IN SITU EVALUATION OF SUPERSOLIDUS LIQUID PHASE
SINTERING PHENOMENA OF STAINLESS STEEL 316L:
DENSIFICATION AND DISTORTION

A Thesis in
Engineering Science and Mechanics
by
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Supersolidus liquid phase sintering (SLPS) is a variant of liquid phase sintering. In SLPS, prealloyed powders are heated between the solidus and liquidus temperature of the alloy. This thesis focuses on processing of stainless steel 316L via SLPS by adding boron. Various amounts of boron were added to study the effect of boron on densification and distortion. The sintering window for water atomized 316L with 0.2% boron ranges from 1430 to 1435°C and 1225 to 1245°C for water atomized 316L with 0.8% boron. The rate of change of liquid content with temperature $\frac{dV_L}{dt}$ decreases from 1.5%/°C to 0.1%/°C for an increase in boron content from 0 to 0.8%, giving a wider range and better control during sintering.

Further, effect of boron on mechanical properties and corrosion properties was researched. It was possible to achieve tensile strength of 476±21 MPa and an yield strength of 250±5 MPa with an elongation of 15±2% in water atomized 316L with 0.8% boron. Fracture analysis indicates the presence of a brittle boride phase along the grain boundary causing intergranular fracture resulting in poor ductility.

The crux of this thesis discusses the evolution of apparent viscosity and its relation to the microstructure. Beam bending viscometry was successfully used to evaluate the \textit{in situ} apparent viscosity evolution of water atomized 316L with 0.2 and 0.8% boron additions. The apparent viscosity drops from 174 GPa.s at 1200°C to 4 GPa.s at 1275°C with increasing fractional liquid coverage in the water atomized 316L with 0.8% boron. The apparent viscosity calculated from bending beam and was used as an input into a finite element model (FEM) derived from constitutive equations and gives an excellent fit between simulation and experiment.

The densification behavior of boron doped stainless steel was modelled using Master Sintering Curve (MSC) (based on work of sintering) for the first time. It is proven that MSC can be used to identify change in densification rate upon liquid formation during SLPS.
# Table of Contents

List of Figures viii  
List of Tables xvi  
List of Symbols xvii  
Acknowledgments xix  

## Chapter 1
**Introduction**  
1.1 Introduction ................................................. 1  
1.2 Outline of Thesis ............................................ 2  

## Chapter 2
**Background**  
2.1 Liquid Phase Sintering ........................................ 3  
2.2 Supersolidus Liquid Phase Sintering (SLPS) ..................... 6  
  2.2.1 Densification Mechanism during SLPS ....................... 8  
2.3 Effect of Processing Variables ................................. 10  
  2.3.1 Particle Size and Distribution ............................. 10  
  2.3.2 Internal Powder Microstructure ............................ 11  
  2.3.3 Green Density ............................................. 11  
  2.3.4 Role of Sinter Temperature and Liquid Fraction .......... 12  
  2.3.5 Additives ................................................ 14  
  2.3.6 Sintering Atmosphere and Sintering Time ................. 16  
  2.3.7 Heating Rate ............................................. 17  
2.4 Modelling of Densification during SLPS ....................... 17  
  2.4.1 Rheology Considerations ................................. 21
Chapter 2

2.5 Distortion during SLPS .................................................. 23
2.6 Corrosion of PM Steels .................................................. 25
2.7 Master Sintering Curve .................................................... 27
   2.7.1 Construction of MSC .............................................. 29
2.8 Significance of Research ................................................. 32

Chapter 3

Experimental Procedures .......................... 34

3.1 Powder Characterization ................................. 34
   3.1.1 Particle Size ..................................................... 34
   3.1.2 Particle Shape ................................................... 35
   3.1.3 Powder Microstructure ....................................... 36
   3.1.4 Apparent Density .............................................. 36
   3.1.5 Tap Density ...................................................... 37
   3.1.6 Pycnometer Density ........................................... 38
3.2 Alloy Composition ................................................... 39
3.3 Powder Preparation ................................................. 40
   3.3.1 Powder Mixing .................................................. 40
3.4 Compaction ............................................................ 40
3.5 Pressing Gas Atomized Powders ....................... 41
3.6 Debinding ............................................................... 41
3.7 Sintering Procedure .................................................. 42
3.8 Dilatometer Study ..................................................... 42
3.9 Distortion Quantification ......................................... 43
   3.9.1 CMM ............................................................... 44
3.10 Synchrovision ......................................................... 45
3.11 Metallography ........................................................ 46
3.12 Image Processing .................................................... 47
   3.12.1 Image Analysis ................................................ 48
3.13 Tensile Testing ....................................................... 49
3.14 Corrosion Testing .................................................... 49

Chapter 4

Results ......................................................... 51

4.1 Melting ............................................................... 51
4.2 Densification ......................................................... 59
4.3 Effect of Boron Content on Densification ............. 63
   4.3.1 Dilatometer Results ........................................... 63
   4.3.2 Effect of Green Density on Densification ................... 66
4.4 Microstructural Evolution ....................................... 67
4.5 Distortion .............................................. 70
  4.5.1 Comparison of Densification and Distortion in Water and
Gas Atomized Powders and their Mixtures ............. 72
  4.5.1.1 In situ Distortion Observation ................. 72
4.6 In situ Observation of Sintering of Hand Pressed and Cold Isostatically Pressed Compacts .......... 73
4.7 Bending Under Gravity .................................. 78
4.8 Beam Bending Viscometry ............................... 78
  4.8.1 Bending Beam Theory .............................. 78
  4.8.2 Apparent Viscosity of Boron Doped Stainless Steel ... 82
  4.8.3 Accuracy and Sources of Error .................... 84
4.9 Mechanical Properties .................................. 85
4.10 Fracture Analysis ..................................... 90
4.11 Corrosion Studies ..................................... 91

Chapter 5
Discussion .................................................. 98
  5.1 Densification and Distortion ........................... 98
  5.2 Effect of Microstructural Evolution on Densification and Distortion 99
    5.2.1 Liquid Volume Fraction .......................... 100
    5.2.2 Contiguity and Fractional Grain Boundary Coverage .... 103
    5.2.3 Grain Size ...................................... 106
    5.2.4 Grain Size Distribution .......................... 108
    5.2.5 Second Phase Identification ....................... 112
  5.3 Apparent Viscosity Evolution .......................... 115
    5.3.1 Relating Apparent Viscosity Evolution to Microstructure 118
  5.4 Distortion Mechanisms ................................ 119
    5.4.1 Lubricated Flow ................................ 122
    5.4.2 Diffusional Flow ................................. 122
    5.4.3 Deformation by Grain Boundary Sliding ............ 122
    5.4.4 Derivation of Creep Equation ...................... 123
    5.4.5 Presence of Yield Stress ........................ 126
  5.5 Application of Master Sintering Curve Concepts to SLPS 127
    5.5.1 MSC for Grain Growth ............................ 134
  5.6 Density-Distortion-Mechanical Properties ............... 134
  5.7 Corrosion of 316L Stainless Steel ...................... 137
  5.8 Finite Element Simulation of Bending and Viscosity Evolution Based on Experimental Measurements of Viscosity ..... 141
  5.9 Sinter Factor ......................................... 143
Chapter 6
Conclusions 144

Bibliography 147

Appendix A
Data 164

Appendix B
Yield strength measurement of a semisolid according to Pashias [152] 165

Appendix C
Modelling 168
C.1 Constitutive Equations for Sintering . . . . . . . . . . . . . . . . . . . . . . . . . . 168
C.2 Finite Element Modelling . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 170
List of Figures

2.1 Schematic of basic densification process during SLPS. .......................... 7
2.2 The geometry of a nodoid liquid profile which connects two unequal sized spheres. ................................................................. 9
2.3 Phase diagram characteristics of SLPS alloys. ................................. 12
2.4 Evolution of microstructure during supersolidus sintering of prealloyed powders [1]. .............................................................. 19
2.5 Sintering curve for SLPS illustrating the sinter window concept. ... 24

3.1 SEM micrograph showing the shape of as-received gas atomized stainless steel 316L powder. ................................................. 36
3.2 SEM micrograph showing the shape of as-received water atomized stainless steel 316L powder. ............................................. 37
3.3 SEM micrograph showing the microstructure of as-received gas atomized stainless steel 316L powder. .................................. 38
3.4 SEM micrograph showing the microstructure of as-received water atomized stainless steel 316L powder. .............................. 39
3.5 Schematic showing the CM horizontal furnace used for sintering. .. 42
3.6 Schematic of the dilatometer. ......................................................... 44
3.7 Schematic of the co-ordinate measuring machine probe measuring compact profile. .............................................................. 46
3.8 Schematic of Synchrovision to observe in situ bending. ................. 47
3.9 Schematic potentiodynamic anodic polarization wiring diagram. ... 50

4.1 DTA plot showing melting behavior of as-received water atomized 316L stainless steel powder. ............................................. 51
4.2 DTA plot showing melting behavior of as-received gas atomized 316L stainless steel powder. ............................................. 53
4.3 DTA plot showing melting behavior of as-received water atomized 316L stainless steel powder with different amounts of boron. The % is indicative of wt.% boron added. ........................................... 53
4.4 DTA plot showing melting behavior of as-received gas atomized 316L stainless steel powder with different amounts of boron. ........ 54
4.5 DTA plot showing melting behavior of a 70:30 mixture of water and gas atomized 316L stainless steel powders with different amounts of boron. ................................................................. 55
4.6 DTA plot showing melting behavior of as-received water atomized 316L stainless steel powder with boron additions upto 5 wt.% .... 56
4.7 First heat melting temperatures for water atomized 316L powders with boron additions upto 5 wt.%. .................................................. 56
4.8 Dilatometric plot of shrinkage of water atomized 316L stainless steel powder heated at 10°C/min to 1420°C. ...................... 59
4.9 Dilatometric plot of shrinkage versus temperature for water atomized 316L stainless steel powder with 0.2 wt.% boron sintered at 5°C/min to maximum sintering temperature. ......................... 60
4.10 Dilatometric plot of shrinkage rate versus temperature for water atomized 316L stainless steel powder with 0.2 wt.% boron sintered at 5°C/min to maximum sintering temperature. ......................... 60
4.11 Dilatometric plot of shrinkage versus temperature for water atomized 316L stainless steel powder with 0.2 wt.% boron sintered at different heating rates. ...................................................... 62
4.12 Dilatometric plot of shrinkage rate versus temperature for water atomized 316L stainless steel powder with 0.2 wt.% boron sintered at different heating rates. ...................................................... 62
4.13 Log shrinkage versus log time for water atomized 316L stainless steel powder doped with 0.2 wt.% boron showing the effects of heating rate on shrinkage kinetics. ............................................. 63
4.14 Dilatometric plot of shrinkage versus temperature for water atomized 316L with different amount of boron additions. .............. 64
4.15 Dilatometric plot of shrinkage rate versus temperature for water atomized 316L with different amount of boron additions. ........ 65
4.16 Sintered density of water atomized 316L powder with different amounts of boron sintered at 5°C/min in hydrogen atmosphere for 30 min. .. 65
4.17 Dilatometric plot of shrinkage versus temperature for water atomized 316L with 0.2 wt.% boron heated at 5°C/min to 1400°C with different starting green density indicated as percent of theoretical. .. 66
4.18 Density and distortion versus sinter temperature for water atomized 316L with 0.2 wt.% boron heated at 5°C/min to the peak sintering temperature in hydrogen with different starting green densities indicated as percent of theoretical. The hold time was 30 min. TD-%theoretical density 67

4.19 Microstructure of water atomized stainless steel powder with 0.2 wt.% boron sintered at 1350, 1400, 1425, 1430, 1435, and 1440 °C read left to right from top, respectively. The samples were sintered in hydrogen for 30 min. 68

4.20 Microstructure of gas atomized stainless steel powder with 0.2 wt.% boron sintered at 1300, 1350, 1375, and 1440 °C read left to right from top, respectively. The samples were sintered in hydrogen for 30 min. 69

4.21 Plot showing sinter density and distortion parameter versus temperature for water and gas atomized 316L with 0.2 wt.% boron alloy sintered for 30 min. The heating rate was 5°C/min and the atmosphere was hydrogen. 71

4.22 Photograph showing water atomized 316L with 0.2 wt.% boron sintered at various temperatures for 30 min in hydrogen atmosphere. Notice distortion at 1440°C, and complete loss of shape at 1450°C. The distortion shape shown is representative of that seen in the case of other alloys. 71

4.23 Plot showing density and distortion parameter versus temperature for water atomized, gas atomized and a mixture of 70:30 water and gas atomized powders mixed with 0.8 wt.% boron heated at 5°C/min to peak sinter temperature. The hold time is 30 min. 73

4.24 In situ images during sintering of water (left) and gas (right) atomized stainless steel powders with 0.2 wt.% boron. Top left-1250°C right-1350°C, middle left-1365°C right-1375°C, bottom left-1400°C right-1425°C. The compacts were heated at a constant heating rate of 5°C/min to the peak temperature. 74

4.25 In situ images during sintering of water (left) and gas (right) atomized stainless steel powders with 0.2 wt.% boron at 1440°C with hold time. Distortion is visible in gas atomized powder compact. Time scale-0, 2, 3, 4, 5, 6, 7, and 30 min read left to right from top. 75

4.26 Plot showing distortion parameter versus time for gas atomized powders mixed with 0.2 wt.% boron at 1440°C. 76
4.27 In situ images during sintering of cold isostatically pressed (right) and hand pressed (left) water atomized steel powders with 0.2 wt.% boron. Temperature scale- 1300°C, 1350°C, 1400°C, and 1430°C read left to right from top.

4.28 In situ images during isothermal sintering of cold isostatically pressed (on the right) and hand pressed (on the left) water atomized steel powders with 0.2 wt.% boron at 1437°C. Time scale-0, 2, 4, 7, 10, 15, 20 and 30 min read left to right from top.

4.29 In situ bending pictures of water atomized 316L with 0.2% boron showing beam deflection at different temperatures along the sinter cycle. Temperature scale-1200°C, 1260°C, 1320°C, and 1380°C read left to right from top.

4.30 In situ bending pictures of wrought 316L with showing beam deflection at different temperatures. Top left-1260°C hold time of 0 min, right- 1440°C with a hold time of 30 min.

4.31 Plot of mid-point deflection versus temperature for a water atomized 316L with 0.2% boron beam. The bending experiment is performed at 5°C/min in 100% hydrogen.

4.32 Schematic showing the bending beam placement in the furnace.

4.33 Mid point deflection versus temperature during sintering of stainless steel 316L with 0.2 wt.% boron during heating at 5°C/min in hydrogen atmosphere.

4.34 Density versus temperature during dilatometry on a water atomized stainless steel 316L with 0.2 wt.% boron compact. The heating rate was 5°C/min and the atmosphere was hydrogen. The thermal expansion was taken into account for calculation of density from shrinkage data.

4.35 Ultimate tensile strength of boron doped water atomized 316L alloys sintered at peak temperature for 30 min in hydrogen atmosphere. An average of three tests at each temperature with the error bars are reported.

4.36 Yield strength (at room temperature) of boron doped water atomized 316L alloys sintered at peak temperature for 30 min in hydrogen atmosphere. An average of three tests at each temperature with the error bars is reported.

4.37 Elongation of boron doped water atomized 316L alloys sintered at peak temperature for 30 min in hydrogen atmosphere. An average of three tests at each temperature is reported.
4.38 Fracture surfaces of water atomized stainless steel powders sintered at 1200, 1225, 1250, and 1275°C read left to right from top, respectively. ........................................... 89
4.39 Fracture surfaces of water atomized stainless steel powders with 0.2 wt.% boron sintered at 1200, 1225, 1250, and 1275 °C read left to right from top, respectively. ........................................... 90
4.40 Fracture surfaces of water atomized stainless steel powders with 0.4 wt.% boron sintered at 1200, 1225, 1250, and 1275 °C read left to right from top, respectively. ........................................... 91
4.41 Fracture surfaces of water atomized stainless steel powders with 0.8 wt.% boron sintered at 1200, 1225, and 1250 °C read left to right from top, respectively. Tensile bar sintered at 1275 °C distorted and was not subjected to tensile testing. ........................................... 92
4.42 Anodic potentiodynamic polarization curves run in 0.1M NaCl for wrought 316L, water atomized 316L with 0.2% boron sintered at 1350°C, 1435°C and, gas atomized 316L with 0.2% boron sintered at 1350°C. ........................................... 93
4.43 Anodic potentiodynamic polarization curves run in 0.1M NaCl for wrought 316L, water atomized 316L with 0.8% boron sintered at 1245°C, 1260°C and, gas atomized 316L with 0.8% boron sintered at 110°C, 1245°C. ........................................... 94
4.44 Anodic potentiodynamic polarization curves run in 0.1M NaCl comparing wrought 316L to water atomized, and gas atomized 316L powders with 0.2 and 0.8 % boron sintered to full density. ........................................... 95
4.45 Wrought and sintered microstructures. Top left-wrought 316L, top right-WA316L 0.2% boron 1350°C, middle-left WA316L 0.2% boron 1435°C, middle right-WA316L 0.8% boron 1260°C, bottom left-GA316L 0.2% boron 1350°C, bottom right- GA316L 0.8%boron 1245°C ........................................... 97

5.1 Distortion as a function of sintered density for boron added 316L. . 99
5.2 Liquid volume fraction as a function of sinter temperature for gas and water atomized 316L determined from DTA. ...................... 100
5.3 Liquid volume fraction Liquid volume as a function of sinter temperature for gas and water atomized 316L with 0.2% boron addition determined from DTA. ...................... 102
5.4 Liquid volume as a function of sinter temperature for water atomized 316L with 0.8% boron measured from microstructural analysis. . . . . . . . . . . 102
5.5 Contiguity as a function of liquid volume for water atomized 316L with 0.8% boron measured from microstructural analysis. . . . . . . . . . . 105
5.6 Grain size as a function of sinter temperature for water atomized 316L with 0.2% boron addition. 107
5.7 Grain size as a function of sinter density for water atomized 316L with 0.2% boron addition. 107
5.8 Evolution of grain size in water atomized 316L with 0.2% boron addition sintered at the peak temperature for 30 min in hydrogen. The peak temperature indicated in the legend is in °C. 109
5.9 Normalized grain size distribution for water atomized 316L with 0.2% boron addition showing self similar distribution at all sinter temperatures indicated in legend (in °C). A Rayleigh distribution function for grain size distribution which has a and n values of 0.7 and 2, respectively is also shown for comparison. Model with a=0.64 and n=3.32 gives a better fit to the data. 109
5.10 Evolution of grain size in gas atomized 316L with 0.2% boron addition sintered at the peak temperature for 30 min in hydrogen. The peak temperature indicated in the legend is in °C. 111
5.11 Normalized grain size distribution for gas atomized 316L with 0.2% boron addition showing self similar distribution at all sinter temperatures indicated in legend (in °C). A Rayleigh distribution function for grain size distribution which has a and n values of 0.7 and 2, respectively is also shown for comparison. Model with a=0.59 and n=3.85 gives a better fit to the data. 111
5.12 SEM of second phases present in gas atomized 316L with 0.2% boron sintered at 1440°C for 30 min. 1-light phase, 2-dark phase and 3-bulk. 112
5.13 SEM of second phases present in water atomized 316L with 0.2% boron sintered at 1440°C for 30 min. 1-dark phase and 2-bulk. 113
5.14 SEM of second phases present in water atomized 316L with 0.8% boron sintered at 1260°C for 30 min. 1-dark phase, 2-light phase, and 3-bulk. 114
5.15 Normalized apparent viscosity as a function of temperature during constant heating rate sintering of water atomized 316L with 0.2% boron for four different runs. The normalized viscosity of water atomized 316L with 0.8% boron is also shown for comparison. 116
5.16 Apparent viscosity as a function of temperature during constant heating rate sintering of water atomized 316L with 0.8% boron. Apparent viscosity calculated for isothermal sintering at 1245, and 1265°C is also shown. 116
5.17 Apparent viscosity and relative density as a function of temperature during constant heating rate sintering of water atomized 316L with 0.2% boron. Microstructure of water atomized stainless steel powder with 0.2 wt.% boron quenched at 1210, 1240, 1350, 1400, and 1440 °C for 0 min hold at peak temperature are also shown along the density evolution curve. ............................. 120

5.18 Master plot showing the evolution of various microstructural parameters and viscosity with temperature during constant heating rate sintering of WA316L with 0.8% boron. The axis from left to right are distortion (%), Grain size (µm), Apparent viscosity (GPa.s), liquid volume (%), contiguity and Fractional grain boundary coverage ($F_C$). Curves: black-Apparent viscosity, blue-contiguity, red-liquid volume, light green- fractional grain boundary coverage, dark green-distortion and brown-grain size. ................................. 121

5.19 Activation energy for densification of water atomized 316L with 0.2% boron with and with out grain growth consideration. .......................... 128

5.20 Master sintering curve for sintering of water atomized 316L with 0.2 wt.% boron showing the densification parameter as function of work of sintering. ........................................................................ 129

5.21 Master sintering curve for water atomized 316L with 0.2 wt.% boron showing the densification ratio as a function of work of sintering. .......... 129

5.22 Modified MSC for densification with consideration of grain growth effect for water atomized 316L with 0.2 wt.% boron showing the densification parameter as function of work of sintering. ............. 130

5.23 Modified MSC with consideration of grain growth effect for water atomized 316L with 0.2 wt.% boron showing the densification ratio as function of work of sintering. ................................. 130

5.24 MSC comparing the densification behavior of atomized 316L with 0.2 wt.% boron and without boron addition. ................................. 131

5.25 Master sintering curve for water atomized 316L with 0.2 wt.% boron showing showing a good correlation between experiment and model. 131

5.26 Modified MSC with consideration of grain growth effect for water atomized 316L with 0.2 wt.% boron showing showing a good correlation between experiment and model. ................................. 132

5.27 Activation energy for densification of water atomized 316L with 0.2% boron using Master Curve software [98]. ................................. 133

5.28 Master sintering curve for densification of water atomized 316L with 0.2% boron using Master Curve software [98]. ................................. 133

5.29 Activation energy for grain growth of water atomized 316L with 0.2% boron. ................................. 134
5.30 Master sintering curve for grain growth of water atomized 316L with 0.2% boron showing good correlation between experiment and model.

5.31 Plot showing the range of UTS and YS from previous work on 316L stainless steel and its alloys with boron. The vertical window represents the optimum conditions for achieving full density with minimal distortion, and good mechanical properties. Solid diamonds represent UTS values from prior work, solid circles represent UTS values from this work. Hollow circles represent YS values from prior work, hollow squares represent YS values from this work. Stars represent the distortion values.

5.32 Corrosion rate as a function of sinter density for 316L with different amounts of boron. The corrosion rate for wrought 316L is very small.

5.33 Corroded surface of water atomized 316L with 0.2% boron showing pitting. The pit marked by the arrow is magnified in the bottom picture. The porosity of the sintered compact was 31%.

5.34 Pitting corrosion of gas atomized 316L with 0.8% boron. The porosity of the sintered compact was 36%.

5.35 Finite element simulation showing excessive deformation of the beam due to poor definition of the shear viscosity.

5.36 Comparison of viscosity from experiment to that calculated based on continuum modelling using FEM.

B.1 Schematic diagram of the initial and final state stress distribution.
### List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Table showing the powder characteristics. (NR-not reported)</td>
<td>35</td>
</tr>
<tr>
<td>3.2</td>
<td>Composition of the as-received gas and water atomized stainless steel 316L powders. The elemental composition is reported in wt.%</td>
<td>40</td>
</tr>
<tr>
<td>4.1</td>
<td>Solidus and liquidus temperatures for water atomized, gas atomized and a 70:30 mixture of water and gas atomized powders with different amounts of boron additions. (NR-not reported)</td>
<td>58</td>
</tr>
<tr>
<td>4.2</td>
<td>Compilation of tensile data on 316L steels. $\delta$ is the elongation and $\rho$ the density. (NR-not reported)</td>
<td>86</td>
</tr>
<tr>
<td>4.3</td>
<td>Compilation of tensile data on 316L steels. $\delta$ is the elongation and $\rho$ the density. (NR-not reported)</td>
<td>88</td>
</tr>
<tr>
<td>4.4</td>
<td>Data obtained from anodic polarization testing of wrought 316L and powders with boron additions at different sintering conditions. The temperature in the bracket indicates the sintering temperature. (NA-not applicable)</td>
<td>95</td>
</tr>
<tr>
<td>5.1</td>
<td>Elemental composition (% atomic) of the various phases seen in sintered microstructure of GA 316L with 0.2% boron as seen in Figure 5.12</td>
<td>113</td>
</tr>
<tr>
<td>5.2</td>
<td>Elemental composition (% atomic) of the various phases seen in sintered microstructure of WA 316L with 0.2% boron as seen in Figure 5.13</td>
<td>114</td>
</tr>
<tr>
<td>5.3</td>
<td>Elemental composition (% atomic) of the various phases seen in sintered microstructure of WA 316L with 0.8% boron as seen in Figure 5.14</td>
<td>115</td>
</tr>
<tr>
<td>5.4</td>
<td>Yield strength values calculated from $in situ$ distortion observed in water atomized 316L with 0.2% boron (seen in Figure 4.28) based on analysis of Pashias [152]</td>
<td>127</td>
</tr>
</tbody>
</table>
List of Symbols

\( T_m \)  Melting point of the alloy
\( T_s \)  Solidus temperature
\( T_l \)  Liquidus temperature
\( X_s \)  Composition of solid
\( X_l \)  Composition of liquid
\( X_a \)  Alloy composition
\( A \)  Slope of liquidus line
\( B \)  Slope of solidus line
\( \rho_s \)  Density of the solid phase in the alloy
\( \rho_l \)  Density of liquid phase in the alloy
\( M_s \)  Solid mass fraction
\( N_G \)  Grain coordination number
\( \phi \)  Solid volume fraction
\( F_C \)  Fractional grain boundary coverage
\( C_{SS} \)  Solid-solid contiguity in a two phase microstructure
\( G \)  Grain size
\( D \) Particle size  
\( \tau_Y \) Yield strength of a semisolid system  
\( \eta \) Viscosity (in general)  
\( \frac{d\gamma}{dt} \) Shear strain rate  
\( \frac{\Delta L}{L_o} \) Shrinkage  
Master Sintering Curve- Symbols  
\( \Gamma_v \) Scaling factor for volume diffusion  
\( \Gamma_b \) Scaling factor for grain boundary diffusion  
\( \Omega \) Atomic volume  
\( \rho_o \) Green density  
\( \rho \) Instantaneous density during sintering  
\( \Psi \) Densification parameter  
\( \Phi \) Sinter density difference ratio parameter  
\( Q \) Activation energy (in general)  
\( \Theta_p \) Work of sintering for densification  
\( \Theta_{p/G} \) Work of sintering for densification with grain growth consideration  
\( M \) Bending moment  
\( E \) Elastic modulus  
\( I \) Moment of Inertia  
\( \delta \) Mid point deflection of the free standing beam  
\( \dot{\delta} \) Mid point deflection rate  
\( \eta_{app} \) Uniaxial apparent viscosity
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Dedication

“Be fearless and pure; never waver in your determination or your dedication to the spiritual life. Give freely. Be self-controlled, sincere, truthful, loving, and full of the desire to serve...Learn to be detached and to take joy in renunciation. Do not get angry or harm any living creature, but be compassionate and gentle; show good will to all. Cultivate vigor, patience, will, purity; avoid malice and pride. Then, you will achieve your destiny.” —- Krishna (Bhagavadgita)

This thesis is dedicated to my family for supporting me in all of my endeavors. To my sister Silpa for being there for me throughout.
Chapter 1

Introduction

1.1 Introduction

Powder Metallurgy (P/M) is a metal working technique to fabricate high quality, complex parts with close tolerances in an economical manner. The prime advantage of P/M is the ability to manufacture components with unique compositions and microstructures. P/M process comprises of shaping (compaction) and sintering. Shaping can be done by either die pressing, injection molding, extrusion, or slip casting. In practice, binders and lubricants are added to facilitate the shaping process. After shaping is accomplished these binders are removed by using thermal, solvent debinding or a combination of both. The final microstructure and properties are tailored during sintering. Sintering is a thermal treatment for bonding particles into a coherent structure via diffusion processes. In practice, majority of sintering happens by liquid phase sintering, a process in which liquid exits during some part of the sinter cycle.

