a strain rate of $1.2 \times 10^5$ s$^{-1}$ which is an order of magnitude less than which they reported of $400 \times 10^{15}$ m$^{-2}$ at a strain rate of $0.05 \times 10^5$ s$^{-1}$. It should be noted that this dislocation density may be off by an order of magnitude due to it being measured via HRTEM using an inverse Fourier transformation instead of diffraction-based techniques [34]. While in uniaxial high strain rate deformation the expected dislocation density for this material would be expected to be much lower. Simulations by Msolli et al. have shown that a higher dislocation density is expected at the prior particle interface compared to the prior particle interior via simulations [35]. Keeping in mind that the measurements in this research obtained via CMWP are an average over both the prior particle interface and prior particle interior it is likely that the value for the dislocation density is a gradient from the prior particle interface to prior particle center. Additionally, a few possible explanations for this higher dislocation density in the cold spray material including the deformation temperature and the total strain in the material.
It is also worthwhile to scrutinize the method by which these dislocation density measurements are made and the overall accuracy of this method. In addition to the limitations due to the measurements being an average over a nonhomogeneous structure outlined above it is also worth noting that the effects of a bimodal grain structure, such as that seen in cold spray coatings, on the accuracy of the CMWP method have not been investigated before in literature. While the effects of a bimodal grain structure have not been thoroughly investigated the CMWP process has been used successfully on many types of bimodal grain structures in literature [36-39]. The CMWP process uses theoretical functions to calculate the effects of various parameters on the peak broadening and assumes a single crystallite size in the material in order to fit the diffraction profile. The basic effects of a bimodal grain structure on the peak profile in copper processes via ECAP has been outlined by Gubicza et al [40]. In this work it is shown that the peak profile for a bimodal structure is a superset of the combined profile created by superimposing the peak due to a fine (< 1µm) and large (> 1µm) crystallite size (Figure 3.13), similar to work shown by Gubicza et al [40]. Other work such as that by Sjogren-Levin et al. has worked to further deconvolute the effects of a bimodal grain structure on diffraction profiles [41]. Future work could focus on deconvoluting this bimodal effect in cold spray to further understand the behavior of the cold spray material.
Figure 3.12 Example of the effects of a bimodal grain structure on peak fitting. It can be seen that the peak is made up of two peaks with different breaths. It should be noted that deconvoluting these effects is not as simple as fitting each apparent peak.

Table 3.3 Relevant dislocation densities measured via line profile analysis.

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal Structure</th>
<th>Deformation Mechanism</th>
<th>Diffraction Type</th>
<th>Analysis Method</th>
<th>Dislocation Density (10^{15} m^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>304*</td>
<td>fcc</td>
<td>Cold Spray</td>
<td>Neutron</td>
<td>CMWP</td>
<td>5</td>
</tr>
<tr>
<td>316L[28]</td>
<td>fcc</td>
<td>Cold Rolling</td>
<td>Neutron</td>
<td>CMWP</td>
<td>2.8</td>
</tr>
<tr>
<td>Al-Cu[7]</td>
<td>fcc</td>
<td>Cold Spray</td>
<td>XRD</td>
<td>CMWP</td>
<td>0.4-0.8</td>
</tr>
<tr>
<td>AA7075[4]</td>
<td>fcc</td>
<td>Cold Spray</td>
<td>XRD</td>
<td>W-H</td>
<td>0.95</td>
</tr>
<tr>
<td>304[42]</td>
<td>fcc</td>
<td>Cold Rolling</td>
<td>XRD</td>
<td>W-H</td>
<td>0.5</td>
</tr>
<tr>
<td>304[29]</td>
<td>fcc</td>
<td>ECAP</td>
<td>XRD</td>
<td>mW-H</td>
<td>6</td>
</tr>
<tr>
<td>316L[43]</td>
<td>Bcc(α')</td>
<td>HPT</td>
<td>XRD</td>
<td>CMWP</td>
<td>13.5</td>
</tr>
<tr>
<td>304[30]</td>
<td>fcc</td>
<td>Tensile (10^{-4} s^{-1})</td>
<td>XRD</td>
<td>CMWP</td>
<td>4.5</td>
</tr>
</tbody>
</table>

* Results from the current work

3.4.2 Recrystallization kinetics in cold spray coatings

Previous literature has observed an increase in recrystallization kinetics in cold spray coatings, and this behavior has been quantitatively shown in various studies. For example, Zahiri
et al. calculated the activation energy for cold-sprayed CP titanium to be 13 kJ/mol, much lower than the 88 kJ/mol for 50% cold-worked CP titanium [44]. Brassart et al. looked at the effects of various heat treatments on cold sprayed 316L stainless steel using a Gleeble system and noted both the increased kinetics for cold spray coatings and the preference for recrystallization first at the prior particle interface [17]. In previous work by Roper et al. it was proposed that the cause of this increased recrystallization kinetics for 304L could be a result of both an increased dislocation density in cold spray coatings and/or nanocrystalline dynamically recrystallized grains at the prior particle interface which act as a nucleation site for recrystallization in this area [3]. Additionally, it has been seen experimentally in EBSD data that around 750 °C during laser heating recrystallization occurs preferentially at the prior particle interface before the prior particle interior. This preferential recrystallization first at the prior particle interface means that the recrystallization process in cold spray can be viewed as a two-step process where first the highly deformed fine grains at the prior particle interface recrystallize followed by the prior particle interior. This two-step behavior indicates that there is likely increased kinetics of recrystallization at the prior particle interface beyond the increased kinetics in cold sprayed material as a whole.

This two-step process of recrystallization in cold sprayed coatings has been shown previously in work by Brassart et al. which looked at the recrystallization behavior of SS316L at various heating profiles using a Gleeble system [17]. Heating rates of up to 300 °C/s were used, hold times of 3 seconds to 24 hours, and temperatures up to 1000 °C. It was found that a heat treatment of 650 °C for 24 hours results in little change in the cold spray microstructure, consistent with the results seen in this paper. A heat treatment of 725 °C for 11 minutes show the beginnings of recrystallization but does not show clear evidence of the “necklacing” at the prior
particle interface. Further they found that a heat treatment of 1000 °C for only 2 seconds and 800 °C for 3 seconds resulted in a microstructure with “necklacing” around the prior particle interior. This increase in kinetics particularly at the prior particle interface has further implications beyond recrystallization as it could lead to more aggressive corrosion or diffusion kinetics at the prior particle interface [45]. In the following sections we will look at both the increased kinetics of cold sprayed material as a whole as well as the proposed property gradients in the material which cause non-homogenous behavior and increased kinetics at the prior particle interface.

When investigating the cause for the rapid recrystallization kinetics in the cold sprayed material, many intrinsic and extrinsic factors can affect the recrystallization rate in metals. The factors that are relevant to cold spray, and should be considered, include intrinsic factors such as the prior strain level, prior grain size, dislocation density, bimodal grain structure in cold spray, and the presence of dynamically recrystallized grain at the particle interface. The extrinsic factors that should be considered include annealing conditions such as the annealing temperature and heating rate.

In general, it can be assumed that material with a fine grain size will recrystallize more rapidly than larger grain material. This can be due to many effects of a small grain size including orientation effects. However, these small grain sizes tend to effect the recrystallization rate as grain boundaries can act as nucleation sites for recrystallization. Additionally, other inhomogeneities such as deformation bands or shear bands can act as sites for nucleation.

The effects of the prior strain level on the rate of recrystallization are well documented. Humpherys highlights that the rate of recrystallization increases with increasing strain until a true strain of ~2-4 at which point the effect levels out [46]. The prior strain rate does not directly influence the recrystallization rate, but strain causes multiple effects such as an increase in
dislocation density and decrease in grain size, which are direct causes of an increased recrystallization rate. This is not because the average strain in a cold spray particle interior can be easily calculated based on the flattening ratio and is typically reported to be between 0.5 and 1 [2, 47-52]. However, at the prior particle interface simulations often indicate that the total strain is well over 1 [53-55], which further strengthens the claims of increased kinetics at the prior particle interface. Prior strain provides an easy value to correlate to recrystallization rate however other properties can be more directly related to the increase in recrystallization kinetics.

When looking at the factors that affect recrystallization kinetics the factor that has the largest impact on the recrystallization kinetics is arguably the dislocation density of the material. The dislocation density of a material works to increase the driving pressure of recrystallization. The driving pressure of recrystallization can be expressed as:

\[ P_d = \alpha \rho G b^2 \]

Equation 3.2

Where \( P_d \) is the driving force or pressure, \( \alpha \) is a constant around 0.5, and \( b \) is the burgers vector. This shows that the driving force for recrystallization has a direct linear relationship to the dislocation density.

The annealing temperature and heating rate can have a major effect on the kinetics of recrystallization in a material. The annealing temperature is one of the largest factors that can effect the rate of recrystallization. This can be shown simply by using an Arrhenius equation to represent the time for 50% recrystallization:

\[ \frac{1}{t_{0.5}} = C \exp \left( -\frac{Q}{RT} \right) \]

Equation 3.3
It can be seen from this equation that an increasing temperature will decrease the time needed to reach 50% recrystallization exponentially.

Since laser heating results in rapid heating the effects of the heating rate on recrystallization are important to consider when looking at the recrystallization kinetics in LHCS. The main effect of rapid heating on the recrystallization kinetics is that the rapid heating rate can reduce the recovery that occurs prior to recrystallization. Slower heating rates can allow for more recovery prior to recrystallization reducing the driving pressure for recrystallization. While recovery is seen in both the in-situ neutron measurements and DSC results these heating rates are still relatively slow compared to laser heating. This recovery peak can be seen easily in the DSC results carried out at 20 °C/s; while the recovery peak is limited in the derivative of the in-situ neutron results taken at 60 °C/s, and limited recovery likely occurs under laser heating.

It is believed that this two-step process of recrystallization seen in LHCS is most likely due to an increase in kinetics at the prior particle interface and not a lowering of the temperature necessary for recrystallization, furthermore, it is believed that this phenomenon is likely due to both the property gradient in each prior particle (bimodal microstructure) and possibly dynamically recrystallized grains at the prior particle interface. Two distinct peaks can be seen in the DSC data at 575 °C and 730 °C. The first peak at 575 °C correlates to a decrease in the dislocation density as measured using CMWP but shows minimal change in the microstructure as seen in EBSD. After the peak centered around 730 °C complete recrystallization could be seen in the material heated in the DSC. The heating rate of 20 °C/s used in DSC allowed for further evolution of the microstructure after heating to a particular temperature than the higher heating rate of 50 °C/s used in neutron diffraction which are much slower than the rapid heating rate seen in laser heating. At the higher heating and cooling rates seen in laser heating the presence of
“necklacing” becomes present where the prior particle interfaces are recrystallized prior to the prior particle interior. It is believed that this “necklacing” is because of the increased kinetics, since the DSC results and in-situ neutron diffraction heating only show the evidence for two regimes the first of which shows recovery and the second shows complete recrystallization in DSC. Increased kinetics coupled with the short heating time of laser heating allow for the recrystallization of the prior particle interface but not the prior particle center. Based on the literature highlighted above, there is believed to be good evidence for this increase in kinetics at the prior particle interface. A dislocation gradient likely exists toward the prior particle interface, and this coupled with dynamically recrystallized grains in the area act as preexisting nucleation sites allows for the rapid recrystallization. Future testing using a TEM could help to identify this gradient toward the prior particle interface more clearly.

In order to deconvolute the effects of various properties in the DSC data the derivative of each of the properties measured via neutron diffraction in figure 3.7 was taken, these derivatives were scaled arbitrarily to be visible in figure 3.8 and the sign of the dislocation density derivative was flipped to match the curves with the expected exothermic heat flow due to recrystallization. Both of the exothermic peaks seen in DSC correlate with the two peaks seen in the derivative of the dislocation density calculated using CMWP and neutron diffraction. The area between these two peaks correlated with the derivative of the BCC to FCC phase transition in the material. It should be noted that due to the low BCC phase percentage not much heat flow is expected from this phase transition. The sign of the derivative for the dislocation density has been multiplied by -1 to be representative of the exothermic release of heat that would be expected from the reduction in dislocations. The amount of energy released due to grain growth is expected to be minimal compared to the reduction of dislocations which is why minimal effect due to this
derivative is seen in the DSC. It is believed that this DSC data shows that the decrease in dislocation density between 500 and 675 °C seen in the CMWP results is real and not due to any artifact in the data. From looking at the EBSD of the DSC data it appears that this first peak shows recovery in the cold spray material. Recovery does not seem to be contained to either the prior particle interior or interface. The second peak between 650 °C and 800 °C correlates to the complete recrystallization and grain growth of the cold spray material.

