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Additive Manufacturing of High-Performance 316L Stainless Steel Nanocomposites via
Selective Laser Melting

A dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy in Materials Science and Engineering

by

Bandar Abdulaziz AlMangour

2017

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ABSTRACT OF THE DISSERTATION

Additive Manufacturing of High-Performance 316L Stainless Steel Nanocomposites via
Selective Laser Melting

by

Bandar Abdulaziz AlMangour

Doctor of Philosophy in Materials Science and Engineering

University of California, Los Angeles, 2017

Professor Jenn-Ming Yang, Chair

Austenitic 316L stainless steel alloy is an attractive industrial material combining outstanding corrosion resistance, ductility, and biocompatibility, with promising structural applications and biomedical uses. However, 316L has low strength and wear resistance, limiting its high-performance applicability. Adding secondary hard nanoscale reinforcements to steel matrices, thereby forming steel-matrix nanocomposites (SMCs), can overcome these problems, improving the performance and thereby the applicability of 316L. However, SMC parts with complex-geometry cannot be easily achieved limiting its application. This can be avoided through additive manufacturing (AM) by generating layer-by-layer deposition using computer-aided design data. Expanding the range of AM-applicable materials is necessary to fulfill industrial demand. This dissertation presents the characteristics of new AM-processed high-performance 316L-matrix nanocomposites with nanoscale TiC or TiB₂ reinforcements, addressing specific aspects of material design, process control and optimization, and physical metallurgy theory.

The nanocomposites were prepared by high-energy ball-milling and consolidated by AM selective laser melting (SLM). Continuous and refined ring-like network structures were obtained with homogenously distributed reinforcements. Additional grain refinement occurred with reinforcement addition, attributed to nanoparticles acting as nuclei for heterogeneous nucleation. The influence of reinforcement content was first investigated; mechanical and tribological behaviors improved with increased reinforcement contents. The compressive yield strengths of composites with TiB_2 or TiC reinforcements were approximately five or two times those of 316L respectively. Hot isostatic pressing post-treatment effectively eliminated major cracks and pores in SLM-fabricated components. The effects of the SLM processing parameters on the microstructure and mechanical performance were also investigated. Laser re-melting through double-scanning created higher-density SLM-processed parts with improved mechanical properties but longer production times. Certain scanning patterns minimized texture, creating near-isotropic structures. The energy density η crucially improved densification at the expense of increased grain size, causing mechanical behavior tradeoffs. It also influenced the size and dispersion state of TiC . In-situ SMCs were fabricated by SLM, an encouraging low-cost processing approach for high-performance parts. Interestingly, in-situ SMCs exhibited higher microhardness values in comparison to the ex-situ composites under fixed SLM processing conditions because of fine, uniform reinforcement distribution. The developed nanocomposites show promise as high-performance materials. Future research is suggested for strategic material developments.

The dissertation of Bandar Abdulaziz AlMangour is approved.

Jaime Marian

Jiann-Wen Ju

Jenn-Ming Yang, Committee Chair

University of California, Los Angeles

2017

Dedicated to

My respected parents

For being my first teachers and earning an honest living for us and for supporting and advising

My dear spouse

For being my love and unwavering support during my higher education journey

My lovely kids

For their laughs, hugs, and peace

Table of Contents

ABSTRACT OF THE DISSERTATION	ii
List of Figures	xi
List of Tables	xvii
Chapter 1 Introduction	1
1.1. Motivation and Background	1
1.2. Research Problem and Approach	4
1.3. Scope of the Thesis	5
Chapter 2 Literature Review	8
Abstract	8
2.1. Historical Background	8
2.1.1. Development History of Laser-Based AM Technology	8
2.1.2. Invention of SLM	10
2.2. General SLM Process and Kinetics	11
2.3. Comparison between AM and Traditional Manufacturing	14
2.4. Advantages and Limitations of AM	18
2.5. Material and Processing Considerations in SLM	20
2.5.1. Feedstock Powder Properties and Characteristics	20
2.5.2. Processing Parameters	21
2.5.3. Solidification Mechanism and Microstructure of the Melt Pool	22
2.5.4. Material Textures	24
2.5.5. Grain Size	25
2.5.6. Densification Level and Laser-Based Defects	26
2.6. Grain Size Refinement Strengthening Via Mechanical Alloying	28
2.6.1. Mechanisms of Nanostructure Formation	29
2.6.2. Ball-Milling of Metal Matrix Composites (MMCs)	31
2.6.3. Mechanical Behavior of Bulk-Nanostructure Metallic Materials	33

2.7.	<i>Nanomaterials in AM</i>	35
2.8.	<i>Influence of Post-Treatment</i>	36
Chapter 3 Fabrication of TiB₂/316L Composites by Selective Laser Melting: Influence of Nanoscale Reinforcement Content, Powder Preparation Method, and Hot-Isostatic Pressing Post-Treatment		38
	<i>Abstract</i>	38
3.1.	<i>Introduction</i>	39
3.2.	<i>Experimental Procedures</i>	42
3.2.1.	Powder Preparation	42
3.2.2.	SLM Process and Hot-Isostatic Pressing Post-Treatment	44
3.2.3.	Microstructural Observation	44
3.2.4.	Mechanical and Wear Behaviors	45
3.3.	<i>Results and Discussion</i>	47
3.3.1.	Characterization of Feedstock Powder	47
3.3.1.1.	Phases and Crystallite Sizes	47
3.3.1.2.	Microstructural Evolution of MA-Processed Powders	50
3.3.2.	Characterization of SLM-Processed Nanocomposites: Influence of Nanoscale Reinforcement Content	53
3.3.2.1.	XRD Analysis	53
3.3.2.2.	SEM Microstructural Characterization	54
3.3.2.3.	TEM Characterization	58
3.3.2.4.	EBSD Analysis	60
3.3.2.5.	Hardness and Wear Performance	63
3.3.2.6.	Microcompression Testing	66
3.3.2.7.	Strengthening Mechanisms	68
3.3.3.	Effect of HIP Post-Treatment	71
3.3.3.1.	Densification Mechanism	71
3.3.3.2.	Hardness and Wear Behavior	78
3.4.	<i>Conclusions</i>	83

Chapter 4 Selective Laser Melting of TiC/316L Nanocomposites: Influence of Starting TiC Particle Size and Volume Content	85
<i>Abstract</i>	85
4.1. <i>Introduction</i>	85
4.2. <i>Experimental Procedures</i>	88
4.2.1. Powder Feedstock	88
4.2.2. SLM Process	89
4.2.3. Microstructural Characterization	90
4.2.4. Hardness and Wear Performance	90
4.3. <i>Results</i>	91
4.3.1. Phases	91
4.3.2. Effects of Starting TiC Size and Volume Content on Densification Behavior	94
4.3.3. Microstructural Observation Using SEM	97
4.3.4. Microstructural Observation Using TEM	101
4.3.5. Microhardness and Wear Performance	102
4.4. <i>Discussion</i>	107
4.5. <i>Conclusions</i>	110
 Chapter 5 Scanning Strategies for Texture and Anisotropy Tailoring During Selective Laser Melting of TiC/316L Nanocomposites	 111
<i>Abstract</i>	111
5.1. <i>Introduction</i>	111
5.2. <i>Experimental Procedures</i>	115
5.2.1. Fabrication of Test Specimens	115
5.2.2. Material Characterizations	117
5.3. <i>Results</i>	119
5.3.1. Morphologies of As-Deposited Specimens and Densification Behavior	119
5.3.2. Microstructural Evolution	121
5.3.3. EBSD Analysis	125
5.3.3.1. EBSD Orientation Maps	125
5.3.3.2. EBSD Misorientation Angles	129

5.3.4.	Texture Development	130
5.3.4.1.	Texture Coefficients Derived From the XRD Analysis	130
5.3.4.2.	Pole Figures Derived From the EBSD Analysis	131
5.3.5.	Mechanical Properties	134
5.4.	<i>Discussion</i>	136
5.4.1.	Densification Behavior	136
5.4.2.	Crystallographic and Morphological Textures	137
5.4.3.	Additional Remarks	141
5.5.	<i>Conclusions</i>	142
Chapter 6 Densification Behavior, Microstructural Evolution, and Mechanical Properties of TiC/316L Nanocomposites Fabricated by Selective Laser Melting		143
	<i>Abstract</i>	143
6.1.	<i>Introduction</i>	144
6.2.	<i>Experimental Procedures</i>	148
6.2.1.	Powder Preparation and SLM Processing	148
6.2.2.	Microstructural Characterization	150
6.2.3.	Mechanical and Tribological Properties	151
6.3.	<i>Results and Discussion</i>	152
6.3.1.	Phase Analysis	152
6.3.2.	Densification Behavior	154
6.3.3.	Microstructure and Texture	159
6.3.3.1.	Effects of the Applied η on the Distribution State of TiC	159
6.3.3.2.	Effects of the Applied η on the TiC Particle Size	163
6.3.3.3.	Microstructural Examination by EBSD	165
6.3.3.4.	Texture Development	168
6.3.4.	Mechanical Properties	170
6.3.4.1.	Microhardness and Wear Performance	170
6.3.4.2.	Micro-Compression Properties	175
6.4.	<i>Conclusions</i>	176

Chapter 7 In-Situ Formation of Novel TiC-Particle-Reinforced 316L Stainless Steel Bulk-Form Composites by Selective Laser Melting	179
<i>Abstract</i>	179
7.1. <i>Introduction</i>	180
7.1.1. Ex-Situ vs. In-Situ MMCs	180
7.1.2. Fabrication of MMC Components by Conventional Methods vs. Additive Manufacturing	181
7.1.3. Present State of Knowledge in Laser Processing of In-Situ MMCs and Outline of the Chapter	182
7.2. <i>Experimental Procedures</i>	184
7.2.1. Powder Preparation	184
7.2.2. SLM Processing	185
7.2.3. Microstructural Characterization	186
7.2.4. Mechanical Properties	186
7.3. <i>Results and Discussion</i>	187
7.3.1. Densification Behavior	187
7.3.2. Phase Prevalence	190
7.3.3. Microstructural Evolution	192
7.3.4. Synthesis of TiC Particles by SLM	195
7.3.5. Hardness	199
7.3.6. Wear Rate and Morphology	201
7.4. <i>Conclusions</i>	204
Chapter 8 Conclusion and Outlook	206
8.1. <i>Current Research Accomplishments</i>	206
8.2. <i>Recommendations for Future Work: Ongoing Research Activities and Re-Invention Issues, Opportunities, and Strategies</i>	208
References	211