Supersolidus liquid phase sintering (SLPS) is a variant of liquid phase sintering. In SLPS, prealloyed powders are heated between the solidus and liquidus temperature of the alloy. Liquid forms along the grain boundaries within the particles, fragmenting them into individual grains. The semisolid compact densifies in response to the capillary force exerted by the liquid film along the grain boundaries. The rheological response of the compact during sintering determines the densification and distortion response. Above the solidus temperature the liquid formation decreases the apparent viscosity of the compact. The compact densifies when the
sintering stress is higher than the inherent strength of the compact. If the viscosity drops too low, the inherent strength of compact is less than gravitational forces leading to distortion. Hence, there exists a critical viscosity window in which full density is achieved with minimal distortion.

SLPS is an important processing route for stainless and tool steels. Stainless steel 316L is an important class of steel which combines high strength to weight ratio, corrosion resistance, impact resistance along with its aesthetic appearance. This thesis focuses on processing of stainless steel 316L via SLPS by adding boron. The crux of this thesis is to understand the evolution of apparent viscosity and its relation to the microstructure. The densification behavior was modelled using Master Sintering Curve (MSC) concepts. The optimization of mechanical and corrosion properties by boron additions is researched.

1.2 Outline of Thesis

Chapter 2 presents the current understanding of supersolidus liquid phase sintering and reviews prior studies. Chapter 3 gives the details of experimental procedures used in this study, followed by results in Chapter 4, and discussion in Chapter 5. The findings are summarized in Chapter 6.
The process of sintering has been known for thousands of years, but it evolved into a science in the past few decades. Sintering is defined as a thermal treatment for bonding particles into a coherent, predominantly solid structure via mass transport events that often occur on atomic scale. The bonding leads to improved strength and a lower system energy. Mass transport during sintering is primarily diffusion aided. Reduction in the surface energy acts a driving force for sintering [1].

Based on the key processing parameters, sintering can be classified into pressureless and pressure assisted. Under pressureless sintering, solid state sintering and liquid phase sintering are key processes. Under pressure assisted sintering, sintering is done with the aid of creep, viscous or plastic flow.

2.1 Liquid Phase Sintering

Although solid state sintering is the most understood form, liquid phase sintering has greater industrial utilization. However, in spite of large scale application it is not well understood. Liquid phase sintering is defined as sintering involving a co-existing liquid and particulate solid during some part of the thermal cycle [2].

The major advantage of liquid phase sintering is faster sintering times and ability to achieve full density in the presence of a liquid. The liquid phase provides for faster atomic diffusion than the concurrent solid state processes. Typically diffusion through the liquid phase is 100 times faster than solid-state diffusion. The capillary attraction due to a wetting liquid gives rapid compact densification
without the need for an external pressure. The liquid also reduces the interparticle friction, thereby aiding rapid rearrangement of the solid particles. The uses of LPS include electrical contacts, wearfacing alloys, tool steels, super alloys, diamond metal composites, high temperature ceramics and other applications.

In spite of all the advantages LPS offers, a common problem associated with LPS is compact slumping (shape distortion) which occurs when too much liquid is formed during sintering.

Liquid phase sintering is generally carried out on a two phase or a multi phase system which involves mixed powders with different melting points. The sintering temperature is high enough to ensure formation of liquid phase during sintering. The presence of liquid does not ensure complete densification; some thermodynamic and kinetic factors need to be satisfied for full density liquid phase sintering. A few of them are

- **Wetting**: A low solid-liquid surface energy compared to the solid-vapor and liquid-vapor surface energies, enhances the final densification.

- **Solubility**: The two solubilities of concern in LPS are the liquid solubility in the solid and the solid solubility in the liquid. For classic LPS, the solid should have good solubility in the liquid, but the reverse solubility must be low.

- **Diffusion**: The diffusion rate through the liquid phase should be high enough to promote rapid densification.

A typical liquid phase sintered microstructure consists of solid phase dispersed in a continuous solidified matrix. The unique two phase composite microstructure provides superior properties over monolithic materials. Liquid phase sintering is classified into four overlapping stages, namely: chemically driven solid state diffusion, rearrangement, solution-precipitation and solid state sintering.

During heating there is solid state sintering driven by chemical concentration gradient in the microstructure. Farooq *et al.* [3] have shown that as much as 90% of the total densification can take place before liquid formation in the W-Ni-Fe system. Systems which have a high amount of solid solubility in the liquid have a higher amount of solid state sintering before liquid formation [4, 5, 184]. Various
parameters like heating rate, solubility of the base in the additive, particle size, and homogeneity of the blend have a marked influence on solid state sintering.

Upon formation of the liquid, there is a burst in the degree of densification. If the solid has a considerable amount of solubility in the liquid, a chemical gradient is established. The wetting liquid dissolves the solid-solid bonds. The capillary force exerted by the liquid on solid particles, pulls the solid grains together, packing them to give a higher density. Good wetting is observed when the contact angle is low or a low solid-liquid surface energy exists in comparison to the solid-vapor and liquid-vapor surface energies. Hupmann and Riegger [6] observed that for low contact angle the forces are attractive and hence densification occurs, where as for large contact angles the forces become repulsive and contact swelling occurs. A powder mix with good homogeneity, small particle size and high volume percent of liquid promotes densification by rearrangement [7, 8].

Cubic packing of monosized spheres gives 64 % density in theory, at least 36 % liquid is needed to obtain full density by rearrangement [9]. In most cases such high liquid contents are not realized and further densification occurs by solution reprecipitation. Densification is also associated with grain shape accommodation, which takes place by contacts flattening at grain contacts. The solid grains deviate from the spherical shape to fill space better. This releases excess liquid which fills the pores. The reduction in energy associated with pore elimination exceeds the total solid surface energy, leading to a net decrease in the system energy. Coalescence involving grain boundary migration further reduces the system energy with concurrent grain growth. The final grain shape is dictated by the dihedral angle and the volume contact of the liquid [10, 11]. The various shapes assumed by the liquid phase in the S+L mixture may be mapped in $\theta - V_L$ space [10]. The liquid structure is connected for $\theta$ (dihedral angle) < $60^\circ$, independent of the volume fraction of the liquid, $V_L$. Alternatively, for low volume fractions of liquid and high dihedral angles, the liquid forms a discrete discontinuous microstructure.

As liquid phase sintering progresses, a solid skeleton forms. Densification rate slows down while microstructural coarsening continues through a process of solution-reprecipitation. The solid skeleton provides rigidity and inhibits pore elimination. Depending on the atmospheres, the pores stabilize or may be totally eliminated. The solubility of the trapped gas, if any, affects the final stage densi-
The other important process which takes place is grain growth. The smaller grains have higher solubility and hence preferentially dissolve and reprecipitate on the larger ones. This leads to a grain size distribution skewed to large grain sizes. Also the number of grains per unit volume decreases with time. The kinetics of grain growth give the mean grain size versus time as \( G^n \sim t \) where \( t \) is the time and \( n \) varies from 2 to 4 for most materials [2, 12]. Several theories have been proposed to explain grain growth. The key parameters that effect grain growth are diffusivity through liquid, mean separation distance between grains, solid volume fraction and also grain coalescence.

2.2 Supersolidus Liquid Phase Sintering (SLPS)

Supersolidus liquid phase sintering has been employed to sinter nickel based superalloys [13, 18, 19, 24, 26, 27, 28], bronze [20, 21, 22, 28], stainless steel [22, 23, 32, 34, 35, 36, 38, 49, 50, 51, 54], aluminium alloys [30, 31], tool steels [37, 39, 40, 41, 42, 43, 44, 45, 46, 55, 56, 57, 58, 59], low alloy steels [47] with considerable success. Supersolidus sintering is a variant of liquid phase sintering. Coarse alloy powders can be processed to full density by supersolidus liquid phase sintering (SLPS). In this process, the prealloyed powder is heated between the solidus and liquidus temperature leading to the formation of a liquid phase inside the particles, compared to classic LPS, where the mixed powders are heated above the liquidus of the liquid phase element. The newly formed liquid spreads to the particle boundaries resulting in capillary force acting on the semisolid particles. Once sufficient liquid forms to fragment particles into individual grains, rapid densification ensues due to capillary induced rearrangement [1]. A sketch of the basic densification process that occurs when a polycrystalline prealloyed powder is heated to a temperature between the solidus and liquidus temperatures is shown in Figure 2.1.

Early investigations of sintering behavior of nickel based superalloys of the Nimonic type show that densification rate increases rapidly on liquid formation, allowing the prealloyed powders to be sintered to almost theoretical densities in short sintering times [13]. It was ascertained that the rapid densification was caused by a small amount of liquid phase at the grain boundaries, which apparently originated by incipient melting at temperatures considerably below those at which macro-
scopic melting occurred (liquidus). The term supersolidus liquid phase sintering has been introduced by Cambal and Lund [14] based on their studies of sintering behavior on loose steel powders. They observed that heating the specimen between the solidus and liquidus causes partial melting of the powder and the force provided by the surface tension of the liquid acts to rearrange the solid particles and to eliminate interparticle voids. Furthermore, since the particles in a loosely
packed aggregate are relatively mobile, and the effective viscosity of the material is drastically reduced when it is heated above the solidus, rapid densification occurs. Further experiments on cupro-nickel [15] show clear evidence of liquid along the grain boundaries responsible for rapid densification in short sintering times.

2.2.1 Densification Mechanism during SLPS

Phase diagrams provide insight into the behavior of mixed powders and prealloyed powders during various sintering cycles. Although sintering is not an equilibrium process, phase diagrams do indicate the phases that might form and aid in the selection of process variables [60]. At supersolidus temperatures, liquid forms within the particles along the grain boundaries and also along the particle boundaries. Microstructures of the cupro-nickel alloy show a clear indication of a liquid phase along the solid particles. Particle rearrangement process, facilitated by the shape change of particles, is responsible for densification [15]. Quenching studies on Astroloy powders revealed microstructures with liquid along the particle boundaries (intergranular) or intraparticular sites. If the maturation period is long or when a high amount of liquid is present, the intragranular liquid can coalesce and migrate to the grain periphery promoting sintering [18, 19].

Another phenomena called particle fragmentation can occur during SLPS leading to considerable densification during short sintering times. Particle fragmentation explains why certain alloy systems, such as nickel based alloys, [20, 22, 24, 26, 27, 28, 29, 61] and high speed steel [44], show faster densification when compared to bronze [20, 21, 22, 24]. The grain boundary liquid which forms above solidus is present as a film, whose thickness depends on the sintering temperature, and dihedral angle [62]. Above a critical temperature, the liquid film is sufficiently thick to initiate grain sliding due to a shear stress adjacent to neck region. The shear stress is induced by a normal stress (usually the capillary stress) at the neck region whose magnitude depends on the particle size, the wetting angle, and the neck liquid volume [63, 64]. Grain sliding will lead to pore filling above a critical temperature. The additional freedom for individual grains to rearrange is provided by the liquid film causing significant densification. Model experiments performed using oil droplets floating on water in which particles of cellulose acetate butyrate
were dispersed show that the time for fragmentation is less than 1 s. Experiments based on the stainless steel system calculate the time required for particle fragmentation as 0.37 s which agrees well with the oil drop experiment [24, 62]. Hence, particle fragmentation coupled with the decrease in the viscosity of solid-liquid mixture results in a favorable condition for rapid grain rearrangement.

![Figure 2.2. The geometry of a nodoid liquid profile which connects two unequal sized spheres.](image)

Figure 2.2. The geometry of a nodoid liquid profile which connects two unequal sized spheres.

The capillary force due to the wetting liquid between solid particles/grains is responsible for agglomeration and pulling the particles together, acting as the driving force for densification. A model consisting of two solid spherical particles connected by a liquid bridge is considered for calculation of capillary force. The capillary force depends on the shape of the liquid bridge, which is a function of the contact angle, particle size, and amount of liquid [65]. Based on the nodoid liquid profile which connects two identical spheres (as shown in figure 2.2) the capillary force is calculated by the force equation:

\[
F = \pi y^2 P + 2\pi y \gamma_{lv} \cos \phi
\]  

(2.1)
The first term, $\pi y^2 P$, is due to pressure deficiency in the liquid acting on the area of any cross section of the liquid bridge. The second term, $2\pi y \gamma_{lv} \cos \phi$, is due to the surface tension $\gamma_{lv}$ acting along the contact perimeter of that cross section of the liquid. A large capillary force results from a small separation distance between the spheres, a small contact angle $\theta$, and uniform distribution of the liquid [65].

Liu et al. [63] have numerically calculated capillary force during SLPS taking into account particle coalescence and liquid volume increase. The capillary force is shown to be dependent on the amount of liquid volume in the neck region which, in turn, is a function of temperature and shrinkage during SLPS. A low wetting angle and higher amount of liquid lead to a greater capillary force causing rapid densification during SLPS.

### 2.3 Effect of Processing Variables

The past research on supersolidus liquid phase sintering provides a basis for analysis of the processing parameters. This section summarizes these various parameters, with a focus on densification and microstructure control.

#### 2.3.1 Particle Size and Distribution

Supersolidus liquid phase sintering can work with relatively coarse powders (>30 $\mu$m). This is an advantage in comparison to classical liquid phase sintering where very fine particle sizes (<10 $\mu$m) must be used in order to achieve homogeneity in the final microstructure. There is an advantage of lower cost and less contamination with coarse powders [21, 66]. In SLPS, near full density can be achieved with powders as large as 500 $\mu$m. However, smaller particle sizes give more initial densification, especially at temperatures below optimal temperature.

Particle size and chemical composition are strongly linked and mainly governed by the cooling rate during atomization. Jeandin et al. [19] observed that in the case of Astroloy, fine particles are less prone to liquid formation than coarser powders and liquefaction kinetics are more rapid with coarse powders. On the contrary, Bee et al. [45] have seen that in tool steels smaller powders have a larger surface area and a higher dissolved carbon content, which tend to lower the
melting point. Although particle size influences the liquid formation, the amount of liquid and where liquid forms during sintering will depend on the alloy content and the segregation behavior exhibited during solidification. However, particle size becomes unimportant at sintering temperatures higher than solidus temperature. In practice SLPS employs mean particle sizes in the range of 50-80 \( \mu \text{m} \) to process alloys to near full density which is more economical than using more expensive gas atomized powders to achieve the same purpose.

A broad particle size distribution will increase the packing density and coordination, thereby speeding densification while reducing net dimensional change. The sintering behavior of the bimodal and the monosized distributions of nickel based superalloys suggest that particle packing plays an important role at low sintering temperatures, where the low fraction of liquid phase may not be able to provide sufficient capillary force. At high temperatures, the excessive liquid phase can override the initial packing density difference between the two distributions and result in almost the same sintered densities. However, the overall shrinkage is much less for the bimodal distribution as compared to monosized distribution [27]. These results agree well with the particle packing studies done by German [67]. Typically, small particles control initial bonding. Thus, their presence is beneficial in widening the temperature range over which SLPS can be practiced.

### 2.3.2 Internal Powder Microstructure

The process by which the powder is manufactured dictates the powder microstructure. In gas atomization some of the gas can be trapped in the particles as spherical pores which prove difficult to eliminate during sintering. Internal voids present in large particles result in a slight reduction of apparent density obtained by using bimodal distribution of superalloys. The internal pores also generate large pores in the sintered microstructure [26]. In all cases, better densification occurs with a smaller initial grain size.

### 2.3.3 Green Density

In practice there is no evidence of a green density effect other than smaller dimensional changes in sintering. Below the optimal sintering temperature higher
green density will lead to a higher sinter density but at supersolidus temperatures, liquid formation and the amount of liquid formed controls densification. Injection molding of superalloys with different starting solid volume fractions sintered to near full density with very little dependence on the initial solid volume fraction of feedstock [20]. In practice most SLPS starts with green density of 70 % or less.

2.3.4 Role of Sinter Temperature and Liquid Fraction

Liquid formation is the most important step in SLPS. The amount of liquid formed, its location and spreading depend on the sintering temperature. The sintering temperature must exceed the solidus temperature to induce densification. Phase diagrams help identify candidate SLPS systems based on the solidus and liquidus temperatures which are important phase diagram characteristics. However, the actual temperature for first liquid formation will differ from the equilibrium phase diagram since the particles solidify in a nonequilibrium manner during atomization [16]. The phase chemistry and quantity of liquid will typically change after initial liquid formation as the system establishes equilibrium.

![Figure 2.3. Phase diagram characteristics of SLPS alloys.](image-url)
A schematic phase diagram plot showing the desired features for SLPS processing is shown in Figure 2.3. The diagram identifies the alloy composition $X_a$, solidus and liquidus temperature for the alloy $T_s$ and $T_l$, and the compositions of the liquid and solid, $X_l$ and $X_s$, at the sintering temperature $T$. A high concentration of alloying additions gives greater separation of solidus and liquidus. Since the liquid volume fraction dependence on temperature is inversely proportional to this separation, a large value for $T_l - T_s$ is desired. To minimize the sensitivity to normal compositional fluctuations in the alloy, it is desirable to have moderately large compositional difference $X_l - X_s$. Temperature control is less critical if the volume fraction of liquid does not change rapidly with temperature fluctuations. Eutectic systems are good candidates for SLPS. At the eutectic temperature a sudden and discontinuous amount of liquid forms along the grain and particle boundaries which aids in densification. If the amount of liquid exceeds a certain critical fraction then there will be concomitant distortion and problems with dimensional control [32, 81].

For multicomponent systems, phase diagrams are not readily available. In such cases differential thermal analysis (DTA) [26, 29, 30, 34, 41, 42, 43] provides valuable information on liquid formation temperatures in various alloy systems. For high speed steels Wright et al. [40, 42, 43] have used pseudo binary phase diagrams to correlate the phase diagrams with densification and microstructural data. Melting and solidification of high speed steel powders, which occurs over a 200°C temperature interval, is a complex process involving peritectic and eutectic reactions and, depending on composition, several phase fields are crossed before the liquidus or solidus is reached. Wright et al. [40, 42] have shown that for T1, M2, M3/2 alloys of standard composition, successful sintering requires heating within an austenite ($\gamma$) + carbide ($M_6C$ in T1 and $M_6C$ + MC in M2 and M3/2) + liquid (L) region. In these systems one of the critical factors influencing alloy sinterability is not the separation between liquidus and solidus, but the temperature range separating the phase boundaries which define the limits of the $\gamma$ + carbide + L region for a given HSS composition. The sintering window over which acceptable microstructures and properties can be obtained is narrow, ranging from 1-5°C for M2 to at best 10-15°C for alloys such as T1, T15 and T42 [43]. Compositions which do not cause a sudden increase in the amount of liquid with an slight
increase in temperature are most successful to process via SLPS. Use of pseudo binary phase diagrams allowed identification of compositions which can exhibit broader sinter windows for better density and dimensional control. In some tool steels, every 3.5°C increase in temperature increases the liquid by 1% [16]. Takajo and Nitta [45] have observed that liquid phase volume decreases in the first few minutes at the sinter temperature and then increases with hold time. Based on the microstructures and the densification curves, a liquid phase of about 5% seems to attain full density in the steel powder. Hence it is necessary to identify the sinter window and choose the sinter temperature in such a way as to form sufficient liquid necessary for densification without causing distortion.

2.3.5 Additives

Additives enhance densification by increasing the sintering driving force through physical or chemical processes. A host of additives have been used to sinter Fe powders [48, 25, 68, 69, 70]. There is an optimum additive concentration which produces the maximum benefit. Uniform distributions of the additives are advantageous.

Alloying elements affect the gap between solidus and the liquation temperature. In the case of M2 steel a decrease in vanadium concentration from the upper limit will reduce the gap and, presumably, the sintering window. An increase in tungsten content in M2 steel will produce a similar effect [40]. Hence any minor changes in chemical compositions which occur from batch to batch (during powder production) will cause the shifting of sinter window and creating problems with respect to controlling the density and microstructure. Increasing the carbon content of T1 from 0.8 to 1.4 % increased the sintering window from 10 to about 40°C and lowered the optimum sintering temperature from 1320 to 1240°C, creating a material more suitable for processing. However there is a upper limit for carbon content enrichment of T1 beyond which the development of deleterious skeletal structures of an Fe-Cr rich phase occurs [42]. Studies on high speed steels with varying Mo content show widening of the sintering window and much lower optimum sintering temperatures [43]. High speed steels sintered with phosphorus additions in the form of Cu-P and Fe-P reduce the sintering temperature required to produce near
full density by 100°C [46].

Since this study involves sintering of austenitic stainless steels, we shall look into the effect of different additives on 316L austenitic steels. Boron addition, either in elemental form or borides, proves to be beneficial in widening the solidus-liquidus gap and lowers the optimum sintering temperature required to achieve full density [22, 23, 33, 34, 35, 36, 37, 38, 49]. Boron is a well known solidus depressant used to sinter Fe powders. It lowers the solidus by forming a low melting eutectic [45]. Fe-B phase diagram is readily available whereas the pseudo binary phase diagram for austenitic steel with boron is not readily available. Differential thermal analysis is used to identify the solidus and liquidus for such complex alloy systems [34, 38, 41, 42, 62, 71]. SIMS analysis on boron doped samples indicates that boron is mainly distributed in the network along the grain boundaries and no appreciable diffusion into the matrix is observed [35]. Energy dispersive analysis of x-rays for electron beams directed at solidified eutectic liquid show traces of boron in boron doped austenitic steels [34]. Similarly, the grain boundaries were enriched in titanium in Astroloy [18] and boron and tantalum in the case of superalloys [26]. The additives, owing to their small size, segregate to the grain boundaries and form a liquid phase once the solidus temperature is exceeded. Although boron addition aids the formation of liquid phase and helps improve mechanical properties, there exists an optimal boron content beyond which the microstructure consists of brittle eutectic along the grain boundaries and coarse grains, leading to brittle failure and poor ductility [23, 34, 36, 37, 38, 49, 70, 72].

Apart from boron, silicon additions also aid in sintering of austenitic steels. Higher shrinkage took place in 316L compacts which contained higher silicon contents and shrinkage was both more pronounced and more rapid once the temperature exceeded approximately 1150°C. The pseudo binary phase diagram of Fe-Ni-Cr-Si indicate the extremely complex reactions that could occur during sintering and also suggests that a homogenous stainless steel containing up to 5% silicon could be capable of undergoing supersolidus liquid phase sintering within the $\gamma + \delta$ + liquid phase field at temperatures above 900 °C [50]. The effect of additions of silicon powder on the sintering behavior and microstructure of compacted 304L stainless powder has shown that the shrinkage ratio increases substantially with silicon content. Silicon profoundly activates the sintering process through
the formation of a eutectic and delta ferrite, which is pseudoperitectically formed during sintering [51]. Silicon was relatively ineffective as a sintering aid despite its potential for reactive sintering and its ability to form liquid phases when combined with 316L stainless steel. This failure to reach full density was caused by localized melting around prior silicon particles and the subsequent formation of annular groups of pores which were not removed by the later liquid phase sintering process. Overall, boron additions in the elemental form prove most beneficial with respect to densification during sintering.

2.3.6 Sintering Atmosphere and Sintering Time

Vacuum sintering is usually the best choice for supersolidus sintering of austenitic steels, tool steels and high speed steels [39, 40, 41, 42, 43, 44, 46, 50]. In the final stage of sintering, the environmental gas becomes trapped in the pores, thereby limiting the final density. An inert gas like argon gives a limiting density of approximately 94-96%. Hydrogen is usually employed in sintering of boron doped austenitic steels [22, 23, 26, 34, 35, 36, 37, 38, 47, 49] and silicon doped austenitic steels [51]. Hydrogen, being soluble in most metals, allows a higher limiting density. In the case of boron doped 316L, it was shown that boron interacts with steel grains only when sintering is carried out in pure hydrogen atmosphere (only a weak interaction occurs at 1240°C in 75H₂-25N₂). Nitrogen in the sintering atmosphere impedes boron interaction with the matrix and induces a combined boron and nitrogen grain boundary segregation phenomena [35]. In M2 steels, hydrogen based atmospheres improve binder burnoff, cause decarburization at higher temperature, lower the densification temperature, and improve interparticle bonding compared to nitrogen based atmospheres. Carbon control can be achieved through atmosphere and temperature control [39].

In practice sintering times range from 10 to 60 minutes [21, 23, 26, 29, 34, 35, 36, 42, 43]. Time dependent densification of Ni-base alloy show that densification is achieved in as little as 5 min for optimal sintering temperature [22]. Sintering of austenitic stainless steel with 0.4% boron for prolonged times did not provide microstructural benefits due to coarsening of the microstructure [23, 38]. During isothermal sintering at optimum temperatures densification occurs first after which
distortion sets in, which results in poor dimensional and mechanical properties. Hence, it is very important to optimize sintering time in order to achieve full densification with minimal distortion.

### 2.3.7 Heating Rate

Heating rate is dictated by furnace capabilities and a need to reduce surface oxides prior to significant densification. Faster heating gives faster densification in SLPS since less homogenization occurs. With slow heating, the compositional gradients are reduced, giving less densification at temperatures below optimal sintering temperature. Murley and German [20] observed that bronze samples heated at a faster heating rate (75°C/min) showed more grain boundaries and grain boundary liquid than did samples heated at slower rate (10°C/min). The nickel system however was unaffected by heating rate. Ravi and German [73] observed higher shrinkage at lower heating rate of 1°C/min when compared to 15°C/min during liquid phase sintering of tungsten heavy alloys. Over the range of 1 to 15°C/min solid state sintering prior to liquid formation did not have a significant effect on distortion. The amount of liquid phase, contiguity and connectivity determined the dimensional stability of the compact. Typical ramps in practice are between 0.5 and 10°C/min.

### 2.4 Modelling of Densification during SLPS

Densification during SLPS is analogous to viscous flow sintering, because the semisolid particles turn mushy and flow once liquid spreads along the grain boundaries. The viscosity decreases as the liquid volume fraction increases, so more liquid makes for faster sintering, but less dimensional precision. Consequently, temperature (which controls solid-liquid ratio) is a main determinant of sintered density and dimensional precision. Models to describe densification during SLPS have been based on rheology and microstructural parameters [63, 64, 74, 75, 76, 77].