Figure 3.13 DSC results from SS304L, EBSD at key inflection points in the DSC results (indicated by vertical lines), and comparison of the data to the derivative of the properties measured from neutron diffraction.
3.5.0 Conclusion

Neutron Diffraction, DSC, and thermal simulations of the heating profile provided valuable information on the microstructural evolution and kinetics of laser heat treated, cold sprayed 304 stainless steel, and the requirements needed for complete recrystallization of the material. The key conclusions of this paper are as follows:

- Neutron diffraction has allowed for the quantification of dislocation density through the bulk of cold sprayed deposits laser heated with different heat inputs. Furthermore, it was shown that laser heating can rapidly recover and recrystallize the cold sprayed material.
- The kinetics of recrystallization at the prior particle interfaces was shown to be faster than that in the prior particle interior, giving rise to “necklacing” of recrystallized grains under laser heating.
- Using the results from CMWP combined with neutron diffraction alongside DSC allowed for the deconvolution of the individual heat flow components in DSC and provided a clear picture of the temperatures required for recovery, recrystallization, and the reverse of the BCC to FCC phase.
- DSC showed distinct peaks for recovery and recrystallization in the CS material centered around 575 °C and 730 °C respectively, with the BCC to FCC transition occurring between the peaks around 670 °C.

Acknowledgements

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CHAPTER 4: EFFECTS OF LASER HEATING ON MICROSTRUCTURE AND DEPOSITION PREPERTIES OF COLD SPRAYED SS304L

Abstract

This paper investigates the effects of laser heated cold spray on the microstructure and mechanical properties of cold sprayed 304L stainless steel (SS304L). In this study, three samples were made by depositing SS304L powder onto SS304L substrates using cold spray (CS) with a nitrogen carrier gas. A laser was used to heat the surface of two of the deposits after cold spray to 750 °C and 950 °C, and the resulting microstructure and mechanical properties were studied. Electron backscatter diffraction (EBSD) and X-ray line profile analysis (XLPA) were used to determine the microstructure and dislocation density in the three depositions both near the surface of the deposition and near the interface of the deposition with the substrate. Vickers microhardness was used to measure the hardness of the material as a function of depth in the samples. It was found that laser heating caused recrystallization in the material and ultimately grain growth, which correlated with a significant decrease in dislocation density in the material and a reduction in hardness for the laser heated deposits. The measured hardness of the material was found to be strongly related to the inverse square root of the grain size as measured by EBSD when accounting for ultrafine grains at the prior-particle interfaces. This paper points to the ability of laser surface heating for effective microstructural manipulation of cold sprayed materials.
Keywords: Austenitic stainless steels, dislocation density, X-ray diffraction (XRD), cold spray, EBSD

4.1.0 Introduction

The US department of energy (DOE) has identified the need for repair processes for the nuclear dry cask storage system (DCSS) and for this they have funded additive research projects in both cold spray and additive friction stir deposition as possible candidates for repair. DCSS’s are used in the United States as a storage solution for spent nuclear fuel waste from energy production. The DCSS were originally created for interim shortage. However, this interim storage solution is currently projected to be used for more than 60 additional years[1]. The DCSS’s are made of austenitic stainless steels that are constructed through traditional fusion based welding techniques. Because of their construction technique and the fact that these canisters often are stored outside in humid and/or coastal environments, the canisters are susceptible to stress corrosion cracking (SCC)[2]. Cold spray is a possible repair technique for these canisters due to the low heat input of the process.

Cold gas-dynamic spray, or cold spray (CS), is a technique of solid-state additive manufacturing during which particles (typically 5-40 µm) are accelerated using high-pressure gas to supersonic velocities causing the particles to impact a substrate at high velocity (typically 300 - 1500 m/s)[3]. The particles carry enough kinetic energy to plastically deform when they impact the substrate creating a strong metallurgical and mechanical bond. Cold spray is a promising additive repair process due to the low heat input during deposition. Welding or other thermal spray techniques can produce high temperatures, which may cause damage or undesirable properties in the substrate or material being repaired[4]. Due to the amount of plastic deformation experienced by the deposited particles during cold spray, small equiaxed grains can
be formed (100 - 300 nm) through the cold work process[5]. This cold spray microstructure ultimately leads to the deposited material having high tensile strength and Vickers hardness, and low ductility. Previous studies have shown the Vickers hardness of cold spray austenitic stainless-steel material to be 400 - 450 HV$_{0.1}$ in contrast to a hardness of about 150 HV$_{0.1}$ for annealed material[6-9]. Similarly, the strain at failure for as-sprayed cold spray austenitic stainless steel is <0.5% while that for wrought SS304 is approximately 70%[6].

Several studies have investigated the microstructure and mechanical properties of cold sprayed austenitic stainless steels[6, 10-16] as well as traditional furnace heat treatments of cold sprayed austenitic stainless steel[8, 17-20]. These papers, looking at traditional ex-situ furnace heat treatments of austenitic stainless steel, have shown recrystallization and grain growth in the cold sprayed material corresponding with a reduction in hardness and increase in ultimate tensile strength and strain at failure. However, repairs often need to be done on large parts on which post process furnace heat treatments are not an option due to either the size of the part being repaired or that heat treating the entire part could have an undesirable effect on the overall system. Previous studies have shown improvement in mechanical properties can be achieved in cold sprayed material during laser assisted cold spray (LACS), where both the laser and spray process are running at the same time[21, 22]. In this current study, this process is decoupled by first cold spraying and then laser heating the deposited material to isolate the effects of the laser on the deposition from the effects of the cold spray process itself. One known study has investigated post cold spray laser heating to improve mechanical properties in CS titanium material[23]. For titanium the post CS laser heating was found to cause grain growth as a function of depth which correlated with a change in hardness in the deposition. According to the
knowledge of the authors, no known studies exist investigating this process for austenitic stainless steel.

The goal of this study is to use a post laser heating process on cold sprayed 304 stainless steel (SS304L) to improve the microstructural characteristics and mechanical properties of the coating through recrystallization. To investigate how the microstructure changed with laser temperature, three SS304L CS coatings were made on top of 3.18 mm (1/8”) SS304L stainless steel substrates. One of the samples was left as-sprayed, one had laser heat treatment with a fixed surface temperature of 750 °C and another at 950 °C. The microstructure of the coatings was characterized using scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and X-ray line profile analysis (XLPA). Vickers microhardness was used to determine the hardness depth profile in the samples.

4.2.0 Experimental Methods

4.2.1 Sample Fabrication

SS304L powder from Carpenter technology (see compositions from manufactures in Table 4.1) was deposited onto plate SS304L (3.18 mm thick) using a Gen III high pressure cold spray system (VRC Metal Systems, Rapid City, SD) equipped with a 1.75 mm throat - 200 mm length de Laval converging-diverging nozzle (Figure 4.1). N₂ working gas was used for the depositions at a gas pressure and temperature of 5.5 MPa (800 psi) and 650 °C, respectively. The dimensions of the deposited pads were 50 mm × 30 mm with a thickness of approximately 2 mm. Prior to deposition the SS304L plate was sanded with P-80 grit abrasive paper to improve deposition efficiency and adhesions. After deposition an LDM-4000-100 variable power 940 nm wavelength diode laser (Laserline, Mülheim-Kärlich, Germany) was used to heat the surface of the deposition to 750 °C and 950 °C, respectively. A closed-loop feedback system was used with
an optical pyrometer to maintain the surface temperature at the specified value. The laser spot (an 8 mm by 6 mm ellipse) was translated across the surface in a raster pattern at 10 mm/s for all laser heated samples so that the entire surface of the deposition was covered once.

![Laser geometry with respect to the sample and spray nozzle.](image)

After deposition the deposition efficiency (DE) of the cold spray was calculated by taking the ratio of the mass of the powder deposited to that of the mass of powder that was sprayed:

$$DE(\%) = \frac{M_{sf} - M_{si}}{M_{pi} - M_{pf}}$$

Equation 4.1

where $M_{sf}$ refers the mass of substrate after deposition, $M_{si}$ is the mass of substrate before deposition, $M_{pi}$ is the mass of powders loaded for spray, and $M_{pf}$ is the mass of powders at the completion of the spray, respectively. A digital scale with an accuracy of 0.0001 g was used for the measurement of mass.

Table 4.1 Chemical composition of the 304L stainless steel powder (wt. %).

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
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<tr>
<td>0.03</td>
<td>2.00</td>
<td>0.045</td>
<td>0.03</td>
<td>1.00</td>
<td>18.00/20.00</td>
<td>8.00/12.00</td>
<td>Balance</td>
</tr>
</tbody>
</table>
4.2.2 Characterization of Microstructure

After deposition all the samples were cross sectioned, mounted in Bakelite, and polished perpendicular to the deposition raster direction. The powder samples were mounted into Bakelite and lightly polished so that the cross section of the powder particles would be visible in an SEM. Optical analysis of the samples was done using a Leica optical microscope with measurements and porosity analysis performed using Leica suite of integrated software. Backscattered electron (BSE) images were obtained using a combination of a Tescan Lyra FIB-FESEM, Thermo-Fisher Apreo SEM, and JEOL 7000 SEM. All EBSD measurements were obtained on a JEOL 7000 SEM using an Oxford Aztec EBSD system. All EBSD maps were taken with an accelerating voltage of 20 keV, specimen tilt of 70°, and a step size of 0.125 µm for the maps. Low-angle grain boundaries were identified in the software as those ≤ 15° while high-angle grain boundaries were marked as those with a misorientation angle >15°. Grain orientation spread (GOS) maps were generated using the Channel 5-Tango software with a set scale of 0° to 25° for all maps.

The microstructure was studied at the top and bottom of the CS and LHCS deposits by using X-ray diffraction (XRD). For this measurement the samples were electropolished at 25 V and 1 A using an A8 electrolytic solution (made by Struers) at room temperature. The diffraction domain size and the dislocation density were investigated by X-ray line profile analysis (XLPA). The XRD measurements were carried out using a Smartlab X-ray diffractometer operating at 1.2 kW (manufacturer: Rigaku, Japan) with CuKα1 radiation (wavelength: \( \lambda = 0.15406 \text{ nm} \)), Ge monochromator, and parallel-beam optics with an incidence angle of 30°. The step size was 0.02° and the range of 2θ was from 30° to 145°. The X-ray beam size was 2×2 mm². The diffraction patterns were evaluated by the Convolutional Multiple Whole Profile (CMWP) fitting.
method [24]. The instrumental broadening was measured on a LaB₆ standard material. The CMWP method gave the parameter q which describes the edge/screw character of dislocations, the area-weighted mean diffraction domain size \(<x>_{\text{area}}\) and the dislocation density \(\rho\) with good statistics. The value of \(<x>_{\text{area}}\) is calculated as \(<x>_{\text{area}} = m \exp(2.5\sigma^2)\), where \(m\) is the median and \(\sigma^2\) is the log-normal variance of the diffraction domain size distribution. In the CMWP process, one fitting parameter is \(\bar{C}_{h00}b^2\rho\), where \(b\) is the modulus of the Burgers vector of dislocations and \(\bar{C}_{h00}\) is the dislocation contrast factor for reflections with the indices \(h00\). The Burgers vector for FCC structures is given as \(a/2 <110>\), where \(a\) is the lattice parameter, thus \(b\) equals 0.2539 nm for the SS304L deposits. The knowledge of the dislocation contrast factors is necessary for the CMWP evaluation method, since \(\bar{C}_{h00}\) depends on the anisotropic elastic constants. Using the elastic constants of the austenite phase [25, 26] two parameters of the dislocation contrast factors, \(\bar{C}_{h00}\) and \(q\) were determined for pure edge and pure screw dislocations by the software ANIZC [27]. The values of \(q\) were 1.59 and 2.38 for edge and screw dislocations, respectively. The average values of \(\bar{C}_{h00}\) obtained for pure edge and pure screw cases (0.29) was used since \(\bar{C}_{h00}\) is almost independent of the edge/screw character of dislocations.

4.2.3 Hardness Measurements

Microhardness data was collected using a Buehler Model 1600-6100 hardness tester. A load of 100 gf was used with a hold time of 11 seconds. Fifteen data points were taken per sample with a spacing of 175 µm extending from the surface of the deposition to the baseplate.
4.3.1 Powder Characterization

The powder used in the experiments was water atomized leading to the powder having irregular powder geometry (Figure 4.2). The as-received powder from Carpenter had a particle size distribution of 15 to 45 microns. EBSD analysis of the particles showed an average grain size of approximately 6 µm inside each particle. EBSD analysis additionally showed the powder to be predominantly γ austenite with small areas of α or δ ferrite in the particles. Within each particle, an equiaxed grain structure was found.