List of Figures

Figure 1.1: Research methodology adopted in the thesis.....	5
Figure 2.1: Surface morphologies of M2 high-speed steel parts processed by (a) SLS [21], (b) SLM [22].	9
Figure 2.2: Process chain for obtaining parts by AM route, from initial 3D design to final fabricated part.	12
Figure 2.3: Schematic of typical SLM system setup [52].	13
Figure 2.4: Percentages of materials in products, waste, and tool steel in AM versus injection molding (IM) processes, for a production volume of 500,000 units [56, 57].	15
Figure 2.5: Comparison of the microstructures of 17-4 stainless steel after etching for (a) SLM; (b) casting. Notice the difference in the scale bars [59].	17
Figure 2.6: SLM of 316L stainless steel. (a) Lateral cross-section of built parts; (b, c) SEM micrographs of built parts at higher magnifications [62].	18
Figure 2.7: Schematic demonstrating the major processing parameters influencing SLM.	21
Figure 2.8: Schematic of solidification process in SLM.	22
Figure 2.9: Effect of laser beam scanning speed on strength and depth of convection during SLM.	23
Figure 2.10: (a) Optical micrograph; (b) SEM image showing 17-4 stainless steel microstructure that is typical of an SLM process with strongly oriented fine austenite grains [73].	24
Figure 2.11: High-magnification SEM micrographs showing the cellular dendrites of SLM-processed 316L parts at different parameters: (a) 104.17 J/mm ³ , 1200 mm/s; (b) 125.00 J/mm ³ , 1000 mm/s; (c) 156.25 J/mm ³ , 800 mm/s; (d) 178.57 J/mm ³ , 700 mm/s [75].	25
Figure 2.12: Variation in relative density of SLM-processed 316L parts under various energy densities [75].	27
Figure 2.13: SEM images of pore morphology using (a) 195-W laser power and 1200-mm/s scan speed, (b) 95-W laser power and 389-mm/s scan speed, (c) 70-W laser power and 287-mm/s scan speed [83].	28
Figure 2.14: Evolutionary stages during ball milling (edited from [88]). The schematic shows the characteristic repeated fragmentation and coalescence events during MA.	30
Figure 3.1: Microstructures of starting (a) 316L and (b) TiB ₂ powders and (c) homogenously mixed 15 vol.% TiB ₂ /316L powder. (d) TEM image of feedstock 15 vol.% TiB ₂ /316L powder.	43
Figure 3.2: XRD patterns obtained for the 2.5% TiB ₂ /316L powders (a) after 8 h of direct mixing and after milling for (b) 2, (c) 4, (d) 6, and (e) 8 h.	47
Figure 3.3: Changes in the crystallite size and lattice parameters observed for the γ -Fe phase of the 316L composite after ball milling for specific times.	49

Figure 3.4: SEM images showing characteristic microstructures of milled powders after (a) 2, (b) 4, (c) 6, and (d) 8 h of milling. The inset in the upper right corner of Fig. 3.4(d) describes the particle morphology after 8 h of milling.	52
Figure 3.5: Average particle diameter plotted as function of ball-milling time.....	52
Figure 3.6: Effect of milling time on the particle size distribution for milled powders.....	53
Figure 3.7: XRD spectra of SLM-processed samples of (a) pure 316L and nanocomposites with different TiB ₂ reinforcement volume contents: (b) 2.5%, (c) 5%, (d) 10%, and (e) 15%.	54
Figure 3.8: SEM images showing characteristics of etched microstructures of SLM-processed samples of (a) pure 316L and TiB ₂ /316L nanocomposites with different TiB ₂ reinforcement volume contents: (b) 2.5%, (c) 5%, (d) 10%, and (e) 15%.	55
Figure 3.9: High-magnification SEM images showing characteristics of etched microstructures of TiB ₂ /316L nanocomposites with different TiB ₂ reinforcement contents: (a) 2.5%, (b) 5%, (c) 10%, and (d) 15%. The dispersion states of the reinforcements can be seen in the images.	56
Figure 3.10: SEM images showing the characteristics of the cross-sections of the SLM-processed samples of (a) pure 316L and (b) the 15 vol.% TiB ₂ /316L nanocomposite, (c) low-magnification image of the 15 vol.% TiB ₂ /316L nanocomposite showing the overlapping of the melt pool and the layer-wise microstructural features along the building direction (BD); pores can be seen clearly in the image.	58
Figure 3.11: (a, b) TEM images of 15 vol.% TiB ₂ /316L nanocomposite obtained in two different regions and showing spherical precipitates at the interface as well as an increase in the dislocation density of the 316L austenitic matrix.	59
Figure 3.12: (a, b) EBSD orientation maps of the 15 vol.% TiB ₂ /316L nanocomposite showing both the FCC 316L and the TiB ₂ phases; (c, d) grain boundary misorientation maps superimposed on an image quality map of the 316L matrix.....	61
Figure 3.13: (a, b) Pole figures for γ -Fe phase; (c, d) inverse pole figures for γ -Fe phase indicating the random texture of the material.	62
Figure 3.14: Evolution of microhardness of the nanocomposites as a function of the TiB ₂ reinforcement volume content.....	63
Figure 3.15: Coefficients of friction of SLM-processed (a) pure 316L sample and samples of the TiB ₂ /316L nanocomposites with different TiB ₂ reinforcement volume contents: (b) 2.5%, (c) 5%, (d) 10%, and (e) 15%.....	65
Figure 3.16: SEM images showing morphologies of worn surfaces of samples of (a) pure 316L and TiB ₂ /316L nanocomposites with different TiB ₂ reinforcement volume contents: (b) 2.5%, (c) 5%, (d) 10%, and (e) 15%.....	66
Figure 3.17: Compressive stress-strain curves of pillars of the TiB ₂ /316L nanocomposites.....	67

Figure 3.18: TEM image of compressed pillar of 15 vol.% TiB ₂ /316L nanocomposite showing the dislocation arrangement and the nanograins: (a) low- and (b) high-magnification images.	69
Figure 3.19: Low-magnification SEM images showing un-etched characteristic morphologies of SLM-processed 316L composites reinforced with 15 vol.% TiB ₂ (a) before HIP treatment and using directly mixed powder (b) before HIP treatment and using ball-milled powder (c) HIP-1 and (d) HIP-2 treatment cycles.	75
Figure 3.20: SEM images showing characteristic morphologies of etched SLM-processed nanocomposites after (a, b) HIP-1 and (c, d) HIP-2 treatments.	78
Figure 3.21: Average microhardness of SLM-processed TiB ₂ /316L composites parts.	79
Figure 3.22: Coefficient of friction and wear rate obtained for SLM-processed 15 vol.% TiB ₂ /316L composites.	80
Figure 3.23: SEM images showing morphologies of the worn surfaces of the 316L composite reinforced with 15% TiB ₂ (a) before HIP treatment and using directly mixed powder (b) before HIP treatment and using ball-milled powder and (c) after HIP-1 (d) after HIP-2.	82
Figure 4.1: Microstructures of the starting materials. (a) 316L stainless steel powder; (b) microscale TiC; (c) nanoscale TiC. Ball-milled 316L feedstock nanocomposite powder with the starting (d) microscale TiC; (e) nanoscale TiC.	89
Figure 4.2: XRD spectra of the 316L SLM-processed nanocomposites reinforced with coarse starting TiC reinforcements with volumes of (a) 2.5%, (b) 5%, (c) 10%, (d) 15%.	92
Figure 4.3: XRD spectra of the 316L SLM-processed nanocomposites reinforced with fine starting TiC reinforcements with volumes of (a) 2.5%, (b) 5%, (c) 10%, (d) 15%.	92
Figure 4.4: SEM images showing surface morphology and densification level of SLM-processed 316L nanocomposites reinforced with TiC particles at various volume reinforcements and size: coarse TiC (a) 2.5%, (b) 5%, (c) 10%, (d) 15%; fine TiC (e) 2.5%, (f) 5%, (g) 10%, (h) 15%.	95
Figure 4.5: Densification levels of SLM-processed parts.	96
Figure 4.6: SEM images showing characteristics of SLM-processed coarse starting TiC/316L nanocomposites at various volume reinforcements: (b) 2.5%, (c) 5%, (d) 10%, (e) 15%.	99
Figure 4.7: SEM images showing characteristics of SLM-processed fine starting TiC/316L nanocomposites at various volume reinforcements: (b) 2.5%, (c) 5%, (d) 10%, (e) 15%.	99
Figure 4.8: EDS elemental mapping showing distribution of major elements in the produced 316L stainless steel nanocomposites samples with: (a, b) 2.5% TiC; (c, d) 5% TiC; (e, f) 10% TiC; (g, h) 15% TiC.	100