Figure 2.3 shows a schematic phase diagram showing the solidus and liquidus as straight lines, providing a simple means to estimate the effect of temperature on the liquid content and densification for an alloy of composition $X_a$. Assuming a
linear relationship between the liquidus and solidus temperatures and composition allows estimation of the solid volume fraction as a function of temperature. The solidus and liquidus temperatures ($T_s$ and $T_l$) change linearly with composition $X_a$ as follows:

$$T_l = T_m + AX_a$$  \hspace{2cm} (2.2)  

$$T_s = T_m + BX_a$$  \hspace{2cm} (2.3)

where $T_m$ is the baseline melting temperature, as sketched in Figure 2.3; $X_a$ is the alloying content on a weight basis; and A and B are the slopes. Actual alloy melting behavior may be more complicated, but usually is not documented such that we can invoke any more realistic model. With the assumed linear relation, the compositions at the liquidus and solidus lines ($X_l$ and $X_s$, respectively) for any composition and temperature given as

$$X_l = \frac{T - T_m}{A}$$  \hspace{2cm} (2.4)  

$$X_s = \frac{T - T_m}{B}$$  \hspace{2cm} (2.5)

The tie-line between these two compositions allows calculation of the solid mass fraction $M_s$ for the particle at a given sintering temperature $T$:

$$M_s = \frac{X_l - X_a}{X_s - X_a}$$  \hspace{2cm} (2.6)

In turn, the volume fraction of solid $\Phi$ depends on the solid mass fraction and the densities of the solid $\rho_s$ and liquid $\rho_l$ phases as follows:

$$\Phi = \frac{M_s/\rho_s}{M_s/\rho_s + (1 - M_s)/\rho_l}$$  \hspace{2cm} (2.7)

Thus, for a given alloy composition and sintering temperature, the solid volume fraction inside the alloy particles can be calculated from the liquid and solid densities, if the solidus and liquidus temperature dependencies are known.

Observing the quenched microstructures during sintering, liquid is seen in three
different places: at the interparticle neck N, along the grain boundaries inside the particles B, and at pockets located inside the grains I [19, 20, 22, 62]. The liquid located at the interparticle necks provides the capillary force for densification, while the liquid located on the grain boundaries lubricates grain sliding during densification.

![Diagram](image)

**Figure 2.4.** Evolution of microstructure during supersolidus sintering of prealloyed powders [1].

Figure 2.4 shows the sintering microstructure and its evolution. Key features
are the particles, grains, necks, grain boundary liquid, and pores. The grain size $G$, particle size is $D$, neck size between the particles is $X$, and width of grain boundary liquid film is $\delta$. As densification progresses, spherical pores form with diameters of size $d_p$. For the model German [76] assumes constant film thickness until most grain boundaries are wetted. The particles are assumed to be spheres and the grains are assumed to be polygons. The grain shape is a tetrakaidecahedron and the grain coordination number $N_G$ can be estimated from the solid volume fraction $\Phi$ for a zero dihedral angle as

$$\log_{10}(N_G) = 1.15 + 1.25\log_{10}(\Phi) \quad (2.8)$$

The total liquid volume is represented by the sum $V_L = V_B + V_N + V_I$, where $V_B$, $V_N$, and $V_I$ designate the liquid volumes (per particle) at the boundary, neck and grain interior, respectively. With respect to a single spherical particle, the liquid volume fraction tied up in these three forms gives the solid volume fraction as

$$\Phi = 1 - \left( \frac{V_B + V_N + V_I}{\frac{\pi}{6} D^3} \right) \quad (2.9)$$

The liquid film on the grain boundaries inside the particles is assumed to be relatively small compared to the grain size $G$; thus,

$$V_B = S_G(\frac{\delta}{2})F_C n_G \quad (2.10)$$

with $S_G$ being the surface area per grain, $\delta/2$ being the width of the grain boundary film assigned to each grain, $F_c$ being the fractional grain boundary coverage by liquid. As liquid spreads on the grain boundaries, the volume of liquid and solid associated with each grain $V_G$ is

$$V_G = \frac{(G + F_c \delta)^3}{2} \quad (2.11)$$

Accordingly, number of grains becomes

$$n_G = \frac{D^3}{G^2(G + 3F_c \delta)} \quad (2.12)$$
Hence volume of grain boundary liquid per particle is [76]

\[ V_B = 1.5F_C \delta G^2 n_G \] (2.13)

The volume of liquid per particle located at the necks between particles is given by [76]

\[ V_N = \frac{\pi}{8} G^2 \delta F_C N_P \] (2.14)

The particle packing coordination varies with the fractional density \( \rho \) for the system and can be estimated as [1]

\[ N_P = 14 - 10.4(1 - \rho)^{0.38} \] (2.15)

The quantity of liquid at the grain interior is assumed to remain a constant fraction of the total liquid \( V_L \) [74]

\[ V_I = F_I V_L \] (2.16)

where \( F_I \) is a fraction of liquid at the grain interior \( (0 < F_I < 1) \).

Summing the contributions of liquid from different locations \( (V_B + V_N + V_I) \), the liquid volume in a particle is given by

\[ V_L = \frac{G^2 \delta F_C}{1 - F_I} (0.4N_P + 1.5n_G) \] (2.17)

### 2.4.1 Rheology Considerations

The viscosity of a semisolid particle is a novel rheological problem. There is a yield strength because the solid structure starts as a rigid, connected microstructure. As liquid spreads on the grain boundaries, the yield strength declines rapidly above the solidus temperature. Yield strength of semisolid systems have been reported over a wide range from 0.01 kPa to 100 MPa. A fit to available data shows that the yield strength \( \tau_Y \) variation with solid fraction \( \Phi \) can be approximated as [76]

\[ \tau_Y = \tau_o (\Phi - \Phi_Y) \] (2.18)
where $\Phi_Y$ is the solid content corresponding to loss of strength and $\tau_o$ is the alloy strength just prior to liquid formation. The capillary induced shear stress follows a Bingham response [78]:

$$\tau - \tau_Y = \eta \frac{d\gamma}{dt}$$  \hspace{1cm} (2.19)

where $\tau$ is the capillary-induced shear stress, $\tau_Y$ is the yield stress, $\eta$ is the apparent viscosity, and $d\gamma/dt$ is the shear strain rate. In the range in which SLPS occurs, a realistic yield strength is below 1MPa. Calculations for various assumptions of $\Phi_Y$ (from 0.3 to 0.6) and $\tau_o$ (from 0.01 to 1 MPa) determined that the densification temperature was not sensitive to these parameters.

For conditions where the fractional grain boundary coverage by liquid allows viscous flow, the apparent viscosity is calculated as follows:

$$\eta = \frac{\eta_o G_0^3}{G^3 \left( \frac{d\gamma}{dt} \right)^m} \exp \left( \frac{Q}{RT} \right) \frac{(\tau - \tau_Y)^2}{(1 - \frac{\Phi}{\Phi_C})}$$  \hspace{1cm} (2.20)

where $\eta_o$ is a combination of factors that includes numerical constants, the liquid viscosity pre-exponential, and a grain agglomeration factor; $G_0$ is the normalized grain size characteristic to the rheocasting measurements; $Q$ is the activation energy for viscous flow; $R$ is the gas constant; $T$ is the absolute temperature; $m$ is the strain-rate-sensitivity exponent; and $\Phi_C$ is the critical solids loading for viscous flow. When the solid content above the critical level, the system strength resists viscous deformation.

From percolation concepts [17, 74, 76] the critical bonding condition (where long range connectivity is established) occurs when

$$N_c P = 1.5$$  \hspace{1cm} (2.21)

where $N_c$ is the bonding coordination number for the lattice and $P$ is the probability of a connection. The probability of a connection is assumed to depend on the fractional coverage of grain boundaries,

$$P = 1 - F_C$$  \hspace{1cm} (2.22)

Assuming a tetrakaidecahedron shape ($N_C=14$) the particles exhibit viscous
flow when 89 % of the grain boundaries within a particle are coated with liquid [17, 76].

Viscous flow sintering modelling analysis by Dawson and Jagota [79] and Liu et al. [64] indicate that the sintering shrinkage during isothermal sintering $\Delta L/L_o$ is given as

$$\frac{\Delta L}{L_o} = \frac{\gamma_{LV} t}{D \eta}$$  \hspace{1cm} (2.23)

where $\gamma_{LV}$ is the liquid-vapor surface energy, $\eta$ is the semisolid apparent viscosity, $t$ is the sintering time, and $D$ is the particle diameter. This is valid for shrinkages up to 10 %. The sintered fractional density $\rho_s$ for a compact starting at a fractional green density $\rho_g$ is given as

$$\rho_s = \frac{\rho_g}{(1 - \Delta L/L_o)^3}$$  \hspace{1cm} (2.24)

Combining the above equations, the evolution of sintered density is given as

$$\rho_s = \rho_g[1 - 0.75\alpha(1 - (\Phi/\Phi_m))^2]^{-3}$$  \hspace{1cm} (2.25)

where the solids loading is temperature dependent.

### 2.5 Distortion during SLPS

This section summarizes the current knowledge on dimensional stability and distortion during supersolidus liquid phase sintering. Distortion can be defined as undesired shape change that occurs during sintering of the compact, causing lack of dimensional precision. Distortion severely limits the use of SLPS as a net shaping process and hence understanding distortion is critical in producing quality parts in the present day industry. In liquid phase sintering, alloys with an excess of liquid exhibit solid-liquid segregation, leading to shape loss, compositional and microstructural gradients and property variations [12, 80].

On the other hand distortion during SLPS is a time and temperature dependant phenomena [32, 71]. Dilatometer studies indicate that distortion follows densifica-
Studies on SLPS systems show the sintering window concept which helps us understand the temperature beyond which distortion occurs [40, 41, 42, 43]. The typical shape of the sinter window is shown in Figure 2.5. Three temperatures are identified; the temperature needed to initiate sintering $T_{os}$, the minimum temperature for sintering to full density $T_m$, and the distortion temperature $T_d$ [40, 42]. Wright et al. [42] show a close correlation between the solidus determined by DTA and the value of $T_{os}$, and a correlation between $T_d$ and the phase boundary defining the upper limit of the $\gamma$+carbide+L region in sintering of T1 high speed steels.

Formation of liquid between solid particles above solidus temperature creates a capillary stress which causes densification. Once the voids are filled with liquid, the capillary force approaches zero, while gravitational force acts downward and distortion occurs when solid-liquid structure is weak in comparison to gravity [81]. German [76] hypothesized that shape loss occurs when the fractional grain boundary coverage by liquid ($F_C$) approaches unity (no solid-solid contact). Lal [71] has shown that distortion occurs inspite of incomplete liquid coverage. A control microstructure softening parameter $\zeta$, which combines the effects of grain size, liquid volume fraction, and contiguity, was proposed to separate densification and distortion events. Slumping during SLPS is not a sudden event, rather it is a time-
dependant event that occurs by viscous deformation (akin to creep). This research aims at better understanding this creep behavior which causes deformation after full densification.

2.6 Corrosion of PM Steels

The corrosion resistance of stainless steels (SS) can be attributed to the natural, protective layer (passive film) that forms on the surface of these metals. This protective oxide film is subject to localized breakdown, yielding pitting, crevice corrosion, and intergranular corrosion of the underlying substrate. In the case of sintered metals, inherent pores or crevices are part of the material and, depending on their size, these pores can act as initiation sites for breakdown of the protective oxide leading to establishment of crevice corrosion [82]. In assessing the corrosion behavior of PM alloys, anodic polarization curves provide useful information concerning the potential range over which a material is passive, the amount of protection afforded by the film, the susceptibility to pitting, and the ease with which passivity is obtained [83]. Austenitic stainless steels owe their corrosion resistance to chromium, nickel, and other passivity enhancing elements such as molybdenum. Chromium is the primary element responsible for corrosion resistance of stainless steels. Nickel stabilizes the austenitic structure and promotes repassivation, especially in reducing environments. Molybdenum stabilizes the passive film, especially in combination with chromium, and improves pitting and crevice-corrosion resistance.

Lower corrosion resistance of sintered steels is attributed to high surface area due to high porosity, alloying effects, sigma phase formation during sintering cycle, and various atmosphere effects [84]. In most cases, higher sinter density leads to better corrosion resistance. However, increasing sinter density improves corrosion resistance only in acid solutions but in the case of saline solutions, the situation is not so clear [83, 85]. In some cases, higher sinter density causes inferior resistance to crevice corrosion. In highly concentrated saline solution, small pores indicative of tighter crevices, caused the wrought 434L specimens open circuit potentials and current densities to approach those of PM alloys [86, 87, 88]. Hence, it is to be noted that corrosion in PM is influenced by many factors other than just sinter
Lei and German [84] were the first to perform potentiodynamic scanning on 304L, 316L and 304LSC in the 3.5% salt water to characterize the corrosion resistance versus processing parameters. They have shown that higher sinter density reduced the corrosion rate even in the salt water solutions which is contrary to that observed by Pao and Klar [89]. Optimal processing corresponds to a high sintered density, and high sintering temperature. In addition, a low dew point atmosphere with a low content of interstitial elements provides minimal opportunity for forming deleterious chromium compounds. Rapid cooling from the sintering temperature minimizes the precipitation of chromium complexes. The removal of chromium from the exposed surface is identified as the greatest cause for low corrosion rates in sintered stainless steels [84]. Nayar et al. [90] have shown that depletion of chromium by nitride formation is the main cause of poor corrosion resistance in steels sintered in nitrogen. However, minimal corrosion can be obtained by sintering in a low dew point nitrogen atmosphere, at high temperatures, followed by rapid cooling.

Alloying additives such as copper and tin [84, 85, 89] and boron [91, 92] help achieve full density via liquid phase sintering. Higher sinter densities correspond to lower corrosion rates. Pao and Klar [89] observed that copper/tin modified 316L has higher resistance to corrosion in 5% NaCl solution. Similarly, based on the corrosion studies of Lei and German [84], the alloy rank order for corrosion resistance was determined to be 316L > 304LSC > 304L + Cu + Sn > 304L. Fedrizzi et al. [91] have shown that boron addition in stainless steel powders, when sintered under proper temperature and atmosphere conditions, leads to full density materials with excellent corrosion resistance in sulphuric acid. However they have hinted that presence of a biphasic material could promote intergranular corrosion. Investigations of Maahn et al. [92] have shown sintered 316L stainless steel with additions of either B, BN, CrB or NiB have shown an improvement of corrosion properties compared with conventional sintered stainless steel. Development of additives requires careful optimization of the metallurgy in order to avoid forming structures during solidification that are sensitive to corrosion.

In this study, research is focussed on the effect of particle morphology, percent boron addition, and sinter density on the corrosion resistance of 316L stainless
steel powders.

2.7 Master Sintering Curve

Sintering is a very complicated process involving the evolution of microstructure through action of several different transport mechanisms. For decades sintering has been modelled based on ideal geometries that represented only one of the three stages in the process [1]. It is well known that sintering behavior of any particular material depends upon several characteristics of the powder, including composition, the particle size, and size distribution, heating rate, sintering temperature, sintering time and atmosphere. A predictive model would require knowledge of all diffusion coefficients and their temperature dependencies, as well as grain growth kinetics as a function of density. Presence of a liquid phase further complicates the prediction of densification behavior, requiring us to know the solubility of major phase in the liquid and liquid transport as a function of temperature. More recently Hansen et al. [95] have attempted to model the sintering process by a single equation. It describes densification through all stages of sintering by characterizing the microstructure through two separate parameters representing geometry, and scale. A generalized model has been proposed by assuming that grain boundary and volume diffusion are the primary mechanisms of densification. This combined stage sintering model predicts the instantaneous linear shrinkage rate as:

\[
-\frac{dL}{Ldt} = \frac{\gamma \Omega}{kT} \left( \frac{\delta D_b \Gamma_b}{G^4} + \frac{D_v \Gamma_v}{G^3} \right)
\]

(2.26)

where each of the scaling factors \( \Gamma_v \) and \( \Gamma_b \) for volume and grain boundary diffusion represent a specific feature of the microstructure that influences the kinetics of sintering. Various other sintering models [99, 104, 105] can be considered as specific cases derived from the above combined-stage sintering model. Determination of these scaling factors is difficult, and deviate significantly from experiments [95, 96].

The master sintering curve concept is derived from the combined-stage sintering model by noting that the lumped scaling factors are dependent on density but are usually independent of heating schedule, unless significant surface diffusion or
exaggerated grain growth occurs [96]. For isotropic shrinkage, the linear shrinkage rate can be converted to the densification rate by

\[- \frac{dL}{Lt} = \frac{d\rho}{3\rho dt}\]  (2.27)

where \(\rho\) is the relative density. By assuming only one dominant diffusion mechanism (either volume or grain boundary) in the sintering process, Equation 2.26 can be simplified to

\[\frac{d\rho}{3\rho dt} = \gamma \Omega (\Gamma(\rho)) D_o \exp \left( - \frac{Q}{RT} \right)\]  (2.28)

where \(Q\) is the apparent activation energy; \(R\) the gas constant; \(D_o\) is the pre-exponent for either grain boundary or volume diffusion depending on which is the dominant mechanism. The exponent is \(n=3\) for volume diffusion and \(n=4\) for grain boundary diffusion. By assuming that scaling factor and grain size are functions of only density alone, Equation 2.28 can be rearranged and integrated as follows:

\[\int_{\rho_o}^{\rho} \frac{(G(\rho))^n}{3\rho \Gamma(\rho)} d\rho = \int_0^t \frac{\gamma \Omega D_o}{kT} \exp \left( - \frac{Q}{RT} \right) dt\]  (2.29)

where \(\rho_o\) is the initial density of the compact.

Rearranging Equation 2.29 to bring all the microstructural and material parameters to one side except for \(Q\), a density dependent parameter \(\Phi\) is obtained

\[\Phi(\rho) = \frac{k}{\gamma \Omega D_o} \int_{\rho_o}^{\rho} \frac{(G(\rho))^n}{3\rho \Gamma(\rho)} d\rho\]  (2.30)

The remaining terms are collected to equal \(\Theta\)

\[\Theta(t, T) = \int_0^t \frac{1}{T} \exp \left( - \frac{Q}{RT} \right) dt\]  (2.31)

which depends only on \(Q\) and the time-temperature profile.

Thus Equation 2.29 becomes

\[\Phi(\rho) = \Theta(t, T)\]  (2.32)
Φ(ρ) incorporates the changes of both microstructure scale, G(ρ), and the scaling parameter Γ(ρ). Thus, Φ(ρ) is considered a characteristic that quantifies the effects of the microstructural evolution on the sintering kinetics as densification occurs.

The relationship between ρ and Θ(ρ) is defined as the master sintering curve [96]. The MSC is unique for a given powder and green body process, including fixed green density, and it is independent of the sintering path.

Su and Johnson [96] have made several assumptions in developing the MSC and these are stated below.

- The master sintering curve (MSC) can be applied only to powder compacts made from the same powder and by the same consolidation process, and green density.

- The microstructural evolution (both grain size and geometry) are dependent only on density for any given powder and green-body process and that one diffusion mechanism dominates in the sintering process.

The master sintering curve has been successfully applied to different sintering systems: isothermal or constant heating rate, metals (nickel), ceramics (Al₂O₃, ZnO), and alumina containing a second phase (Al₂O₃(TiO₂), Al₂O₃(ZrO₂)) [96, 102, 103]. Recently Kutty et al. [97] have used MSC to evaluate the activation energy for ThO₂-UO₂ sintering in air.

2.7.1 Construction of MSC

The MSC is generated from measured densities as a function of Θ, using isothermal or non-isothermal methods as long as the temperature as a function of time during the sintering cycle is known. It is necessary to include the early stages of cooling if significant densification could occur during cooling. ρ-Θ data can be obtained with ease by performing constant heating rate (CHR) experiments in a dilatometer. Three to five runs are made over a wide range of heating rates. The final densities are measured, and the instantaneous density evolution is computed from linear shrinkage data. Isothermal sintering over a range of temperatures can also be used as long as shrinkage during the non-isothermal portion of the run is recorded.
accurately. Individual sinter runs can be performed at different sinter temperatures to calculate $\rho-\Theta$ data. This usually entails a large amount of experiments and there generally more scatter than with dilatometry.

Once a set of data is obtained, the value of $\Theta$ is computed for each data point, using a known or assumed value of the activation energy. The data then is plotted as density vs. $\log(\Theta)$, maintaining the identity of each heating rate (for CHR) or temperature (for isothermal) and the dispersion of the data is assessed. The activation energy is better found using error analysis. The data is lumped into a single set irrespective of heating rates. A function is fitted to the data, the predicted and residual is computed at each data point, and the mean square residual computed. The mean square residual is plotted as a function of activation energy, and the activation energy at which minimum of the mean residual is achieved is chosen as the activation energy for the sintering process. The form of the function chosen to fit the data can result in different activation energy values for the same set of data. Su and Johnson [96] used polynomial fits to the ZnO data and they found an activation energy of 310 kJ/mol. Teng et al. [98] used a sigmoidal curve with five adjustable parameters (Equation 2.33) which yielded a better fit to the data. The activation energy calculated was 350 kJ/mol which is greater than found by Su and Johnson [96]. It is also greater than the 210 kJ/mol assumed by Chu et al. [99] and the 276±13 kJ/mol observed by Gupta and Coble reported in [96].

The sigmoidal function used by Teng et al. [98] is

$$\rho = \rho_o + \frac{a}{1 + \exp\left(-\frac{\log(\Theta) - \log(\Theta_o)}{b}\right)^c}$$  \hspace{1cm} (2.33)

where $a$, $b$, $c$ are constants, $\rho_o$ is the green density, and $\log(\Theta_o)$ is the abscissa coordinate of the reflection point of the curve. The five parameters, $a$, $b$, $c$, $\log(\Theta_o)$, and $\rho_o$, determine the exact form of the S-curve, which gives a smooth MSC and is a better fit to the data.

Park et al. [100] have used densification parameter $\Psi$, sinter density difference-ratio parameter $\Phi$, and work of sintering ($\Theta$) to construct their master sintering curve. The definition of these parameters is given below:

$$\Psi = \frac{\rho - \rho_o}{1 - \rho_o}$$ \hspace{1cm} (2.34)
\[ \Phi = \frac{\rho - \rho_o}{1 - \rho} \quad (2.35) \]

\[ \Theta_{\rho} = \int_0^t \frac{1}{T} \exp \left( - \frac{Q_{\rho}}{RT} \right) dt \quad (2.36) \]

where \( \rho \) is the instantaneous density, \( \rho_o \) is the starting density, \( Q_{\rho} \) is the activation energy for densification. The relation between sinter density difference-ratio parameter \( \Phi \) and work of sintering \( (\Theta_{\rho}) \) is modelled based on a power law as follows:

\[ \Phi = \frac{\rho - \rho_o}{1 - \rho} = \left( \frac{\Theta_{\rho}}{\Theta_{\text{ref}}} \right)^n \quad (2.37) \]

Equation 2.37 in logarithmic form yields a straight line with slope \( n \) (power law exponent) and \( \ln(\Theta_{\text{ref}}) \) is the logarithmic value of work of sintering at \( \rho = (1 + \rho_o)/2 \), a densification parameter \( \Psi \) of 0.5. The equation for densification can be derived as

\[ \Psi = \frac{\rho - \rho_o}{1 - \rho} = \frac{1}{1 + \exp \left[ - \ln(\Theta_{\rho}) - a \right] b} \quad (2.38) \]

where \( a = \ln(\Theta_{\rho}) \) and \( b = 1/n \).

Park et al. [100] have attempted to model grain growth using master sintering curve ideas based on the assumption that grain size is dependent only on the density for any given powder and green-body process, and independent of the thermal history. By plotting Chu et al. [99] ZnO data Su and Johnson [96] show that their data does fall on a MSC indicating the independence of grain-size-density trajectory on thermal history. Hence, independence of grain size on thermal history is valid.

The grain growth equation is [1]

\[ \dot{G} = \frac{k_g \exp[-Q_G/RT]}{G^2} \quad (2.39) \]

Integrating the above equation and putting it in master sintering form gives
\[ G = \sqrt[3]{G_o^3 + 3\Theta_G} \]  

(2.40)

where \( \Theta_G = \int_0^t K_g \exp[-Q_G/RT]dt \). The two parameters \( K_g \) and \( Q_G \) can be determined by curve fitting the experimental data. The dependence of grain growth rate constant \( K_g \) on time and temperature is not totally stated, and in reality it could be a function of time and temperature. In liquid phase sintering the \( K_g \) varies with the liquid volume fraction as [175]

\[ K_g = K_I + K_L/V_L^{2/3} \]  

(2.41)

where \( K_I + K_L \) represents the infinite dilution rate constant and \( V_L \) the liquid volume fraction. In alloy systems the amount of liquid increases with temperature between solidus and liquidus, and hence \( K_g \) is a function of temperature.

Application of MSC to liquid phase sintering systems has been minimal so far. Park et al. [100] have modelled densification of tungsten heavy alloys (W-Ni-Fe) using master sintering curve with satisfactory results [101]. However, the full implications of MSC applied to liquid phase sintered systems is yet to be realized.

In this work, modelling of densification and grain growth during supersolidus liquid phase sintering of boron doped 316L stainless steel is attempted using MSC concepts.

2.8 Significance of Research

Supersolidus liquid phase sintering is a promising route to process coarse powders to full density. Processing of stainless steel 316L with boron additions via SLPS will be researched. The objective of the study is to find sintering routes to achieve full densification while avoiding distortion. Densification and distortion are sequential events and a sinter window is defined to separate the two.

Beam bending technique is used to evaluate the \textit{in situ} viscosity during sintering of 316L with boron additions. Contribution to the field is quantification of viscosity for 316L, and how the changing viscosity affects the densification and distortion behavior. The rheology of the compact follows the Bingham model and it is intended to find a yield stress value for 316L during sintering. The apparent vis-
cosity will be correlated to the evolving microstructure, to tailor microstructures for achieving full densification with minimal distortion and optimal mechanical, and corrosion properties.

Master Sintering Curve concepts are applied to model densification during supersolidus liquid phase sintering for the first time. A sinter factor is introduced which is directly proportional to density, strength and inversely proportional to distortion parameter and corrosion rate. Sintering conditions responsible for high sinter factor are desired.
Experimental Procedures

This chapter describes the experimental procedures, techniques, and equipment used in this research study.

3.1 Powder Characterization

The as-received powders were characterized for their size, size distribution, morphology, surface area, apparent, tap and pycnometer densities. Most characterization techniques require only a small quantity of powder, hence it is important that the sample selected for the analysis is representative of the bulk. A Quantachrome sieving riffle was used to draw representative samples for characterization as per MPIF standard [106].

Table 3.1 summarizes the characteristics of the stainless steel 316L and boron powders used for the experiments. The characterization techniques used in the present study have been described in the following sections.

3.1.1 Particle Size

Powder size and the size distribution was determined by using a laser scattering analyzer (Horiba LA 920). Laser scattering is a streaming technique where the particles are dispersed in a moving fluid stream which scatters light beam. The scattered light intensity is measured by using photodiode detectors. The signal from the detectors is converted to particle size distribution through mathematical
algorithms based on Fraunhofer and Mie scattering theories. Since the technique uses a liquid to disperse the particles agglomeration has to be minimized. Agglomeration skews the particle size distribution to higher particle sizes. To ensure proper dispersion, the powders were agitated both ultrasonically and mechanically. Distilled water was used as dispersion medium and 10% sodium meta-phosphate was used as surfactant to ensure good dispersion. The particle analyzer was checked for precision by measuring particle size of standard carbonyl iron powder with known distribution. Three measurements were made for each powder for statistically accurate results and the average value is reported here. The overall standard deviation was less than 3 µm in all cases.

3.1.2 Particle Shape

The particle shape was observed using a TopCon ABT-32 scanning electron microscope (SEM). Figures 3.1 and 3.2 show the representative shape of the as received powders. The as-received water atomized stainless steel powder was coarse and had an irregular shape. On the other hand the gas atomized stainless steel powder was finer and had a spherical shape. The particle shapes were characteristic of the processing route used to manufacture these powders.