4.3.2 Microstructure and Phase Transformation of Coatings

The macrostructure and porosity of the cold sprayed SS304L showed no appreciable change with laser heating temperature in BSE images (Figure 4.3). In each image the prior-particle interfaces can be seen, indicated with arrows, and do not show any change with laser heating. In the 750 °C top image and both the top and bottom images of the 950 °C laser heated specimen, some contrast can be seen from the larger grain size in these areas. The porosity of
these coatings, sprayed with nitrogen gas, is higher than could be achieved using helium but it is not a central concern for this paper since the main focus is to study the recrystallization of the microstructure with laser heating and not the tensile properties of the material.

![Figure 4.3 SEM backscatter images of deposition near the surface (A, B and C) and near the interface of the substrate and deposition (D, E and F). Examples of prior-particle interfaces denoted with black arrows.](image)

Vickers microhardness of the three samples shows a marked decrease in hardness in the laser heated samples (Figure 4.4). The as-sprayed material had an average microhardness of 450 HV$_{0.1}$. Heat treating the material with a laser temperature of 750 °C influenced the CS material down to a depth of ~700 µm from the top surface and reduced the hardness in that area down to around ~350 HV$_{0.1}$. Below 700 µm the hardness of the material heat treated at 750 °C was indistinguishable from the as-sprayed material. The material heat treated with a temperature of 950 °C shows a very different story. The hardness of this material was decreased throughout the depth of the deposition to a hardness value of 250-300 HV$_{0.1}$ with a slight upward trend to the hardness value with depth. For reference, the hardness of the 304SS substrate was 175 HV$_{0.1}$. 

114
Figure 4.4 Hardness depth profile of deposition. The substrate is not included in this graph. The hardness of the substrate material was 175 HV0.1. Error bars in data were taken as one standard deviation of 10 random points taken on rolled SS304L.

EBSD measurements of the three samples show a notable increase in grain size and transformation of grain shape due to laser heating (Figure 4.5). Both the top and the bottom of the as-sprayed material show a typical CS microstructure with very clear prior-particle interface boundaries (Figure 4.5A and 4.5D). At the prior-particle boundaries, the CS material has a refined microstructure with a grain size less than 0.5 µm, and larger grains retained in the prior-particle interior that are deformed but not highly refined due to plastic deformation. The 750 ºC material shows a similar microstructure to the CS material near the top of the deposition with pancake like grains and refined microstructure at the particle interface boundaries (Figure 4.5E). Near the top of the 750 ºC material a microstructure that has begun to undergo recrystallization particularly in the fine grains near the particle interfaces boundaries can be seen (Figure 4.5B).
However, the 750 ℃ material at the top still retains some of the overall characteristics of the as-sprayed material. For the 950 ℃ material a recrystallized microstructure with equiaxed grains and very little remaining characteristics of the as-sprayed material is present (Figure 4.5C and 4.5F). The top and bottom of the 950 ℃ material are similar with more grain growth in the material at the top near the surface. Twinning can also be seen in the 950 ℃ material which is to be expected in SS304L due to the low stacking fault energy (SFE) for austenitic stainless steels.

Figure 4.5 IPF orientation maps with respect to z direction (sample normal and direction of spray gun translation) of samples, with top row taken within 200 µm of surface (A, B and C) and bottom taken within 200 µm of baseplate (D, E and F). Columns correspond to

The average grain size obtained from EBSD is listed below (Table 4.2). Note that this is the average of the grain size of those grains which are detected in EBSD and does not take into account the small grains at the prior particle interfaces in CS material which are not detected in EBSD. For this reason the grain size in cold spray is not typically reported, however, this is listed below as the grain size and area fraction detected in the EBSD scans are used in a weighted function (Eq. 2) to fit this data to the Hall-Petch equation.
Table 4.2 Grain size data obtained from EBSD scans (µm)

<table>
<thead>
<tr>
<th></th>
<th>No laser</th>
<th>750 °C</th>
<th>950 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>0.543 ± 0.07</td>
<td>0.610 ± 0.05</td>
<td>0.973 ± 0.1</td>
</tr>
<tr>
<td>Bottom</td>
<td>0.548 ± 0.06</td>
<td>0.542 ± 0.06</td>
<td>0.815 ± 0.12</td>
</tr>
</tbody>
</table>

GOS data assigns a number to each grain based on the average of the misorientation angles to the grain mean orientation inside each grain with blue being 0° spread inside the grain and increasing to red at the maximum, which was chosen to be 15° for all images in this paper (Figure 4.6). Small grains consisting of a small number of pixels might not be assigned a GOS number by the software if the results are not statistically significant, these pixels are colored white. High levels of grain orientation spread show that the crystal lattice inside of a grain is being deformed due to dislocations. Recrystallization of a grain will create a new lattice which has significantly fewer dislocations and therefore lower GOS. In the as-sprayed material and the bottom of the 750 °C material there is significant amounts of deformation and very few grains with a low GOS value (Figure 4.5A, 4.5D and 4.5E). The top of the 750 °C material shows low grain orientation spread, typical of recrystallized grains, particularly near the particle interface boundaries, with non-recrystallized, pancake shaped grains still present in the prior particle interiors (Figure 5B). The 950 °C material at both the top and the bottom shows material that is fully recrystallized with a very low grain orientation spread in the material (Figure 5C and 5F).
As expected, phase maps of the deposited material show most of the material to be austenite (FCC) (Figure 4.7). However, the as-sprayed material near the bottom of the as-sprayed deposition shows a large fraction of BCC material compared to the other samples. This BCC material is not seen in either of the heat-treated samples including at the bottom of the 750 °C sample. It is possible that this apparent BCC material is actually strain-induced α’ martensite. It should be noted that EBSD cannot distinguish between the two BCC phases in stainless steel, δ ferrite and α’ martensite, for that reason in the remaining of this paper the BCC phase is referred to as simply ferrite except when the phase transformation “strain-induced martensite” is being referenced.
4.3.3 Characterization of the microstructure by XLPA

The XLPA measurements did not reveal any BCC (ferrite) peaks for the present material, indicating that the ferrite fraction is below X-ray diffraction sensitivity (less than 5%). Therefore, the average diffraction domain size and dislocation density in the CS and LHCS deposits were determined for the FCC phase by CMWP. As an example, figure 4.8 shows the CMWP fitting on the X-ray diffraction pattern obtained for the top of the CS deposit. For the LHCS deposits with a 950 °C surface temperature, the diffraction domain size was larger while the dislocation density was lower than the detection limits of the present diffraction configuration (~1 μm and ~10^{13} m^{-2}, respectively).
Figure 4.8 The X-ray diffraction pattern in logarithmic intensity scale for the top of the CS deposit. The open circles and the solid line represent the measured and the fitted X-ray diffraction patterns, respectively. A part of the pattern is presented in the inset with linear intensity scale. The difference between the measured and the fitted patterns is also shown at the bottom of the inset.

Between the dislocation density and diffraction domain size of the top and bottom of CS depositions only a slight difference was observed, in contrast with the 750 °C LHCS where significant differences were measured (see Figure 4.9). The dislocation density value was higher and the diffraction domain size lower in the bottom of the 750 °C LHCS deposition with comparing the values at the top of the deposition at the same time. It is noted that the diffraction domain size determined by XLPA is much smaller than the grain size measured from EBSD measurements. This difference could be explained by the fact that XRD is more sensitive to slight misorientations than EBSD. It is clear from the XLPA results that the dislocation density in the bottom of the 750 °C samples is similar to the as-sprayed samples while the dislocation density in the top of the 750 °C samples is significantly less, as would be expected with recovery.
or recrystallization. For the 750 °C LHCS sample the diffraction domain size was larger than the detection limit due to the recrystallization.

The \( q \) values at the top and bottom of the CS and the bottom of the 750 °C LHCS deposits were 2.17, 2.24, and 2.18, respectively, suggesting a more screw dislocation character. In the top of the deposit at 750 °C laser heat treatment the \( q \) parameter value was 1.59, indicating an edge character of dislocations. These results suggest that dislocation annihilation could have occurred. The change of the dislocation character could be explained by the fact the screw dislocation annihilates considerably easier than edge dislocation in FCC crystals.

![Figure 4.9](image)

Figure 4.9 XLPA results showing A) the dislocation density and B) the diffraction domain size in the CS and LHCS with 750 °C samples

### 4.4.0 Discussion

#### 4.4.1 Recrystallization of deposition due to laser heating

Laser heating caused clear recrystallization and grain growth in the cold spray deposition. The amount of grain refinement after deposition in CS, particularly at prior-particle interfaces due to the solid-state deformation is well documented [5, 28, 29]. Additionally, some papers have studied the effects of furnace heat treatment on the recrystallization and grain growth in CS stainless steel coatings [6]. As expected, these papers show that heat treating cold spray deposits
in stainless steels can cause recrystallization and grain growth. In this paper recrystallization, similar to what would be expected from a traditional ex-situ furnace heat treatment, was activated by heating the surface of the deposition via laser. This recrystallization can be seen in the EBSD data with the increase in grain size and decrease in GOS values. In the as-sprayed condition, highly deformed grains exist with a refined structure, in the 750 °C sample grain growth begins at the top of the sample, and in the 950 °C sample almost no remnants can be seen of the prior grain structure and significant grain growth has occurred. Recrystallization can be seen even more prominently in the GOS maps taken from the EBSD data. GOS data shows us the level of deformation within each grain, by averaging the change in grain orientation over an entire grain resulting in one value per grain. Before recrystallization the grains have a high dislocation density resulting in a large variation in lattice orientation (and correspondingly large GOS) compared to a fully recrystallized grain. The as-sprayed material has a high level of deformation in all grains. Moving to the top of the 750 °C heat treated sample necklacing of recrystallized grains (low GOS) at the prior-particle interfaces begins to occur. Moving to the 950 °C material significant recrystallization can be seen resulting in almost no grains with a high level of deformation as in other samples and significant grain growth. It is worth noting that the bottom of the 950 °C sample still has some remnant of refined grains at the prior-particle interface. Future work aimed at simulating the temperature distribution in the material during laser heating could reveal the heating curves at the top and bottom of this material giving an indication of the time and temperature needed for full recrystallization. This information could then be used to optimize the temperature and speed of the laser for more complete recrystallization throughout the material. It should be noted that in deformed SS304L recovery does not occur due to the low stacking fault energy of SS304L, which does not allow
dislocations to cross slip and rearrange [20]. Since recovery does not occur in deformed SS304L, upon heating the material will only undergo recrystallization and grain growth.

Of particular interest is that the stainless steel cold spray deposit rapidly recrystallized with laser heating in seconds compared to a typical furnace heat treatment of hours. According to the ASTM standard, a typical furnace annealing time and temperature for austenitic stainless steel is 1010 °C to 1120 °C for 60 minutes per 25.4 mm (1 inch) of thickness, minimum [9]. In the case of these laser heated samples the laser was moving at a speed of 10 mm/s which corresponds to a time of 0.667 seconds that the laser spends over a spot on the samples and a total time of 85 seconds to laser heat the entire sample (50 × 30 × 2 mm). There are two hypothesized reasons that the recrystallization and grain growth occurred so quickly in these cold sprayed samples. One is that the high levels of plastic deformation in the CS material create a buildup of dislocations resulting in a high dislocation density in the material which is unique to the cold spray process. This high dislocation density creates a strong driving force for recrystallization since the higher levels of stored energy mean that less thermal energy needs to be applied to overcome the activation barrier to move grain boundaries and create new grains, which reduces the overall energy in the material. Two, the cold spray process may have created ultra-fine, defect free crystallites at the prior particle interfaces, which may act as nuclei for defect free grains, essentially eliminating the nucleation portion of the recrystallization and grain growth process. Previous work by Liu et. al. on cold spray Al-Cu alloys shows ultra-fine grains at the prior particle interfaces with a uniform low grain reference orientation deviation (GROD) angle, thus possibly indicating the presence of these nuclei in cold sprayed material [29]. Both hypotheses line up well with the behavior seen in the top of the 750 °C cold spray material where necklacing of recrystallized grains is seen at the prior particle interfaces. The prior particle
interfaces undergo the highest level of plastic deformation and exist closest to the area where these defect free nuclei would be created. Additionally, literature outlines how the recrystallization time is much shorter for materials with high grain refinement and high dislocation densities [20]. The existence of ultrafine grains at the prior particle interfaces in cold spray has been outlined in previous literature extensively [5, 28-32]. However, no literature exist that the author is aware of that shows the decrease in recrystallization time to the extent observed in this paper.