Figure 4.9: TEM images for 316L reinforced with the starting (a) coarse TiC, (b) fine TiC nanocomposite, revealing spherical precipitates at the interface and in increased dislocation density in the 316L matrix.	101
Figure 4.10: Influence of the starting particle sizes and volume contents of the TiC particle on the variation of microhardness of SLM-processed nanocomposites.	103
Figure 4.11: SEM images showing the worn morphologies of 316L/TiC nanocomposites using the coarse starting TiC particles with different volume contents: (a) 2.5%; (b) 5%; (c) 10%; and (d) 15%.	106
Figure 4.12: SEM images showing the worn morphologies of 316L/TiC nanocomposites using the fine starting TiC particles with different volume contents: (a) 2.5%; (b) 5%; (c) 10%; and (d) 15%.	107
Figure 5.1: An overview of the four scanning methodologies used in this study.	117
Figure 5.2: SEM images of the TiC/316L nanocomposites processed by SLM scanning methods (a) I and (III). The obtained data demonstrate an overlap between the melt pool and the individual layer microstructural features (such as pores and cracks) along the building direction.	120
Figure 5.3: High-magnification SEM images of the 15 vol.% TiC/316L nanocomposite sample cross-sections obtained by SLM scanning methods (a) I, (b) II, (c) III, and (d) IV.	123
Figure 5.4: High-magnification SEM images of the top sides of the 15 vol.% TiC/316L nanocomposite samples obtained by SLM scanning methods (a) I, (b) II, (c) III, and (d) IV.	123
Figure 5.5: EBSD orientation maps of the 15 vol.% TiC/316L nanocomposite samples, which were obtained by scanning methods (a, b) I, (c, d) II, (e, f) III, and (g, h) IV.	127
Figure 5.6: Grain boundary misorientation maps superimposed on the image quality maps of the FCC 316L matrix, which was obtained by scanning methods (a, b) I, (c, d) II, (e, f) III, and (g, h) IV.	130
Figure 5.7: Pole figures obtained for the FCC 316L matrix, which was produced by scanning methods (a, b) I, (c, d) II, (e, f) III, (g, h) and IV.	133
Figure 5.8: Effect of the scanning strategy on the hardness of the obtained SLM nanocomposite samples.	135
Figure 5.9: The influence of overlap factor and the type of scanning method on the appearance of consecutive melt pools: (a) small overlapped area that result in poor bonding between the two adjacent layers (i.e., lower densification) and (b) large overlapped area that result in good bonding between the two adjacent layers (i.e., higher densification).	136
Figure 6.1: (a, b) TiC/316L nanocomposite feedstock after 8 h of milling, (c) “alternate-hatches” method of scanning.	149
Figure 6.2: XRD spectra of SLM-processed TiC/316L parts produced using various laser energy densities (η): (a) 67 J/mm ³ ; (b) 125 J/mm ³ ; (c) 200 J/mm ³ ; (d) 300 J/mm ³	152

Figure 6.3: SEM micrographs showing the effect of processing laser energy density (η) on sample porosity. The above two rows of micrographs show the variations in the microstructure and porosity with the applied laser energy density. The bottom row quantifies the relative densities as a function of the laser energy density.	154
Figure 6.4: High-magnification SEM images showing the evolution dispersion states of nanoscale TiC reinforcement in SLM-processed TiC/316L nanocomposites at various applied laser energy densities (η): (a,e) $\eta = 67 \text{ J/mm}^3$; (b,f) $\eta = 125 \text{ J/mm}^3$; (c,g) $\eta = 200 \text{ J/mm}^3$; (d,h) $\eta = 300 \text{ J/mm}^3$	161
Figure 6.5: Schematic of the movement mechanisms of TiC nanoparticles in the melt pool under various scanning speeds: (a) high scan speed; (b) moderate scan speed; (c) low scan speed.....	163
Figure 6.6: TEM images showing the TiC particle size of SLM-processed TiC/316L nanocomposites obtained at (a, c) $\eta = 67 \text{ J/mm}^3$; (b, d) $\eta = 300 \text{ J/mm}^3$. Notice the size of the nearly spherical TiC particles at the interface as well as an increase in the dislocation density of the 316L austenitic matrix.	164
Figure 6.7: EBSD orientation maps of SLM-processed TiC/316L nanocomposite parts produced using different laser energy densities (η): (a) 67 J/mm^3 ; (b) 125 J/mm^3 ; (c) 200 J/mm^3 ; (d) 300 J/mm^3	166
Figure 6.8: Pole figures of the γ -Fe phase in the SLM-processed TiC/316L parts produced using different laser energy densities (η): (a) 67 J/mm^3 ; (b) 300 J/mm^3 . Notice that the maximum texture intensity of the SLM sample processed at 300 J/mm^3 was almost fourfold that of the sample processed at 67 J/mm^3	169
Figure 6.9: Effects of the applied laser energy densities (η) of SLM-processed TiC/316L nanocomposite parts on microhardness.	171
Figure 6.10: Effect of the applied laser energy densities (η) of SLM-processed TiC/316L nanocomposite parts on average wear rate.....	172
Figure 6.11: SEM images showing typical morphologies of the worn surfaces of TiC/316L parts processed at (a) $\eta = 67 \text{ J/mm}^3$, (b) $\eta = 125 \text{ J/mm}^3$, (c) $\eta = 200 \text{ J/mm}^3$, and (d) $\eta = 300 \text{ J/mm}^3$	173
Figure 6.12: Microcompression stress-strain curves of unreinforced 316L stainless steel and nanocomposite pillars.	176
Figure 7.1: SEM images of (a) 316L stainless steel powder; (b) Ti powder; (c) graphite powder.	184
Figure 7.2: Influence of the energy density on the relative density of SLM-processed composites. (a) 67 J/mm^3 , (b) 100 J/mm^3 , (c) 200 J/mm^3 , (d) 300 J/mm^3 . The top panel shows low-magnification micrographs of different SLM samples, with relative density against laser energy density input shown in the bottom panel.....	188
Figure 7.3: XRD patterns of the (a) starting feedstock powder and SLM-processed samples at various energy densities (η): (b) 67 J/mm^3 ; (c) 100 J/mm^3 ; (d) 200 J/mm^3 ; and (e) 300 J/mm^3	191
Figure 7.4: SEM images showing characteristics of etched microstructures of SLM-processed parts at various applied energy densities. (a) 67 J/mm^3 , (b) 100 J/mm^3 , (c) 200 J/mm^3 , (d) 300 J/mm^3	193

Figure 7.5: SEM images showing high-magnification characteristics of etched microstructures of SLM-processed parts processed using energy density of (a) 67 J/mm ³ , (b) 300 J/mm ³	193
Figure 7.6: Schematic of formation mechanism of TiC–316L in situ composite by SLM.....	198
Figure 7.7: Influence of the energy density on the variation in microhardness of SLM-processed nanocomposites.....	200
Figure 7.8: Influence of the energy density on the variation in wear rate of SLM-processed nanocomposites.	201
Figure 7.9: Influence of the energy density on the variation of worn morphologies of SLM-processed composite components with various applied energy densities. (a) 67 J/mm ³ , (b) 100 J/mm ³ , (c) 200 J/mm ³ , (d) 300 J/mm ³	203

List of Tables

Table 2.1: Powder properties and characteristics influencing SLM process	20
Table 3.1: Variation in 2θ locations and intensities of γ -Fe diffraction peaks of 2.5% vol. TiB ₂ /316L nanocomposite powders with different milling times.....	48
Table 3.2: Average wear rates for pure 316L and 316L nanocomposite samples	64
Table 4.1: Variation of 2θ locations and intensities of the γ -Fe diffraction peaks in SLM-processed nanocomposites with different starting 15% vol. TiC particle sizes.....	93
Table 4.2: Average coefficient of friction (COF) and wear rate of the 316L nanocomposites parts.....	104
Table 5.1: Relative densities of the 15 vol.% TiC/316L nanocomposite samples obtained by various SLM scanning methods.....	121
Table 5.2: TiC volume contents determined by XRD for the 15 vol.% TiC/316L nanocomposite samples, which were obtained by various SLM scanning methods.....	124
Table 5.3: Texture coefficients T_c derived from the XRD data for the 15 vol.% TiC/316L nanocomposite samples, which were obtained by various SLM scanning methods.....	131
Table 6.1: Variation of 2θ locations and intensities of the γ -Fe diffraction peaks in SLM-processed nanocomposites with various applied energy densities	153
Table 7.1: Milling conditions used for powder preparation.....	185
Table 7.2: SLM processing parameters	185
Table 7.3: Changes in sub-stoichiometric and the lattice parameters of TiC _{1-x} with various applied energy density	198

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VITA

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Chapter 1

Introduction

1.1. Motivation and Background

The industrial demand for “mass customization” and “design for function” is rapidly outweighing that for “mass production” and “design for manufacturing,” giving rise to a need to develop advanced technologies to enable the economical production of customized parts. The manufacture of high-performance functional parts using traditional methods, such as casting and machining, is a time-consuming multiple-step procedure. In response to this need, additive manufacturing (AM, commonly referred to as 3D printing) has been developed. As defined by the ASTM, AM is the “process of joining materials to make objects...usually layer upon layer,” using three-dimensional (3D) computer-aided design (CAD) data [1].

AM techniques enable the direct production of complex parts in small and medium lot sizes. In contrast to subtractive approaches, in which excess material is removed to yield the end shape, AM techniques produce end-useable parts by adding subsequent layers (i.e., layer-by-layer addition) to obtain nearly or fully net-shaped parts [2]. AM thereby directly translates virtual 3D models into physical parts, both quickly and easily. The model data is sliced into a series of thin sections that are passed to the AM machine, which creates them in a layered sequence [3]. Clearly, AM reduces not only the cost but also the lead time in parts production, due to the absence of molds or tools, and produces complex parts with a high material yield, unlike more wasteful subtractive processing. AM techniques also have the potential to attain zero wastage because they can use recycled feedstock materials. This consequently reduces emissions, because

less of the raw material must be produced. Moreover, AM processes do not require the direct use of toxic chemicals, unlike traditional manufacturing technologies requiring coolants or lubricants.

The increasing pressure to put products on the market quickly has led to the creation of several AM processes. Currently, several AM processes are in use, including laser metal deposition (LMD), selective laser melting (SLM), fused deposition modeling (FDM), stereolithography, inkjet printing, and selective laser sintering (SLS). Each technology is distinguished by the raw materials used, such as wire, powder, photosensitive liquid resin, printing ink, or thermoplastic filament, and by the method of consolidation, such as photopolymerization, laser heating and melting, conductive heating, and chemical reaction.

Several AM techniques used in the production of metal parts use energy-beam sources to consolidate section layers [4-8]. These different approaches (processing mechanisms) can be categorized as follows:

- Indirect processing, in which metal powders are mixed with polymer binders. This method exploits the presence of the low-melting-point binder to consolidate the green part. Post-processing by thermal treatment or infiltration densifies the final parts.
- Partial melting, using a mixture of two metal powders or a metal alloy. This involves the partial melting of the powder (i.e., semi-solid consolidation mechanism). Processing problems such as insufficient densification, heterogeneous microstructures, and property variations commonly occur; therefore, post-processing treatments such as hot-isostatic pressing (HIP) or secondary infiltration with low-melting-point materials are often used to improve the mechanical properties.