Table 3.1. Table showing the powder characteristics. (NR—not reported)
3.1.3 Powder Microstructure

The as-received powders were observed to examine the powder microstructure. The powders were mounted in epoxy and diamond polished on automatic polishing machine (Rotopol). The powder microstructure for gas and water atomized stainless steel 316L powders is shown in Figures 3.3 and 3.4. As seen in the powder microstructures the powders are non porous.

3.1.4 Apparent Density

The apparent density of the powder gives a measure of the degree of packing of the powder in the loose form without agitation, expressed as a fraction of the theoretical density. The apparent density was measured using an Arnold meter according to the MPIF standard 48 [107].

This test method consists of slowly sliding a brass bushing partially filled with powder over a hole in a hardened steel block. The powder in the cavity is collected
and weighed and this weight divided by the cavity volume \((20 \text{ cm}^3)\) gives the apparent density of the powder. Three measurements were made for each powder and the average value is reported. The standard deviation was less than 2 %.

### 3.1.5 Tap Density

Tap density is the highest density that can be achieved by vibration of a powder without the application of external pressure. The packing of the powder is function of friction between particles. An irregular shape powder has more interparticle friction and hence a lower tap density. Tap density measurements were made according to the MPIF standard 46 [108].

The mass of the powder used depends on the apparent density of the powder. Depending on the apparent density, the adequate amount of powder is placed in a graduated cylinder. The contained powder mass was tapped for 3000 cycles in tap meter (Quantachrome dual autotap) at a tap rate of 260 taps per minute. The occupied volume will decrease rapidly and eventually reach a plateau value, giving tap density as the weight divided by the final volume occupied. The precision of the test is limited by the resolution of the volume measurement. The smallest
increment on the cylinder is 0.2 cm³, which limits the accuracy of volume measurement to ±0.1 cm³. For a 20 cm³ sample, this results in an accuracy of ±0.025 g/cm³. For each batch of the powder three measurements were made and the mean value is reported. The standard deviation in the measurements was less than 2%.

3.1.6 Pycnometer Density

Pycnometer density gives a measure of the true density of the powder. The actual density of the powder can be less than the theoretical value due to presence of internal porosity or impurities such as oxides. The true density of the as-received powders was measured using a helium pycnometer (Micrometrics Accupyc 1330). The unit was calibrated using factory supplied stainless steel calibration balls of known volume and density. The calibrated density was within 0.05% of the given value. A known mass of powder is placed in the sample cell of volume $V_0$. A reference cell of volume $V_c$, is pressurized to $P_1$. The sample cell is then connected to the reference chamber. This results in a drop in chamber pressure to an equilibrium value of $P_2$. Applying the ideal gas law gives,
Figure 3.4. SEM micrograph showing the microstructure of as-received water atomized stainless steel 316L powder.

\[ P_1(V_s - V_p) = P_2(V_s - V_p + V_c) \]  \hspace{1cm} (3.1)

Thus, as the only unknown, the powder volume \( V_p \) can be calculated,

\[ V_p = V_s + V_c (1 - P_1/P_2)^{-1} \] \hspace{1cm} (3.2)

The true density of the powder was determined to an accuracy of 0.01 g/cm\(^3\). Ten measurements were performed for each powder. Less than 1% variation was observed between the measured readings.

### 3.2 Alloy Composition

In this study, the experiments were performed using water atomized and gas atomized stainless steels doped with different amounts of elemental boron. The alloy composition is shown in Table 3.2
Table 3.2. Composition of the as-received gas and water atomized stainless steel 316L powders. The elemental composition is reported in wt.\%

<table>
<thead>
<tr>
<th>Element</th>
<th>GA316L</th>
<th>WA316L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>16.9</td>
<td>16.3</td>
</tr>
<tr>
<td>Fe</td>
<td>67</td>
<td>66</td>
</tr>
<tr>
<td>Mn</td>
<td>1.8</td>
<td>0.21</td>
</tr>
<tr>
<td>Ni</td>
<td>11.7</td>
<td>13.4</td>
</tr>
<tr>
<td>Mo</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>P</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Si</td>
<td>&lt; 0.10</td>
<td>&lt; 0.10</td>
</tr>
</tbody>
</table>

3.3 Powder Preparation

The as-received powders need to be mixed, compacted and sintered and the techniques used are discussed in detail below.

3.3.1 Powder Mixing

Water atomized and gas atomized 316L powders were weighed accurately and mixed with different amounts of elemental boron (0.2, 0.4, 0.8 wt.\%) to make up the desired final composition. The powders were weighed with an accuracy of 0.001 g using an electronic balance. The balance was calibrated using a standard set of weights supplied by NIST (National Institute of Standards and Technology). The weighed powders were placed in a 500 cm$^3$ capacity polypropylene jar and mixed in a turbula mixer (Glen Mills T2C) for 30 min. Turbula imparts a 3D spiral motion which imparts sufficient energy for the powder to mix homogenously.

3.4 Compaction

The homogenously mixed powders were compacted using a hand press (Carver) to various compaction pressures to manufacture cylindrical compacts with different densities. The bending beam and tensile specimens were pressed in a hydraulic press to achieve tensile bars with 60 % theoretical density.

A few compacts were made by cold isostatic press (Fluitron ISI-CP 30) to give minimal density gradients in the compacted parts and hence to minimize
the effect of density gradients on distortion. The powders were taped and sealed in cylindrical polyurethene rubber molds. The inside of the rubber molds was sprayed with zinc stearate to lubricate them. Lubrication helps compaction and easy removal of subsequent compacted samples. The cold pressed isostatic green compact density was 72 % of theoretical density of the alloy, where the theoretical density of the alloy was calculated using the inverse rule of mixtures using the following formula:

$$\frac{1}{\rho_T} = \sum_{i=1}^{N} \frac{w_i}{\rho_i}$$  \hspace{1cm} (3.3)

Where N is the number of elements in the mixture, $w_i$ is the weight fraction of the $i^{th}$ component, and $\rho_i$ the theoretical density of the $i^{th}$ element. The sintering behavior of the cold isostatically pressed compacts and the die pressed compacts were compared using in situ video imaging technique.

### 3.5 Pressing Gas Atomized Powders

A unique processing technique was developed to press the gas atomized powders. A novel binder system was used to compact the gas atomized powder which are otherwise very difficult to press due to their spherical morphology [109].

### 3.6 Debinding

The green compacts were debound in a vertical retort to remove the binder. The compacts were heated in a dry hydrogen atmosphere at a heating rate of 5°C/min to 500°C and held at this temperature for 1h to burn out the binder. Further the compacts were heated to 900°C and held at this temperature for 1h to impart handling strength to the compacts. Appropriate care needs to be taken to handle the compacts to avoid any damage after the debind step.
### 3.7 Sintering Procedure

The green parts were sintered in a horizontal alumina tube batch type furnace (CM, Bloomfield, NJ) with MoSi$_2$ heating elements placed outside the protective alumina tube. Figure 3.5 shows the a schematic diagram of the CM horizontal batch type sintering furnace. Sintering was performed in dry H$_2$ atmosphere. A gas flow rate of 2000 cm$^3$/min was maintained in the furnace throughout the sintering cycle. Dew point lower than -40 °C was maintained in the furnace. A low dew point indicates the lower moisture content of the carrier gas. A fully programmable Honeywell universal digital controller controlled the power output of the furnace.

![Schematic diagram of the CM horizontal sintering furnace](image)

**Figure 3.5.** Schematic showing the CM horizontal furnace used for sintering.

The compacts were heated at 5°C/min to sinter temperature. The sinter temperatures were different based on different alloy compositions. The dwell time at the peak sinter temperature was 30 minutes. After sintering the samples were cooled at 5°C/min to room temperature.

### 3.8 Dilatometer Study

The dimensional change in a powder compact is one of the widely applied sintering monitors. A dilatometer is employed for determination and *in situ* measurement of sintering events such as shrinkage, shrinkage rate and phase changes. Figure
3.6 is a schematic diagram of a vertical push rod dilatometer (Unitherm -1161 Al, Anter, Pittsburgh, PA) used in this study. It consists of a 1750°C (maximum temperature, but only operated to 1500°C) alumina sintering furnace capable of operating in various atmospheres: air, H\textsubscript{2}, N\textsubscript{2}, and Ar. The tube, specimen holder and the push rod are made of high density alumina.

A photoptic grating sensor converts the linear displacement of the push rod into an electrical signal which is processed by a microcomputer. The weight of the push rod is balanced by a counter weight so that the probe moves in accordance with the linear displacement of the sample without exerting much pressure. An alumina disc is placed on top of the sample to distribute the load evenly on the sample. To eliminate any expansion contribution due to the alumina probe, alumina tube or alumina disc the dilatometer is calibrated using a single crystal sapphire. Further calibration was done using a high purity Fe at \( \alpha \)-Fe to \( \gamma \)-Fe transformation temperature of 910°C. This unit measures the dimensional changes over the entire sintering cycle with a precision of 1\( \mu \)m. The temperature of the sample was measured within 2°C accuracy by a sheathed S-type thermocouple placed next to the sample. The same sinter cycle is programmed as that run in the furnace to obtain the shrinkage and shrinkage rate during sintering. The experiments were performed in flowing hydrogen (100%).

### 3.9 Distortion Quantification

Sintering induces a change in the dimension of the compact. Depending on the composition, and sintering conditions the shape change can be isotropic or non isotropic. The objective of sintering in most cases is not only to produce a component with desired properties but also maintain the tolerance on dimensions. Hence it is important to quantify any distortion that occurs so that control can be implemented to avoid it. The distortion was quantified in this study by using a coordinate measuring machine (CMM).
3.9.1 CMM

The sintered compact dimension was measured using a manual touch probe coordinate measuring machine (CMM). Figure 3.7 shows the photograph of CMM probe measuring the profile of a compact. The machine consists of a piezoelectric sensor (probe) which moves on frictionless air bearing in the x, y, z directions. The equipment is coupled with a data acquisition device via a personal computer,
which gives real time display of probe position. The probe is first calibrated on a stainless steel sphere of 3 mm diameter. The equipment has programs which can calculate various geometries to an accuracy of 10 $\mu$m. Since the samples used were cylinders the sample dimensions were quantified by measuring the sectional diameter at various heights. The measurements were made on half of the cylindrical compact. The compacts were divided into 10 equidistant subsections along their height and the corresponding diameter of each circular section was measured. The measured sectional radii and heights were normalized with respect to the maximum radius and the maximum height, respectively. The normalized radii were plotted against the normalized height to give a profile of the sample shape. These profiles provide a frame work for comparing the slumped geometry of the super-solidus liquid phase sintered compacts. The distortion parameter was calculated by measuring the standard deviation in the normalized radial measurements as given in Equation 3.4. A higher standard deviation, indicates higher deviation from the cylindrical shape, translating into higher amount of % distortion.

\[
%\text{Distortion} = 100 \sqrt{\frac{\sum_{i=1}^{N} (X_i - \bar{X})^2}{N}}, \tag{3.4}
\]

where $X_i$ is the normalized radius ($R_i/R_{\text{max}}$) and $\bar{X}$ is the mean of the normalized radius measurements and $N$ is the number of observations.

### 3.10 Synchrovision

The Synchrovision system uses high intensity strobe lighting in combination with high speed shuttering to obtain high definition images of samples inside a furnace with good contrast at high temperatures. The apparatus consists of a controller unit, a camera with high speed shuttering, and a strobe with xenon flash lamp as shown in Figure 3.8. Both the camera and the strobe light were triggered in unison by the controller. A Fresnel lens was used in conjunction with the strobe light to focus a parallel beam of light into the furnace tube. The controller unit controls the strobe intensity and frequency. The horizontal tube furnace was fitted with specially designed quartz window to allow for viewing inside the furnace.
The camera collected the strobe light reflected from the sample through a mirror placed at 45° angle in the center of the Fresnel lens. The in situ image was displayed on a television and also recorded in a standard video tape on an 8 mm tape. The recorded images were transferred to an image analysis system (Clemex Image Analyser) to measure the beam midpoint deflection.

3.11 Metallography

Standard metallographic techniques were employed for preparing samples for microstructural examination. The sintered samples were sectioned using the Accutom automatic cutter. The as cut samples were mounted using red bakelite in a LECO mounting press (Pr-25). During polishing the pores present may lead to comet tails and other artifacts which need to be avoided in order to get good images. Hence, where it was necessary the samples were vacuum impregnated by epoxy resin. The polishing was done using a Rotpol-22 automatic polishing machine (Struers) using
a series of magnetic cloths. The polishing procedure involves polishing using 9 \( \mu \text{m} \) diamond spray followed by 6, 3 and 1 \( \mu \text{m} \). In between each step a 5 min ultra sonic cleaning was done to remove any debris that the sample might have. A mirror like finish is obtained by giving a final OPS polish. To enhance the contrast in some cases between the grains and the matrix the sample was electrolytically etched using Kalling’s reagent.

### 3.12 Image Processing

The images were obtained by using a Nikon EPIPHOT microscope. The number of images collected depends on the number of grains one needs to measure to get statistically accurate results. In this study, data was collected on at least 600 grains. Images should be collected at random areas on the section but care should be taken as to avoid regions around pores as grains may be smeared and would not be representative of the microstructure. Eight to ten images were taken for each sample. A commercial image processing software package called CLEMEX image analyser is used for this process.

In order to analyze the grain sizes and other characteristics, the image should be transferred to a binary image, which represents the two phases in two different
colors. Obtaining a good binary is the key to obtain a good final image for measurements. Grain relief is one of the main reasons for a bad image. Another reason could be uneven illumination of the image, i.e., some regions appear more brighter than some. The contrast between the liquid and solid phase also affects the quality of the image. Some times sputtering with a platinum oxide layer can enhance the contrast between the grains and the matrix. In spite of all these factors, Clemex offers some features for digitally enhancing the quality of the image to perform microstructural analysis.

3.12.1 Image Analysis

Once the processing of the image is done, further feature analysis can be done to extract the necessary information from the microstructure. Liquid volume fraction, contiguity, connectivity, and grain size were measured. The liquid volume fraction can be obtained by measuring the area fraction of the liquid along the grain boundaries in the polished surface. The liquid phase was present as a thin layer along the grain boundary and it was difficult to calculate contiguity using routines. Hence, manual point count method was employed to measure contiguity. Contiguity is the average degree of contact between grains of the same phase in a two-phase microstructure. The ratio varies from 0 to 1 as the distribution of phase changes from completely dispersed to fully agglomerated structure [110]. Although contiguity varies with dihedral angle, grain size ratio, and volume fraction solid, it can determined using principles of stereology [111]. It is shown that the relative areas of 2 kinds of interfaces in a volume are directly proportional to the number of interfaces of each type intersected by a random line [112]. Hence, contiguity (C_{SS}) can be calculated by counting the number of solid-solid (N_{SS}) and solid-liquid (N_{SL}) interfaces intersected by random lines superimposed on the microstructure using the following formula:

$$C_{SS} = \frac{2N_{SS}}{2N_{SS} + N_{SL}}$$

(3.5)

The grain connectivity C_{g} is measured by counting the number of grains mutually in contact with a given central grain. The connectivity determines the rigidity of the compact during liquid phase sintering, which in turn determines the
densification rate and shape distortion [113].

Grain size, and size distribution were measured using routines developed on the Clemex analysis software. The two dimensional grain areas were measured, and converted to equivalent spherical diameter.

Image analysis has been successfully used before and the results have been compared to manual count methods. Yang [114] showed that the volume fraction measurements gave an error below 0.1 % in comparison to manual point count method.

3.13 Tensile Testing

Mechanical properties were measured using standard flat tensile bars of 6.45 cm$^2$ projected area pressed using a uniaxial hydraulic press (Gasbarre) to 61±2% green density. Tests were done on the boron added water atomized 316L powders sintered to different sinter temperatures for 30 min in a hydrogen atmosphere. Tensile tests were performed at a constant cross head speed of 2.54 mm/min. The stress-strain data was analyzed for yield strength (YS), and ultimate tensile strength (UTS). To facilitate the calculation of elongation, 1 inch mark was made on the tensile test specimen prior to test, and the mark was remeasured after tensile test. The percent elongation was calculated from the difference in the marker spacing.

3.14 Corrosion Testing

Anodic polarization scans were conducted in an EG and G Princeton Applied Scientific Model 0373 flat cell using a standard three electrode (reference, counter, and working) technique. The reference electrode used was a saturated calomel electrode. A platinum mesh served as the counter electrode system and the alloy under test was the working electrode. The experimental set up is shown in Figure 3.9. Anodic potentiodynamic polarization scans were performed using a Gamry potentiostat and CMS100 DC framework software in accordance with ASTM G5 [93] using a 0.2 mV/s scan rate. The polarization tests were performed under ambient laboratory conditions in a 0.1M NaCl solution. The ASTM G5 [93] standard calls for preparing the working electrode surface within 1 h of the experiment by
wet grinding on 240-grit SiC paper and wet polish with 600-grit SiC paper until previous coarse scratches are removed, and then rinsing and drying the specimen. This particular step was avoided as corrosion properties of as-sintered specimens were under investigation. An initial delay of 7200 s was used prior to polarization in order to allow for stabilization of the open circuit potential, \( E_{oc} \). The \( E_{oc} \) was monitored during the initial hold period. The current density was recorded continuously with change in potential (which was recorded with reference to \( E_{oc} \)) from -0.2 V to 1.8 V. Anodic scans were performed on each alloy three times for repeatability.

**Figure 3.9.** Schematic potentiodynamic anodic polarization wiring diagram.
Results

4.1 Melting

The non-equilibrium nature of the powders makes it difficult to accurately predict their melting behavior using phase diagrams. Further, phase diagram information for multi-component alloys is often not available. Hence, techniques like differential thermal analysis (DTA), differential scanning calorimetry (DSC), and quenching studies are employed to study the melting behavior.

Figure 4.1. DTA plot showing melting behavior of as-received water atomized 316L stainless steel powder.
All DTA tests were performed at 10°C/min in an argon atmosphere. The DTA was calibrated using indium, bismuth, aluminum, silver, and nickel to scan the entire temperature range from 100 to 1450°C. The DTA was accurate in predicting the melting temperature of indium (156°C), bismuth (271°C), aluminum (662°C), and silver (962°C) to ±1°C. However, at higher temperatures it was off by 6°C. The melting point of nickel was observed to be 1446°C, whereas, the correct melting point is 1452°C. This offset is taken into account by the software, and the subsequent tests indicate the corrected solidus, and liquidus temperatures. The solidus and liquidus were calculated from the DTA curves as outlined in the thermal analysis book [117]. The DTA plot for the as-received water atomized 316L stainless steel powder is shown in Figure 4.1. The as-received powder was heated to 1500°C at 10°C/min in 100 % argon atmosphere. The onset of liquid formation is 1448°C and the powder melts completely by 1465°C. The test was repeated with a different powder sample from the same batch to measure the variation of the melting temperature. The onset of liquid formation was found as 1441°C and complete melting occurred by 1459°C. The temperature measurements are accurate to ±2°C. The observed difference in solidus and liquidus can be attributed to the variation in powder sample used in DTA study. The DTA plot for gas atomized stainless steel 316L powder is shown in Figure 4.2. Gas atomized stainless steel powder has a lower solidus and liquidus as compared to the water atomized powder owing to smaller particle size. The melting range is quite narrow (<20°C) for both gas and water atomized powders, and at relatively high temperatures. Thus, the as-received 316L powder is not suitable for processing via SLPS due to its high temperature sensitivity.
**Figure 4.2.** DTA plot showing melting behavior of as-received gas atomized 316L stainless steel powder.

**Figure 4.3.** DTA plot showing melting behavior of as-received water atomized 316L stainless steel powder with different amounts of boron. The % is indicative of wt.% boron added.
Figure 4.4. DTA plot showing melting behavior of as-received gas atomized 316L stainless steel powder with different amounts of boron.

Boron is known to be a solidus depressant that enhances densification. Hence, the as-received powder was modified by addition of elemental boron in the amounts of 0.2, 0.4 and 0.8 wt.%. The DTA plots obtained for water and gas atomized stainless steel powder with boron additions are shown in Figures 4.3 and 4.4 respectively. As seen from the DTA plots the solidus is lowered to around 1230°C for both water and gas atomized stainless powders with different amounts of boron additions. The liquidus is lower for alloys with higher amounts of boron content. The second melting event at higher temperature as seen in Figure 4.3 is the complete melting of the stainless steel. The melting range has been increased by boron additions hence giving more temperature control during the sintering process. DTA on a mixture of water atomized and gas atomized powders in the ratio 70:30 with different boron contents is shown in Figure 4.5. The melting characteristics are similar to that of gas and water atomized powders with boron additions with liquid formation around 1230°C. The present results compare well with those reported by Molinari et al. [35]. They estimated the temperature of eutectic liquid formation in 316L powder with 0.4 wt.% of boron addition to be between 1200 and 1240°C. The Fe-B phase diagram shows the eutectic at 1174°C, the increase in the eutectic tempera-
Figure 4.5. DTA plot showing melting behavior of a 70:30 mixture of water and gas atomized 316L stainless steel powders with different amounts of boron.

ture for 316L is attributed to the presence of substitutional elements like Mo and Cr [35, 36].

The melting behavior of water atomized 316L powders with different amounts of boron additions up to 5 wt.% is shown in Figure 4.6. With an increase in boron content the solidus temperature decreases and the gap between solidus and liquidus increases hence giving a wider temperature range in which liquid persists. The first heat melting characteristics are shown in Figure 4.7 for water atomized 316L steel powders with varying boron content. At boron content near 2.75 wt.% the solidus and liquidus are almost convergent indicating a eutectic phase diagram for stainless steel with boron. DTA results for various powders with different amounts of boron are summarized in Table 4.1, along with results from previous works and the handbook values. The solidus-liquidus separation is quite narrow for as-received stainless steel powder whereas additions of 0.2 wt.% boron to water atomized 316L powder increases the gap from 18°C to 212°C. Further increases in boron do not significantly alter this gap. Hence, further studies were primarily focused on stainless steel powders with 0.2 wt.% boron additions which gives better temperature control during sintering than the unalloyed steel powder.
Figure 4.6. DTA plot showing melting behavior of as-received water atomized 316L stainless steel powder with boron additions upto 5 wt.%.

Figure 4.7. First heat melting temperatures for water atomized 316L powders with boron additions upto 5 wt.%. 
The handbook values (shown in Table 4.1) for solidus and liquidus are for wrought stainless steel with standard 316L compositions. In the case of 316L powders the elemental composition in the alloy can vary slightly in production, which causes a shift in the solidus and liquidus temperatures. The solidus and liquidus temperatures reported by Lal [71] for water atomized 316L powders $D_{50} = 53 \mu m$ (similar particle size as this study) with and without boron additions are relatively close to those determined in this study. In another study [38] differential calorimetry was used to determine the solidus temperatures for water atomized 316L with boron additions and the solidus temperatures were $10^\circ C$ lower than identified in this study. The lower solidus temperature can be attributed to the finer particle size of the starting powder ($D_{50}=15\mu m$) and less segregation during atomization. Higher amount of boron additions leads to large amounts of liquid formation at higher temperature, resulting in poor dimensional control. Moreover sintering in the presence of excess boron forms a brittle boride phase along the grain boundaries leading to premature fracture as will be shown in Section 4.9 and 4.10. Hence, identifying the optimum sintering temperature is paramount to process precise fully dense components via SLPS. This sinter window ranges from 1430 to 1435$^\circ C$ for water atomized 316L with 0.2% boron and 1225 to 1245$^\circ C$ for water atomized 316L with 0.8% boron.
<table>
<thead>
<tr>
<th>Composition</th>
<th>Solidus (°C)</th>
<th>Liquidus (°C)</th>
<th>Melting range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wrought 316L</td>
<td>1438</td>
<td>1459</td>
<td>21</td>
</tr>
<tr>
<td>WA316L</td>
<td>1441</td>
<td>1459</td>
<td>18</td>
</tr>
<tr>
<td>WA316L 0.2% boron</td>
<td>1233</td>
<td>1445</td>
<td>212</td>
</tr>
<tr>
<td>WA316L 0.4% boron</td>
<td>1230</td>
<td>1427</td>
<td>197</td>
</tr>
<tr>
<td>WA316L 0.8% boron</td>
<td>1224</td>
<td>1393</td>
<td>169</td>
</tr>
<tr>
<td>70:30 WA:GA</td>
<td>1432</td>
<td>1458</td>
<td>26</td>
</tr>
<tr>
<td>70:30 WA:GA 0.2% boron</td>
<td>1234</td>
<td>1440</td>
<td>206</td>
</tr>
<tr>
<td>70:30 WA:GA 0.4% boron</td>
<td>1232</td>
<td>1428</td>
<td>196</td>
</tr>
<tr>
<td>70:30 WA:GA 0.8% boron</td>
<td>1226</td>
<td>1391</td>
<td>165</td>
</tr>
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<td>1452</td>
<td>20</td>
</tr>
<tr>
<td>GA316L 0.2% boron</td>
<td>1234</td>
<td>1429</td>
<td>195</td>
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<tr>
<td>GA316L 0.4% boron</td>
<td>1230</td>
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<td>186</td>
</tr>
<tr>
<td>GA316L 0.8% boron</td>
<td>1228</td>
<td>1393</td>
<td>165</td>
</tr>
<tr>
<td>Hand book 316L [116]</td>
<td>1405</td>
<td>1445</td>
<td>40</td>
</tr>
<tr>
<td>WA316L [71]</td>
<td>1436</td>
<td>1457</td>
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<td>215</td>
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<tr>
<td>WA316L 1.0% boron</td>
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<td>1415</td>
<td>203</td>
</tr>
<tr>
<td>WA316L 0.25% boron [38]</td>
<td>1223</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>WA316L 0.5% boron [38]</td>
<td>1220</td>
<td>NR</td>
<td>NR</td>
</tr>
</tbody>
</table>

**Table 4.1.** Solidus and liquidus temperatures for water atomized, gas atomized and a 70:30 mixture of water and gas atomized powders with different amounts of boron additions. (NR-not reported)
4.2 Densification

Shrinkage and shrinkage rate are monitored by dilatometry. Furnace sintering runs were also performed to calculate the final density achieved outside of the dilatometer. Figure 4.8 shows the dilatometric plot of as received water atomized 316L heated at 10°C/min to the peak temperature. The compact shrunk by 4% and this is not sufficient to achieve full density. (Note: For a starting green density of 66% the compact needs to shrink 12.8% to achieve full density). Boron additions proved helpful is achieving higher shrinkages, and therefore higher densities, at lower temperatures when compared to as-received powder. Water atomized 316L compacts with 0.2 wt.% boron were sintered at 5°C/min to maximum temperatures of 1400°C or 1425°C and held at the peak temperature for 10 minutes. The plot of shrinkage versus temperature is shown in Figure 4.9.

![Figure 4.8. Dilatometric plot of shrinkage of water atomized 316L stainless steel powder heated at 10°C/min to 1420°C.](image-url)
Figure 4.9. Dilatometric plot of shrinkage versus temperature for water atomized 316L stainless steel powder with 0.2 wt.% boron sintered at 5°C/min to maximum sintering temperature.