4.4.2 Dislocation density changes as observed by XLPA

The XLPA results quantify the dislocation density reduction that corresponds with the recrystallization that could be seen qualitatively in the EBSD data. The XLPA results show that the dislocation density in the top of the 750 °C heated sample was reduced by a factor of 10. This reduction correlates to the necklacing and recrystallization seen in the GOS maps from EBSD, further confirming that recrystallization has begun. Additionally, recrystallization lowers the dislocation density, and it makes the material softer, as we can see from the hardness data in figure 4.4. Conversely, a high value of the dislocation density was observed in the CS and in the bottom of the 750 °C LHCS deposits. For comparison, XLPA was successfully used in a recent paper to determine the dislocation density for a series of low-pressure CS Al-Cu coatings with copper contents from 2 mass% to 5 mass% [31]. The dislocation densities of the Al-Cu coatings increased with copper alloy additions from $4.3 \times 10^{14} \text{ m}^{-2}$ for Al-2%Cu to $7.5 \times 10^{14} \text{ m}^{-2}$ for Al-5%Cu. These values are smaller compared with the cold-sprayed 304L steel in this paper, ~68-79×10^{14} \text{ m}^{-2} (see Figure 4.9A). This can be explained by the high pressure applied during CS of the present 304L stainless steel while the Al-Cu deposits were produced by low-pressure CS. The higher pressure can yield a more severe plastic deformation during CS.
The dislocation densities as measured by XLPA have some similarities and distinct differences with studies of other deformation methods applied to austenitic stainless steels. Similar dislocation density values to the present study were achieved in 316L stainless steel processed by the high-pressure torsion (HPT) process for a 1/4 turn deformation [33]. In the HPT work, the researchers studied the thermal stability of the deformed microstructure in 316L steel using both differential scanning calorimetry (DSC) and XLPA. The dislocation density was very large $\sim 66 \times 10^{14}$ m$^{-2}$ in the main BCC/martensite phase even after 1/4 HPT turn, and during the DSC annealing the BCC/martensite phase transformed into the FCC phase. It should be noted that it is very difficult to distinguish between BCC and martensite in the X-ray diffraction measurements. In the temperature range of 467–727°C the matrix of the material gradually transformed from BCC/martensite to primarily FCC, and the dislocation density decreased from $\sim 13–14 \times 10^{14}$ m$^{-2}$ to $\sim 6–10 \times 10^{14}$ m$^{-2}$ in the main FCC phase [33]. These changes in the dislocation density in HPT of 316L steel are similar to the measurements in this present study after laser heating of cold sprayed material. It should be noted, that after the heat treatment in 316L steel processed by HPT, the diffraction domain size did not change significantly compared with the present laser heat treated CS samples, for which the diffraction domain size did increase. This difference could be due to the relatively low temperature range for the HPT experiments. For other studies on recrystallization of cold rolled 304 and 316L, recrystallization was observed at temperatures above 700 and 900 °C, respectively [34]. As a reminder, the nominal surface temperature in these present laser heat treating experiments was 750-950 °C.

XLPA can also provide some insight into how different deformation processing results in different dislocation character or type in austenitic stainless steels. The work of Shintani et. al. studied the dislocation type shifts from predominantly screw to the mixed type of screw and edge
dislocations in the FCC phase with increasing strain in the cold rolling process [35]. While the dislocation character in the BCC phase does not show any dominant type of dislocations, in this phase mixed type of screw and edge dislocations exists. In the current paper, the dislocation character shows more screw type characters at the top and bottom of the “as-sprayed” CS deposit. This can be attributed to the fact that cross-slip is more difficult in metals with low stacking fault energy, like 304L stainless steel. At the same time, the dislocation character shows a significant difference between the bottom and top of the 750 °C LHCS deposit. This could be explained by the fact that during recovery and recrystallization the screw dislocations annihilated first at the top of the 750 °C LHCS and the character of the dislocation became more edge type. It is confirmed by the fact the dislocation density decreased at the top of the 750 °C LHCS deposit.

4.4.3 Strengthening Mechanisms

The reduction in hardness due to laser heating correlates well to the recrystallization seen in the EBSD results, and the reduction in dislocation density seen in the XLPA results. The Hall-Petch equation can be used as a first approximation to estimate to what level the grain refinement is responsible for the observed changes in hardness of the material. To do so, requires a few assumptions. First the hardness value used is an average over the top and bottom 500 µm of the sample thickness. This combination of data gives us an average hardness for these areas. Secondly, the most important assumption made is that the combination of EBSD and XLPA measurements should estimate the grain or crystallite size. The EBSD data analysis used a minimum threshold of 5 pixels when identifying grains. Particularly for the cold spray-only sample and the top portion of the 750 °C samples, some regions of the microstructure could not be consistently indexed by EBSD because of the high level of deformation and the small size of
the grains/crystallites. To compensate, the percentage of the microstructural area that was not measurable by EBSD was assumed to have an average grain size equal to the average crystallite size derived in the XLPA analysis (i.e. 0.05 μm). This is a rough approximation since the true grain size in the boundary areas between prior particles cannot be reliably measured via EBSD. This grain size measurement is a fair one based on results from literature, which all show the formation of ultrafine grains less than 0.5 μm with some particles being as small as 0.01 μm [5, 29, 30]. Additionally, the fact that the grain size in the area that was not indexed by EBSD is over a small spread in grain size means that the selected grain size for the undetected area has little effect on the overall grain size regardless of distribution. This approach resulted in the average grain size of the total area being calculated as:

\[ d_{\text{average}} = (1 - A_{\text{detected}}) \cdot d_{\text{crystallite(XLPA)}} + A_{\text{detected}} \cdot d_{\text{grain(EBSD)}} \]

Equation 4.2

where \( d_{\text{average}} \) is the composite grain size calculated and used below (Figure 4.10), \( A_{\text{detected}} \) is the total area fraction of each EBSD map covered by grains consisting of 5 pixels or greater, \( d_{\text{crystallite(XLPA)}} \) is the crystallite size/diffraction domain size determined by XLPA, and \( d_{\text{grain(EBSD)}} \) is the average grain size from each EBSD map of all grains 5 pixels or greater (the same set used to calculate \( A_{\text{detected}} \)). It can be seen that the average hardness in the CS material follows the Hall-Petch relationship with the average hardness matching the inverse square root of the grain size within one standard deviation for the calculations (Figure 4.10a). The Hall-Petch relationship for hardness versus grains size is given as:

\[ HV = HV_0 + k d^{-1/2} \]

Equation 4.3
where HV is the Vickers hardness, $HV_0$ is the hardness as the grains size approaches infinity, d is the grain size, and k is a fitting constant. For this paper the value of $HV_0$ is 70.8 HV and the value of k is 191.2 HVµm$^{1/2}$.

While the results of this application of the Hall-Petch equation are interesting the limitations of this application should also be noted. As sprayed CS material has a bimodal microstructure as seen above (Figure 4.5) with fine grains at the prior particle interface and elsewhere. This method averages the strengthening effect of the two areas together into one number, furthermore the size of the prior particles is of the same length scale as Vickers hardness which could lead to fluctuating hardness values and varying levels of contribution to hardness from the prior particle interface depending on indent placement.

We can attempt to estimate the contribution of dislocation density to the hardness ($HV_{0,1}$) of plastically deformed metallic materials through the Taylor-equation [36]:

$$HV = HV_0 + 3\alpha M^T G b \rho^{1/2}$$

Equation 4.4

where $HV_0$ is the hardness of non-strain hardened material, $\alpha$ is a constant, $G$ is the shear modulus, $b$ is the modulus of the Burgers vector, $M^T$ is the Taylor factor, and $\rho$ is the dislocation density. The measured hardness values did not correlate well with the measured dislocation densities through the Taylor-equation. At this point, the data suggests that the reduction in grain size has a greater proportional effect on the increase in hardness than does the increase in dislocation density, however, further experiments should be made to clarify this point. In the Taylor equation (4), $\alpha$ is a parameter describing the strength of the interaction between dislocations and $M^T$ is the Taylor factor, for untextured polycrystalline FCC materials this value is 3.06. The shear modulus and the Burgers vector for SS304L steel are $G = 77$ GPa and $b =$
0.2539 nm, respectively. The slope of the measured data from Figure 4.10B is 1845 HV·nm and the $3aM^\alpha Gb = 1830$ HV·nm, using $\alpha = 0.1$.

Figure 4.10 A) Hall-Petch relationship between calculated grain size and hardness, error bars in y axis correspond to one standard deviation in the data collected and error bars in x axis correspond to minimum and maximum achievable values by varying undetected grain size values B) Taylor relationship between the measured hardness of the cold spray deposit and the dislocation density as measured by XLPA.

The hardness values presented here agree well with that reported in literature for cold sprayed SS304L [6, 7]. Both Coddet et. al. and Yeom et. al. reported a maximum hardness in cold sprayed SS304L to be in the range of 450 Vickers hardness. Additionally, Coddet et. al. reports a Vickers hardness of approximately 200 HV$_{0.1}$ for a 4 hour heat treatment at 950 °C [6].

The similarity of this hardness value to the hardness value seen here for laser heat treatment at 950 °C indicates that the material undergoes the majority of its recrystallization in the first few seconds of heat treatment for cold spray material due to the low grain size lowering the activation energy for recrystallization.
4.4.4 Comparison of phases in deposition to powder

A significant concentration of ferrite (BCC phase) was seen in the as-sprayed deposition near the substrate-deposition interface that was not seen in the depositions that were laser heated. For CS deposition, ferrite seen in the final deposition is either retained from the original powder or is developed during the cold spray deposition process. The SS304L powder used for these depositions did show some initial fraction of ferrite (~2%), and it is hypothesized that the phases in the powder are maintained in the deposited particles. However, it is of interest that the bottom of the coating in the as-sprayed deposition shows a significantly higher fraction of ferrite than in any of the other depositions. It is possible that this is the result of the strain induced martensite phase transformation, a well-understood phenomenon in austenitic stainless steels that has been documented in a number of studies [35, 37, 38]. It is generally accepted in cold spray literature that the amount of plastic deformation in the deposited material will increase deeper into the sample due to the further plastic deformation of initial layers by the subsequent impact of particles above them [5]. It is possible that the $\gamma \rightarrow \alpha'$ phase transformation seen here in the material is strain induced. Similar results were shown in cold sprayed SS316 by Bandar et. al., in which as-sprayed austenitic material showed the presence of a ferrite phase (BCC (110)) in XRD measurements, that was not seen after heat treatment at 800 °C and 1000 °C [39]. Similarly, in the current work a ferrite phase was also present in the powder prior to deposition. It should be noted other work by Yeom et. al. did not note the formation of ferrite in cold sprayed SS304L [7]. It was theorized in Chen et. al. that strain induced martensite was not formed in the material due to the tendency of 304 stainless steel to impede $\alpha'$-martensite transformation at high strain rates (above $10^5$ s$^{-1}$) due to deformation twinning [40]. Dislocation activity and deformation-induced martensitic transformations are more common at lower strain rates of 10 to $10^3$ s$^{-1}$. The
paper further cites the typical strain rate in cold sprayed material to be $10^7$ to $10^9$ s$^{-1}$, which could explain the lack of strain induced martensite seen in this paper [14]. If this theory is true, the presence of ferrite in both the current study and that done previously by Bandar et. al. would be due to the presence of ferrite in the powder prior to deposition. This initial fraction of ferrite in the powder could be simply retained through the deposition process into the deposited material. This aligns well with the work of Brewer et. al. which studied the connections between feedstock powders and cold spray coating microstructures in austenitic stainless steels and found that powders with an initial fraction of ferrite retain that phase in the cold spray deposited material [41]. Brewer et al. did not see evidence of ferrite in coating made with powder without an initial ferrite fraction. It should be noted that standard EBSD indexing algorithms are not capable of consistently distinguishing between the $\alpha$ ferrite and the $\alpha'$ martensite phases. The two laser-heat-treated samples show a significant reduction in the amount of ferrite present to the point where almost no ferrite is seen in the bottom of the sample heated at 950 °C. The reduction of the ferrite is expected with heating; however, the speed at which this transformation happens is unique in the laser heat treated samples. It is worth noting that in the as-sprayed material, as well as at the bottom of the 750 °C sample, there is some uncertainty as to what phases are present at the particle interface boundaries since the highly refined microstructure at the interfaces cannot be reliably indexed by the EBSD system.