- Full melting, the most recently developed method, using fully melted metal powders. The laser melting mechanism was developed to obtain fully dense parts and to reduce the time processing cycle. The concept of full melting is supported by continuous improvements in laser processing conditions, including laser types, higher laser powers, smaller focus spot sizes, and smaller layer thicknesses, which have in turn led to significant enhancements in the densification, microstructure, and mechanical properties of produced parts, relative to those made with earlier lasers [8]. Among these methods, SLM uses metal powder and a high-power laser to consolidate a useable part. SLM can produce parts that are fully dense and which require a minimal amount of post-processing.

The results yielded by the first two approaches are two-phased materials with low-melting-point constituents. These are mainly applied to rapid tooling. On the other hand, the full melting of metal powders is currently more suitable for producing end-usable metal parts for the medical, dental, aerospace, and tooling industries [9-16]. However, the performance of these parts, in terms of their mechanical properties, dimensional accuracy, residual porosity, and surface roughness, is closely related to the complex metallurgical and atomic mechanisms involved in both heat adsorption of, and transmission through, the powders, as well as the melting and consolidation of powders [17-20].

In SLM, the metallic powder is completely melted to the liquid phase and then rapidly cooled. The homogeneity of the product is easily controllable, but there are drawbacks. Because of the wide temperature variation during melting and cooling, residual stresses introduced into the product from thermal expansion and contraction may compromise the strength of the material.

Additionally, defects such as porosity and balling may form during the phase transitions inherent to the build process.

1.2. Research Problem and Approach

The present study set out to develop high-performance 316L stainless-steel-matrix nanocomposites. Typically, 316L stainless steel, containing around 16–18 wt.% chromium and around 10–14 wt.% nickel, is used for applications requiring high ductility and corrosion resistance. The promising mechanical properties of stainless steel matrix composites (SMCs), as well as nanocomposites, are limited in terms of their applicability by the geometric limitations of traditional manufacturing methods. These drawbacks limit the engineering applications of SMCs in industries. The present study involves a unique approach to the research and development of laser-based AM technology: high-performance components formed from 316L stainless-steel nanocomposites were processed by the alternative route of SLM. The components showed promising results regarding their structural integrity and resulting mechanical and tribological performances. In this research, the integration of designed materials, tailored processing, and controllable properties are emphasized as key strategies.

The nanocomposite feedstock was first synthesized by mechanical alloying via high-energy ball milling followed by SLM consolidation. The mechanisms of both the ball-milling and SLM were studied in detail. After consolidation, the relationships between the processing, microstructure, and mechanical properties were investigated. In this dissertation, the processing details of SLM will be discussed, particularly regarding the ways in which the processing parameters affect the build behavior of the material. The influence of the reinforcing content and processing parameters on the microstructure were investigated by X-ray diffraction (XRD),

scanning electron microscopy (SEM), electron backscattering diffraction (EBSD), and transmission electron microscopy (TEM), while the mechanical and tribological properties were evaluated by hardness testing, micro-compression testing, and wear testing. Figure 1.1 briefly demonstrates the research methodology adopted in the thesis.

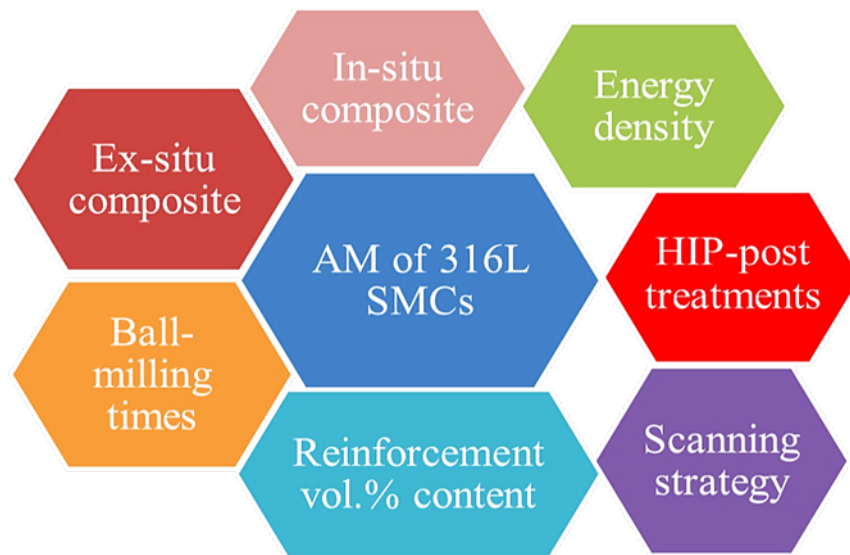


Figure 1.1: Research methodology adopted in the thesis.

1.3. Scope of the Thesis

This thesis is divided into eight chapters. Briefly, the content is as follows:

Chapter 2 reviews the literature addressing current state-of-the-art research on SLM, including the developmental history of laser-based AM technologies, a general process overview, and the main advantages and limitations of SLM. Traditional manufacturing methods and AM are compared. An in-depth review of the materials and processing aspects, including the physical aspects of the feedstock materials for SLM, the main process parameters, solidification and microstructural characteristics, and major laser-based AM defects, is presented. The techniques

applied to the processing of bulk-form nanostructured alloys and composites through mechanical alloying are discussed, as well as the mechanisms and mechanical properties of mechanically alloyed materials. A brief survey of the use of nanomaterials in metal AM is given. A brief discussion highlights the effects of post-processing treatments on the microstructure and mechanical properties.

Chapter 3 introduces the SLM process, as a newly developed powder-bed-based AM process for fabricating TiB₂/316L composite parts with various TiB₂ contents and by either direct mixing or ball milling powder. First, the evolution of constituent phases, microstructural characteristics, and size distribution with milling time is investigated. The microstructures of the developed nanocomposites are investigated by XRD, SEM, TEM, and EBSD. The effect of the TiB₂ content on the densification kinetics is then discussed. The mechanical properties of the developed nanocomposites are evaluated by performing hardness tests and the compressive testing of fabricated micro-pillars. The deformation mechanism is analyzed via TEM. The tribological performance is evaluated by wear testing. The effect of the initial powder characteristics on the hardness and wear performance is analyzed. Finally, the composites processed using ball milling of 15% TiB₂/316L powder are subjected to the HIP-post treatment in order to examine the influence of this post treatment on the composite densification, microstructural evolution, and mechanical properties.

Chapter 4 discusses the influence of the TiC reinforcement content and particle size on the microstructural evolution (using SEM, XRD, and TEM), hardness, and tribological performance (by wear testing) of the 316L stainless steel nanocomposites. The underlying role of the

reinforcement size and volumetric content on the densification of the processed parts is elucidated.

Chapter 5 presents the effects of several SLM scanning strategies on the tailoring of the densification, microstructure, texture, and anisotropic behavior of the produced TiC/316L nanocomposite. A detailed microstructural and mechanical examination using SEM, EBSD, XRD, and hardness tests reveals that the alternate-hatching pattern with the single pass of the laser beam minimizes the behavioral anisotropy and reduces unwanted textures.

Chapter 6 further examines the effects of the applied energy density on the densification, microstructure (i.e., particle size and distribution state, grain size, and texture), mechanical properties (i.e., hardness and micro-compressive behavior), and tribological behavior (i.e., wear testing) of the fabricated TiC/316L nanocomposites.

Chapter 7 introduces the feasibility of in-situ TiC formation, reinforced in 316L by SLM. A short comparison of ex-situ and in-situ composites is provided. The mechanisms underlying the formation of the TiC particles by SLM are elucidated. The effects of the applied laser energy density on the densification, microstructure, hardness, and tribological behavior of the SLM-processed parts are also investigated.

Chapter 8 summarizes the main results and conclusions of this work. Further important issues and opportunities for future research and development are also outlined.

Chapter 2

Literature Review

Abstract

This chapter begins with a brief introduction to the development history of laser-based AM technology. The development of SLM from the separate technique of SLS is discussed. A general overview of the process of SLM is provided. Traditional manufacturing and SLM are compared in terms of environment, efficiency, energy consumption, microstructure, and properties. The major advantages and limitations of SLM are elaborated. The general SLM processing parameters, features, laser-based defects, solidification and microstructural characteristics, materials, and physical aspects of components are all addressed. SLM-produced metallic structures are discussed, including the kinetics of microstructural formation and features specific to SLM products. The process and mechanisms of mechanical alloying are introduced. Finally, the roles of nanomaterials and post-treatment methods in current AM technology are discussed.

2.1. Historical Background

2.1.1. Development History of Laser-Based AM Technology

SLM is a relatively recent development from the previously established technique of selective laser sintering (SLS), in which sintering or partial melting is the only mechanism causing the rapid consolidation of powder. SLM uses a high-energy-density fiber laser emitting short-wavelength light to melt thin layers of metal powder, while SLS machines use classical CO₂ lasers. Figure 2.1 demonstrates the significant improvement in the surface morphologies, densification, and microstructural homogeneity when SLM is used, in comparison to SLS.

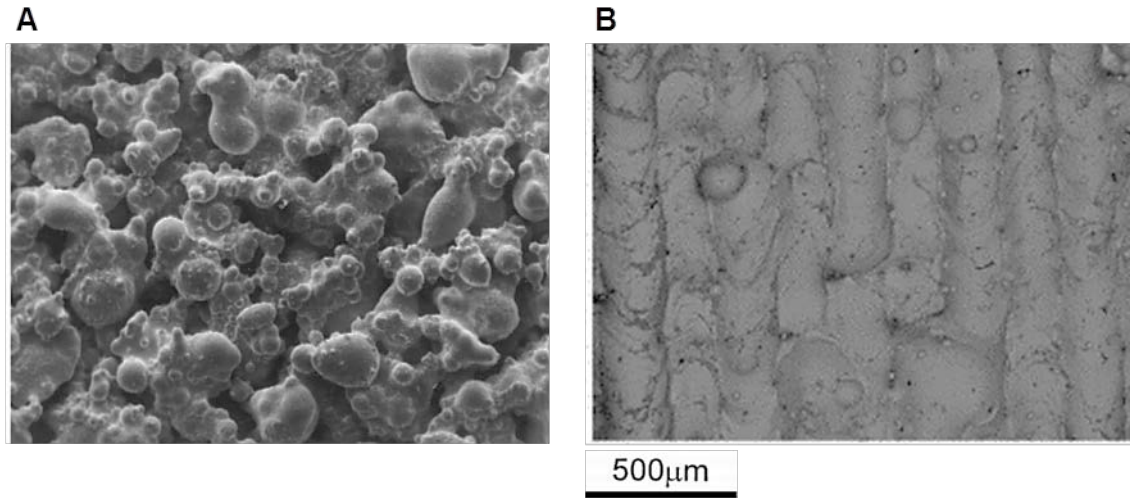


Figure 2.1: Surface morphologies of M2 high-speed steel parts processed by (a) SLS [21], (b) SLM [22].