Figure 4.10. Dilatometric plot of shrinkage rate versus temperature for water atomized 316L stainless steel powder with 0.2 wt.% boron sintered at 5°C/min to maximum sintering temperature.
Near full density was achieved for compacts sintered above 1400°C. The shrinkage increases rapidly in the case of heating a compact to 1425°C indicating a slumping event. Observation of the sintered dilatometer sample confirmed this. The rapid increase in shrinkage with temperature can be used as a slumping monitor. The peak shrinkage rate indicates the temperature of most active sintering which is near 1240°C as seen in Figure 4.10. This correlates to the liquidus temperature in this alloy system measured from DTA.

The development of master sintering curve (MSC) model, specifically its predictive ability, is an important step toward understanding the system. Four dilatometer runs with different thermal profiles were performed and the data obtained were used as an input for master sintering curve determination. The dilatometer plots for 316L with 0.2 wt.% boron sintered at different heating rates are shown in Figures 4.11 and 4.12. Initially, the compact expands, and then starts shrinking around liquid formation temperature, beyond which it shrinks rapidly to achieve full density. The higher the heating rate, the more significant the liquid formation event as can be seen from the peak shrinkage rate for different heating rates (seen in Figure 4.12). As heating rate increases, the peak shrinkage rate increases, however the temperature of maximum sintering activity is still relatively close for different heating rates.

Figure 4.13 shows a plot of log shrinkage versus log time during constant heating rate dilatometry indicating a linear relationship between log shrinkage and log time which has been observed by Kingery [134] in diffusion rate control and boundary reaction control case. From the plot shown in Figure 4.13 it can be observed that higher heating rates give faster densification kinetics, n being the value of the time exponent. Prior studies exploring heating rate effects on densification, and distortion behavior of liquid phase sintered tungsten heavy alloys indicate that higher shrinkage was observed for lower heating rate at a given temperature, but upon liquid formation there is a sudden burst of densification taking the compact to full density. However, little effect of heating rate was observed on distortion [73]. Microstructure is the first dictate on densification and distortion behavior.
Figure 4.11. Dilatometric plot of shrinkage versus temperature for water atomized 316L stainless steel powder with 0.2 wt.% boron sintered at different heating rates.

Figure 4.12. Dilatometric plot of shrinkage rate versus temperature for water atomized 316L stainless steel powder with 0.2 wt.% boron sintered at different heating rates.
4.3 Effect of Boron Content on Densification

4.3.1 Dilatometer Results

Dilatometry was performed on the water atomized compacts with boron additions by heating them at 10°C/min to the 1265°C and holding them for 30 minutes at this temperature. The green density of the compacts was 66 ± 1 % of theoretical. The compact with no boron additions was heated to 1420°C instead of the 1265°C. The dilatometer results are shown in Figure 4.14. The addition of boron forms a complex Fe-Cr-Mo-B eutectic at lower temperatures, and hence lower temperatures were employed in the dilatometry study for compacts with boron.

The water atomized 316L with 0.8% boron shows rapid densification starting at 1210°C and the compact is fully dense by about 1237.5°C. With less amounts of boron (0.2 and 0.4 wt.%), the shrinkage is not sufficient enough even at 1267°C, to achieve full density. However, this is still more than 316L with no boron addition.
which shrinks 3.75% at 1406°C (at least 12.8% shrinkage is needed for full density starting from a green density of 66% of theoretical density). Hence, we can achieve higher densities by sintering 316L with an optimized amount of boron additions at a lower temperature. As can be seen from Figure 4.14, the rate of change of shrinkage with temperature (slope of the curve) is highest for 316L with 0.8 wt.% boron and lowest for 316L with no boron.

![Figure 4.14. Dilatometric plot of shrinkage versus temperature for water atomized 316L with different amount of boron additions.](image)

Observation of the shrinkage rate helps identify the temperature of most active sintering. The peak in the shrinkage rate versus temperature curve indicates the temperature where most intense sintering is occurring. For water atomized 316L with boron additions, this temperature is close to 1231°C as seen in Figure 4.15. The peak for the water atomized 316L lies at a much higher temperature.

The effect of temperature and boron on the sintered density is shown in Figure 4.16. The sintered density increases with increases in the amount of boron additive and sintering temperature. With an increase in boron content in the alloy and sintering temperature, the amount of liquid phase formed increases. Hence, compacts with 0.8 wt.% boron sintered to 1275°C show the highest density.
Figure 4.15. Dilatometric plot of shrinkage rate versus temperature for water atomized 316L with different amount of boron additions.

Figure 4.16. Sintered density of water atomized 316L powder with different amounts of boron sintered at 5°C/min in hydrogen atmosphere for 30 min.
It is to be noted that although the compacts achieve full density, they also distorted. Therefore, there exists a narrow sinter window in which one needs to operate to achieve full density without distortion.

![Dilatometric plot of shrinkage versus temperature for water atomized 316L with 0.2 wt.% boron heated at 5°C/min to 1400°C with different starting green density indicated as percent of theoretical.](image)

**Figure 4.17.** Dilatometric plot of shrinkage versus temperature for water atomized 316L with 0.2 wt.% boron heated at 5°C/min to 1400°C with different starting green density indicated as percent of theoretical.

### 4.3.2 Effect of Green Density on Densification

Figure 4.17 shows the shrinkage with temperature of water atomized 316L with 0.2 wt.% boron, with varying green density. At a given temperature, a lower density compact shrinks more than a higher density compact. More dimensional change occurs in a lower density compact for achieving full density when compared to a high density compact. Figure 4.18 shows the density and distortion of compacts sintered from different initial green densities. Compact with a starting green density of 65% is 85% dense after sintering at 1425°C for 30 min. Compacts with higher green densities sinter to density >95% sintering at 1350°C, for 30 min. Compacts sintered with starting green densities of 85 and 88% sintered at 1425°C undergo distortion. Higher starting green densities is beneficial in lowering the sintering temperature in supersolidus liquid phase sintering of boron doped 316L stainless
Figure 4.18. Density and distortion versus sinter temperature for water atomized 316L with 0.2 wt.% boron heated at 5°C/min to the peak sintering temperature in hydrogen with different starting green densities indicated as percent of theoretical. The hold time was 30 min. TD- %theoretical density

steel. However, the advantage of SLPS is the ability to achieve full density from lower starting green densities, meaning slip casted and injection molded parts can be sintered to full density.

4.4 Microstructural Evolution

The evolution of microstructure during sintering of water atomized stainless steel powder with 0.2% boron addition is shown in Figure 4.19. The microstructure at 1350°C is porous, similar to a green microstructure, the pores being irregular and homogenously distributed in the compact. With an increase in the sinter temperature the compact begins to densify. This is clearly seen in Figure 4.19 as a reduction in porosity. At a sinter temperature of 1430°C the compact is almost fully dense with some closed, round pores. The compact is fully dense at 1435°C, distortion setting in a temperature between 1435°C and 1440°C. The eutectic liquid phase is not visible until 1440°C.
Figure 4.19. Microstructure of water atomized stainless steel powder with 0.2 wt.% boron sintered at 1350, 1400, 1425, 1430, 1435, and 1440 °C read left to right from top, respectively. The samples were sintered in hydrogen for 30 min.
This could be due to low amounts of liquid phase at lower sinter temperatures. The liquid phase along the grain boundaries was indiscernible, and hence the microstructural measurement was not possible.

The microstructural evolution of gas atomized 316L with 0.2% boron is shown in Figure 4.20. The compact reaches full density at 1300°C. The eutectic liquid phase is present along the grain boundaries. This liquid phase spreads along the grains and causes distortion when the liquid covers the majority of the grain boundaries. The compact does not distort till it reaches a much higher temperature between 1375°C, and 1440°C. Microstructure of a distorted compact at 1440°C shows a two phase structure with a solidified eutectic liquid phase distributed in the steel grains. As the liquid phase was adequately visible in the microstructural
images, the measurement of microstructural parameters was possible in the case of gas atomized 316L with 0.2% boron compacts. Microstructural measurements were also possible on water atomized 316L with boron additions of 0.8 wt.%.

4.5 Distortion

Densification and distortion are sequential events, with distortion occurring after the compact has achieved full density. Water atomized 316L with 0.2 wt.% boron was chosen as a representative material to study distortion during supersolidus liquid phase sintering. Distortion can be qualitatively judged by looking at the distortion profiles of the sintered compacts. Distortion is quantified using a distortion parameter which is defined based on the standard deviation of ten normalized radial measurements measured along the height of the compact. Sintered density and distortion parameter are plotted as function of temperature in Figure 4.21. There exists a narrow window of about 10°C in which full density is attained with minimal amount of distortion. Boron addition of 0.2 wt.% did not lower the sinter temperature as much as anticipated in water atomized steel powders. In the case of gas atomized powders with 0.2 wt.% boron, full density was achieved at a much lower temperature of 1300°C. The reason for this could be loss of boron due to formation of boron oxides from boron reacting with the oxygen present in the water atomized steel powder and leaching the boron available for forming a sufficient amount of liquid phase necessary for densification. The amount of oxygen measured in gas atomized powder is 0.077 % whereas water atomized powder had 0.167 % oxygen content. Loss of boron to reducing the oxides in water atomized powders leads to higher sintering temperatures when compared to gas atomized powders. Boron can possibly react with O₂ above 1100°C forming B₂O₃ [118] and existence of various borides has been reported by Elliot [119]. In fact, B₂O₃ in liquid form is stable in the temperature range 627-1527°C [120]. Baczewska and Rosso [37] observed that boron showed a strong affinity to oxygen; in the sintering process it reacted with a chemically bound oxygen on the surface of powder particles.
Figure 4.21. Plot showing sinter density and distortion parameter versus temperature for water and gas atomized 316L with 0.2 wt.% boron alloy sintered for 30 min. The heating rate was 5°C/min and the atmosphere was hydrogen.

Figure 4.22. Photograph showing water atomized 316L with 0.2 wt.% boron sintered at various temperatures for 30 min in hydrogen atmosphere. Notice distortion at 1440°C, and complete loss of shape at 1450°C. The distortion shape shown is representative of that seen in the case of other alloys.
Increasing the amount of boron lowers the sinter temperature significantly as seen in Figure 4.16. With a higher amount of boron (0.8 wt.% in this case) full density was achieved at 1260°C, which is significantly lower than 1435°C as in the case of alloys with 0.2 wt.% boron. Figure 4.22 shows a photograph of compacts of water atomized 316L with 0.2 wt.% boron, sintered at various temperatures for 30 min. As can be observed from the photograph the compacts distort significantly in a very narrow temperature range (<20°C).

4.5.1 Comparison of Densification and Distortion in Water and Gas Atomized Powders and their Mixtures

Water and gas atomized steel powders were mixed in 70:30 weight ratio respectively to achieve better packing. Gas atomized powders which have a smaller size will help densification in the initial stages. Figure 4.23 shows the density and distortion of water atomized, gas atomized stainless steel powders and a 70:30 mixture with 0.8 wt.% boron. After sintering at 1245°C for 30 min, the gas atomized powder achieved full density, whereas the water atomized powder was only 75% dense. The smaller particle size of the gas atomized powders aids densification in the 70:30 mixture leading to a higher density (83%) than the water atomized powder (75%), but lower than that of gas atomized powders (100%). At a higher sinter temperature of 1260°C, and beyond the particle size does not effect density as all compacts achieve full density. Since distortion follows full densification, it sets in early for the gas atomized powder with 0.8 wt.% boron when compared to the water atomized or the 70:30 mixture with boron.

4.5.1.1 In situ Distortion Observation

Figure 4.24 shows the in situ images during sintering of water atomized and gas atomized steel powders with 0.2 wt.% boron next to each other. The liquid spreads in gas atomized compact in 2 minutes as seen from images taken at 1365°C and 1375°C. In comparison, the water atomized compact does not show any significant shrinkage or liquid spreading.

Complete densification is achieved in boron doped gas atomized compact by 1440°C and further hold at this temperature leads to compact slumping. Figure
Figure 4.23. Plot showing density and distortion parameter versus temperature for water atomized, gas atomized and a mixture of 70:30 water and gas atomized powders mixed with 0.8 wt.% boron heated at 5°C/min to peak sinter temperature. The hold time is 30 min.

4.25 shows the distortion of gas atomized powder compact with 0.2 wt.% boron sintered at 1440°C for 30 min. The distortion of the compact occurs in the first few minutes of the hold period. The distortion increases steadily with time akin to creep behavior. The amount of distortion with time is shown in Figure 4.26.

4.6 **In situ** Observation of Sintering of Hand Pressed and Cold Isostatically Pressed Compacts

Hand pressed and cold isostatically pressed boron doped water atomized 316L steel compacts with same green density \((\approx 72\% \text{ of theoretical})\) were observed *in situ* to study their densification and distortion behavior. Constant heating of compacts did not show a significant difference in their sintering behavior as seen in Figure 4.27. However, isothermal sintering at 1437°C reveals interesting sintering behavior in these compacts. The cold isostatically pressed compacts shows liquid spreading and distortion (hour glassing) with time as seen in Figure 4.28. This
is contrary to expectations, where the isostatically pressed compact should show isotropic shrinkage and the hand pressed compact with density gradients should undergo hour glassing. It is hypothesized that strain in the outer layer can be preventing distortion in hand pressed compacts.
Figure 4.25. In situ images during sintering of water (left) and gas (right) atomized stainless steel powders with 0.2 wt.% boron at 1440°C with hold time. Distortion is visible in gas atomized powder compact. Time scale-0, 2, 3, 4, 5, 6, 7, and 30 min read left to right from top.
Figure 4.26. Plot showing distortion parameter versus time for gas atomized powders mixed with 0.2 wt.% boron at 1440°C.

Figure 4.27. *In situ* images during sintering of cold isostatically pressed (right) and hand pressed (left) water atomized steel powders with 0.2 wt.% boron. Temperature scale- 1300°C, 1350°C, 1400°C, and 1430°C read left to right from top.
Figure 4.28. *In situ* images during isothermal sintering of cold isostatically pressed (on the right) and hand pressed (on the left) water atomized steel powders with 0.2 wt.% boron at 1437°C. Time scale-0, 2, 4, 7, 10, 15, 20 and 30 min read left to right from top.
4.7 Bending Under Gravity

So far distortion of cylindrical compacts slumping under their own weight was investigated. Similarly, gravity will induce distortion in unsupported horizontal sections due to softening upon liquid formation. In situ video imaging was performed on a water atomized stainless 316L with 0.2 wt.% boron beam with dimensions of 10.45 mm wide, 57.60 mm long and 10.05 mm thick. The span length was 40 mm. No external force was applied. Figure 4.29 shows representative images during bending beam experiment of a water atomized 316L with 0.2 wt.% boron. Figure 4.30 shows the bending of wrought 316L beam (thickness =1.05 mm) for comparison. The wrought 316L beam does not bend even after heating to 1440°C for 30 min. Note although [116] reported melting range of wrought 316L is 1405-1445°C, we see at 1440°C there is no melting. The DTA analysis of as-received wrought 316L indicates the melting range as 1438-1459°C (seen in Table 4.1) which were higher than the handbook values. As temperature increases, the compact becomes less viscous and hence deforms under its own weight. The mid-point deflection versus temperature is plotted in Figure 4.31 indicating that the bending is gradual during supersolidus liquid phase sintering of water atomized 316L with 0.2 wt.% boron.

4.8 Beam Bending Viscometry

The in situ apparent viscosity of water atomized 316L with 0.2 wt.% boron beams during SLPS was determined using the beam bending technique. The theoretical background is presented in the following section. Finally, a discussion on the sources of error and the test accuracy is presented.

4.8.1 Bending Beam Theory

Bending beam analysis allows the calculation of the viscosity of the solid-liquid mixture during sintering. In the case of uniform loading of elastic beams, the general deflection equation is expressed as [153]
Figure 4.29. *In situ* bending pictures of water atomized 316L with 0.2% boron showing beam deflection at different temperatures along the sinter cycle. Temperature scale-1200°C, 1260°C, 1320°C, and 1380°C read left to right from top.

Figure 4.30. *In situ* bending pictures of wrought 316L with showing beam deflection at different temperatures. Top left-1260°C hold time of 0 min, right- 1440°C with a hold time of 30 min.
Figure 4.31. Plot of mid-point deflection versus temperature for a water atomized 316L with 0.2% boron beam. The bending experiment is performed at 5°C/min in 100% hydrogen.

\[
\frac{d^2\delta/dx^2}{[1 + (d\delta/dx)^2]^{3/2}} = \frac{M}{EI}
\]  

(4.1)

where \(M\) is the bending moment, \(I\) is the moment of inertia, \(E\) is elastic modulus at temperature, \(\delta\) is the deflection of the beam, and \(x\) is the distance from the left support (see Figure 4.32). For a beam of rectangular cross section (b*h) bending under its own weight (q)

\[
M = \frac{qlx}{2} - \frac{qx^2}{2}
\]  

(4.2)

\[
I = \frac{bh^3}{12}
\]  

(4.3)

Where \(l\) is the span length, \(q = \rho gh\) is the distributed load due to the beam’s own weight, \(g\) the gravitational constant, and \(\rho, b,\) and \(h\) are the density, width, and thickness of the specimen, respectively.

For small deflections, i.e. \(d\delta/dx < 0.15\), the second order term \((d\delta/dx)^2\) can be
neglected and Equation 4.1 can be expressed as

\[
\frac{d^2\delta}{dx^2} = \frac{M}{EI}
\]  

(4.4)

Solving Equation 4.4 with appropriate boundary conditions gives the maximum deflection occurring at the middle of the span as

\[
\delta_{\text{max}} = \frac{5\rho g L^4}{32Eh^2}
\]  

(4.5)

In sintering experiments, materials undergoing densification and distortion demonstrate linear viscous rather than linear elastic behavior. Using the viscoelastic analogy between these deformation modes, one simply replaces \(E\) by uniaxial viscosity, \(\eta\), and deflection, \(\delta\) by the deflection rate, \(\dot{\delta}\).

Assuming linear viscous flow allows Equation 4.5 to be rearranged to give the analogous viscous form; \textit{in situ} viscosity is calculated as

\[
\eta = \frac{5\rho g L^4}{32\dot{\delta}h^2}
\]  

(4.6)

Gulati \textit{et al.} \cite{133} verified the theory by measuring the viscosity of glass discs in a disc bending viscometer and comparing it with the values obtained by beam bending and parallel plate methods; good agreement was found. Hence, beam bending in its simplicity can provide us with viscosity estimates during sintering.
4.8.2 Apparent Viscosity of Boron Doped Stainless Steel

As the viscosity measured by means of Equation 4.6 includes effects that evolving porosity has on resistance against flow, it is termed the *in situ* or apparent viscosity. As can be deferred from the name, this is also the viscosity that would be measured during a test similar to a uniaxial tension used to measure the elastic modulus. Apparent viscosity of water atomized 316L with 0.2 wt.% boron was calculated during constant heating rate experiments using *in situ* video imaging. The constant heating rate experiments were repeated 4 times to check the repeatability of the bending experiments. The results were repeatable and the average of the 4 bending curves was considered for further analysis. Figure 4.29 shows the *in situ* images of the bending beam during sintering in one such experiment. Figure 4.29 shows the bending of the beam increases with temperature during sintering. This is due to several factors, such as increasing liquid content with temperature, grain growth, and decreasing viscosity. The deflection of the beam was calculated using image analysis software. The mid point deflection of the beam as a function of temperature is shown in Figure 4.33 for four replica runs. The plot indicates that the bending increases with temperature, but there is a ± 25% variation in bending between runs.

From the knowledge of the heating rate, the deflection can be plotted as a function of time during sintering. Curve fitting the data gives the deflection as a function of time. Deflection rate is calculated as a function of time by taking the time derivative of the deflection curve. Equations 4.7 and 4.8 show the regression analysis expressions for average deflection in mm, and deflection rate (cm/s) with respect to time (min).

\[
\delta = 1.228 + 0.0021t^2 \quad (4.7)
\]

\[
d\delta/dt = 7 \times 10^{-6}t \quad (4.8)
\]

\(t= 0\) in the above equations corresponds to 1150°C. Dilatometer runs were performed at 5°C/min to sinter temperature to determine shrinkage as a function of temperature. Using the continuity equation along with shrinkage data, the changes in density and thickness were calculated as a function of temperature.
Figure 4.33. Mid point deflection versus temperature during sintering of stainless steel 316L with 0.2 wt.% boron during heating at 5°C/min in hydrogen atmosphere.

Figure 4.34. Density versus temperature during dilatometry on a water atomized stainless steel 316L with 0.2 wt.% boron compact. The heating rate was 5°C/min and the atmosphere was hydrogen. The thermal expansion was taken into account for calculation of density from shrinkage data.
The evolution of sinter density with temperature based on shrinkage data from dilatometry is shown in Figure 4.34. The shrinkage data was corrected for thermal expansion of stainless steel compact during heating. The coefficient of thermal expansion was calculated from the cooling curve and it has a value of 16.6 \times 10^{-6} /°C. The thermal expansion increases the shrinkage by about 2% which translates into a 2-3% increase in sinter density. The deflection rate, density and thickness changes were input into Equation 4.6 along with the gravitational constant and span length to calculate the apparent viscosity during sintering. The viscosity evolution will be dealt in discussion chapter.

4.8.3 Accuracy and Sources of Error

- Thermal expansion effect will result in a change in the support span length, which was measured at room temperature. This effect was minimized by choosing alumina as the material for fabrication of the support assembly. Measurement of span length at room temperature and at the typical test temperature revealed negligible change.

- The mathematical relation used in determining the viscosity is valid for small deflections. Timoshenko [153] showed that this small deflection theory works for dδ/dx ratios of 0.3 to 0.4. Further, Hagy [137, 150] observed no errors up to deflections of dδ/dx about 25% of the span length. In the present case, deflections up to only about 15% of the length were used for calculations.

- The uncertainty in the temperature was estimated to be ±2°C.

- The apparent viscosity marks a linear relationship between stress and strain rate once deflection occurs. The deflection occurs when the stress exceeds the yield strength of the beam (\(\sigma_{ys}\)).

- The density and height values were calculated from the shrinkage data obtained from the dilatometer. Two runs were made in the dilatometer and viscosities were calculated based on both the shrinkage data sets and the error in the viscosity was less than 10%. For a given shrinkage data set the viscosities changed from experiment to experiment due to error in deflection data which translates into an error of 60% in the apparent viscosity.
4.9 Mechanical Properties

The ultimate tensile strength (UTS) for water atomized 316L with different amounts of boron sintered to different sintering temperatures for 30 min in hydrogen is shown in Figure 4.35. At a sintering temperature of 1200°C, the ultimate tensile strength is not significantly enhanced with higher boron content but with an increase in sintering temperature to 1225°C the ultimate tensile strength increases. The increase is highest for an alloy with 0.8 wt.% boron. Further increase in sintering temperature is detrimental in the case of 0.8 wt.% alloys but beneficial for others. The UTS depends on both the final density and microstructure. Full density does not necessarily imply higher UTS. In the case of alloys with 0.8 wt.% sintering at 1250°C creates a microstructure with brittle connected phase hence lowering the UTS.

Figure 4.35. Ultimate tensile strength of boron doped water atomized 316L alloys sintered at peak temperature for 30 min in hydrogen atmosphere. An average of three tests at each temperature with the error bars are reported.
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<th>T,t,Atm</th>
<th>UTS</th>
<th>Y.S</th>
<th>δ, %</th>
<th>ρ(%TD)</th>
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<td>NR</td>
<td>82</td>
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<td>96</td>
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<td>NR</td>
<td>100</td>
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<td>92.2</td>
<td>62</td>
<td>1.49</td>
<td>65.7</td>
</tr>
<tr>
<td>316L+0.4%B [38]</td>
<td>1200,30,H₂</td>
<td>96.2</td>
<td>70.5</td>
<td>2.10</td>
<td>65.8</td>
</tr>
<tr>
<td>316L+0.6%B [38]</td>
<td>1200,30,H₂</td>
<td>112.8</td>
<td>76.6</td>
<td>1.17</td>
<td>64.2</td>
</tr>
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<td>316L [39]</td>
<td>1225,30,H₂</td>
<td>90</td>
<td>70.1</td>
<td>0.2</td>
<td>65.8</td>
</tr>
<tr>
<td>316L+0.2%B [39]</td>
<td>1225,30,H₂</td>
<td>124.5</td>
<td>76.9</td>
<td>5</td>
<td>68.6</td>
</tr>
<tr>
<td>316L+0.4%B [39]</td>
<td>1225,30,H₂</td>
<td>259.9</td>
<td>125.9</td>
<td>15.0</td>
<td>80.9</td>
</tr>
<tr>
<td>316L+0.8%B [39]</td>
<td>1225,30,H₂</td>
<td>476.8</td>
<td>235.1</td>
<td>15.03</td>
<td>95.3</td>
</tr>
<tr>
<td>316L [39]</td>
<td>1250,30,H₂</td>
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<td>74.1</td>
<td>0.2</td>
<td>66.8</td>
</tr>
<tr>
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<td>133.5</td>
<td>77.7</td>
<td>7.4</td>
<td>69.8</td>
</tr>
<tr>
<td>316L+0.4%B [39]</td>
<td>1250,30,H₂</td>
<td>318.4</td>
<td>150.5</td>
<td>14.7</td>
<td>88.3</td>
</tr>
<tr>
<td>316L+0.8%B [39]</td>
<td>1250,30,H₂</td>
<td>350.8</td>
<td>250.6</td>
<td>2.2</td>
<td>98.5</td>
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<tr>
<td>316L [40]</td>
<td>1275,30,H₂</td>
<td>99.5</td>
<td>73</td>
<td>0.2</td>
<td>66.5</td>
</tr>
<tr>
<td>316L+0.2%B [40]</td>
<td>1275,30,H₂</td>
<td>138.6</td>
<td>82.0</td>
<td>8.6</td>
<td>70.5</td>
</tr>
<tr>
<td>316L+0.4%B [40]</td>
<td>1275,30,H₂</td>
<td>346.8</td>
<td>162.8</td>
<td>15.3</td>
<td>92.91</td>
</tr>
<tr>
<td>316L+0.8%B [40]</td>
<td>1275,30,H₂</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
</tr>
</tbody>
</table>

Table 4.2. Compilation of tensile data on 316L steels. δ is the elongation and ρ the density. (NR-not reported)
Figure 4.36. Yield strength (at room temperature) of boron doped water atomized 316L alloys sintered at peak temperature for 30 min in hydrogen atmosphere. An average of three tests at each temperature with the error bars is reported.