**4.4.5 Summary of effect of Laser heating on properties of deposition**

Laser heat treatment of the cold sprayed deposit may improve the durability of repairs for DCSS’s. Cold spray is a portable technique and thus has generated a lot of interest for field repair of DCSS’s. However, several studies of CS have shown limited ductility [6, 39], these results suggest improvement of strength and higher ductility. The results seen here suggest that
in-situ laser heat treatment after cold spray can improve microstructure and possibly the mechanical properties. More work needs to be done to investigate how the laser heat treatment effects the corrosion properties of the material which is important for its use to repair stress corrosion cracking in DCSS’s. The improvement in mechanical properties and lower hardness will likely lead to an increase in the longevity and durability of the repair. Furthermore, the decrease in total grain boundary area due to laser heating is likely to improve the overall corrosion properties of the repair material as well. There is room for future work in optimization of the laser heat treatment to minimize the excess heat added to the system while improving the properties of the material. This could possibly be performed by lowering the overall heat of the laser and slowing down the laser speed to allow for more heat to soak into the material. Overall, this process has shown promise as a means of repair using austenitic stainless steel that can match the mechanical and microstructural properties of the base material.

While the temperatures used in this research show the ability to rapidly recrystallize the 304L stainless steel, one should also consider the possibility of sensitization for this alloy. 304 stainless steel has the known problem of grain boundary sensitization, through the formation of chromium carbides at the grain boundaries when held at temperatures in the 650-850°C range. The upper temperature for laser heat treatment of 950°C is well above this range, and as long as the material cools rapidly, sensitization should not be a concern. For 304 stainless steel, the work of Ikawa et al. [42], predicts that sensitization will begin after approximately 6 seconds at 750°C. For 304L stainless steel (with a lower carbon content of <0.03 wt% carbon), the start of sensitization is delayed to approximately 80 minutes. The 304L steel samples in this study were heated for 150 seconds (2.5 minutes), so sensitization is unlikely, even at a surface temperature of 750°C. Nonetheless, the degree of sensitization of laser heat treated, cold sprayed material
would be an important measurement as this technique is further developed for repair of austenitic stainless steel structures.

4.5.0 Conclusion

This paper examines the microstructural evolution produced by *in situ* laser heat treatment of cold sprayed 304SS material. The following, key conclusions were developed from this research.

- Laser heating, after CS results in recrystallization and grain growth in CS coating microstructure. It is notable that this microstructural evolution is quite rapid, requiring only 85 seconds of laser heating.

- Using detailed X-ray line profile analysis, a significant decrease in dislocation density was measured in areas with recrystallization.

- Recrystallization to a depth of 0.5 mm observed when laser heating to a surface temperature of 750 °C post cold spray, while recrystallization was observed through the entire depth of the 2 mm thick deposit at the 950 °C surface temperature.

- The hardness of the laser heat treated material decreased with the inverse square root of the measured grain size and was well-described by the Hall-Petch relationship.

- These results suggest that the detrimental effects of strain hardening can be mitigated via *in situ* laser heating of cold sprayed stainless steel.
Acknowledgements

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References


CHAPTER 5: RESIDUAL STRESS IN COLD SPRAYED SS304L MEASURED VIA NEUTRON DIFFRACTION AND COMPARISON OF ANALYTICAL MODELS TO PREDICT THE RESIDUAL STRESS

Abstract

This study employs neutron diffraction to investigate the relationship between residual stress and coating thickness in cold-sprayed 304L austenitic stainless steel. Results show that shot peening predominantly impacts the residual stress profile, leading to substantial in-plane compressive force. The impact of laser heating, a widely used method to alter cold spray's microstructural properties, on the coating's residual stress is also analyzed. The findings indicate that the maximum compressive residual stress in the in-plane component is mainly independent of coating thickness, which suggests that the material properties determine the maximum residual stress. The cold sprayed deposits possessed compressive, nearly biaxial strain and stresses. After laser heating, these stresses were replaced by tensile residual stresses. Two analytical models, the Tsui and Clyne and the Boruah models, for predicting residual stresses are also evaluated and both models provide reasonable fits to the experimental data. At this point, the deviations between the experimental results and the models are principally caused by the inability of the current models to address plastic deformation and relaxation and the residual stresses generated by thermal gradients.

5.1.0 Introduction
One of the many proposed applications of cold spray is the repair of corrosion damage due to stress corrosion cracking [1]. The high deformation in cold spray results in characteristic properties of the cold spray material, specifically high hardness, a refined grain structure, and the accumulation of significant amounts of compressive residual stress [2]. The significant amounts of compressive residual stress in cold spray are often cited as being beneficial to prevent future stress corrosion cracking [3]. However, it has been shown that cold spray coatings can exhibit poor corrosion performance compared to their wrought counterparts [4] but that post-spray heat treatments can improve the coating's corrosion performance [5]. For this reason, laser heating has been investigated as it can recrystallize cold spray coatings and improve the material properties of the coatings. While it is well known that cold spray can accumulate significant residual stresses in both cold spray coatings and the substrate, the evolution and characterization of these residual stresses in literature is a severely understudied area of cold spray literature due to the difficulty of making residual stress measurements on cold sprayed materials.

Cold spray is often quoted as having compressive residual stresses due to the effects of peening by the subsequently deposited particles. However, work by Luzin et al. showed that in the case of titanium coatings on copper, tensile stresses could exist at the deposit's surface due to a thermal mismatch between the deposited material and substrate. In further work by V Luzin et al., it is described that the residual stress in cold spray coatings is a combination of three factors: a quenching stress which is tensile, a peening stress which is compressive; and the thermal expansion mismatch stress between the substrate and coating, which can be either compressive or tensile [6]. The quenching and peening stress are intrinsic stresses; for cold spray, peening stress is the primary dominant stress. The thermal mismatch stress is formed upon cooling after
the spray and is zero for self-sprayed cold spray, i.e. the same material is used for both the deposit and the substrate.

Analytical models of the residual stress in cold spray coatings are desirable due to the ease of use when compared to analytical models. Furthermore, analytical models allow for an predictive understanding of how changing input parameters will affect the final residual stress. Currently, the Tsui and Clyne model [7] is the primary analytical model used to predict the residual stresses in cold spray coatings. The Tsui and Clyne model was initially developed to predict the residual stress in thermal spray coatings and had been used by Luzin et al. to predict the residual stress in cold spray coatings by using negative intrinsic stress to predict the peening stress. Similar to the Tsui and Clyne model, Boruah et al. developed a model in 2019 for use with cold spray [8]. The Boruah model is similar to the Tsui and Clyne model in principle but uses a force balance approach instead of the bending/curvature approach of the Tsui and Clyne model to simplify the model further. Both models, in their current form, handle certain aspects of the residual stress generation in cold spray well, but both also have deficiencies which will be covered in detail in the discussion of this paper. For example, neither model can account for material yielding in the deposit or substrate and both models in their current state are used primarily as descriptive models instead of as predictive models due to their lack of ability to predict the magnitude of the peening effect during cold spray.

High quality measurements of the residual stress profile in the coatings must be made for many material combinations to further develop predictive models of residual stress in cold spray coatings. Many methods exist for measuring the residual stress in cold spray coatings, including stress relaxation and diffraction based methods. Diffraction methods include X-ray diffraction, synchrotron diffraction, and neutron diffraction, while stress relaxation methods include
incremental hole drilling and crack compliance; an additional in-situ curvature method also exists [6]. The stress relaxation methods are valuable due to the relatively limited equipment needed to perform the experiments, but they can suffer due to noise in the measurements. In addition, in-situ curvature methods cannot measure the residual stress in the through-thickness. Of the diffraction-based nondestructive techniques, the differentiating factor for each is the penetrating depth of the technique. X-ray diffraction is fairly limited in its penetrating depth and can only measure surface stresses; synchrotron X-Ray can measure up to 2.5 mm of material with its penetrating depth; neutron diffraction can measure through 10’s mm of depth and is one of the most precise techniques for residual stress measurement with its main drawback being the accessibility of neutron sources.

All the above methods have been used to measure the residual stress in cold spray coatings in literature. The primary material studied for residual stress in cold spray includes aluminum and aluminum alloys, copper, titanium, ODS steels, and Inconel 718. Aluminum and aluminum alloys are the most well-studied materials on this list regarding residual stress, with commercially pure aluminum, 7075, and 6061, being studied using diffraction and stress relaxation methods. The literature shows that aluminum alloys typically create primarily compressive residual stresses in the cold spray coatings [9-14], though it has been shown that commercially pure aluminum can develop tensile residual stresses under the correct conditions [3, 9]. The magnitude of the residual stresses typically seen in aluminum and its alloys are well below the material's yield stress and can be modified by changing the spray parameters or heating/cooling of the substrate [13]. The second most studied material is copper, which has been shown to show primarily compressive stresses during deposition, with the thermal history and substrate altering the final residual stress significantly, allowing for tensile residual stresses to be
created under some situations in the coating [3, 15, 16]. Finally, work on CP Ti, ODS alloys, and IN 718 is limited, with only one paper discussing each alloy. Current literature for IN 718 and ODS alloys suggests compressive residual stress in these coatings [17, 18]. In the case of titanium in-situ residual stress measurements, substantial tensile stresses have been seen during deposition, and depending on the substrate and thermal history, compressive stresses can be formed after spraying [3].

This paper uses neutron diffraction to measure the residual stress in cold sprayed SS304L sprayed onto SS304L plate. The residual stress is measured in samples of thickness of 2, 4, and 6 mm to evaluate how the residual stress evolves as a function of the sample thickness. Additionally, the residual stress in a 2 mm thick cold spray sample laser heated to 750 °C via the LHCS process was analyzed. The LHCS process has become increasingly popular to alter the material properties of cold spray but the residual stresses from this process have not been analyzed. For the as-sprayed samples, the measured residual stress is compared to the two current models used for residual stress in cold spray coatings, and these methods are evaluated to see how they may be improved to predict the residual stress more accurately in the coatings. This paper is the first paper to measure the residuals tress in cold sprayed SS304L on SS304L, and the first paper to look at the residuals stress evolution in coatings as a function of coating thickness. Additionally, two analytical models, the Tsui-and-Clyne and Boruah Model, are investigated and the modifications needed for more accurate modeling of residuals tress in cold spray coatings are discussed.

5.2.0 Experimental Methods

5.2.1 Manufacturing of test samples
SS304L was deposited using a VRC Gen III high pressure cold spray system (VRC Metal Systems, Rapid City, SD). SS304L powder was obtained from Sandvik and had a nominal powder size of 15-45 µm (see compositions in Table 5.1). A DeLaval converging-diverging nozzle was used with a throat size of 2.0 mm and a total length of 196 mm. Helium gas was used to spray the powder at a temperature and pressure of 350 ºC and 600 psi, respectively (Table 5.2). A 25 x 25 mm deposition was made for each of the four samples onto a ½” thick SS304L substrate with 53 x 53 mm dimensions. Varying thicknesses of as-sprayed material were made with nominal thicknesses of 2 (6 passes), 4 (12 passes), and 6 (18 passes) mm.

Table 5.1 Chemical composition of the 304L stainless steel powder (wt. %).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>N</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.02</td>
<td>0.14</td>
<td>1.5</td>
<td>0.023</td>
<td>0.006</td>
<td>0.73</td>
<td>18.7</td>
<td>8.3</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Table 5.2 Spray conditions for manufacturing samples

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>He</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>600 psi</td>
</tr>
<tr>
<td>Gas temperature</td>
<td>350 ºC</td>
</tr>
<tr>
<td>Nozzle</td>
<td>VRC NZL0060, 196 mm, 2mm throat</td>
</tr>
</tbody>
</table>

An LHCS sample was made with a thickness of 2 mm and was heated to 750 ºC in increments of 100 ºC starting at 150 ºC (Figure 5.1). For each increment, the laser was rastered at 10 mm/s over the surface of the samples with a spacing of 1 mm between passes to cover an area of 20 x 20 mm (80s total). The substrate for both the LHCS and the thickest 18-pass sample was polished to 1 µm prior to deposition, as this provided the best adhesion for the coatings so that delamination did not occur. Duplicates of all four samples were made from which 0.2 mm cross
sections were taken from the center of each deposit. These cross sections were stress relieved by making cuts every 1.5 mm from top to bottom so that variations in \( d_0 \) due to changes in chemical composition between the depositions and substrate could be checked and accounted for.