The major research leading to the development of SLM provides a history of laser usage in AM techniques. Many publications have addressed material investigations, such as the study of the laser sintering of copper and tin powder mixtures to create bronze parts by Klocke et al. [23]. Prabhu and Bourell [24] researched the supersolidus liquid-phase laser sintering of pre-alloyed bronze powder for rapid prototyping. Niu and Chang exclusively studied the laser sintering of high-speed steel powders [25-27]. The laser sintering of a mixture of nickel superalloy and cermet powders to produce turbine blade tips was reported by Das et al. [28]. Laoui et al. studied the sintering of WC-Co hard metal powder [29]. A hard-metal-based powder mixture for rapid tooling was introduced by Petzoldt et al. [30]. The viability of SLM for the manufacture of engineering parts using ceramic, Ti, and WC-Co powders was also investigated [31]. Further studies tested the feasibility of using the heat of exothermal reactions together with the laser energy to provide the bulk of the energy required for consolidation [32].

Other publications have focused on the fundamentals of the SLS process. Bourell et al. [33] provided an overview of the basic principles of SLS machine operation, as well as the bonding mechanisms of different powder particles. Bunnell et al. [34] described metallurgical mechanisms whereby loose metal powder beds are sintered to nearly full density using a scanning laser beam. Among these mechanisms was the resolidification of a sub-cooled semi-infinite metal powder bed with a mobile Gaussian heat source. Lewis and Schlienger illustrated the practical considerations, as well as the capacity, for laser-assisted direct-metal deposition [35]. Several authors have published detailed results for the microstructural characterization of materials produced by metal laser sintering to better understand the mechanisms of particle bonding and the microstructures produced by the laser sintering of metallic powders [36-40].

2.1.2. Invention of SLM

In 1971, Pierre Ciraud filed a patent application [41] describing a method that could be used to manufacture objects of any given geometry by placing powdered material, such as metal, on a substrate and condensing the powder using a beam of energy, such as a laser beam. In 1989, Deckard [42] at the University of Texas at Austin, patented SLS, which was commercialized with the development of the DTM Sinterstation 2000/2500 machines and feedstock powder materials. The EOS EOSINT M250 direct metal laser sintering (DMLS) machines were developed in 1995 to produce metal tools for plastic injection molding; this is regarded as the start of rapid tooling [43]. In 2004, EOS GmbH obtained all the rights to the patents related to laser sintering from the University of Texas and 3D Systems [44].

SLM was formalized in 1995 at the Fraunhofer Institute for Laser Technology (Fraunhofer ILT) in Germany, with a research project that yielded the ILT SLM patent DE 19649865 [45]. Early in

the development process, Fockele and Schwarze of Fockele and Schwarze (F&S) Stereolithographietechnik GmbH (Paderborn, Germany) began working with Wissenbach and Meiners, both Fraunhofer ILT researchers, on the development of SLM technology [46]. F&S Stereolithographietechnik GmbH later partnered with what later became SLM Solutions GmbH (Luebeck, Germany) [47]. At the time, the company was called MCP HEK GmbH, which was later changed to MTT Technology GmbH, and finally to SLM Solutions GmbH [48]. While Fockele founded his own company (Realizer GmbH), Schwarze chose to stay at SLM Solutions GmbH [49].

Today, the major leading vendors and manufacturers of SLM machines are SLM Solutions GmbH, 3D Systems Corporation, Concept Laser GmbH, Phenix Systems, and EOS GmbH [50].

2.2. General SLM Process and Kinetics

The manufacturing of parts by AM including SLM begins with the creation of a CAD model of the part, which is subsequently converted into a stereolithography (STL) file (i.e., the standard format for the AM industry) (see Fig. 2.2). The STL format is a 3D triangulated representation of the model's surface geometry; the surface is tessellated into a set of oriented triangular facets. The number and parameters of the triangular grids can be manipulated to optimize the results. Larger numbers of triangles improve the accuracy of the surface approximation, but entail larger file sizes and hence increased build times. The data is then processed into planes; the STL file is sliced into thin 2D cross-sectional layers of a specific thickness, as the required deposition paths for each layer are simultaneously developed. The orientation of the deposition path determines the time required to build the part. This data is then sent to the SLM machine to direct and focus the laser beam onto a layer of deposited metal powder. The powder melts, according to preset

specifications, on the fabrication substrate. As each layer sets, the substrate moves to maintain a constant distance between the laser and powder. As defined by the model, the laser continues to build the required part layer-by-layer by melting the powder so that it fuses together.

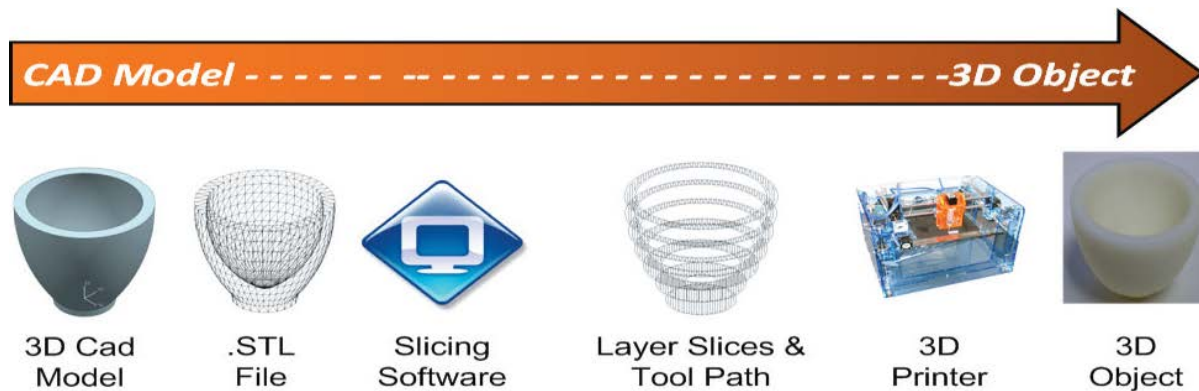


Figure 2.2: Process chain for obtaining parts by AM route, from initial 3D design to final fabricated part.

The basic setup of the SLM apparatus is shown in Fig. 2.3. The build piston supports the build platform, consolidated part, and any unconsolidated metal powder. A high-power laser traces the sections and slices the surfaces constituting the geometry of any built part. The resulting slices are then welded to the previously drawn sections of the part. Once the building of the layer is completed, the build piston moves vertically downwards by an amount equal to the thickness of one layer, after which a fresh layer of unconsolidated powder is deposited on the build platform by the recoater arm sweeping across it. This process continues until the part is completed. Most SLM processing is performed under inert shield gases (such as nitrogen or argon) to reduce the oxidation, electrical charging, and porosity of a build [51].

Once the part is completed, the residual powder is unloaded and the build platform is removed from the machine. Grinding is sometimes necessary to remove the supports from the build

platform and parts to ready them for use. In some cases, additional post-processing such as heat treatment, hot isostatic pressing (HIP), polishing, and shot peening may be performed after SLM to improve the densification, surface characteristics, and mechanical properties.

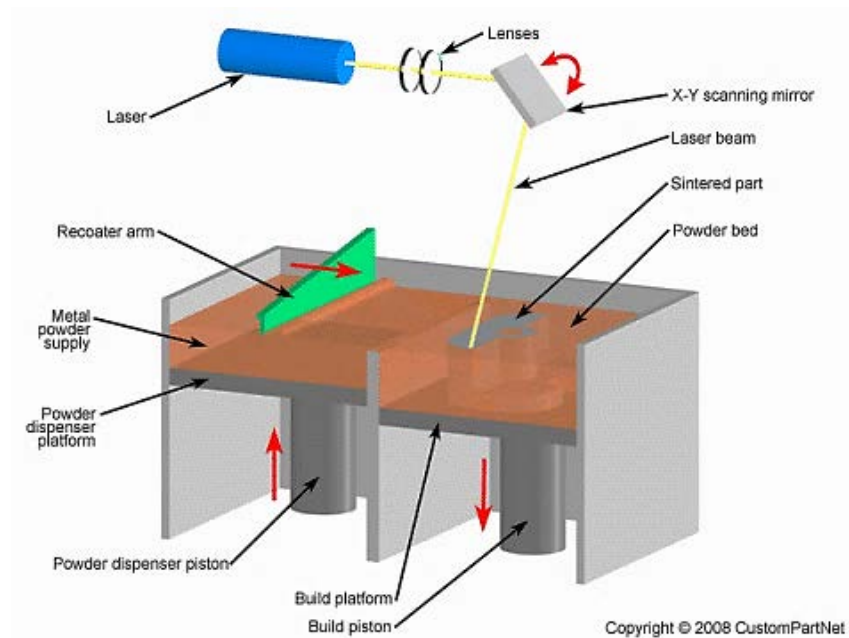


Figure 2.3: Schematic of typical SLM system setup [52].

The cooling–heating cycle of the building process must be considered when selecting SLM over other AM methods, because materials that are sensitive to constant thermal cycling may exhibit properties that are different to those which were originally intended under constant temperature fluctuations. The effects of thermal expansion and contraction occurring during the thermal cycles of the SLM build process often lead to the development of more residual stress in products than in those procured through traditional manufacturing processes; these stresses can lead to critical defects of cracking and delamination. Furthermore, if the build temperature is poorly controlled, the molten powder may ball up, which effectively ruins the build [51]. If the powder feedstock is allowed to melt, the grain formation and orientation become inconsistent,

adversely affecting the quality of the build. Therefore, temperature control is necessary for the success of an SLM build.