Figure 4.37. Elongation of boron doped water atomized 316L alloys sintered at peak temperature for 30 min in hydrogen atmosphere. An average of three tests at each temperature is reported.
<table>
<thead>
<tr>
<th>Composition</th>
<th>T,t,Atm</th>
<th>UTS</th>
<th>Y.S</th>
<th>δ, %</th>
<th>ρ(%TD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIM316L[123]</td>
<td>1340,60,H_2</td>
<td>369.5</td>
<td>199.2</td>
<td>18.6</td>
<td>NR</td>
</tr>
<tr>
<td>MIM316L[123]</td>
<td>1340,60,75H_2-25N_2</td>
<td>460.1</td>
<td>316.9</td>
<td>11.8</td>
<td>NR</td>
</tr>
<tr>
<td>MIM316L[123]</td>
<td>1340,60,50H_2-50N_2</td>
<td>475.8</td>
<td>341.0</td>
<td>10.4</td>
<td>NR</td>
</tr>
<tr>
<td>316L[126]</td>
<td>1327,NR,Ar</td>
<td>462</td>
<td>177</td>
<td>33</td>
<td>90</td>
</tr>
<tr>
<td>316L[126]</td>
<td>1327,NR,N_2</td>
<td>517</td>
<td>258</td>
<td>25</td>
<td>90</td>
</tr>
<tr>
<td>MIM316L[125]</td>
<td>1375,60,N_2</td>
<td>688</td>
<td>451</td>
<td>25</td>
<td>NR</td>
</tr>
<tr>
<td>MIM316L[125]</td>
<td>1375,60,N_2-10H_2</td>
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<td>451</td>
<td>32</td>
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<td>MIM316L[125]</td>
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<td>52</td>
<td>98</td>
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<tr>
<td>MIM316L[125]</td>
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<td>98</td>
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<td>95</td>
</tr>
<tr>
<td>GA316L[124]</td>
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<td>575</td>
<td>210</td>
<td>44</td>
<td>NR</td>
</tr>
<tr>
<td>GA316L[124]</td>
<td>1280,60,H_2</td>
<td>575</td>
<td>210</td>
<td>44</td>
<td>NR</td>
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<tr>
<td>GA316L[124]</td>
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<td>210</td>
<td>52</td>
<td>NR</td>
</tr>
<tr>
<td>GA316L[124]</td>
<td>1340,60,H_2</td>
<td>500</td>
<td>210</td>
<td>58</td>
<td>NR</td>
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<tr>
<td>GA316L+25%WA316L[124]</td>
<td>1280,60,H_2</td>
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<td>201</td>
<td>22</td>
<td>NR</td>
</tr>
<tr>
<td>GA316L+25%WA316L[124]</td>
<td>1280,60,H_2</td>
<td>360</td>
<td>201</td>
<td>22</td>
<td>NR</td>
</tr>
<tr>
<td>GA316L+25%WA316L[124]</td>
<td>1320,60,H_2</td>
<td>400</td>
<td>201</td>
<td>28</td>
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<tr>
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<td>1320,60,H_2</td>
<td>400</td>
<td>201</td>
<td>28</td>
<td>NR</td>
</tr>
<tr>
<td>GA316L+50%WA316L[124]</td>
<td>1280,60,H_2</td>
<td>320</td>
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<td>11</td>
<td>NR</td>
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<td>GA316L+50%WA316L[124]</td>
<td>1280,60,H_2</td>
<td>320</td>
<td>192.5</td>
<td>11</td>
<td>NR</td>
</tr>
<tr>
<td>GA316L+50%WA316L[124]</td>
<td>1320,60,H_2</td>
<td>420</td>
<td>192.5</td>
<td>26</td>
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<td>GA316L+50%WA316L[124]</td>
<td>1320,60,H_2</td>
<td>420</td>
<td>192.5</td>
<td>26</td>
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<td>205</td>
<td>183.7</td>
<td>8</td>
<td>NR</td>
</tr>
<tr>
<td>GA316L+75%WA316L[124]</td>
<td>1320,60,H_2</td>
<td>335</td>
<td>183.7</td>
<td>28</td>
<td>NR</td>
</tr>
<tr>
<td>GA316L+75%WA316L[124]</td>
<td>1320,60,H_2</td>
<td>335</td>
<td>183.7</td>
<td>28</td>
<td>NR</td>
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<tr>
<td>WA316L[124]</td>
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<td>175</td>
<td>25</td>
<td>NR</td>
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<tr>
<td>WA316L[124]</td>
<td>1280,60,H_2</td>
<td>330</td>
<td>175</td>
<td>25</td>
<td>NR</td>
</tr>
<tr>
<td>WA316L[124]</td>
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<td>380</td>
<td>175</td>
<td>35</td>
<td>NR</td>
</tr>
<tr>
<td>WA316L[124]</td>
<td>1320,60,H_2</td>
<td>380</td>
<td>175</td>
<td>35</td>
<td>NR</td>
</tr>
</tbody>
</table>

Table 4.3. Compilation of tensile data on 316L steels. δ is the elongation and ρ the density. (NR-not reported)
Figure 4.38. Fracture surfaces of water atomized stainless steel powders sintered at 1200, 1225, 1250, and 1275°C read left to right from top, respectively.

The room temperature yield strength of water atomized 316L alloys doped with boron, sintered to various temperatures for 30 min in hydrogen is shown in Figure 4.36. At a given temperature the yield strength is higher for an alloy with higher boron content. In the case of alloys with 0.8 wt.% there exists an optimum temperature to attain maximum yield strength beyond which the compact fractures in a brittle manner. Figure 4.37 shows elongation of boron doped water atomized stainless steel 316L alloys sintered at different temperatures. With no boron additions the elongation is almost same at all sinter temperatures from 1200 to 1275°C. The elongation increases and then decreases for 316L with 0.8 wt.% boron. The optimum temperature for achieving highest elongation in this alloy system is 1225°C. The tensile data from this study are compiled with data from prior studies and presented in Tables 4.2, and 4.3.
Figure 4.39. Fracture surfaces of water atomized stainless steel powders with 0.2 wt.% boron sintered at 1200, 1225, 1250, and 1275 °C read left to right from top, respectively.

4.10 Fracture Analysis

Undoped water atomized 316L and water atomized 316L with 0.2 wt.% boron tensile bars have high final porosity (about 30% see Figure 4.16) and have isolated sintering contacts translating into poor mechanical properties. The fracture surfaces shown in Figures 4.38 and 4.39 are indicative of brittle failure in these alloys at all the sinter temperatures.

Figure 4.40 shows the fracture surfaces for water atomized 316L with 0.4% boron sintered to different sintering temperatures. The fracture surface at 1200°C indicates isolated sintering contacts and a brittle failure. At 1275°C the pores are isolated and the fracture is ductile, characterized by an increase in UTS, yield strength, and elongation.

Figure 4.41 shows the fracture surfaces for water atomized 316L with 0.8 wt.%
Figure 4.40. Fracture surfaces of water atomized stainless steel powders with 0.4 wt.% boron sintered at 1200, 1225, 1250, and 1275 °C read left to right from top, respectively.

boron sintered to 1200°C, 1225°C, and 1250°C. The fracture surface at 1200°C indicates that the fracture propagates through the interconnected pores. With an increase in sinter temperature to 1225°C the fracture mode changes from predominantly ductile indicated by the dimples, to brittle fracture at 1250°C due to the brittle phase at the grain boundaries. This indicates that the optimum sintering temperature for 0.8 wt.% boron samples is 1225°C. Hence optimum mechanical properties can be achieved by not only controlling the density but also the final microstructure during sintering.

4.11 Corrosion Studies

Figure 4.42 compares the anodic polarization curves for water and gas atomized steels with 0.2% boron, sintered to full density, to wrought 316L. Zero current
potentials for wrought 316L were always more positive than PM components. The formation of a passive film enhances the corrosion resistance of stainless steels. The formation of such a passive film is hindered in most PM alloys due to the presence of porosity. Anodic potentiodynamic polarization curves for PM alloys indicated either initial passivation followed by a more uniform corrosion process or general attack throughout the scan. Water atomized 316L with 0.2% boron sintered to 1435°C is nearly fully dense and it displays more of a classical passive behavior. The passive film is subject to pitting corrosion in presence of chloride species. The pitting potential of WA316L with 0.2% boron sintered to full density at 1435°C is 585.7 mV which is lower than the pitting potential of wrought 316L (700mV) as shown in Table 4.4. The higher the pitting potential, the less susceptible the material is to pitting. In comparison, the WA316L with 0.2% boron sintered at
1350°C which contains 30% porosity shows a uniform corrosion behavior, (seen in Figure 4.42) with the pores acting as hydrogen concentration cells reducing the ability to passivate. It should be noted that the current density is based on the apparent area rather than the actual surface area of the pores. An approximate calculation of the surface area assuming spherical pores indicates that the actual surface area of the pores is about 10-12 times higher than the apparent surface area. This would shift the anodic polarization curves for the specimens with high porosity to the left in Figures 4.42 and 4.43. For specimens with porosity less than 8%, the pores are not interconnected and the effect of pore surface area is negligible on corrosion as compared to high porosity specimens. Sinter density does enhance the corrosion resistance.

![Graph](image-url)

**Figure 4.42.** Anodic potentiodynamic polarization curves run in 0.1M NaCl for wrought 316L, water atomized 316L with 0.2% boron sintered at 1350°C, 1435°C and, gas atomized 316L with 0.2% boron sintered at 1350°C.

Anodic polarization curves for water and gas atomized powder with 0.8% boron additions sintered at different sinter temperatures to study the sinter density effect on corrosion are shown in Figure 4.43. Water atomized powder with 0.8% boron goes from being 75% dense at 1245°C to full density at 1260°C leading to better corrosion properties marked by higher corrosion potential and lower current density in the fully dense compact. A similar trend is observed in sintering of gas atomized
Figure 4.43. Anodic potentiodynamic polarization curves run in 0.1M NaCl for wrought 316L, water atomized 316L with 0.8% boron sintered at 1245°C, 1260°C and, gas atomized 316L with 0.8% boron sintered at 110°C, 1245°C.

powders with 0.8% boron at 1150°C (36% porosity) and 1245°C (full density). This is in agreement with studies done by Fedrizzi et al. [91] who have observed that sintering of water atomized 316L powders with 0.4% boron in hydrogen atmosphere above the solidus temperature shows a noticeable corrosion resistance improvement when tested in sulphuric acid solution.

Gas atomized 316L with 0.2% boron sintered at 1350°C which is fully dense exhibits uniform corrosion as compared to the passive behavior exhibited by fully dense WA316L with 0.2% boron sintered at 1435°C. This may be due to the sinter sensitization caused by formation of boride phases along the grain boundaries in gas atomized 316L with 0.2% boron specimen as seen from the microstructure shown in Figure 4.45. In comparison the water atomized 316L with 0.2% boron exhibits a superior microstructure close to that of wrought 316L but only with a larger grain size (seen in Figure 4.45).

In Figure 4.44, we see that fully dense water atomized 316L powder with 0.2 and 0.8 % boron exhibit different corrosion behavior. The WA316L with 0.2% boron shows classic passive behavior whereas the WA316L with 0.8% boron shows quasi-passive behavior with lower pitting potential (399 mV) and lower current
Figure 4.44. Anodic potentiodynamic polarization curves run in 0.1M NaCl comparing wrought 316L to water atomized, and gas atomized 316L powders with 0.2 and 0.8 % boron sintered to full density.

Table 4.4. Data obtained from anodic polarization testing of wrought 316L and powders with boron additions at different sintering conditions. The temperature in the bracket indicates the sintering temperature. (NA—not applicable)

<table>
<thead>
<tr>
<th>Composition</th>
<th>$i_{corr}$ ($\mu$ A/cm$^2$)</th>
<th>$E_{corr}$ (mV)</th>
<th>$E_{pit}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wrought 316L</td>
<td>1.17 $\times$ 10^{-9}</td>
<td>-1.8</td>
<td>698</td>
</tr>
<tr>
<td>WA316L 0.2% boron (1435°C)</td>
<td>1.6</td>
<td>-164</td>
<td>585</td>
</tr>
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<td>0.8</td>
<td>-75</td>
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</tr>
<tr>
<td>WA316L 0.8% boron (1260°C)</td>
<td>6.1</td>
<td>-157</td>
<td>399</td>
</tr>
<tr>
<td>WA316L 0.8% boron (1245°C)</td>
<td>14.1</td>
<td>-317</td>
<td>NA</td>
</tr>
<tr>
<td>GA316L 0.2% boron (1350°C)</td>
<td>3.9</td>
<td>178</td>
<td>NA</td>
</tr>
<tr>
<td>GA316L 0.8% boron (1245°C)</td>
<td>31.5</td>
<td>178</td>
<td>NA</td>
</tr>
<tr>
<td>GA316L 0.8% boron (1150°C)</td>
<td>21.7</td>
<td>-252</td>
<td>NA</td>
</tr>
</tbody>
</table>

densities. The difficulty in obtaining the passive state could be attributed to the presence of a heterogeneous microstructure with the eutectic phase localized at the austenitic grain boundary in the higher boron containing alloys. This is clearly seen in the sintered microstructures shown in Figure 4.45 which shows a higher amount of boride phase and thicker layers in 0.8% boron specimen when compared
to 0.2% boron specimen, causing higher amount of sinter sensitization. Maahn et al. [92] have also observed that sintering additives such as boron, BN, NiB, and CrB produce fully dense microstructures with improved salt-spray corrosion resistance but show sinter sensitization due to formation of Cr-rich and Mo-rich borides during solidification.

Similar to water atomized compacts, gas atomized compacts with 0.2% boron sintered to full density exhibit lower current densities in comparison to the 0.8% boron compacts (seen in polarization curves from Figure 4.44). Water atomized powders with 0.2% boron sintered to full density perform better than gas atomized powders with same amount of boron. This again can be seen in Figure 4.45 where the boride phases evident in the gas atomized 316L with 0.2% boron cause sinter sensitization. Hence, the amount of boron, and process conditions have to be optimized in order to achieve full density at lower sinter temperatures and have a microstructure that is not susceptible to sinter sensitization.
Figure 4.45. Wrought and sintered microstructures. Top left-wrought 316L, top right-WA316L 0.2% boron 1350°C, middle-left WA316L 0.2% boron 1435°C, middle right-WA316L 0.8% boron 1260°C, bottom left- GA316L 0.2% boron 1350°C, bottom right-GA316L 0.8% boron 1245°C
Discussion

5.1 Densification and Distortion

Densification critically depends on the sintering stress exceeding the threshold strength. In sintering large particles, the sintering stress that causes densification is small, and often insufficient to overcome the inherent compact strength that resists densification. Thermal softening during heating decreases the yield strength of the sintering compact, allowing densification in response to the sintering stress. During sintering of stainless steel 316L, at a temperature of 1300°C the sintering stress equals the in situ strength of 5 MPa [115]. However, in SLPS of 316L with boron additions formation of liquid phases in 316L at lower temperatures in the presence of boron weakens the compact. Compact strength as low as 1 MPa is associated with liquid films on the grain boundaries [115]. In fact, Yu et al. [129] measured tensile strengths as low as 5 MPa for carbon steels near their solidus temperatures. At temperatures close to the solidus the in situ compact strength is lower than the sintering stress causing rapid densification as observed from the increase in shrinkage above the solidus, seen in the dilatometry plots (section 4.3).

During densification, the compact consists of semisolid particles and considerable porosity. The liquid assists densification in two ways. Firstly, the liquid can flow and fill the pores. Secondly, the liquid at the grain boundaries exerts a capillary force causing localized deformation in a small region near the neck (where capillary stress provides a high compressive stress) resulting in neck growth and contact flattening [64]. Since the capillary stress is much larger (a few MPa) than
the gravitational force (1 kPa for a sample of height 0.01 m) during densification, the effect of gravity is negligible [81]. After densification, the compact consists of solid grains with liquid film along the grain boundaries and almost zero porosity. Once the pores are filled the capillary force approaches zero, while the gravitational force exceeds the in situ compact strength resulting in distortion [64]. Distortion happens after full densification [127, 128, 185]. This phenomena is shown in Figure 5.1 for 316L stainless steel, and its alloys with boron, where full densification occurs before distortion. Similar behavior has been observed in supersolidus sintering of nickel base alloys [22] and 316L stainless steel with boron [32, 71].

![Figure 5.1. Distortion as a function of sintered density for boron added 316L.](image)

5.2 Effect of Microstructural Evolution on Densification and Distortion

Microstructural evolution plays a very important role in the viscosity evolution during SLPS. It is necessary to understand the evolution of microstructure, and microstructural parameters to fully understand the mechanisms involved in densification and distortion during SLPS. The evolution of the microstructural pa-
rameters such as liquid volume, contiguity, fractional liquid coverage, liquid film thickness, and grain size will be discussed in this section.

Figure 5.2. Liquid volume fraction as a function of sinter temperature for gas and water atomized 316L determined from DTA.

5.2.1 Liquid Volume Fraction

Unlike liquid phase sintering systems where the amount of liquid remains constant with temperature, SLPS systems show an increase in liquid content with temperature, above the solidus. The liquid volume determined from the DTA analysis for 316L and its alloys with 0.2 wt.% boron additions is shown in Figures 5.2 and 5.3, respectively. The amount of liquid increases with temperature, and the rate at which the liquid content increases with temperature \((dV_L/dT)\) indicates the temperature sensitivity of the particular alloy. The as-received water and gas atomized 316L alloy has a narrow melting range and liquid volume varies from 0 % to 100 % within 25°C and 30°C, respectively. In the case of gas atomized 316L with 0.2 wt.% boron addition, the liquid volume changes from 1.5% to 30% in 19°C \((dV_L/dT= 1.5%/°C)\) whereas as it varies from 1% to 12% for water atomized 316L with 0.2 wt.% boron \((dV_L/dT=0.57%/°C)\). The difference in the behavior of gas
and water atomized 316L with boron can be attributed to the leaching of boron by the oxygen present in water atomized powders. Boron oxide has low vapor pressure and hence volatilizes at high temperature. The liquid volume calculated from microstructural analysis as a function of sinter temperature for water atomized 316L with 0.8% boron is shown in Figure 5.4. The $dV_L/dT$ from microstructural analysis for WA316L with 0.8 wt.% boron is calculated to be 0.1%/°C. From DTA observations by Wright et al. [42] on T1 high speed steels with varying carbon content, $dV_L/dT$ varies in the range 0.45-0.7 %/°C for carbon content variation from 1.6% to 0.6%, respectively. Data from Bee et al. [45] gives $dV_L/dT$ of 0.39 %/°C for M2 steel, and 0.54 %/°C for T15 steel powders. For bronze, Lal [71] observed $dV_L/dT$ of 0.65 %/°C. For nickel based super alloys $dV_L/dT$ of 0.72%/°C was calculated based on the DSC data [61]. This suggests that the rate of increase of liquid content with temperature varies depending on the nature of the alloy. A high rate could lead to a large amount of liquid in a narrow temperature range, leading not only full density, but also microstructural coarsening, and poor dimensional control. On the other hand, a lower rate indicates better temperature control that can be achieved during the sintering process. Hence, a lower rate of increase in the liquid content with temperature is desirable in the optimum sintering range to better control the densification and dimensional precision during sintering.
Figure 5.3. Liquid volume fraction Liquid volume as a function of sinter temperature for gas and water atomized 316L with 0.2% boron addition determined from DTA.

Figure 5.4. Liquid volume as a function of sinter temperature for water atomized 316L with 0.8% boron measured from microstructural analysis.
German [16] has compiled data for the optimum amount of liquid necessary for densification in various alloys. Within the optimal working temperature range the reported liquid content varies from 5% to 65%. In the case of boron doped 316L we observe that the liquid content necessary for densification could be as little as 5%. Similar observations were made by Takajo and Nitta [45] on M2 type Fe-6W-5Mo-4Cr-2V high speed steel, where near full density was achieved with 5% liquid phase. Chan et al. [61] found that a minimum liquid volume fraction of 11% is required to achieve near full density in SLPS of nickel based superalloys via MIM. The amount of liquid content is important during densification, equally important is the location of the liquid in the microstructure. Jeandin et al. [18, 19] have observed distribution of liquid within the grains (intra) and along the grain boundaries (inter) in astroloy and nickel base super alloys. The temperature at which both intragranular and intergranular liquids become connected has a critical influence both on the kinetics of natural densification and rheology of liquid-solid astroloy. In an another study, Lal [71] observed that in bronze system, most liquid formed at the grain boundaries and some within the grains as isolated pools. The liquid present within the grains does not contribute to densification process. In stainless steel alloys, all the liquid formed at the grain boundaries due to segregation of boron to the grain boundaries. Another important factor to be considered is the wetting and spreading of liquid along the grain boundaries. This will be further discussed in the following subsections.

5.2.2 Contiguity and Fractional Grain Boundary Coverage

Contiguity ($C_{SS}$) is defined as the fraction of internal surface area of a phase shared with grains of the same phase in a two phase microstructure. The fractional grain boundary coverage $F_C$ by the liquid is $1-C_{SS}$. The contiguity and fractional grain boundary coverage for water atomized 316L alloy with 0.8 wt.% boron as a function of liquid volume are shown in Figure 5.5. The fractional grain boundary coverage by liquid increases with increasing liquid volume in the microstructure. Isothermal sintering studies on W-Mo-Ni-Fe alloy, report a sharp decrease in contiguity during the initial stage of the isothermal hold, reaching a minimum after 120 min. The contiguity subsequently increases due to grain coalescence [130]. The wet-
ting and dihedral angle determines the penetration of interparticle bonds. Flaitz and Pask [131] demonstrate that grain boundary penetration can occur without having "complete wetting" or spreading. The dihedral angle \( \phi \) defines the ability of the liquid to penetrate the grain boundaries. The solid dissolution across the interface into the newly formed liquid causes a reduction a momentary decrease in solid-liquid surface energy [132]. The reduction in surface energy required to cause grain boundary penetration is given by:

\[
- \frac{d\gamma_{SL}}{\gamma_{SL}} = \frac{\phi}{2} \tan(\phi/2)
\]

(5.1)

Although we have not measured the dihedral angle in this study, we can estimate the dihedral angle based on the relationship by Campbell [161]

\[
F_c = 2.64\left(\frac{V_L}{K}\right)^{1/2}
\]

(5.2)

where \( F_c \) is the fractional liquid coverage, \( V_L \) is the liquid volume fraction. The term \( K \) depends only on the dihedral angle \( \phi \) and is given by

\[
K = \sqrt{3} + \frac{3}{\tan[30 - (\phi/2)]} - \left[ \frac{30 - (\phi/2)}{60} \right] \frac{\pi}{\sin^2[30 - (\phi/2)]}
\]

(5.3)

Based on the above equation we calculate the dihedral angle to be nearly zero for 316L with 0.8 % boron. Lal [71] observed the dihedral angle to be between 1 to 5° for 316L with 0.5 % boron. For a dihedral angle of 5°, a 0.19% decrease in the relative solid-liquid surface energy leads to liquid penetration of the grain boundaries. Alternatively, for a dihedral of 1°, a 0.008% decrease in solid-liquid surface energy will lead to grain boundary penetration. Dissolution of the solid grain in the liquid phase can cause a small decrease in the solid-liquid energy which is sufficient to cause grain boundary penetration and an increase in fractional grain boundary coverage. Chan and Lin [130] ascribed the decrease in contiguity during initial stages of isothermal sintering of W-Mo-Ni-Fe alloys to the continuous change in interfacial properties. From percolation concepts, the critical \( F_c \) needed for onset of viscous flow is determined to be 0.89 [76]. However, when the \( F_c \) approaches 1, distortion can occur due to creep under gravitational stress. Based on the compression creep tests on various metals containing low melting intergranular
Figure 5.5. Contiguity as a function of liquid volume for water atomized 316L with 0.8% boron measured from microstructural analysis.

Phases Pharr et al. [164, 172] observe that the dihedral angle when close to zero, as is the case in Cu-Bi alloys, 95% of the grain boundary area is wet enhancing creep. Vaandrager [171] observed no significant effect on creep behavior when only 9% of the grain boundaries were covered in brass. Baudelet et al. [165] and Bordeaux et al. [166] observe the presence of a connected liquid phase along the grain boundaries lowered the axial flow stress above the solidus temperature in aluminum alloys. The strain rate in these tests was $10^{-4}/s$ which is close that in SLPS and hence serve as a good comparison. There exists a critical range for fractional grain boundary coverage ($0.89 < F_C < F_{dist}$) in which sinter densification occurs without the concomitant distortion due to creep mechanisms.

The liquid film thickness observed had a distribution. A rough estimate shows the liquid film could vary from 0.1-10 µm.
5.2.3 Grain Size

Grain growth is a dominant aspect of microstructural evolution which occurs concomitant with liquid formation and spreading during SLPS. There is a change in grain co-ordination number (Equation 2.8) with an increase in the liquid volume fraction. Grains grow rapidly via diffusion through the liquid phase. The driving force for grain growth is the decrease in the interfacial energy (area) at the solid-liquid interface. Hence, with time the mean grain size tends to increase leading to a decrease in the chemical potential of the system. Isothermal grain growth kinetics relate the mean grain size to time as follows [2]:

\[ G^n = G_o^n + Kt \]  (5.4)

where \( G \) is the mean grain size after time \( t \), \( G_o \) is the initial grain size, \( K \) the grain growth rate constant, and \( t \) is the time of sintering. Extensive research has been done on grain growth in liquid phase sintered systems [2, 175, 184]. Most of the models applied to liquid phase sintered structures are extrapolations of classic Ostwald ripening concepts developed for dilute solid contents. Semisolid systems evidence coarsening behavior different from the assumptions in Ostwald ripening models. These materials have intertwined liquid and solid phases that coarsen at elevated temperatures [173]. The grain size increases with solid volume fraction and dihedral angle. Grain growth follows a cube root dependence on time. An important observation was that in LPS systems the grain growth rate constant varies linearly with the volume fraction of the liquid to the \(-2/3\) power [73, 175, 182]. In LPS systems which have significant differences in solid and liquid densities, gravity needs to be taken into account for grain growth [176, 177, 178, 179]. In SLPS sintering of steels, the liquid and solid phase have similar densities and the liquid volume fractions are smaller, hence we can neglect the effect of gravity on grain size.
Figure 5.6. Grain size as a function of sinter temperature for water atomized 316L with 0.2% boron addition.

Figure 5.7. Grain size as a function of sinter density for water atomized 316L with 0.2% boron addition.
The grain size as a function of sinter temperature for water atomized 316L with 0.2 wt.% boron is shown in Figure 5.6. The grain size increases with an increase in sinter temperature. The grain size as a function of sinter density for water atomized 316L with 0.2 wt.% boron is shown in Figure 5.7. Grain size measurements on boron doped stainless steel by Tandon et al. [34, 62] show that the activation energy for grain growth below solidus temperature is 985 KJ/mol and above solidus is 325 KJ/mol. In the case of supersolidus sintering the grain growth rate constant above solidus (solid-liquid region) indicate a 20-fold increase with liquid formation [62]. The grain growth rate constant is sensitive to the liquid content. A hybrid grain growth rate constant has been developed by German [76], which is as follows:

\[ K = (1 - F_C)K_S + \frac{F_CK_L}{(1 - \Phi)^{2/3}} \] (5.5)

where \( F_C \) is the fractional coverage of grain boundaries, \( K_S \) is the solid-state grain growth rate constant, \( K_L \) is the liquid phase rate constant, and \( \Phi \) is the solid volume fraction. Tandon [62] observed K to be in range of 50 to 70 \( \mu m^3/s \) for a boron doped stainless steel. The grain size measured for water atomized 316L with 0.2 wt.% boron increases two fold for an increase in sinter temperature from 1400°C to 1450°C. The change in grain size is relatively rapid, affecting the fractional grain boundary coverage. The number of grains per particle decreases, leading to an increased coverage of remaining grain boundaries.

### 5.2.4 Grain Size Distribution

Grain size distribution is an important aspect of multi-phase systems. The grain size evolution from the initial particle size distribution to the final steady state distribution is an intriguing problem. The grain size distribution for water atomized and gas atomized 316L with 0.2 wt.% boron sintered at peak sintering temperature for 30 min is shown in Figure 5.8 and 5.10, respectively. In the case of WA316L with 0.2 wt.% boron the shape of the distribution is similar, but is wider for higher sintering temperature and the mean grain size increases with sinter temperature. The distribution is much narrow for the sintered GA316L with 0.2 wt.% boron and the mean grain size increases with sinter temperature.
Figure 5.8. Evolution of grain size in water atomized 316L with 0.2% boron addition sintered at the peak temperature for 30 min in hydrogen. The peak temperature indicated in the legend is in °C.