![Figure 5.1 Overview of the heating profile used for LHCS sample](image)

### 5.2.2 Residual stress measurements using neutron diffraction

Residual stress measurements were made using the high intensity diffractometer for residual stress analysis (HIDRA) beamline at the high flux isotope reactor (HFIR) at Oak Ridge National Lab [19, 20]. A gauge volume of 20 x 0.7 x 0.7 mm was used for the neutron beam, and steps of 0.5 mm were taken in the build direction for all measurements such that the results were over-sampled. For both the build direction (BD) as well as the longitudinal direction (LD), the longest direction of the interaction volume was perpendicular to the spray direction, whereas, for the transverse direction (TD), the interaction volume was parallel to the spray direction (Figure 5.1). A collection time of 600 s was used for the BD and LD, and a time of 900 s was used for
the TD. An incident wavelength of 1.54 Å was used for measurements, and the Fe (311) peak located at approximately 82.3° was used to measure the strain in the material. Measured data were reduced from neutron events into 1D diffraction data using the pyRS package[doi:10.1107/S1600576721010554]. Changes in lattice spacing, \(d_{hkl}\), where measured using Braggs law:

\[
\lambda = 2d_{hkl} \sin \theta_{hkl}
\]

Equation 5.1
where \(\lambda\) is the wavelength of the incident neutrons (1.54 Å) and \(2\theta_{hkl}\) is the measured angle of the diffracted peak. The strain free \(d_0\) was measured using a stress relieved “comb” with cuts made every 0.2 mm to check for changes in the strain free lattice parameter as a function of depth. No changes were seen in the lattice parameter as a function of depth. This measured value was also compared to the \(d_0\) from the feedstock powder. A force balance was performed on the final calculated stress results for the Hooke’s law approach and calculated \(d_0\) after this method agreed with the strain relived samples and powder measurements. Elastic strains in the material were then calculated using the change in d-spacing from the d-spacing in strain-free CS material. The elastic strain was calculated as follows:

\[
\varepsilon_{hkl} = \frac{d_{hkl}^0 - d_{hkl}}{d_{hkl}^0}
\]

Equation 5.2
where \(d_{hkl}^0\) is the stress-free lattice spacing and \(d_{hkl}\) is the measured lattice spacing.
Neutron Diffraction was used for residual stress measurements showing the gauge volume size and direction in the cold spray material for each residual stress measurement.

Calculation of the residual stress was performed with two methods, the first traditional approach was to use Hooke’s law to calculate the residual stress and then use a force balance to calculate the final residual stress, and the second is the method outlined by Luzin et al. uses the elastic diffraction strain constants and a set of assumptions to calculate the residuals stress. For the Hooke’s law approach, Young’s modulus and poison’s ratio are used to calculate the residual stress in the material based on the following:

\[
\begin{bmatrix}
\sigma_x \\
\sigma_y \\
\sigma_z
\end{bmatrix} = \frac{E}{(1 + v)(1 - 2v)} \begin{bmatrix}
1 - v & v & v \\
v & 1 - v & v \\
v & v & 1 - v
\end{bmatrix} \begin{bmatrix}
\varepsilon_x \\
\varepsilon_y \\
\varepsilon_z
\end{bmatrix}
\]

Equation 5.3

Using the Hooke’s law approach the residual stress in the x and y direction are identical since the assumption that the strain is biaxial was made. For the approach used by V. Luzin, the following assumptions are made [21]:

1. For a flat geometry, a zero-plane stress state can be assumed with a stress component normal to the cold spray coating to be zero.
2. Coating properties are uniform in the in-plane direction near the center of the coating. However, this will break down at the edge of the coatings and cannot be assumed to be uniform.

3. The stress profile is uniform in both in-plane primary directions. This means that the stress state in cold spray coating can be described by just the in-plane stress component. This means that the stress state can be fully described by measuring just the strain in an in-plane direction and out-of-plane direction.

\[
\sigma_\parallel = \frac{1}{\frac{1}{2}S_2(\text{hkl})} \frac{d_\parallel - d_\perp}{d_0}
\]

Equation 5.4

And

\[
d_0 = \frac{1}{\frac{1}{2}S_2(\text{hkl})} \left( \left( \frac{1}{2}S_2(\text{hkl}) + 2S_1(\text{hkl}) \right) d_\perp - 2S_1(\text{hkl})d_\parallel \right)
\]

Equation 5.5

The constants and parameters used for both methods are given below in Table 5.3.

### Table 5.3 Material constants for residual stress analysis

<table>
<thead>
<tr>
<th>Luzin</th>
<th>Isometric</th>
<th>Young’s Modulus (GPa)</th>
<th>Poisons Ratio</th>
<th>d_0</th>
<th>Threshold to Converge (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>½ S2</td>
<td>196.5</td>
<td>0.27</td>
<td>1.086</td>
<td>50</td>
</tr>
<tr>
<td>-1.59</td>
<td>6.73</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### 5.2.3 Analytical Models of Residual Stress

Analytical Models of the residual stress in cold spray coatings were fitted using MATLAB. The Tsui and Clyne model is a curvature-based model that uses many more physical properties to calculate the residual stress profile after deposition in a material, while the Boruah model is a force-based model that uses the substrate thickness, coating thickness, and intrinsic stress per layer. The parameters used in fitting both models are shown in Table 5.4.
Table 5.4 Input Parameters for Models

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Tsui and Clyne</th>
<th>Boruah</th>
</tr>
</thead>
<tbody>
<tr>
<td>b – Sample Width (mm)</td>
<td>25</td>
<td>12.7</td>
</tr>
<tr>
<td>Youngs Modulus (GPa)</td>
<td>196.5</td>
<td></td>
</tr>
<tr>
<td>Poisons ratio</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>Coefficient of thermal expansion</td>
<td>17.3</td>
<td></td>
</tr>
<tr>
<td>Substrate Thickness (mm)</td>
<td>12.7</td>
<td>12.7</td>
</tr>
<tr>
<td>Intrinsic Stress (MPa)</td>
<td>-400</td>
<td>-450</td>
</tr>
</tbody>
</table>

The Tsui and Clyne Model was originally developed for use with thermal spray and takes into effect many factors. Since the coefficient of thermal expansion is the same for both the substrate and spray material, no residual stress is calculated upon cooling due to a differential in thermal expansion.

5.3.0 Results

5.3.1 CS and LHCS Material Properties

The SS304L powder used for the cold spray deposits showed a spherical shape typical of gas-atomized powders (Figure 5.3a). The cold spray coatings were dense with no apparent porosity.
Tensile tests were performed of the cold rolled SS304L used as the substrate material and compression test were performed on both the wrought material and cold sprayed SS304L. The yield stress of the wrought SS304L material that was used in the spray as the substrate was found to be 270 MPa in both tension and compression. The yield stress of the cold sprayed SS304L was found to be 1200 MPa. The cold spray material was not tested in tension as attempts failed at low stress levels and did not exhibit any plasticity.
Figure 5.4 Stress-Strain Curves for plate used as substrate here. A yield point of 270 MPa was used to determine max residual stress possible in Figure 5.9.

The as-sprayed coatings all exhibited a uniform hardness with a nominal Vickers hardness of 400 HV. The laser heated cold sprayed sample only showed effects due to laser heating on the hardness of the coating in the top 1 mm portion of the deposit. This region showed a gradient in hardness from 250 to 350 HV. The bottom portion of this laser heated sample showed no effects due to laser heating on the hardness of the sample.
Figure 5.5 Hardness results for various conditions show how laser heating softened the material at the deposit's surface (1 mm) but did not bring the hardness back down to that of wrought, likely due to the relatively still fine grain size in the fully recrystallized material.

EBSD of the cold spray microstructure shows the as-sprayed microstructure (Figure 5.5a) at the bottom of the LHCS sample, while the surface of the cold spray samples shows an equiaxed grain structure in the material. Notably, even in the recrystallized microstructure, a bimodal distribution of grains can be seen with a network of much finer grains surrounding areas of larger recrystallized grains. These finer grains are believed to be located at what was previously the prior particle interface between the cold sprayed particles.
Figure 5.6 Inverse pole figure (IPF) maps from EBSD taken with respect to the spray direction (top to bottom) showing A) the cold spray microstructure near the bottom of the LHCS deposit, which exhibits an as-sprayed microstructure and B) the fully recrystallized microstructure from near the surface of the laser heated sample.

5.3.2 Residual Stress Analysis

The strain's longitudinal direction (LD), transverse direction (TD), and build direction (BD) were measured for all four samples. Due to time constraints, only the deposit and the first few millimeters of the substrate were measured in the longitudinal direction. The LD and TD were found to be in good agreement with each other (Figure 5.7), so the data from the TD direction was used to analyze the residual stress at the missing data points in the substrate for the isometric analysis method. The experimental error in the strain measurement was greater in the deposit than in the substrate due to peak broadening caused by the highly deformed microstructure in the cold spray deposit leading to type II and type III microstresses. Type II stresses are discontinuous from grain to grain and self-equilibrate over the length of a grain, and type III microstresses are stresses that exist on the lattice size scale, respectively. These could be stresses varying within a specific grain, such as due to grain subdivision into cell structures. In
this case, the origin of these stresses is misfits, such as crystal defects, with a scale shorter than the grain scale. The Type III category typically includes stresses due to coherency at interfaces and dislocation stress fields. These microstresses represent themselves as peak broadening in diffraction (figure 5.8) [22]. It can be seen that the peak broadening in the cold sprayed material is an order of magnitude greater than in the cold rolled plate due to high values for these Type II and III microstresses. Multiple authors have reported these stresses previously in literature for cold spray [23-25].

Figure 5.7 Residual strain as a function of depth for the LD and TD in the 18-pass as-sprayed material. This data shows that an assumption of biaxial symmetry for strain in the sample is reasonable.
Figure 5.8 Example of the peak broadening in the cold spray material due to type II and type III microstresses. Representative peaks are for the 6-pass BD and the collection time was the same for both peaks.

The in-plane residual stress results profiles showed a maximum compressive residual stress in the cold spray coating of around -400 MPa at a depth between 1-2 mm into the thickness of the coating. A reduction in the compressive residual stress was seen on either side of this most compressive region, with the surface region of the deposit showing a compressive residual stress of around -100 to -200 MPa. Regardless of thickness, the overall stress profiles in the samples are similar, with similar values for the maximum compressive and tensile stresses seen in the samples. It should be noted that it is likely that the gauge volume used was not small enough to capture the gradients that exist in the sample for the 6-pass (2 mm nominal thickness) sample.
Residual stress analysis showed good agreement between the more traditional method of residual stress analysis using Hooke’s law and the measurement of strain in all three primary directions and the method used by Luzin et al. in their works on residual stress analysis except for in the case of the thinnest cold spray specimen.

The residual stress profile due to cold rolling of the substrate material can still be seen in the 2 mm thick coatings. However, this profile is not apparent in the thicker cold spray coatings due to the generation of residual stress via the cold spray process being sufficient to dominate the residual stress profile in the substrate. Residual stress analysis showed good agreement between the more traditional method of residual stress analysis using the strain data from all three primary directions (BD, LD, and TD) and the method used by Luzin et al. in their works on residual stress analysis, which assumes symmetry in the in-plane strain direction. However, in the thinnest cold spray specimen the two methods show agreement in the magnitude of the residual stress in the coating but do not agree to the trend in the coating. This disparity in the trend is likely due to the gauge volume being used for neutron diffraction being insufficient to accurately capture the trend in the coating as only three data points were captured.
Figure 5.9 Residual Stress measurements for cold spray and 750 °C LHCS coatings. The data indicated in red was analyzed using the method by Luzin et al., while the data highlighted in black was analyzed using a more traditional Hooke’s law approach.

5.3.3 Analytical Modeling of Residual Stress

The Tsui and Clyne and the Boruah model both show reasonable agreement with the experimental data, particularly in the case of the 18-pass (6mm) thick coating. Looking at the 18-pass coating, it appears that the Boruah model does a marginally better job at predicting the residual stress in the coating portion of this data, while the Tsui and Clyne does a marginally better job than the Boruah model in the substrate. Overall, both models do a reasonable job of predicting the residual stress in the cold spray coatings; however, both models fail to capture the decrease in compressive residual stress at the surface of these coatings and predict a larger residual stress in the substrate than measured.
Figure 5.10 Fitting of the Tsui and Clyne and Boruah Model to Experimental Data. Hatched grey areas indicate the areas beyond the yield stress measured for the cold-rolled SS304L used in these experiments.
5.4.0 Discussion

The measured residual stresses in the cold sprayed coatings were shown to be compressive in nature, with the magnitude of the compressive residual stress in the coatings being controlled more by the material properties than by the thickness of the coatings. The maximum residual stress seen in the cold spray coatings was just under 400 MPa. It is worth noting that the residual stress showed a compressive trend in all of the as-sprayed materials.

5.4.1 Residual Stress in CS Coatings

Understanding the individual components that make up residual stress in cold spray coatings is essential to understand how residual stresses in cold spray coatings are created and how varying factors may change the final reported residual stress in the coatings. Residual stresses can first be broken down into two buckets, intrinsic stresses that occur during the deposition of the coating and thermal or cooling stresses that evolve during cooling after the cold spray process has been finished. Combinations of these individual stresses combine to create the final residual stress that is measured.