As discussed earlier, AM with metals and alloys is performed using layers of metallic powder that are melted and cooled into the desired configuration. Various parameters and properties must be considered for laser-based metal AM. The powder absorbance of the laser energy varies according to the material properties of the powder, as well as the laser wavelength. In general, the laser energy and part density are positively correlated. The surface tension and wettability of the melt must be considered and accommodated in the SLM process by the inclusion of additives in the feedstock powder and the control of the processing parameters [53]. Additives in the powder can serve many purposes, from reducing oxide formation to adjusting viscosity, the latter allowing the powder to easily spread across the surface without being overly viscous such that balling occurs.

2.3. Comparison between AM and Traditional Manufacturing

One major difference between AM and traditional manufacturing, such as computer numeric control (CNC) machining, is that machining generally employs cutting oil for lubrication, which becomes waste that accompanies the removed material. Huang et al. [54] observed that the pollution of terrestrial, aquatic, and atmospheric systems resulting from AM methods is much lower than that resulting from traditional manufacturing processes; the main health risk associated with traditional manufacturing processes is the oil mist formed by the metalworking fluids. Therefore, it is necessary to measure toxicity and as many other factors as possible, rather than judging the level of environmental friendliness based only on energy use or material waste. Luo et al. [55] investigated the ecological impact of different AM machines, showing that they

can vary by up to an order of magnitude, and that the machining of plastics generally requires no lubrication.

AM is more efficient than traditional manufacturing in terms of resource consumption, because a final product includes a higher proportion of the raw materials. Traditional manufacturing, such as injection molding (IM), uses large amounts of raw material for the likes of mold forms that are not parts of the final products. If the same raw materials are used in both traditional and AM methods, AM clearly has the advantage in terms of efficiency (see Fig. 2.4).

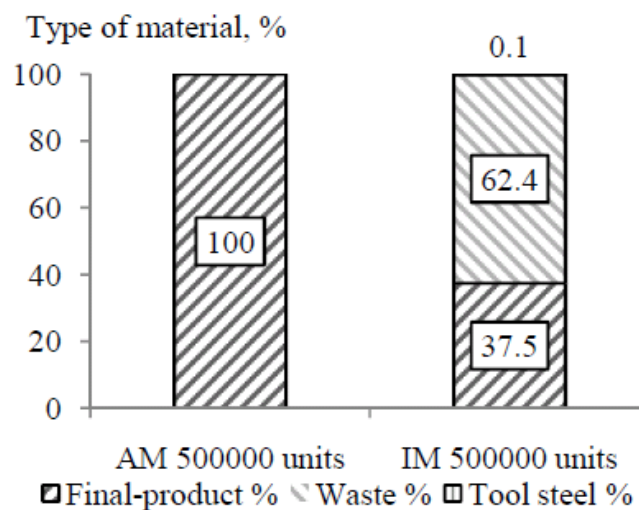


Figure 2.4: Percentages of materials in products, waste, and tool steel in AM versus injection molding (IM) processes, for a production volume of 500,000 units [56, 57].

Considering the energy consumption per unit produced, AM processes always use more energy than traditional methods such as injection molding at higher production volumes. However, AM has the advantage in terms of energy usage at low production volumes. The crossover point of energy versus production volume depends significantly on the raw material choice and product geometry. Analyses of energy consumption have shown that most of the energy used in AM is

used in the creation of the final product, whereas in traditional manufacturing, only a fraction of the total energy is used for the production of the final product [56, 57].

It is always true that different manufacturing methods produce different properties when applied to any one material; for instance, the microstructure and properties of wrought 316L are quite unlike those of cast 316L. Therefore, it is also logical to expect SLM parts to differ from traditional parts in the corresponding material. Although the differences are generally predictable, they can be surprising, as illustrated by the following examples.

Example 1: It is well known that metal parts produced by laser-based processes usually have much finer grain sizes than parts that are cast in comparable materials. This is generally because of the very rapid solidification rate that results from the almost instantaneous removal of heat as the scanning laser spot moves, and from the rapid conduction of heat from the melted zone into the surrounding powder bed and/or solid metal. Figure 2.5 shows micrographs of 17-4 stainless steel parts built using the EOS M280 system with the recommended standard parameters; a comparison with a cast sample made of the same material is also shown. Clearly, the SLM sample displays very fine grains with an average size of approximately 1 μm , in comparison to the cast sample, which has much coarser grains and which differs significantly in its texture.

Example 2: The material kinetics of SLM materials may differ from those produced in the same materials using traditional methods. Conventionally, cast parts made of 17-4 stainless steel, for example, can be post-hardened using post-heat treatment at 482°C (900°F) for 1 h, resulting in precipitation hardening that increases the strength and hardness. However, when such post-processing was first tested on laser-sintered parts in 17-4 stainless steel, it was found that the post-heat treatment unexpectedly decreased the tensile strength, instead of increasing it [58].

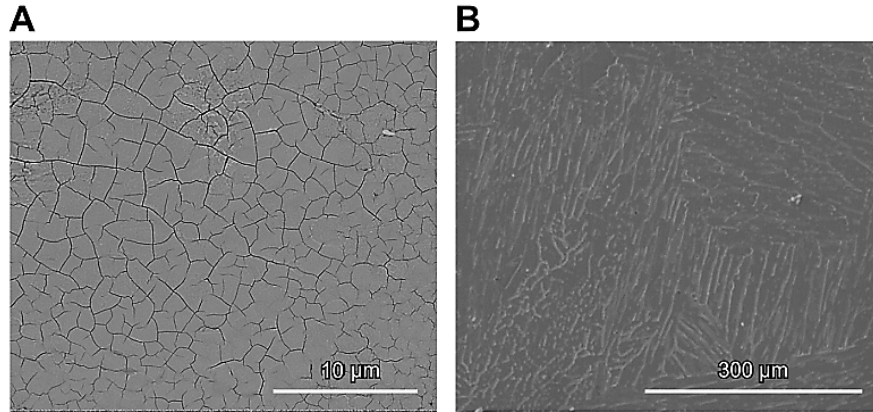


Figure 2.5: Comparison of the microstructures of 17-4 stainless steel after etching for (a) SLM; (b) casting. Notice the difference in the scale bars [59].

In another investigation by Shellabear et al. [60] they indicated that this unexpected behavior arose from the formation of a duplex-type steel structure with interlocked phases of austenite and ferrite/martensite, resulting from the extremely rapid melting and re-solidification. These results differ from those of conventional heat treatment because the duplex-type structure remains, hindering subsequent martensite formation. However, a recent work [61] has contradicted the findings of previously published works, showing that aging at 900°F enhanced the hardness and compressive yield strength of 17-4 stainless steel because of the precipitate phase that developed with aging.

Example 3: When parts are built layer-by-layer by the sequential melting and re-solidification of individual lines of material, the structure would be expected to feature “weld lines” and a fine-grained and dendritic structure, as shown in Fig. 2.6. The crystals are oriented perpendicularly to the applied layer, with a height much greater than the layer thickness (Fig. 2.6 (a)). High-magnification images (Fig. 2.6 (b) and (c)) demonstrate the complexity of the microstructure, a fine cellular substructure with elongated intragranular cells.

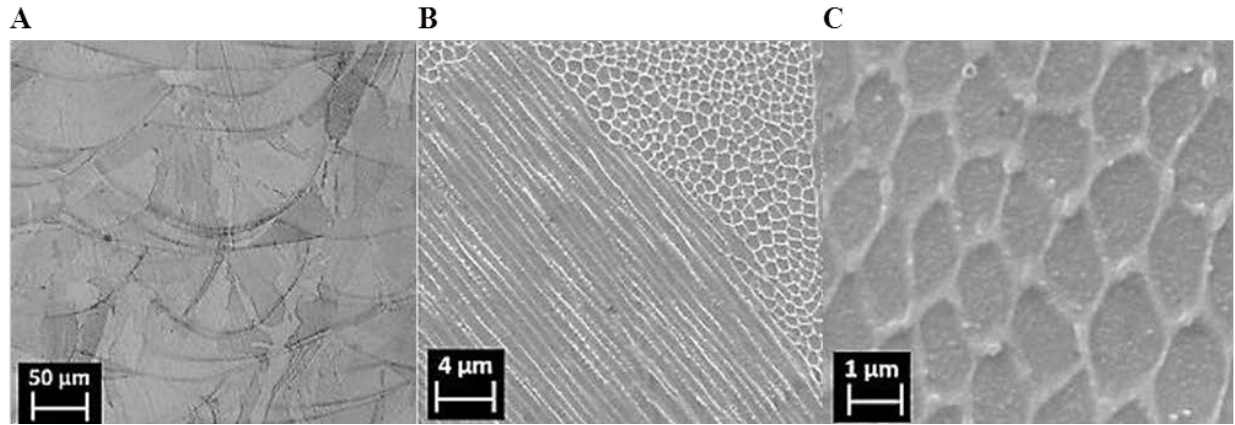


Figure 2.6: SLM of 316L stainless steel. (a) Lateral cross-section of built parts; (b, c) SEM micrographs of built parts at higher magnifications [62].

The material structure and properties always depend on the build strategies, such as the laser exposure patterns, as well as the processing parameters used. The three examples above describe specific build situations; the results are expected to vary with the use of different parameters.

2.4. Advantages and Limitations of AM

The development of laser-based AM offers multiple advantages and the possibility of industrial applications. Generally, the primary advantages offered by AM processes are the ability to create complex geometries that cannot be formed by traditional manufacturing processes and the lack of necessary auxiliary devices and tools. From an industrial standpoint, these advantages present several pivotal implications.

Individual components are often manufactured in different factories with special tooling and are then shipped to assembly sites. With AM, parts are formed without specialized tools, allowing the on-site production of many parts and the elimination of the need for supply chains.

Furthermore, as AM is also capable of printing interlocking parts, AM also decreases the number of parts per component and the need for assembly.