Figure 5.9. Normalized grain size distribution for water atomized 316L with 0.2% boron addition showing self similar distribution at all sinter temperatures indicated in legend (in °C). A Rayleigh distribution function for grain size distribution which has a and n values of 0.7 and 2, respectively is also shown for comparison. Model with a=0.64 and n=3.32 gives a better fit to the data.
A self-similar distribution emerges during diffusion controlled coarsening. This means the distribution has the same shape at all times when plotted versus the relative grain size. The relative grain size is measured size divided by a time-depended characteristic grain size, such as the mean, mode, or median [173]. Fang et al. [181] show that the grain size distributions achieve a self-similar pattern regardless of initial particle size distributions after initial rapid transients. It was also found that the rate of coarsening increased with the width of the initial distribution. Ravi and German [73] observed self-similar grain size distributions regardless of composition and heating rate in liquid phase sintered heavy alloys. German [173] compiled the grain size distributions for several LPS systems and observed a broader distribution than suggested by Ostwald ripening and modelled the distribution using the Rayleigh distribution function. A more generalized model for the cumulative grain size distribution \( F(G) \) can be described by:

\[
F(G) = 1 - \exp\left[-a\left(G/G_M\right)^n\right]
\]

(5.6)

where \( a \) and \( n \) are constants, \( G \) the actual grain size and \( G_M \) is the median grain size. When \( a=0.7 \) and \( n=2 \) the distribution is known as Rayleigh distribution.

The cumulative grain size distribution as a function of normalized grain size (normalized to median grain size) for water and gas atomized 316L with 0.2 wt.% sintered at different temperatures is shown in Figure 5.9 and 5.11, respectively. The Rayleigh model deviates considerably from the observed data. For water atomized 316L with 0.2 wt.% boron, \( a=0.64 \) and \( n=3.32 \) gives a better fit to the data, and in the gas atomized 316L with 0.2 wt.% boron case \( a=0.59 \) and \( n=3.85 \) gives a good fit to the data when compared to the Rayleigh distribution with \( a=0.7 \) and \( n=2 \). The rayleigh distribution is a broader distribution where as the distributions in this study were narrow. The higher values of \( n \) indicate a narrow size distribution. Since initial particle size distribution does not affect the final grain size distribution [181], the narrow grain size distribution is a characteristic of stainless steels. Lu and German [174] have observed deviation from the Rayleigh distribution in microgravity sintered W-Ni-Cu alloys where they observed values of \( a=0.7 \) and \( n=2.6 \). Ravi and German [73] report \( a \) and \( n \) values of 0.73 and 2.35 respectively, for liquid phase sintered W-Ni-Fe alloys. The grain growth mechanisms involved in stainless and heavy alloys are quite different.
Figure 5.10. Evolution of grain size in gas atomized 316L with 0.2% boron addition sintered at the peak temperature for 30 min in hydrogen. The peak temperature indicated in the legend is in °C.

Figure 5.11. Normalized grain size distribution for gas atomized 316L with 0.2% boron addition showing self similar distribution at all sinter temperatures indicated in legend (in °C). A Rayleigh distribution function for grain size distribution which has a and n values of 0.7 and 2, respectively is also shown for comparison. Model with $a=0.59$ and $n=3.85$ gives a better fit to the data.
In heavy alloys solution-reprecipitation, coalescence and gravity play an important role in grain size distributions [178, 179, 190, 191, 192, 193]. In the case of stainless steels the grain growth happens primarily via solution-reprecipitation giving narrow size distributions.

5.2.5 Second Phase Identification

Scanning electron micrographs of second phases in boron doped stainless steels are shown in Figure 5.12, 5.13, and 5.14. Figure 5.12 shows the second phases in gas atomized 316L with 0.2% boron. There are two distinct phases that are visible in the micrograph, a light phase which lines a darker phase. The elemental composition of the phases is shown in Table 5.1. The bulk phase is typical of 316L, where as the dark phase is high in Cr and Mo. The light phase is rich in Cr and Ni. The formation of the chromium rich second phases depletes the region next to the second phase causing sinter sensitization during corrosion testing. Identification of boron was difficult in the compacts with 0.2% boron using EDS as the quantity was below the threshold of the instrument.

Figure 5.12. SEM of second phases present in gas atomized 316L with 0.2% boron sintered at 1440°C for 30 min. 1-light phase, 2-dark phase and 3-bulk.

Figure 5.13 shows the second phases in water atomized 316L with 0.2% boron and Table 5.2 shows the elemental composition of the bulk and dark phase. Once
Table 5.1. Elemental composition (% atomic) of the various phases seen in sintered microstructure of GA 316L with 0.2% boron as seen in Figure 5.12

<table>
<thead>
<tr>
<th>Element</th>
<th>Bulk</th>
<th>dark phase</th>
<th>light phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>17.94</td>
<td>27.02</td>
<td>19.62</td>
</tr>
<tr>
<td>Fe</td>
<td>68.00</td>
<td>61.91</td>
<td>67.04</td>
</tr>
<tr>
<td>Ni</td>
<td>10.81</td>
<td>4.14</td>
<td>9.68</td>
</tr>
<tr>
<td>Mo</td>
<td>1.39</td>
<td>3.99</td>
<td>1.48</td>
</tr>
<tr>
<td>Si</td>
<td>1.86</td>
<td>2.95</td>
<td>2.17</td>
</tr>
</tbody>
</table>

Figure 5.13. SEM of second phases present in water atomized 316L with 0.2% boron sintered at 1440°C for 30 min. 1-dark phase and 2-bulk.

again we see a light phase which is rich in Mo along the periphery of dark phase. The bulk phase is a typical 316L composition where as the dark phase is rich in Cr and Mo and depleted in Fe and Ni.

Figure 5.14 shows the scanning electron micrograph of water atomized 316L with 0.8% boron sintered to 1260°C for 30 min. The amount of boron being higher it was identifiable in the EDS scans. The elemental composition for the different phases in given in Table 5.3. The broad area scan indicates a typical 316L composition. The bulk area next to the precipitate is depleted in Cr which causes sinter sensitization (refer to section 4.11). The dark phase is rich in Cr, Fe and boron and is believed to be a (Cr,Fe)_2B type [52, 53]. The bright eutectic
<table>
<thead>
<tr>
<th>Element</th>
<th>Bulk</th>
<th>dark phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>18.24</td>
<td>26.99</td>
</tr>
<tr>
<td>Fe</td>
<td>65.17</td>
<td>61.63</td>
</tr>
<tr>
<td>Ni</td>
<td>13.30</td>
<td>5.98</td>
</tr>
<tr>
<td>Mo</td>
<td>1.64</td>
<td>3.09</td>
</tr>
<tr>
<td>Si</td>
<td>1.65</td>
<td>2.31</td>
</tr>
</tbody>
</table>

Table 5.2. Elemental composition (% atomic) of the various phases seen in sintered microstructure of WA 316L with 0.2% boron as seen in Figure 5.13

Figure 5.14. SEM of second phases present in water atomized 316L with 0.8% boron sintered at 1260°C for 30 min. 1-dark phase, 2-light phase, and 3-bulk.

phase on the other hand is a (Cr,Fe,Mo) boride. Molinari et al. [35] observed that the boron is mainly distributed in a network along the steel grains and no appreciable diffusion into the matrix takes place. Based on the EDS analysis they have hypothesized the eutectic to be a (Fe,Cr,Mo)₂B which explains the higher eutectic temperature when compared to 1140°C in Fe-B system. The precipitates were analyzed by XRD after dissolving the steel in sulphuric acid and the analysis indicates that the precipitates are (Cr₀.₈₂₅Fe₀.₁₇₅)₂B. Tandon and German [34] also observe that the eutetic is Mo, Cr, B rich and precipitates are Cr, Fe, B rich.
<table>
<thead>
<tr>
<th>Element</th>
<th>broad area</th>
<th>bulk</th>
<th>dark (no B)</th>
<th>dark (w B)</th>
<th>bright (No B)</th>
<th>bright (w B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>18.08</td>
<td>14.73</td>
<td>56.06</td>
<td>16.84</td>
<td>27.54</td>
<td>5.95</td>
</tr>
<tr>
<td>Fe</td>
<td>65.33</td>
<td>68.34</td>
<td>39.44</td>
<td>11.69</td>
<td>46.23</td>
<td>9.99</td>
</tr>
<tr>
<td>Ni</td>
<td>13.58</td>
<td>13.88</td>
<td>1.85</td>
<td>0.55</td>
<td>8.36</td>
<td>1.81</td>
</tr>
<tr>
<td>Mo</td>
<td>1.89</td>
<td>2.17</td>
<td>2.65</td>
<td>0.74</td>
<td>17.87</td>
<td>3.56</td>
</tr>
<tr>
<td>Si</td>
<td>1.12</td>
<td>1.88</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>B</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
</tr>
</tbody>
</table>

Table 5.3. Elemental composition (% atomic) of the various phases seen in sintered microstructure of WA 316L with 0.8% boron as seen in Figure 5.14

Baczewska and Rosso [37] observed while sintering Distaloy Sa and Astaloy Mo specimens, boron undergoes in situ chemical reaction with the surrounding alloyed powders to form a boride phase. Distaloy samples with boron show a eutectic structure at grain boundaries (containing ferrite) and complex borides of type (FeMoNi)$_3$B. Astaloy samples with boron show a eutectic at grain boundaries and complex borides of type Fe$_2$MoB$_4$. Similarly, Kuroki et al. [47] observed a eutectic liquid containing Fe-Cr-Mo-B-C in a low alloy Cr-Mn-Mo steel. The composition of the liquid and the precipitate phase are identified in this study. The second phase along the grain boundaries are identified as a boride phase, this boride phase being brittle causes poor mechanical properties.

### 5.3 Apparent Viscosity Evolution

Viscosity evolution during supersolidus sintering has a direct effect on densification and distortion. Above the solidus temperature the compact is semi-solid and the microstructural conditions are conducive for viscous flow densification. However, at higher temperatures there is a substantial decrease in the apparent viscosity which leads to poor dimensional control and distortion problems. The normalized apparent viscosity (normalized to viscosity at 1200°C) during constant heating rate experiments on water atomized 316L with 0.2 wt.% boron is shown in Figure 5.15. The viscosity evolution for water atomized 316L with 0.8% boron is also shown for comparison. The normalized viscosity decreases more rapidly in the case of WA316L with 0.8% boron due to higher amount of liquid. The absolute values for viscosity values are in the 0-200 GPa.s range for both alloys.
Figure 5.15. Normalized apparent viscosity as a function of temperature during constant heating rate sintering of water atomized 316L with 0.2% boron for four different runs. The normalized viscosity of water atomized 316L with 0.8% boron is also shown for comparison.

Figure 5.16. Apparent viscosity as a function of temperature during constant heating rate sintering of water atomized 316L with 0.8% boron. Apparent viscosity calculated for isothermal sintering at 1245, and 1265°C is also shown.
For comparison, isothermal experiments were conducted near the solidus temperature at 1245°C and above the solidus at 1265°C for WA316L with 0.8 wt.% boron. The apparent viscosity calculated from constant heating and isothermal heating were grossly different as shown in Figure 5.16. For constant heating rate, the viscosity was 42 and 21 GPa.s at 1245 and 1265°C, respectively. For isothermal heating the viscosity was 135 and 4 GPa.s at 1245 and 1265°C, respectively. Since the deflection rate was calculated from curve fitting the deflection data during constant heating, it over estimates the deflection rate at 1245°C giving lower viscosity value, whereas isothermal heating gives deflection rate which is a true representation of deflection at 1245°C. However, at 1265°C the fractional grain boundary coverage is 0.94, and the liquid along the grain boundaries assists in creep leading to lower viscosity value than calculated from constant heating rate experiment.

Conventionally, viscosity was measured from sinter forging types of experiments [142, 147, 154, 155], compression tests [144], and loading dilatometry [40,42,55]. Beam bending has been proven to be a simple and effective technique in calculating the viscosity evolution during sintering [135, 137, 141, 143, 150, 156, 157]. Viscosity measurements on Distaloy [141, 143, 156, 157] show that the viscosity calculated from bending beam tests are consistent with the data obtained during loading dilatometry tests. Lame et al. [141] have observed effective viscosity values between 60 and 80 GPa.s for sintering of Distaloy which are the same order of magnitude obtained in this study on 316L stainless steel. It has been observed by viscosity studies on glasses [136, 138, 142, 147] that although the viscosity should decrease with a decrease in temperature, the hardening associated with densification almost compensates for the decrease of viscosity with temperature. Boccaccini [146] considers the effect of porosity and pore structure on the viscosity of the porous sintering glass compacts. The compact becomes more viscous with densification during heating and this behavior has been modelled based on porosity evolution. However, the formation of liquid phase during sintering concomitant with evolution of porosity makes the study of viscosity evolution complex. Gillia et al. [151] have observed chaotic sintering stress behavior upon liquid formation beyond 1325°C in WC-Co system. Compressive tests on Astroloy demonstrate that a relatively low uniaxial pressure (a few MPa) can lead to a large deformation of the alloy (≥10) as long as the fraction of liquid exceeds 10% [48]. A rough
viscosity calculation from the relative height reduction versus time plot, shows a viscosity drop with increase in temperature further supporting the viscosity drop in supersolidus sintering process.

In SLPS of stainless steels the densification does not compensate for the drop in viscosity due to liquid formation. Hence, we see a continual decrease in viscosity with temperature, the viscosity plunges after formation of a critical amount of liquid and fractional grain boundary coverage. Whychell [158, 160] and Tingskog et al. [159] have performed sag tests to assess the distortion of 316L and 17-4PH of MIM parts. Based on the final sag observed by Whychell [158, 160] the effective viscosity was calculated using the relationship in [141]. The calculations yield effective viscosity values in the range of 0.5-1 GPa.s for 316L and 17-4 PH steels. These values are in the ballpark of what we have observed during sintering of 316L with boron additions. Calculations based on German’s model for apparent viscosity [76] give viscosity values close to 10 GPa.s and the normalized viscosity values follow a more continual decrease rather than a sudden drop as observed in this study. The values suggest that the model can predict the viscosity evolution during supersolidus sintering. Although the absolute value of viscosity is an important measure, we see a scatter in the data based on different experiments and techniques used. Moreover, the viscosity value in solid state is a very high number (practically infinity) which can not be estimated. Hence, the normalized viscosity is a better parameter to compare and contrast viscosity evolution in different materials. The relationship between normalized viscosity and the microstructure is discussed in the following subsection.

5.3.1 Relating Apparent Viscosity Evolution to Microstructure

Figure 5.17 shows the evolution of microstructure along side viscosity with temperature during sintering of water atomized 316L with 0.2 wt.% boron. The densification does not compensate for the decrease in viscosity with temperature and hence the continual decrease in viscosity. Based on the microstructure it was difficult to measure any microstructural parameters due to low liquid contents, and not being able to resolve liquid at low temperatures. However, at higher temper-
atures liquid was seen along the grain boundaries as seen in Figure 5.17 (1440°C microstructure).

Water atomized 316L with higher amount of boron specifically 0.8 wt.% was used to relate viscosity evolution to microstructure, since measurement of the microstructural parameters was feasible. The viscosity and microstructural evolution are shown in Figure 5.18 along with the evolution of microstructural parameters. As the amount of liquid content increases, the fractional grain boundary coverage increases which causes a drop in the apparent viscosity. The fractional grain boundary coverage is 0.93 at temperatures above 1260°C which is above the critical value of 0.89 from percolation concepts [76] causing distortion in the compact. Figure 5.18 is a summary of the events that occur during supersolidus sintering of stainless steel with boron additions.

5.4 Distortion Mechanisms

Distortion occurs after full densification. After full densification the microstructure consists of solid grains surrounded by a liquid phase. However, the fractional grain boundary coverage is seldom 1. But to realize the distortion many models have been based on this assumption that the grains are completely surrounded by the liquid [164, 165, 166, 172]. Gravitational forces induce anisotropic shrinkage [187] and shape distortion during sintering [188]. We shall here study the effect of liquid phases along the grain boundary on distortion. After full densification the presence of a liquid layer between the solid grains will enhance creep in two ways. The liquid may act as lubricant allowing grains of the material to slide over each other more easily; or liquid may provide a high diffusivity path, allowing diffusional transport away from load bearing points or surfaces [163].
Figure 5.17. Apparent viscosity and relative density as a function of temperature during constant heating rate sintering of water atomized 316L with 0.2% boron. Microstructure of water atomized stainless steel powder with 0.2 wt.% boron quenched at 1210, 1240, 1350, 1400, and 1440 °C for 0 min hold at peak temperature are also shown along the density evolution curve.
Figure 5.18. Master plot showing the evolution of various microstructural parameters and viscosity with temperature during constant heating rate sintering of WA316L with 0.8% boron. The axis from left to right are distortion (%), Grain size (µm), Apparent viscosity (GPa.s), liquid volume (%), contiguity and Fractional grain boundary coverage ($F_C$). Curves: black-Apparent viscosity, blue-contiguity, red-liquid volume, light green-fractional grain boundary coverage, dark green-distortion and brown-grain size.
5.4.1 Lubricated Flow

Lubricated flow occurs when a liquid film of thickness $\delta$ is present between grains of size $D$, allowing the grains to slide over each other. For a simple square geometry assumed by Pharr and Ashby [163], the shear stress $\tau$ produces a shear strain rate $\dot{\gamma}$ of

$$\dot{\gamma} = \left( \frac{\delta}{\delta + D} \right) \frac{\tau}{\eta_l}$$

(5.7)

where $\eta_l$ is the viscosity of the liquid. If the volume remains constant during flow we have

$$\dot{\varepsilon} = \alpha \left( \frac{\delta}{\delta + D} \right) \frac{\bar{\sigma}}{\eta_l}$$

(5.8)

where $\bar{\sigma}$ is the deviatoric stress, $\dot{\varepsilon}$ the axial strain rate and $\alpha$ is a constant, roughly $1/3$. This simple model predicts a linear dependence on deviatoric stress and an exponential dependence on temperature (through $1/\eta_l$).

5.4.2 Diffusional Flow

Diffusional flow involves dissolution and redeposition of the solid phase. The creep rate can be limited by the kinetics of dissolution and the equation is given by [163];

$$\dot{\varepsilon} = \alpha \frac{C_L D_L}{kT} \frac{\delta}{D^3 \bar{\sigma}}$$

(5.9)

where $C_L$ is the solubility of the solid in the liquid, $D_L$ is its diffusion coefficient and $\alpha$ is a constant. If thickness of liquid film $\delta$ is constant, then axial strain rate has a linear dependence on deviatoric stress. However, if the thickness of liquid film depends on stress, the linear dependence on stress is lost.

5.4.3 Deformation by Grain Boundary Sliding

Microstructural observations on Cu-Bi alloys suggest that creep strain is produced in two separate ways: a) by percolation of liquid bismuth around the copper grains, and b) by grain boundary sliding accommodated by cavitation in the liquid. Percolation occurs in a very small amount of time ($10^{-5}s$) in the initial stages of the
deformation [172]. Deformation occurs by the sliding of grains on those boundaries across which a large shear stress \( \tau \) exists. The nucleation and growth of cavities is necessary to accommodate changes during grain boundary sliding. In most cases nucleation of cavities was determined to be the rate limiting step in the process [163, 165, 166, 172]. In SLPS the stresses are low after grain boundary sliding is unlikely to cause deformation.

5.4.4 Derivation of Creep Equation

A creep equation is derived based on a single mechanism of interfacial sliding and viscous flow based on the experimental observations on Sn-Pb alloy by Li [168]. The strain rates determined in Sn-Pb alloy creep studies were in the range that would be expected to be seen in SLPS. There are two kinds of stresses which can be exerted on the fluid layer, a shear stress and a normal stress. The shear stress produces a shear flow and the normal stress will produce a squeeze flow. In a random aggregate, the average shear stress and the average normal stress are about the same but the squeeze flow in much slower than the shear flow. So the squeeze flow may control the creep rate [168]. Jin et al. [183] show that viscous flow of the amorphous intergranular films contributes to the initial stage of tensile creep deformation in silicon nitride. Li [168] has observed a hyperbolic sine stress dependence of the penetration velocity during stress relaxation for the Sn-Pb eutectic alloy. Assume shear flow rate of the interfacial fluid obeys a hyperbolic sine law of the shear stress \( \tau \) as follows:

\[
\dot{\gamma} = \frac{\tau_o}{2\eta_l} \sinh \left( \frac{\tau}{\tau_o} \right) \tag{5.10}
\]

where \( \tau_o \) is a constant and \( \eta_l \) is the viscosity of the liquid phase. The velocity for squeezing flow, \( V \) divided by the size of the solid particles is given by:

\[
\frac{V}{D} = \frac{32\tau_o \delta^2}{3(5.3)\eta_l D^2} \sinh \left( \frac{5.3\sigma \delta}{\tau_o D} \right) \tag{5.11}
\]

where \( \sigma \) is the normal stress applied to liquid layer between the solid particles and \( \delta \) is the thickness of the fluid layer between the solid particles.

The velocity with which the grains move toward each other \( V \) can be related
to squeeze flow velocity $V$ (derivation can be seen in Appendix) by

$$\bar{V} = \alpha \delta \frac{V}{D} \quad (5.12)$$

The grain approach velocity $\bar{V}$ is proportional to the shrinkage rate.

$$\bar{V} = \beta \frac{d(\Delta L/L_o)}{dt} \quad (5.13)$$

Further for small $x$,

$sinh \ x \approx x$.

In this case we see that

$$\frac{(5.3)\sigma \delta}{D \tau_o} \ll 1 \quad (5.14)$$

Putting Equation 5.13 in 5.11 and making the $s inh x \approx x$ simplification we get

$$\frac{d(\Delta L/L_o)}{dt} = \frac{32 \alpha \sigma \delta^4}{3 \beta \eta_l \ D^4} \quad (5.15)$$

The shrinkage rate is equivalent to the strain rate $\dot{\epsilon}$ giving the creep law for distortion as

$$\dot{\epsilon} = \frac{32 \alpha \sigma}{3 \beta \eta_l \ \delta} \left(\frac{\delta}{D}\right)^3 \frac{\delta}{D} \quad (5.16)$$

where $\alpha$ and $\beta$ are constants. The distortion in supersolidus liquid phase sintering is caused from gravitational forces making the compact weak during sintering. Hence the stress in Equation 5.16 refers to the gravitational stress. $\delta/D$ is proportional to the liquid volume fraction ($V_L=3\delta/2D$). From the above derivation we observe that the $\dot{\epsilon} \propto V_L^4$. Realizing that $\sigma/\dot{\epsilon}$ is apparent viscosity we get

$$\eta_{app} = \frac{C \eta_l}{V_L^4} \quad (5.17)$$

Drucker [162] modelled deformation due to a liquid phase at the grain boundary and showed the strain rate is given by;

$$\dot{\epsilon} = \left(\frac{\sigma}{\eta_l \sqrt{3}}\right) \left(\frac{\delta}{D}\right)^3 \quad (5.18)$$
The strain rate in this case is proportional to $V_L^3$. In the present model we observe a higher sensitivity to liquid volume fraction than observed by Drucker [162] and Lal [71].

The above equations were derived on the assumption that the entire grain is surrounded by a thin liquid film. In real systems the solid grains are not completely wetted by the liquid film; there will be solid-solid grain contacts lowering the strain rate. In real systems the strain rate will not be proportional to the absolute liquid volume fraction, $V_L$. Lal [71] states that the strain rate will be proportional to $V_{eff} f(F_C)$, $V_{eff}$ being the liquid directly between the grains (not accounting for the liquid inside the grains and at the triple junctions), and $f$ is function of fractional liquid coverage, $F_C$. For an apparent viscosity of 1 GPa.s and $C=100$ we calculate the liquid volume fraction to satisfy Equation 5.17 is 0.3% which is much lower than observed in stainless steels with boron, the liquid volume fraction is typically between 5 to 10%. This corroborates the idea of an effective liquid fraction and solid-solid contacts leading to higher viscosities. In real systems the grain boundary liquid film thickness is much smaller than the average liquid film thickness. In fact, Clarke [63] calculates that stable liquid films as thin as 1 nm could exist in ceramic materials. The liquid film thickness could also have a size distribution. Jin et al. [183] observed a bimodal thickness distribution in silicon nitride after creep, whereas it was highly uniform before creep.

Liu et al. [81] proposed a microstructural softening parameter $\zeta$, which combines the effects of grain size, liquid volume fraction, and contiguity to separate densification and distortion. $\zeta$ is given by

$$\zeta = \frac{G^{1/3} V_L}{3 V_S}$$  \hspace{1cm} (5.19)

where $G$ is the grain size, $V_L$ the liquid volume fraction and $V_S$ the solid volume fraction. The ideal sintering condition is where $\zeta_{densif}<\zeta<\zeta_{distort}$ where

$$\zeta_{densif} = \left(\frac{\alpha \eta l}{\sigma_{SS}}\right)^{1/3} \frac{(1 - C_{SS})^{5/3}}{(A - C_{SS})^{1/3}}$$  \hspace{1cm} (5.20)

$$\zeta_{distort} = \left(\frac{\alpha \eta l}{\sigma_{SS}}\right)^{1/3} \frac{(1 - C_{SS})^{5/3}}{(B - C_{SS})^{1/3}}$$  \hspace{1cm} (5.21)
where $A$ is dependent particle size and wetting and $B$ depends on compact size and density. Model implementation for water atomized 316L with 0.8% boron onset of densification was observed at 1230°C and onset of distortion was at 1265°C. From the grain size, liquid volume fraction measured from the microstructures we calculate $\zeta_{\text{densif}} = 0.01 \, \mu m^{1/3}$ and $\zeta_{\text{distort}} = 0.06 \, \mu m^{1/3}$.

### 5.4.5 Presence of Yield Stress

The presence of solid-solid contacts and inhomogeneous liquid film thickness in the compact may lead to presence of a yield stress. Yield stress declines rapidly above the solidus temperature. Yield strengths of semisolid systems have been reported over a wide range from 0.01 kPa to 100 MPa [76]. A configurational threshold for distortion has been observed in heavy alloys where above the threshold there is no deviation from the cylindrical shape, whereas the bottom part manifests a considerable amount of slumping. The presence of this threshold suggests a yield strength requirement for the compact. The sintering can be modelled based on a Bingham response;

$$\tau = \tau_o + \eta \frac{d\gamma}{dt} \quad (5.22)$$

where $\tau$ is the shear stress, $\tau_o$ the yield stress, $\eta$ apparent viscosity, and $d\gamma/dt$ is the shear strain rate. The presence of yield stress has been reported in cements and concrete mixes [140], heavy alloys [188, 189] and other material systems such as polymers, solder pastes [76]. Pashias [152] devised a simple slump test which is an effective tool for determining yield stress [see Appendix for details]. Yield strength values calculated from in situ distortion observed in water atomized 316L with 0.2% boron (seen in Figure 4.28) based on analysis of Pashias [152] are given in Table 5.4. The average yield strength was calculated to be 0.34 kPa at 1437°C. Olevsky et al. [188] modelled shape distortion caused by gravity during liquid phase sintering using continuum theory. They realize the importance of modelling the system as a Bingham solid enabling them to introduce yield strength consideration into the model. The yield strength based on continuum theory is given as

$$\tau_o = \frac{\rho gh \sqrt{4 - 3\theta}}{\sqrt{6} \sqrt{(1 - \theta)^2} (1 - z/h)} \quad (5.23)$$
Table 5.4. Yield strength values calculated from \textit{in situ} distortion observed in water atomized 316L with 0.2\% boron (seen in Figure 4.28) based on analysis of Pashias [152].