Intrinsic stresses are created during the cold spray deposition by the splatting of individual particles and are comprised of peening stresses, which are compressive, and “quenching” stresses which are tensile. The ratio of these two stresses determines the stresses generated during deposition. Peening stresses are caused by the subsequent impact of powder particles, or splats, onto already deposited material, causing a peening effect in this material. Since cold spray coatings comprise of hundreds of millions of individual particle impacts, each new particle deposited creates a peening stress which extends in depth multiple particles below the deposited particle. Quenching stress is a term originating from thermal spray where molten droplets of metal that are deposited quench and solidify, creating a tensile stress. The term is still
used in the context of cold spray but has a different meaning and is used to describe the tensile stress that results from micro-scale thermal gradients on the scale of a single particle, where each particle cools when impacting the cooler substrate and thermal expansion causes the material to shrink. The simplest way for the intrinsic stresses to be modeled is to model the deposit as layers where each deposited layer has a set residual stress assigned. This assigned residual stress for each layer would need to be determined by calculating the ratio of peening to quenching stress for a material. The limitations of such an approach quickly become apparent as the deposited layer could induce a compressive stress beyond itself into the layers below it due to the peening effects. Due to the continuous nature of these coatings, this difference is limited, and the current approach of assigning a stress to each new layer is reasonable to provide an approximation to the residual stress.

However, some of the observations of the residual stress in measured profiles, namely the uptick in the residual stress near the surface of the coating, may be better calculated using a more realistic implementation of the effects of peening on the substrate. Typical residual stress profiles in shot peening, laser shock peening, and SMAT show a residual stress profile that is compressive in the coating with a u-shaped residual stress profile that reaches the highest compressive residual stresses at maximum depth of 0.1 to 0.2 mm below the surface [26-28]. The maximum compressive residual stress in these coatings is much further below the surface than what is typically seen in shot peening; however, this effect could be stretched out over a longer distance due to the successive material deposition in cold spray that is not seen in shot peening resulting in the smearing of elastic energy over more distance.

The second source of residual stresses in cold spray arises during cooling. These stresses result from a discrepancy in the coefficient of thermal expansion, as well as from temperature
gradients formed when heat is applied to the deposition side of the material from the spray gas and a temperature gradient exist towards the cooler backside of the plate. The coefficient of thermal expansion mismatch residual stresses exists if mismatched materials are used for the deposit and substrate with different thermal expansion coefficients. Upon cooling, one will contract further than the other creating a bending moment in the sample. This coefficient of thermal expansion mismatch does not exist in all materials and will not exist if the same material is used for the substrate and coating. The other cooling stress exists in all materials and is caused by a temperature gradient existing in the material after deposition, with the top being hotter than the bottom of the sample. This thermal gradient will cause the surface of the deposit to contract more upon cooling than the bottom of the material, putting the surface into tension and the bottom into compression. This effect is not accounted for in thermal spray models or in any current cold spray analytical residual stress models.

Figure 5.11 Graphic of residual stress evolution in Cold Spray coatings, adapted from work by V. Luzin [60]. A ratio of peening and quenching stress is generated during the cold spray deposition process. After deposition, the residual stress from thermal coefficient mismatch is added, if any,
as well as a stress due to a temperature gradient. Finally, these stresses are added up to produce the final stress state.

5.4.2 Analytical Modeling of Residual Stress

Analytical models provide an advantage over numerical models as they provide closed-form solutions that offer insights into the fundamental behavior of the system, and they often require less computational resources, making them computationally efficient. The two analytical models used in this paper, Tsui and Clyne and Boruah models, are currently the only two models which have been used for cold spray.

The Tsui and Clyne model is based on beam theory and works in two parts. First, “layers” are added to a substrate one at a time with a set stress per layer. This is called quenching stress in the Tsui and Clyne model, but Luzin et al. have adapted this model by putting compressive stress here to simulate peening stress. After each layer is added, the force balance, beam bending, and the residual stress at each layer's center and the substrate's top and bottom are calculated. This approach is repeated until the deposition is finished. After this, the thermal mismatch stress due to cooling is calculated and added to the residual stresses from deposition. This makes up the final residual stress. Again, this model does not account for the thermal gradient to the deposition.

The Boruah model seeks to simplify the current analytical models by providing a simple and efficient analytical model that requires considerably fewer material property inputs. The Boruah model uses a force and moment equilibrium calculation to calculate the proposed residual stress compared to the curvature-based model of the Tsui and Clyne method. The Boruah method has proven to have reasonably good agreement with data from literature using a much more simplified approach than other models. Since this model’s main input parameter is the stress in a newly deposited layer, the authors outline that further testing can link the cold
spray parameters to this residual stress per layer to create a more predictive model of residual stress.

Both models suffer from similar drawbacks, namely the lack of ability to predict the extent of the peening effect during deposition and the lack of ability to account for material yield both in the coating as well as the substrate. The current areas of development that are needed for analytical models of residual stress in cold spray to be more useful include the following:

- The prediction of the extent of the peening effect in cold sprayed material
- Consideration of yield stress in the material
- Residual Stress due to thermal gradient upon cooling

The peening stress effect in cold spray can range from above the yield stress of wrought material, such as seen here for SS304L, to only a fraction of the yield stress of similar wrought material, as is seen in many aluminum residual stress measurements [6, 9, 21, 23, 24, 29]. This effect is compounded by the fact that materials that work harden readily will increase the material's compressive yield strength, allowing them to support higher loads, such as is the case for SS304L in the current work. The prediction of the extent of this peening stress is not straightforward and is likely a combination of the spray conditions as well as the deformation mechanisms. Work by Hassani-Gangaraj et al. on particle impact-bonding modes could provide some insight into the deformation type and help to calibrate this parameter [30]. Hassani-Gangaraj works to create a predictive map based on LIPIT work to predict whether impacting particle with a substrate will experience penetration where the majority of deformation is in the substrate, splatting where the deformation occurs mainly in the impacting particle or co-deformation where both materials experience deformation. This approach could be predictive of the level of peening that occurs, where materials that experience more penetration may have
higher levels of peening effects. Another approach to the extent of the peening effect would be to use an existing shot peening model to estimate the magnitude of the peening effect. The limitation of using existing peening models is that the impacting particle remains and has some level of deformation that occurs, absorbing some of the impact energy.

It can be seen from the measurements of residual stress and the tensile properties of the base materials that both models (Tsui-and-Clyne and Bourah) estimate a larger residual stress than is possible in both the 12-pass and 18-pass samples. This is because both models assume linear elastic behavior and cannot account for plastic deformation in the material. The same limit for the residual stress of the yield strength applies in the cold spray material, though the yield stress in the cold spray material may be harder to calculate due to the difficulty of making freestanding cold spray test samples. It is also worth noting that cold spray is likely to perform better in compression than in tension since the failure of cold spray in tension tends to be crack growth and the opening of defects that will be closed in compression. This is likely to affect material which may form a tensile residual stress in the coating or upon laser heating where the compressive stress is converted to tensile stresses in the coating. The residual stress in the cold spray coatings is well above the yield stress in cold rolled material. This is due to the high work hardening coefficient of SS304L leading to high hardness and what is likely a corresponding increase in the yield strength of the cold spray material. The use of in-situ residual stress measurements, as has been performed by Suhonen et al. and Brown et al., could be useful for the determination of how yield occurs in the coatings during the cold spray process as well as the ratio of peening to quenching in the cold spray coatings [3, 31]. The work by both authors showed that either tensile or residual stresses could be created during the cold spray process.
depending on the ratio of peening to quenching stresses, and showed that depending on the CTE mismatch that additional tensile or compressive stresses could be added after deposition.

The easiest possible additional residual stress to calculate would be the residual stress that occurs from a temperature gradient in the material upon cooling. The simplest way to model this effect would be to use the spray gas temperature as the temperature on the surface of the deposit and assume a temperature for the backside of the deposit based on the clamping setup. The steady-state temperature could then be calculated, and subsequently, the resulting residual stress from the thermal gradient. It should be noted that the temperature on the surface of the plate is likely slightly lower than the spray gas temperature, but it has been seen previously that the surface temperature of the plate follows the spray gas temperature within reason. Experimentally the effect of a temperature gradient on the residual stress in cold spray has been observed with work by Marzbanrad et al., where they found that heating and cooling of the substrate material could affect the residual stress profile in the cold spray coating [32].

5.4.3 Effect of Laser Heating on Residual Stress

Laser heating of cold spray coatings is desired to modify the microstructure of cold spray back to that of a wrought-like condition, principally to enhance the material's ductility. However, laser heating changes the compressive residual stresses on the surface of the cold spray coating to a tensile stress state, which could be detrimental to the coating's stress corrosion cracking resistance. Therefore, it is worthwhile to compare the residuals stress from laser-heated cold spray with other additive manufacturing processes such as WAAM, DED, LPBF, and thermal spray to understand better how the cold spray process stacks up to competing processes in the additive repair world.
Additive manufacturing processes such as WAAM, DED, LPBF, and thermal spray tend to generate tensile residual stresses due to the melting and solidification of material during the deposition process. Residual stress trends in fusion-based additive manufacturing processes exhibit unique characteristics influenced by the specific techniques involved. In WAAM, the deposition of molten metal induces thermal gradients, resulting in residual stresses that generally tend to be tensile, especially near the bond line between the deposited material and the substrate [33]. In the DED processes, localized heating and cooling cycles give rise to complex stress distributions, with the type of residual stress being dependent on factors such as material deposition strategy and cooling rates. While the stresses can be either tensile or compressive, they often manifest as compressive in the core of DED processed material and tensile on the outer edges of the material [34]. LPBF experiences rapid heating and solidification, leading to high temperature gradients and rapid cooling rates, which commonly produce tensile residual stresses at the surface with compressive stresses deeper into the build [35]. Additionally, specific laser scanning patterns and material properties can influence the magnitude and distribution of these stresses. In thermal spray, where particles are deposited at high velocities, the mechanical impacts can create compressive residual stresses within the coating; however, unlike in cold spray, the quenching stress can induce significant tensile residual stresses in the coatings due to material shrinkage during solidification [36].

Converting the compressive residual stresses in cold spray to tensile after laser heating can potentially open defects in the cold sprayed material. The compressive mechanical test on freestanding cold spray in this paper shows that cold spray has the potential to carry large loads in compression. However, due to how cold spray is built up, defects such as porosity, oxides, or hairline cracks have a significant potential to exist at the interfaces between the prior particles.
When these defects are put in tension, they can open, significantly reducing the load that the cold spray material can carry in tension as the failure mechanism becomes controlled by these defects rather than the material properties of the cold sprayed material.

5.5.0 Conclusions:

The residual stress distributions and evolution as a function of cold spray coating thickness were investigated in both the coating as well as the substrate using neutron diffraction. The primary findings of the paper are as follows:

- The residual stress in cold sprayed SS304L was dominated by the peening effects of cold spray, creating a large compressive residual stress in the coating.
- The cold spray deposit was found to be able to support a compressive residual stress of 400 MPa due to the increased hardness of the material from cold work during the cold spray process.
- The residual stress gradient in the substrate was shown to be limited by the yield stress in both the 12 pass (4 mm) and 18 pass (6 mm) samples.
- The measured residual stress in the system varied greatly from analytical models (Tsui-and-Clyne and Boruah) due to these models' lack of ability to account for yielding in the material.
- It was proposed that an additional stress due to the temperature gradient at the end of the deposition process must be added to the current models for more accurate residual stress predictions.
- Laser heating induced significant tensile stresses in the cold sprayed material, with over 400 MPa seen at the surface of the coating.
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References


CHAPTER 6 : SUMMARY, OUTLOOK, AND CONCLUSIONS

Summary

The use of cold spray for the deposition of stainless steel 304L coatings was investigated. Cold Spray provides increased portability with a lower heat input over other additive repair technology. However, the high amount of cold work seen in cold spray coatings can result in coatings with less-than-ideal mechanical properties. Additionally, concerns have been raised about the possibility of strain induced martensite formation, as it is detrimental to both the mechanical and corrosion properties of a cold spray coating. For this reason, the laser heated cold spray (LHCS) process was investigated for the stainless steel cold spray coatings to recrystallize the cold spray microstructure and improve the coating quality of SS304L cold spray after deposition.

In this dissertation, key areas of research are investigated to better understand the cold spray process of SS304L and the effects of laser heating on the cold spray material. These key areas are an investigation into how the large amounts of cold work, high strain rates, and elevated temperatures in SS304L affect the formation of strain induced martensite, an investigation into how laser heating affects the microstructure and mechanical properties, the dislocation density in cold sprayed 304L and the kinetics of recrystallization in this material, and finally a look into the residual stress in cold spray coatings and the effect of laser heating on the
residual stress in the coating. Future work is recommended based on the findings in this dissertation as well.