Regarding product distribution, AM could fundamentally change the objects that are distributed. AM products are arguably based on the digital file for the product model; therefore, the file, rather than the physical product, could be distributed. With a digital file, any user with access to the appropriate AM hardware could produce the physical product [63]. From a logistical standpoint, AM allows manufacturers to create parts that are not ordered often, but which must conventionally be warehoused, on an as-needed basis, thus reducing warehouse load. Given the capabilities of AM, these parts could be created at much lower volumes, thereby decreasing the cost of storing many uncommon spare parts. The current state of AM technology is such that several successful applications can already be found, including in custom orthodontics, hearing aids, prosthetics, and other medical devices, since AM processes can be used to form specialized parts.

However, despite the promise of AM, the inherent limitations of AM must be acknowledged. The most notable issue, which relates to industrial applications, is the time required to complete the build, which is an inherent effect of the layer-by-layer construction of the product. For instance, the formation of a small cube could take hours when using AM, but could be completed in minutes with injection molding. Furthermore, metal AM products lack the necessary consistency in the desired properties for commercial distribution. For these reasons, AM requires further advancements in efficiency and process control before it becomes a viable means of mass production [53].

2.5. Material and Processing Considerations in SLM

2.5.1. Feedstock Powder Properties and Characteristics

The powder characteristics and properties must be considered as they influence the SLM process and densification kinetics. Table 2.1 summarizes some of these major properties, some of which are interrelated. For example, the powder size and size distribution both affect the viscosity of the melt and the flow rate of the powder [64]. Finer particles absorb more laser energy, thereby increasing the particle temperature and kinetics of densification, because the powder presents a larger surface area than one with coarser particles. Finer particles can also fill voids and therefore increase the powder density, producing higher solidification rates and finer microstructures [65]. However, the flow of nanopowders is often inferior; nanopowders often agglomerate, increasing the optical reflectivity of the powder bed and thereby decreasing the energy absorption and densification kinetics [66].

Table 2.1: Powder properties and characteristics influencing SLM process

Property type	Examples
Metallurgical and chemical properties	alloy composition, oxygen and carbon concentration, reaction enthalpy, oxidation potential
Granulomorphometric characteristics	particle size and distribution, particle morphology, roughness, powder flowability
Rheological properties	viscosity and surface tension
Mechanical properties	elastic modulus, yield point, tensile strength
Thermal properties	conductivity, specific heat, melting temperature, thermal expansion
Optical properties	reflection/ absorption ratio, optical penetration

2.5.2. Processing Parameters

Figure 2.7 illustrates the SLM processing parameters that have a major influence and which must be considered. One common means of considering combined multiple interdependent process parameters in SLM utilizes the Andrew number [67], which can easily be expressed as an energy density E , given by $E = \frac{p}{vst}$ [53], where p is the laser power, v is the scanning speed, s is the hatch spacing, and t is the layer thickness. In addition, the use of different scanning patterns for the laser can produce different microstructures and properties (e.g., density, hardness, residual stress, etc.). By varying E and the scanning pattern, it is possible to improve the densification, microstructure, and mechanical properties of the SLM product.

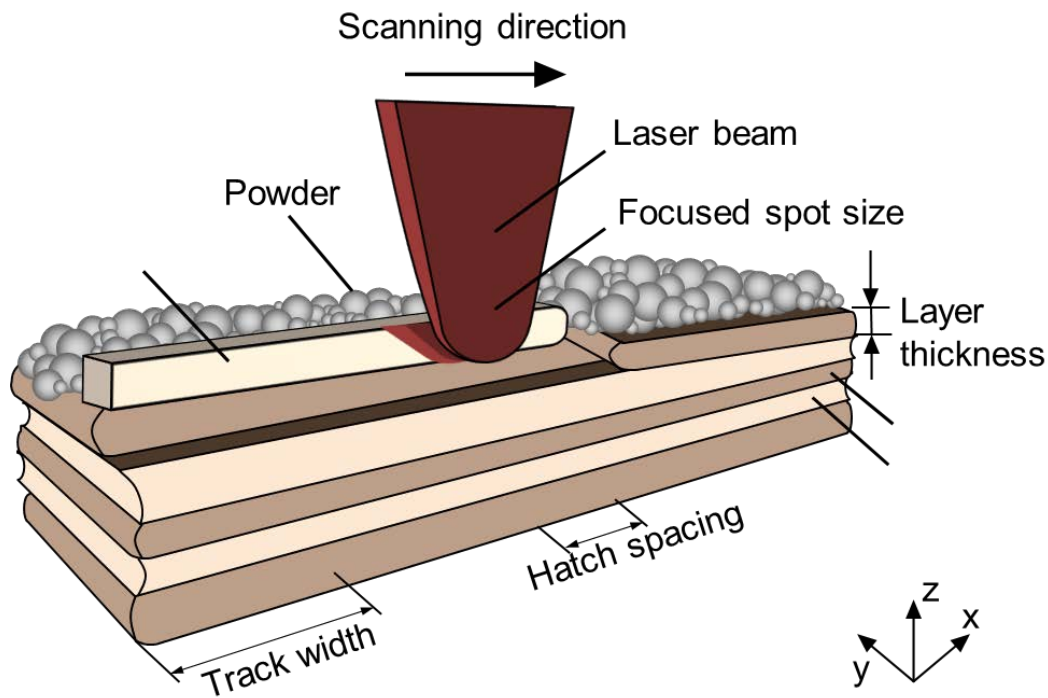


Figure 2.7: Schematic demonstrating the major processing parameters influencing SLM.

2.5.3. Solidification Mechanism and Microstructure of the Melt Pool

During SLM, the laser and powder bed interact for a short time because of the relatively high scanning speed of the laser beam, leading to rapid heating and melting followed by rapid solidification (see Fig. 2.8) [68]. There are several physical phenomena involved with this process, including optical absorption and reflection, heat and mass transfer, phase transformation, motion of the interface between the solid and liquid phases, fluid flow caused by surface tension gradients, and chemical reactions within the molten pool [69]. The cooling rate and melt pool geometry (i.e., size and shape) affect the grain growth and microstructure of the part [70] while generating a temperature gradient between the center and the edge to create surface tension gradients that incline the melt to flow radially toward the center [71]. Figure 2.9 illustrates the effect of decreasing the scanning speed on the strength of the Marangoni flow and the depth of convection. The advantages of achieving the Marangoni flow include the creation of a refined microstructure, the extension of the solid solubility, increased chemical homogeneity, and the formation of metastable phases [72].

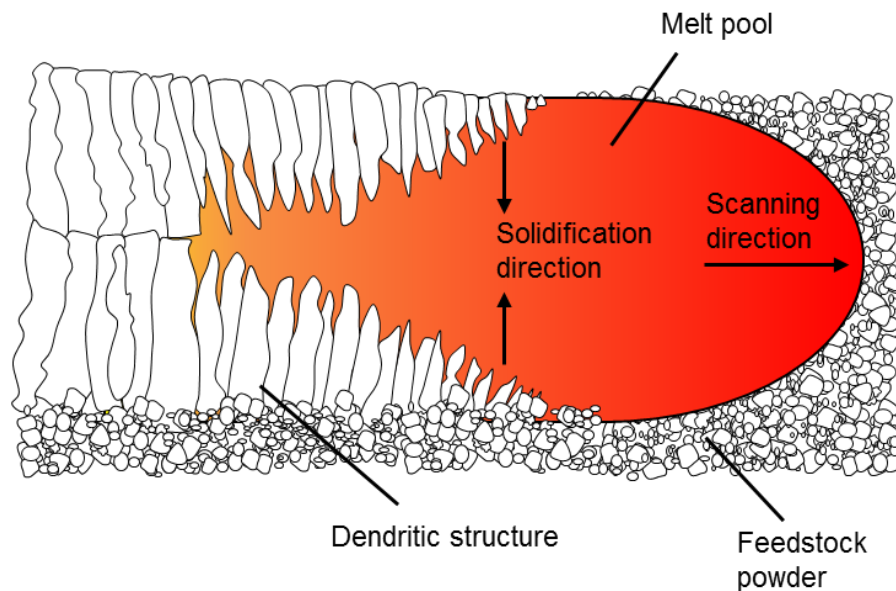


Figure 2.8: Schematic of solidification process in SLM.

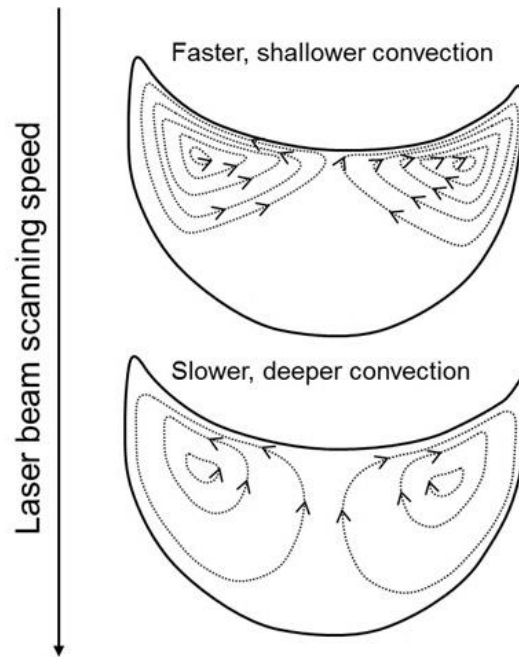


Figure 2.9: Effect of laser beam scanning speed on strength and depth of convection during SLM.

The microstructures formed by SLM can be categorized into two different types. One type contains large grains arranged in columns as formed by the epitaxial growth; this occurs when the grains grow according to the direction of the maximum thermal gradient. In SLM, during successive layer deposition, the previous layers are remelted, which causes each new layer to adopt the same crystallographic orientation as those below; this is the “epitaxial growth mechanism.” The other type encompasses alloy metals with unstable solidification fronts, caused by dissonance of the front. They feature finer grain structures that grow toward the center of the melt pool. The solidification type of the melt can be altered by varying the laser energy density or scan speed. Figure 2.10 shows an example of optical and SEM micrographs of as-built SLM 17-4 stainless steel, which exhibits a unique microstructure. The optical micrograph shows a microstructure typical of an SLM-processed material, featuring overlapping bowl-shaped

features that result from the solidification of the melt pool after each laser scan. The strong grain orientation in the SEM image indicates that solidification occurs for crystals growing perpendicularly to the close-packed austenite planes. The clear, simultaneous appearance of the two microstructures (bundles of columnar grains as well as fine equiaxed grains cutting across the melt pool boundaries in the build direction) is observed.