<table>
<thead>
<tr>
<th>Image</th>
<th>S'</th>
<th>(\tau_y) (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1437-15min</td>
<td>0.061</td>
<td>0.357</td>
</tr>
<tr>
<td>1437-20min</td>
<td>0.083</td>
<td>0.337</td>
</tr>
<tr>
<td>1437-25min</td>
<td>0.077</td>
<td>0.342</td>
</tr>
<tr>
<td>1437-30min</td>
<td>0.1</td>
<td>0.324</td>
</tr>
</tbody>
</table>

where \(z/h\) is the configurational threshold, \(h\) is the final height, \(\theta\) the porosity. The yield stress value calculated based on this equation for W-Ni-Fe system at 1500°C is 0.292 kPa which is the same range that we observe for stainless steel with 0.2\% boron. The yield strength calculated from the above equation for the water atomized 316L with 0.2\% boron at 1437°C is 0.323 kPa which is close to 0.34 kPa calculated from analysis of Pashias [152].

5.5 Application of Master Sintering Curve Concepts to SLPS

The apparent activation energy for densification of water atomized 316L with 0.2\% boron with and without grain growth correction is shown in Figure 5.19. The activation energy was 876 KJ/mol without grain growth consideration and 936 KJ/mol with grain growth consideration. Although the activation energy has increased the mean residual error has decreased indicating a better estimate. Teng \textit{et al.}[98] have defined the MSC to be a sigmoidal curve rather than a polynomial curve [96] giving better fit to the data. Simulation done using Teng’s Master Curve gives us an apparent activation energy of 785 KJ/mol (seen in Figure 5.27). The activation energy calculation is determined by the function that is fitted to the data. Johnson [103] has observed different activation energies for the same data set on ZnO. The activation energy using polynomial fit was 310 KJ/mol, whereas fitting the data to sigmoidal curve [98] it was 350 KJ/mol.

Master sintering curve for densification of water atomized 316L with 0.2\% boron is shown in Figure 5.20. The curve does not have the conventional S shape as ex-
expected from the sigmoidal fit [96, 98, 100, 102, 103]. A closer examination of the curve, we can see that below the solidus ($1230^\circ$C) there is not much densification happening. At liquid formation temperature there is a jump in densification, after which densification occurs steadily. This jump in densification can be better seen from Figure 5.21 which shows $\ln \Psi$ as a function of work of sintering. The densification ratio increases steadily until the solidus temperature and shows a jump in $\ln \Psi$ in the range of 1230-1245$^\circ$C. This correlates well with the liquid formation observed from DTA. The formation of liquid phase enhances the densification process. The amount of liquid increases with temperature and so does densification which can be observed from Figure 5.21. It is interesting to note that densification ratio increases at the same rate (same slope I and II) before and after liquid formation. At higher temperatures however the ratio increases steeply indicating a faster densification process.

Figure 5.19. Activation energy for densification of water atomized 316L with 0.2% boron with and with out grain growth consideration.
Figure 5.20. Master sintering curve for sintering of water atomized 316L with 0.2 wt.% boron showing the densification parameter as function of work of sintering.

Figure 5.21. Master sintering curve for water atomized 316L with 0.2 wt.% boron showing the densification ratio as a function of work of sintering.
**Figure 5.22.** Modified MSC for densification with consideration of grain growth effect for water atomized 316L with 0.2 wt.% boron showing the densification parameter as function of work of sintering.

**Figure 5.23.** Modified MSC with consideration of grain growth effect for water atomized 316L with 0.2 wt.% boron showing the densification ratio as function of work of sintering.
Figure 5.24. MSC comparing the densification behavior of atomized 316L with 0.2 wt.% boron and without boron addition.

Figure 5.25. Master sintering curve for water atomized 316L with 0.2 wt.% boron showing showing a good correlation between experiment and model.
Modified MSC with consideration of grain growth for water atomized 316L with 0.2 wt.% boron showing densification parameter and densification ratio as a function of work of sintering are shown in Figures 5.22 and 5.23, respectively. The curves are of similar form to the ones with out grain growth consideration. The difference is the higher activation energy in the case of grain growth modified MSC meaning a higher sintering work needed to achieve similar densities.

The master sintering curve is modelled based on the three regions observed (Region I, II, III as shown in Figure 5.21). The sigmoidal curve is fit in the three different regions to obtain the \( \ln \theta_{ref} \) and \( n \) values. The model fit to the experimental data collected at a heating rate of 5°C/min is shown in Figure 5.25 and 5.26. The sigmoid model with and without grain growth consideration show an excellent fit to the experimental data asserting the predictive capabilities of MSC. Data analysis using Master curve [98] is shown in Figure 5.28. The sigmoid model used by Teng et al. does not fit the data accurately because it does not consider the different regions of densification.

**Figure 5.26.** Modified MSC with consideration of grain growth effect for water atomized 316L with 0.2 wt.% boron showing showing a good correlation between experiment and model.
Figure 5.27. Activation energy for densification of water atomized 316L with 0.2% boron using Master Curve software [98].

\[ y = 61.714749709414 + \left( \frac{693.547325707052}{(1 + \exp(-0.0696781819886/x - 0.975606177703301)^{0.613254069572809})} \right) \]

Figure 5.28. Master sintering curve for densification of water atomized 316L with 0.2% boron using Master Curve software [98].
The master sintering curve comparing the densification of water atomized 316L with 0.2 wt.% boron and without boron addition is shown in Figure 5.24. Sinter densification starts at lower work of sintering in the case of 316L with boron addition. This is expected due to the formation of liquid phase at lower temperature which enhances the densification process.

### 5.5.1 MSC for Grain Growth

The activation energy for grain growth of water atomized 316L with 0.2 wt.% boron is 1300 KJ/mol. as shown in Figure 5.29. The grain growth prediction is shown in Figure 5.30 along with the experimental data. The model does not fit the data accurately but does give us a starting point to model grain growth using MSC. The error could result from the errors in prediction of activation energy.

![Activation energy for grain growth of water atomized 316L with 0.2% boron.](image)

**Figure 5.29.** Activation energy for grain growth of water atomized 316L with 0.2% boron.

### 5.6 Density-Distortion-Mechanical Properties

Figure 5.31 shows the range of ultimate tensile strength, yield strength, and distortion plotted as a function of sinter density. The UTS and yield strength plotted
from the literature show a scatter, although the trend is increasing UTS and YS with increasing density. In supersolidus sintering distortion sets in after full densification, hence care needs to be taken to work in an optimum range to achieve the desired mechanical properties and microstructure. Alongside sinter density, microstructure has a big influence on the mechanical properties. The UTS obtained for WA316L with 0.8% boron sintered at 1225°C for 30 min was 476 MPa which is a little lower than the value obtained by Tandon and German [34, 49]. An elongation of 15% was also possible in the WA316L with 0.8% boron sintered at 1225°C. The maximum yield strength obtained was 250 MPa for WA316L with 0.8% boron sintered at 1250°C for 30 min. Typical values for UTS and YS for PM 316L steels are 390 MPa and 210 Mpa respectively [121]. MIM stainless steel 316L can achieve an ultimate tensile strength of 520 MPa and a yield strength of 175 MPa [122]. Elongation of 21% for PM 316L steels and 50% for MIM steels is typical. Sintering at higher temperatures gives higher density, but the microstructure has a brittle boride phase along the grain boundary causing brittle failure (See microstructure in Figure 5.14 and fracture surfaces in Figure 4.41) which translates into low ductility. The hardness measured on the grain was about 151 HV where as the secondary phase along the grain boundary had much higher values,
the average being 470 HV. In one case the hardness of the precipitate was as high as 866 HV. Baczewska [37] observed matrix hardness of 150 HV and hardness of eutectic being 203 in Distaloy alloyed with boron. This brittle phase is responsible for intergranular fracture.

![Figure 5.31](image)

**Figure 5.31.** Plot showing the range of UTS and YS from previous work on 316L stainless steel and its alloys with boron. The vertical window represents the optimum conditions for achieving full density with minimal distortion, and good mechanical properties. Solid diamonds represent UTS values from prior work, solid circles represent UTS values from this work. Hollow circles represent YS values from prior work, hollow squares represent YS values from this work. Stars represent the distortion values.

Molinari *et al.* [35] achieved UTS of 464 MPa with 19% elongation for WA316L with 0.4% boron sintered at 1240°C for 1h. Molinari *et al.* [36] observed that for a given sinter temperature increasing the boron content does increase the UTS, YS but there exists a critical amount of boron which gives the optimal mechanical properties. Similar phenomena is observed in sintering of Distaloy SA and Astaloy where 0.4% boron additions give optimal mechanical properties [37, 72]. The nature of boron addition has an effect on the mechanical property evolution [38]. Elemental boron additions prove more effective in achieving higher UTS (575
MPa) but poor elongation (18%) as a result of continuous brittle eutectic phase along the grain boundary [34, 38]. Nickel boride additions give lower UTS (480 MPa) in comparison but achieve higher elongation (38%) due to the discontinuous precipitation at the grain boundary providing an opportunity for ductile fracture [38]. Oliviera et al. [41] observed that when sintering temperature reached 1260°C during SLPS of high speed steel, eutectic M₆C, MC, and M₂C carbides and grain boundary M₆C carbide films appear. The crack initiation occurs at the W-Mo rich M₆C and propagates through the brittle carbide phase. Wright et al. [42] observed development of deleterious skeletal structures of an Fe-Cr rich eutectic phase which may cause brittle failure in T1 high speed steel powders. Bee et al. [45] found that over heating leads to the formation of deleterious grain boundary carbide films and eutectic structures in M2 steels. German et al. [68] observed negative effects from formation of the FeMo₂B₂ intermediate compound on densification and ductility.

Hence, boron additions and sinter cycle are optimized to achieve acceptable microstructures with good mechanical properties.

5.7 Corrosion of 316L Stainless Steel

The prime reason to use 316L is due to its higher corrosion resistance when compared to 304L or other austenitic steels. It is well known that better corrosion resistance mandates high sinter density, high sintering temperature, low absorbed interstitial content (C,O,N) [84, 85, 89]. Figure 5.32 shows corrosion rate decrease with increasing sinter density for stainless steel 316L with boron additions. In chloride environment 316L does exhibit surface corrosion, usually visible as brown staining. A pitting potential of 585 mV and 260 mV were measured for WA316L with 0.2% boron and GA316L with 0.8% boron sintered to full density, respectively. A pitting potential of 138 mV was measured for GA316L with 0.8% boron which has 36% porosity. Wrought 316L and stainless steels 316L processed to full density via MIM show higher pitting potential over a wide range of NaCl concentrations than porous PM steels [94]. Pitting potential also increases with lower oxygen and carbon contents [92].
Figure 5.32. Corrosion rate as a function of sinter density for 316L with different amounts of boron. The corrosion rate for wrought 316L is very small.
Figure 5.33. Corroded surface of water atomized 316L with 0.2% boron showing pitting. The pit marked by the arrow is magnified in the bottom picture. The porosity of the sintered compact was 31%.
Figure 5.34. Pitting corrosion of gas atomized 316L with 0.8% boron. The porosity of the sintered compact was 36%.

Sintered microstructure plays an equally important role on determining the corrosion behavior of an alloy. The corrosion resistance of stainless steel is due to the chromium content in the alloy, corrosion resistance decreases when chromium is lost. The chromium removal can be lost by vaporization during sintering or by compound formation. Although water atomized 316L powder with 0.2 and 0.8% boron are fully dense they exhibit different corrosion behavior. The presence of a heterogeneous microstructure with the eutectic phase localized at the austenitic grain boundary in the higher boron containing alloys makes it difficult to achieve a passive behavior. These borides are rich in chromium and molybdenum (Tables 5.1, 5.2 and 5.3) depleting the chromium in the bulk causing sinter sensitization. Higher the amount of the boron, higher the amount of eutectic phases and higher is the depletion of chromium, hence the poor corrosion resistance. Nayar et al. [90] observed poor corrosion resistance due to Cr$_2$N precipitation during cooling. Precipitation of Cr and Mo rich borides caused sinter sensitization in 316L steels.
with boron additions [91, 92]. Intergranular corrosion is extremely prevalent in sintered ferritic stainless steels because of chromium depletion at the grain boundaries [87, 88]. Therefore, a loss of chromium due to secondary phase formation leads to poor corrosion resistance. Hence, optimization of boron and the sinter cycle is necessary to achieve full density with microstructures which are not susceptible to sinter sensitization.

5.8 Finite Element Simulation of Bending and Viscosity Evolution Based on Experimental Measurements of Viscosity

Sintering has been modelled based on constitutive equations derived using continuum approach, explained in detail in Appendix-C. The finite element simulation was run using ABAQUS 6.4 with the CREEP subroutine, programmed using the constitutive equations defined in reference [194]. The initial result showed excessive deformation, indicating that the shear viscosity is too low to resist material flow. This result is shown in Figure 5.35. Densification results confirmed that the bulk viscosity was well-defined with density values predicted as 73% theoretical at 1280°C, compared to 71% theoretical at this temperature in the experiment [195].

The definition of the shear viscosity was adjusted until a more accurate simulation of the distortional events was achieved. It was found that scaling the shear viscosity equation by a factor 8 resulting in a simulation the closely mimicked deflection from experiments [195]. The comparison between the simulation and experiment of the midpoint deflection against temperature is shown in Figure 5.36.
Figure 5.35. Finite element simulation showing excessive deformation of the beam due to poor definition of the shear viscosity.

Figure 5.36. Comparison of viscosity from experiment to that calculated based on continuum modelling using FEM.
It should be noted that it is difficult to separate the influence of changing density from the temperature influence using this method of measuring apparent viscosity. With the influence of density included in the measurement, it is not possible to evaluate the validity of the linear-viscous assumption for the sinter model. However, simulation results from these experiments indicate that the form of apparent viscosity function yields promising results.

5.9 Sinter Factor

A dimensionless sinter factor $S$ is defined to determine the best process cycle. The factor $S$

$$S \propto \frac{\rho \dot{M}}{(DP)(CR)} \quad (5.24)$$

where $\rho$ is the density as % theoretical, $\dot{M}$ is the UTS or YS normalized to the value in the standard, $DP$ is the dimensionless distortion parameter, $CR$ is the corrosion rate normalized to that of the wrought alloy. It can be readily seen that the a high $S$ value implies a better sintered product. Since all the parameters on the LHS of the equation are microstructure dependent, we do not have to introduce any microstructural parameter. $S_{\text{crit}}$ is the value specified by the necessary application. Any sinter cycle which produces a $S$ value higher than $S_{\text{crit}}$ is a viable sinter cycle.
Conclusions

Supersolidus liquid phase sintering of stainless steel 316L with boron addition is dealt in this research. *In situ* apparent viscosity evolution for stainless steel 316L is reported. To my knowledge this study is the first to report evolution of viscosity of stainless steel 316L. Some of the most important findings are summarized below:

- Densification occurs due to the liquid phase formation and full density is achieved at lower temperatures with boron additions. Distortion happens after full density has been achieved. The sintering window for water atomized 316L with 0.2% boron ranges from 1430 to 1435°C and 1225 to 1245°C for water atomized 316L with 0.8% boron. The rate of change of liquid content with temperature $dV_L/dt$ decreases from 1.5%/°C to 0.1%/°C for an increase in boron content from 0 to 0.8%, giving a wider range and better control during sintering.

- Beam bending viscometry was successfully used to evaluate the *in situ* apparent viscosity evolution of water atomized 316L with 0.2 and 0.8% boron additions. The apparent viscosity drops from 174 GPa.s at 1200°C to 4 GPa.s at 1275°C with increasing fractional liquid coverage in the water atomized 316L with 0.8% boron.

- Contrary to expectations, cold isostatically pressed compacts exhibit hourglassing phenomena when compared to hand pressed compacts.
The grain size measured for water atomized 316L with 0.2 wt.% boron increases two-fold for an increase in sinter temperature from 1400°C to 1450°C. Normalized grain size distributions for gas and water atomized 316L with 0.2% boron at different peak sintering temperatures are self similar. Grain size distribution is narrow for gas atomized 316L with 0.2% boron in comparison to water atomized 316L with 0.2% boron. Grain size distribution is described by a cumulative grain size distribution function F(G) (given in Equation 5.6) with a=0.64 and n=3.32 for water atomized 316L with 0.2% boron, and a=0.59 and n=3.85 for gas atomized 316L with 0.2% boron.

Influence of boron content on mechanical properties has been studied. It was possible to achieve tensile strength of 476±21 MPa and an yield strength of 250±5 MPa with an elongation of 15±2 % in water atomized 316L with 0.8% boron. Fracture analysis indicates the presence of a brittle boride phase along the grain boundary causing intergranular fracture resulting in poor ductility. Higher properties can be achieved with lower amount of boron but need to sinter at higher temperature to achieve those properties. Sinter temperature, time and amount of boron need to be optimized for best mechanical properties.

Corrosion properties of water and gas atomized 316L powders with boron additions were compared. A pitting potential of 585 mV and 260 mV were measured for WA316L with 0.2% boron and GA316L with 0.8% boron sintered to full density, respectively. A pitting potential of 138 mV was measured for GA316L with 0.8% boron which has 36% porosity. Higher density implies that the number of pores is low, which makes pitting difficult. Sinter sensitization occurs due to depletion of chromium from the matrix upon formation of deleterious second phases along the grain boundaries.

Master sintering curve (MSC) (based on work of sintering) was used to model densification and grain growth behavior during SLPS of 316L with boron addition for the first time with considerable success. The activation energy for densification with and without grain growth consideration is 936 kJ/mol and 876 kJ/mol respectively. It is possible to identify change in densification rate upon liquid formation using MSC concepts.
• A creep equation is derived based on a single mechanism of interfacial sliding and viscous flow. The strain rate ($\dot{\epsilon}$) is proportional to liquid volume fraction $V_L^4$ indicating a higher sensitivity to liquid content on distortion than indicated by previous models. The apparent viscosity scales inversely to $V_L^4$, indicating lower viscosities with higher liquid contents.

• The rheology of this system follows a Bingham model with the presence of a yield stress. The yield stress measured from in situ sintering observations on water atomized 316L with 0.2% boron was 0.34 kPa.

• The apparent viscosity as determined through in situ video-imaging of a bending beam during sintering can be used to characterize the constitutive equations of sintering. However, reasonable results are only obtained through scaling this value, assuming that definitions for sintering stress and Poisson’s ratio are correct. This initial study indicates that the linear elastic - linear viscous analogy can be used with success to describe the rheology of supersolidus sintering deformation.

• A dimensionless sinter factor $S$ is defined to determine the best process cycle. A sinter cycle giving an $S$ value higher than $S_{crit}$ is a viable process cycle.
Bibliography


Appendix A

Data
Yield strength measurement of a semisolid according to Pashias [152]

The slump test, initially developed to determine the flow properties of fresh concrete, has been adopted means to accurately measure the yield stress of strongly flocculated suspensions. The slump test measurement consists of filling a cylindrical frustum with the material to be tested, lifting the frustum off and allowing the material to settle under its own weight. The height of the final deformed, or slumped, material is measured. The slump height is defined to be difference between initial height and final height.

Figure B.1. Schematic diagram of the initial and final state stress distribution.

Figure B.1 shows the schematic sketch of a cylindrical compact before and after slumping. At any given height, z, the pressure, P, can be approximated as:
\[ P_z = \rho gh \quad (B.1) \]

For an ideal elastic solid, the maximum shear stress that can act on a body when pressure, \( P \), is applied to it in a normal direction is equal to half the pressure. Hence, the maximum shear stress, \( \tau \), at a height, \( z \), can be expressed as:

\[ \tau_z = \frac{1}{2} \rho gh \quad (B.2) \]

Putting Equation B.2 in dimensionless form, we have:

\[ \tau'z = \frac{1}{2} z' \quad (B.3) \]

Equation B.3 illustrates that there is a linearly increasing stress distribution along the height of the cylinder, ranging from zero at the top to a maximum at the base. Figure B.1 illustrates schematically the slumping behavior and corresponding stress profile throughout the material. Note that the bottom portion of compact slumps when the gravity stress exceeds the yield stress of the material. From Figure B.1, the height of the unyielded material, \( h_o \), can be calculated by substituting the yield stress, \( \tau_y \), in place of \( \tau_z \) into Equation B.3. Thus, the initial height is reduced to a total height, \( h \), that is made up of two components: the height of the yielded regions, \( h_1 \), and the remaining non-yielded region, \( h_o \). In the portion of the material that undergoes yielding, the height can be divided into elements of thickness, \( dz \), which reduce to a thickness \( dz_1 \), once yielding is complete. During the deformation stage it is assumed that all horizontal sections remain horizontal, and slumping is only due to the radial flow. By assuming incompressibility, the thickness, \( dz_1 \), can be related to \( dz \) by:

\[ dz_1 = \left( \frac{r_2^2}{r_1^2} \right) dz \quad (B.4) \]

The height can be evaluated by integrating Equation B.4. Since, it is assumed that there is no flow between horizontal planes, the amount of material above any given plane will be the same before and after slumping. Flow occurs until the cross-sectional area increases so that stress required to support the weight is reduced to the yield stress. Thus, the relationship between the original and final
elements is that the product stress times the cross-sectional area is proportional to the weight of material above the plane. This results in the following expression:

\[(r_z)^2 \tau_z = (r_{z1})^2 \tau_y \] (B.5)

By substituting Equations B.2, B.3, and B.5 into Equation B.4, the following equation is obtained:

\[h t_1 = \int_{h_o}^{1} \frac{\tau_y}{0.5 z t} d z t \] (B.6)

Integrating Equation B.5 yields,

\[h t_1 = -2 \tau_y \ln(h t_o) \] (B.7)

The value of \(h_o\) to be used in Equation B.7 can be evaluated from Equation B.2 as:

\[\tau_y = \frac{1}{2} h t_o \] (B.8)

The dimensionless slump value can then be calculated via

\[st = 1 - h t_o - h t_1 \] (B.9)

Solving Equation B.7 to B.9 yields

\[st = 1 - 2 \tau_y [1 - \ln(2 \tau_y)] \] (B.10)

From the distortion profile observed after sintering or \textit{in situ} sintering, the slump is easily measured. For a given slump height Equation B.10 can be solved for yield stress.
C.1 Constitutive Equations for Sintering

Hooke’s Law, the constitutive equation for behavior of an isotropic linear elastic material is

\[ \sigma_{ij} = 2\mu\epsilon_{ij} + K\epsilon_{kk}\delta_{ij} \]  

(C.1)

where \( \sigma_{ij} \) is the Cauchy stress tensor, \( \epsilon_{ij} \) is the strain tensor (true, not engineering strain) with the deviatoric portion defined as

\[ \epsilon_{ij} = \epsilon_{ij} - \frac{\epsilon_{kk}}{3}\sigma_{ij} \]  

(C.2)

and \( \delta_{ij} \) is the Kronecker delta function. The shear modulus and bulk modulus \( K \) are related to the elastic modulus and Poisson’s ratio \( \nu \) as follows

\[ \mu = \frac{E}{2(1 + \nu)} \]  

(C.3)

\[ K = \frac{E}{3(1 - 2\nu)} \]  

(C.4)

Taking the linear elastic - linear viscous analogy one step further, an equivalent set of constitutive equations for isotropic linear viscous behavior is [188]

\[ \sigma_{ij} = 2G\dot{\epsilon}_{ij} + \zeta\dot{\epsilon}_{kk}\delta_{ij} \]  

(C.5)
Equation C.5 is similar to Equation C.1, except that the strain tensor has been replaced by the strain rate tensor, and the shear $G$ and bulk $\zeta$ viscosity are now defined in terms of the uniaxial viscosity and viscous Poisson’s ratio as

$$
G = \frac{\eta}{2(1 + \nu_{vp})} \tag{C.6}
$$

$$
\zeta = \frac{\eta}{3(1 - 2\nu_{vp})} \tag{C.7}
$$

The potential a porous compact has to shrink during sintering is described by a hydrostatic stress term called the sintering stress $\sigma_{ij}$. The constitutive equations of sintering are set up by including this sintering stress into Equation C.5 as follows

$$
\sigma_{ij} = 2G\dot{\epsilon}_{ij} + \zeta\dot{\epsilon}_{kk}\delta_{ij} + \sigma_s\delta_{ij} \tag{C.8}
$$

In this study we will measure the uniaxial apparent viscosity, however, we have to assume models for the sintering stress and viscous Poisson’s ratio in order to fully characterize Equation C.8. The sintering stress is defined as

$$
\sigma_s = \frac{3\gamma}{r_o}D^2 \tag{C.9}
$$

where $\gamma$ is the material surface tension, $r_o$ is the initial particle radius and $D$ is the relative density, defined as the ratio of the current density to the theoretical density of the material. The viscous Poisson’s ratio can be defined through models for the shear and bulk viscosities, as they are directly related to the viscous Poisson’s ratio through Equations C.3 and C.4. There are many models used to describe the density dependence of the shear and bulk viscosities [194]. Typically, the viscous Poisson’s ratio approaches 0.5 as the porous material nears full density and becomes incompressible, and is always non-negative. In this study we use the following models for normalized shear $\phi$ and $\psi$ bulk viscosity, respectively [188]

$$
\phi = D^2 \tag{C.10}
$$

$$
\psi = \frac{2D^3}{3(1 - D)} \tag{C.11}
$$
According to Equations C.6, C.7, C.10 and C.11, the viscous Poisson’s ratio is therefore defined as

\[ \nu^{vp} = \frac{3D - 1}{3D + 1} \]  

(C.12)

Equation C.12 is consistent with the rules described earlier: as \( D \to 1 \), \( \nu^{vp} \to 0.5 \), and \( \nu^{vp} \) is always non-negative over the sintering regime (0.27 \( \leq \nu^{vp} \leq 0.5 \) for \( 0.58 \leq D \leq 1 \)).

C.2 Finite Element Modelling

Equations C.6, C.7, C.8, C.9 and C.12, along with the measured uniaxial apparent viscosity describe the rheological response of the porous body during sintering. These equations are used in a finite element analysis to solve the force-stress equilibrium equation

\[ \sigma_{ij,j} + f_i = 0 \]  

(C.13)

where \( f = \rho g \) is the gravitational body force. Through maintaining the equilibrium in Equation C.13 over the sintering time domain, the shape of the sintered powder compact can be computationally simulated.

The dimensional change, measured by the dilatometer during a 5°C/min heating cycle, is 0.57% expansion from room temperature to 1200°C. During the initial stages of sintering, thermal expansion can have a greater affect on dimensional change that the shrinkage due to sintering. In fact, sintering shrinkage only starts in the intermediate stage of sintering after sinter bonds have reached a theoretical limit defined by the neck size ratio, \( X/D = 0.3 \). Assuming isotropic strain, this means that the dimensions of the beam geometry used at the beginning of the simulation time period, \( T = 1150°C \), \( t = 0 \), are 10.51mm x 58.23mm x 1.00mm. The initial shape of the beam was calculated as a curve with a midpoint deflection of 0.66mm, as this was the midpoint deflection measured in the beam at 1150°C, the beginning point of the simulation. The beam was resting on supports with a 35mm span. The geometry was meshed into 640 elements, 40 along the length, 8 across the width and 2 over the height. This mesh was shown to have converged.
simulation results. The simulated thermal cycle is a heating ramp of 5°C/min from 1150°C to 1400°C.
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