6.1 Strain Induced Martensite

The first paper investigates the strain induced martensite transformation in cold sprayed SS304L and looks at how cold spray can suppress this transformation in the material. It is known that 304L stainless steel can rapidly form large amounts of martensite with increasing strain. Additionally, cold spray material has large total strains due to the deformation process that is essential for cold spray to work. At the total strain seen in cold spray of 0.5 to 0.6, an expected formation of almost 20% could be expected at room temperature from work by Angel et al. However, the results indicate that the extent of martensite transformation is primarily influenced by the spray gas temperature. Neutron diffraction data showed a slight increase in the BCC/BCT phase (martensite) in the cold spray material produced at 350 °C of 0.4%. Meanwhile, a more significant increase of 30% was seen by using a spray gas temperature of 25 °C. The findings suggest that higher spray temperatures can potentially reduce the formation of strain-induced martensite without the need for post-heat treatments.
Figure 6.1 Graph of strain induced martensite percentage at various temperatures as a function of strain. Replotted from the work of Angel et al.

Additionally, BCC/BCT phases in the as-received powder are attributed to the high cooling rate during atomization, which can cause martensite formation. It is unclear whether this initial martensite phase is retained in the deposits or if elevated spray temperatures can further reduce or prevent its formation. Consistent with existing literature, deposits made from powder without the initial BCC phase did not show BCC in the deposit, while deposits with BCC in the powder exhibited BCC in the deposit, indicating a reduction in BCC phase fraction through cold spray.

Furthermore, the change in spray gas temperature from 350 °C to 25 °C showed a significant change in the microstructure at the prior particle interface region. Previous literature suggests that ultrafine grains at particle interfaces are a result of dynamic recrystallization caused by ultra-high strain rate deformation. Various mechanisms have been proposed, including
continuous dynamic recrystallization (CDRX), geometric dynamic recrystallization (GDRX), rotational dynamic recrystallization (RDRX), progressive subgrain misorientation recrystallization (PriSM), static recovery (SRV), and static recrystallization (SRX). The presence of these mechanisms in cold spray is still debated. The low stacking fault energy of SS304L supports static recrystallization (SRX) over static recovery (SRV) in this material. It has also been shown that decreasing the grain size in SS304L promotes CDRX. Diffusion-based rotational dynamic recrystallization has been reported in cold sprayed materials, suggesting that grain boundary reorientation can occur at high strain rates. The PriSM mechanism proposes mechanically driven lattice rotations within adiabatic shear bands, leading to recrystallization without relying on diffusion. The exact mechanism for dynamic recrystallization in cold spray remains unclear and requires further investigation, but the absence of recrystallized grains in lower-temperature sprays adds context to the proposed mechanisms.

6.2 Dislocation density in cold sprayed material

The second paper analyzed the dislocation density in cold sprayed SS304L as a function of position and temperature in the cold sprayed SS304L using neutron diffraction combined with the convolutional multiple width profile (CMWP) method. The measured dislocation density in the as-sprayed coatings was found to be $5 \times 10^{15} \text{ m}^{-2}$, similar to previous studies on cold spray coatings. The recrystallization temperature for cold spray coatings was found to be approximately 725 °C. Furthermore, it was shown that the microstructure resulting from the cold spray process increases recrystallization kinetics in the cold spray coatings. In LHCS, this results in rapid recrystallization of the coatings with short heating times. Additionally, it was seen that Cold spray coatings exhibit a two-step process of recrystallization, with the prior particle interface recrystallizing first, followed by the prior particle interior. The kinetics at the prior
particle interface is believed to be higher than in the overall cold sprayed material. The increase in recrystallization kinetics at the prior particle interface has implications for corrosion and diffusion kinetics.

In-situ heating of freestanding cold spray during neutron diffraction allowed for determining the dislocation density and crystallite size as a function of temperature using the CMWP method. Additionally, the BCC phase fraction was determined from this data. The in-situ heating combined with DSC results showed distinct peaks for recovery and recrystallization in the CS material centered around 575 °C and 730 °C, respectively, with the BCC to FCC transition occurring between the peaks around 670 °C.

6.3 Effects of laser heating on cold spray microstructure

The third paper looked at changes in the microstructure of cold spray SS304L after laser heat treatment at 750 °C and 950 °C. It was seen that the samples heated at 750 °C only recrystallized at the very surface of the material while that laser heated at 950 °C was recrystallized through over half of the cold spray material. A hardness value for the as sprayed coatings was measured at 450 Vickers hardness. After laser heating a minor reduction in hardness was seen in the 750 °C LHCS material, and a reduction in hardness to 250 Vickers hardness was seen in the 950 °C LHCS material.

The Hall-Petch equation is used to estimate the contribution of grain refinement to the changes in hardness. However, certain assumptions are made in this estimation, such as averaging the hardness values over specific sample thickness and approximating the grain size in regions not measurable by EBSD using the average crystallite size from XLPA. The calculated average grain size follows the Hall-Petch relationship, indicating a proportional relationship
between grain size and hardness. The limitations of this approach are noted, including the bimodal microstructure of the material and the potential variability in hardness contributions from different areas. Additionally, the Taylor equation is used to estimate the contribution of dislocation density to hardness, but the data does not strongly correlate with the measured dislocation densities. The study suggests that the reduction in grain size has a greater impact on hardness than the increase in dislocation density, but further experiments are needed to confirm this. The presented hardness values align with previous literature on cold sprayed SS304L material, indicating a significant recrystallization in the early stages of heat treatment.

6.4 Residual Stress in cold sprayed material

The final paper looks at the residual stress in cold spray as a function of coating thickness as well as the effects of LHCS on the residual stress as measured via neutron diffraction. Stainless steel 304L cold spray coatings with 2, 4, and 6 mm thickness were made onto 1/2” thick 304L substrates. Compressive residual stresses were found in all the cold spray coatings with the similar maximum residual stresses regardless of coating thickness of -400 MPa. Measurements of the yield stress of the substrate material in both tension and compression revealed the maximum residual stress in the substrate the be controlled by the yield stress of the material, which was reached in both the 4 and 6 mm thick coating, with a tensile stress at the interface in the substrate of 270 MPa and a compressive stress on the backside of the substrate of 270 MPa. The yield stress in the cold spray coating was measured in compression to be 1.05 GPa, while a maximum compressive residuals stress in the coatings was measured at approximately 400 MPa.
In addition to measuring the residual stress in the coatings, the individual components of residual stress that combine to form the final residual stress profiles is discussed. It can be seen in figure 6.2 that a ratio of peening stress and quenching stress is generated during the cold spray process. Peening dominated material creates a compressive stress which is seen in most cold spray material. However, some quenching stress can be created due to the shrinkage of hot particles to cooler temperatures after deposition, which creates a tensile stress. After the deposition process, some temperature gradient will exist in the coating and substrate. Upon cooling, this will generate a residual stress that is added to the created during the deposition process. Additionally, if the coating material and substrate have mismatched coefficients of thermal expansion, this can generate an additional residual stress in the coatings that need to be accounted for. The sum of all these stresses results in the final residual stress in the coatings.

Figure 6.2 Generation of residual stress in cold spray coatings. Adapted and modified from work by V. Luzin.
Analytical models of the generation of this residual stress can help us to understand the formation of these residual stresses. Currently, two analytical models have been used in literature, the Tsui and Clyne model and the Boruah model. Both models do a reasonable job of estimating the residual stresses in cold spray coatings, as has been seen in literature. However, neither of these models account for material yield, or plastic flow, if the yield stress is exceeded, such as that seen in the current work in the substrate. Additionally, these models fail to consider the presence of residual stresses that arise during cooling due to temperature gradients. Therefore, it was proposed that if the yield in the material could be accounted for, as well as the residual stress that results from a temperature gradient, analytical models could more accurately predict the residual stress for more materials.

**Recommendations for Future Work**

Recommendations for future work around this dissertation focus on three aspects of the cold spray process: the increase in recrystallization kinetics in the cold spray material, the accumulation of residual stress, and the optimization of cold spray and laser heating parameters using the information learned. These three areas of research are closely related to each other as the increase in recrystallization kinetics in the cold spray material, and the understanding of the residual stress in the coatings are both needed in order to fully optimize the cold spray and laser heating process for the best material properties and minimal residual stress in the coating.

The increased kinetics of recrystallization in cold spray, particularly at the prior particle interface, are poorly understood in cold spray. While this dissertation has shown the increase in recrystallization kinetics in the cold spray coating and at the interface, the kinetics and mechanisms of recrystallization at the interface are poorly understood. This work proposes that
the smaller grain size and increased kinetics at the prior particle interface may lead to the increased kinetics and resulting necklacing of recrystallized grains upon rapid heating. However, the possibility of dynamically recrystallized grains at the prior particle interface acting as the initiation site for grain growth at the interface, and eliminating the need for new grains to be recrystallized is also discussed. In order to determine the cause for this rapid recrystallization at the interface, in-situ heating experiments could be performed in a TEM using a DENS chip that can provide in-situ heating. This would allow for a full understanding of how the microstructure at the interface evolves with heating and allow for the determination of where recrystallization begins in various parts of the cold spray microstructure.

Chapter 5 discusses the changes to better model the residual stress in cold spray coatings. These changes involve the addition of stresses due to macro scale thermal gradients after the deposit has finished and the addition of material yield into the model. The development of these models is a natural follow-up to the work shown in this dissertation. Once the improved model is developed and shown to accurately describe the residual stress in cold spray coatings in literature, more data on various material combinations must be collected to validate the model. In addition to developing a better analytical model to better describe the residual stress in cold spray coatings, work can be performed to predict the ratio of peening to quenching stress in cold spray coatings. Prediction of these values would allow the residual stress model to transform from a descriptive model to a predictive model of the residual stress in the coatings.

Finally, the optimization of cold spray and laser heated cold spray parameters can be studied based on the other findings in this study. Most of the current literature work on the optimization of cold spray coatings is focused on the cold spray parameters and is based on experimental studies which require the manufacturing and analysis of numerous samples using
many analysis techniques. The modeling of heat created by a laser and the flow of heat in a part for LHCS is simple to model. While possible the simulation of LACS is a more complicated problem due to the need to account for material addition during the simulation. If the residual stress in the material and the recrystallization kinetics in the cold spray coatings can be modeled, then models could be used to optimize coating properties without manufacturing samples.

In summary, the three recommendations for areas of future work are:

- The development of general residual stress model for CS by incorporating plasticity and macro thermal gradients into the existing models.
- Investigation of kinetics at prior particle interface via in-situ TEM heating.
- Development of optimized cold spray and heating profiles to reduce residual stress generation while still achieving recrystallization through the simulation of heat transfer during LHCS.

Conclusions

In summary, the purpose of this dissertation research was to examine the potential of utilizing cold spray and LHCS SS304L for repairing stress corrosion cracking in dry storage casks for spent nuclear fuel. The use of cold spray for this purpose raises two important considerations: the microstructural and mechanical aspects of the coatings. These factors can have an impact on the corrosion and mechanical properties of the coatings, ultimately influencing the durability of the cold spray repair. Of particular concern is the unique bimodal cold spray microstructure, as previous research has shown that the presence of ultrafine grains at the interface of the prior particles can increase corrosion in those areas. Furthermore, the cold
work involved in the cold spray process leads to high hardness, reduced ductility, and significant residual stresses. Here, we present the key findings of this investigation:

1. This research has now shown that the elevated temperatures during a typical cold spray (350 °C) suppress the strain induced martensite transformation. At lower temperatures, e.g. room temperature, significant strain induced martensite (28.1%) can be formed through the process, which is detrimental to the corrosion properties of the coating.

2. Additionally, reducing the spray temperature resulted in fewer ultrafine grains at the prior particle interface than is typically seen in cold spray performed at higher spray gas temperatures.

3. It was shown that cold sprayed material exhibits increased recrystallization kinetics that allows for rapid recrystallization of the whole cold sprayed material in tens of seconds with minimal heat input through laser heating.

4. It was shown that the recrystallization temperature for cold sprayed SS304L during rapid heating was 730 °C, and that the prior particle interface regions showed increased kinetics over that of the prior particle interior due to the ultrafine grains and higher amounts of cold work in these areas.

5. Both CS and LHCS generate residual stresses. These residual stresses can be compressive or tensile, which can have either beneficial or detrimental effects on the overall performance of the coating. In the case of cold spray, the deposition process's peening effects lead to the generation of compressive stresses. In the substrate, the residual stress reached the material's yield strength (tensile at the interface, compressive at the backside) with as little as 4 mm thick of cold spray layers deposited.
6. In this work our experimental, neutron diffraction-based measurements identified that the current limitation of the existing analytical models for predicting residual stress is the lack of plasticity in these models. Modifications were proposed to existing models to create a better numerical residual stress model in cold spray.