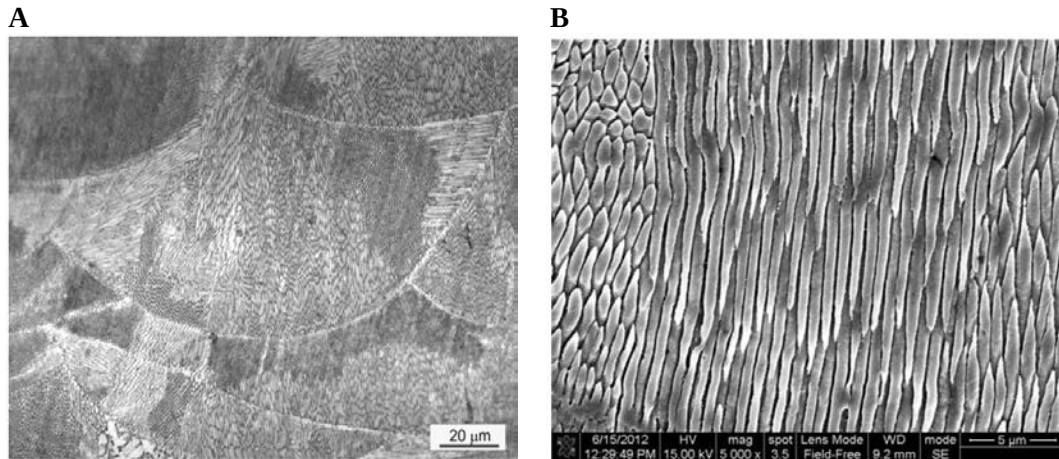


Figure 2.10: (a) Optical micrograph; (b) SEM image showing 17-4 stainless steel microstructure that is typical of an SLM process with strongly oriented fine austenite grains [73].

2.5.4. Material Textures

SLM-processed parts exhibit textures induced by directional solidification. The texture is heavily influenced by the scanning method, which determines the direction of solidification. For example, for high-alloy cubic metals scanned unidirectionally, stronger textures form perpendicular to the scan vector. This creates a $\langle 100 \rangle$ texture, because $\langle 100 \rangle$ is the direction of the maximum thermal gradient for cubic metals [74]. However, when bidirectional scanning is applied, in which the layers are scanned in a zigzag pattern with a 90° rotation between the scan

lines, the columnar grain structure is broken, subsequently creating a weaker texture. For lower-alloy metals, however, this relationship is different.

2.5.5. Grain Size

Compared to metals processed by traditional methods such as casting, SLM metals have finer microstructures [53] that create stronger materials with higher yield stresses (i.e., according to the Hall–Petch relation). The grain sizes of laser-processed materials are generally fine, because of the high cooling rate and limited time in which the grains can grow. However, the microstructural features of SLM parts can be dramatically altered by varying the processing parameters.

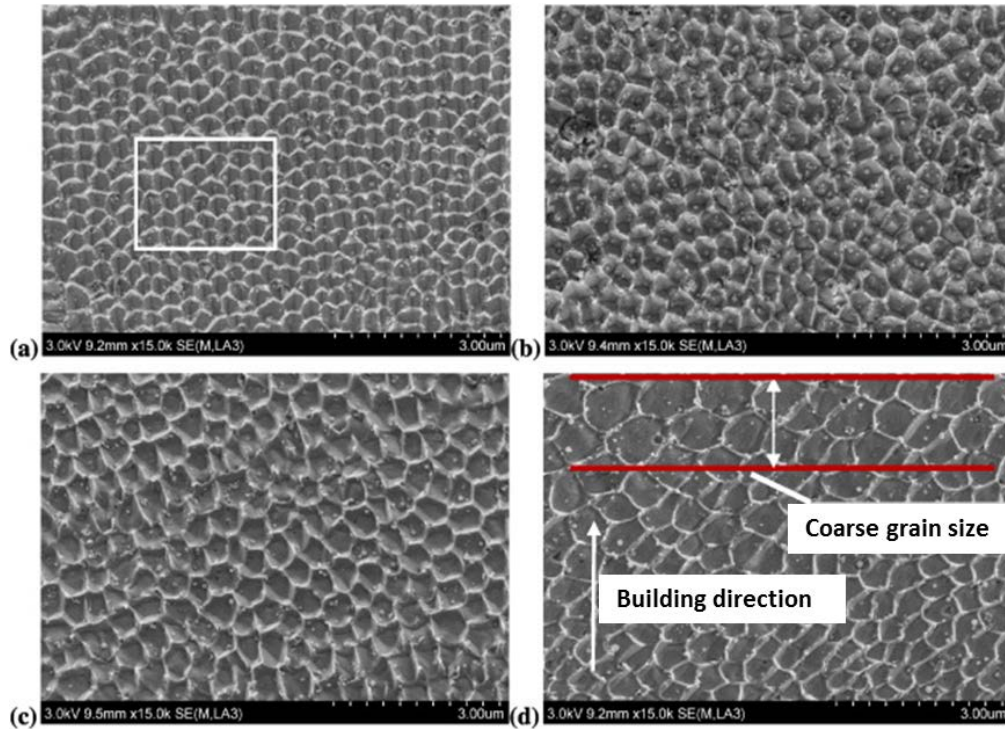


Figure 2.11: High-magnification SEM micrographs showing the cellular dendrites of SLM-processed 316L parts at different parameters: (a) 104.17 J/mm^3 , 1200 mm/s ; (b) 125.00 J/mm^3 , 1000 mm/s ; (c) 156.25 J/mm^3 , 800 mm/s ; (d) 178.57 J/mm^3 , 700 mm/s [75].

Figure 2.11 shows how the mean primary dendritic arm spacing of 316L stainless steel SLM parts increases as the laser scan speed is decreased; when the applied energy density is increased from 104.17 J/mm^3 to 178.57 J/mm^3 , the mean primary dendrite spacing increases from approximately $0.31 \text{ }\mu\text{m}$ to $0.74 \text{ }\mu\text{m}$. This overall trend is attributed to the lower cooling rate at lower scan speeds, as well as the higher average melt pool temperature, which gives the grains more time to grow.

2.5.6. Densification Level and Laser-Based Defects

Powder consolidation in the SLM process is driven by temperature changes, gravity, surface tension, and capillary forces in the absence of external pressure. Under these conditions, SLM parts may suffer from common laser-based defects, such as the emergence of porosity. Large pores can form from insufficient melting, micropores from minimal feeding in the interdendritic zones, and spherical pores from trapped gas [68].

Another defect in SLM processing is known as balling; this occurs when the molten material is unable to wet the underlying substrate, such that it consequently spheroidizes [76, 77]. Balling induces surface coarsening, significantly decreasing the SLM processing quality and increasing the porosity [78]. It is possible to improve the wetting by avoiding oxidation and contamination, as well as by adding alloying elements to the powder [79].

Laser-processing methods such as SLM can introduce residual stresses because of the large thermal gradients that arise as a result of the nature of the process. When the newly molten layer cools and shrinks, the material is subjected to tensile stresses; in addition, the strains on the substrate also contribute to residual stresses, creating a tensile stress in the deposited layer and a compressive stress on the bottom [79, 80]. Residual stresses lower the quality of the SLM parts

because of the shape changes that arise from deformation. Higher cooling rates in SLM increase the occurrence of deformation and cracking, which are exacerbated by residual stresses [81], and greatly decrease both the tensile strength and fatigue strength.

For low-laser-energy densities, samples experience poor wetting and spheroidization. For exceedingly high-laser-energy densities, the density of the part is increased, but the laser tracks are cut off, being present as short strips. Vaporization and the penetration of the melt pool increase, which can form keyholes and vapor cavities in the melt pool. Intermediate laser energy densities create continuous tracks in each deposited layer with improved densification [82].

To demonstrate the influence of energy density on the porosity, Fig. 2.12 shows the average relative densities of 316L stainless steel specimens, as measured by the Archimedes principle, under various energy densities. In general, a proper increase in the applied energy density enhances densification. However, excessive energy input causing very low viscosity may generate thermal stresses and hence cracking.

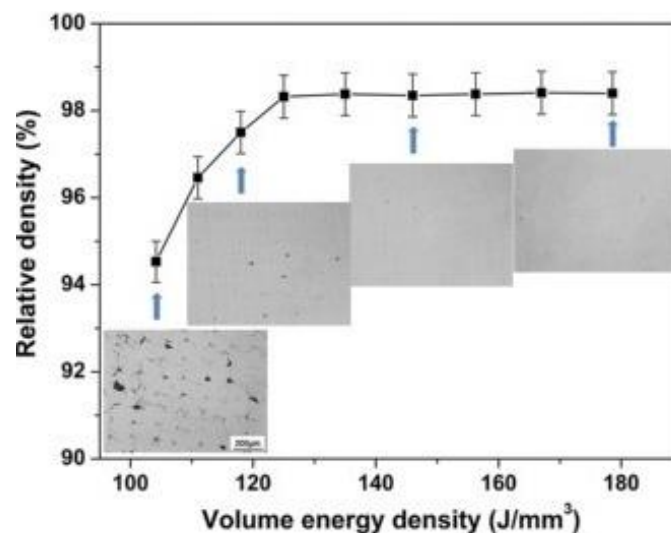


Figure 2.12: Variation in relative density of SLM-processed 316L parts under various energy densities [75].

Figure 2.13 shows SEM images of 17-4 stainless steel specimens that are formed using processing parameters of 195 W and 1200 mm/s, 95 W and 389 mm/s, and 70 W and 287 mm/s, respectively, at which the porosity is significantly higher than that formed under other parameters. For the processing parameters of 195 W and 1200 mm/s, the laser input is sufficient to completely melt the stainless steel powder, given the high laser power. However, the laser scan track shows discontinuities from the balling phenomenon, as shown in Fig. 2.13(b). Notably, more thermally induced cracks are found in specimens formed under such processing conditions, because the extremely high cooling rates caused by the very high scan speeds create greater thermal stresses. For the processing parameters of 95 W and 389 mm/s and 70 W and 287 mm/s, the laser input is low, causing insufficient melting with limited liquid phase formation.

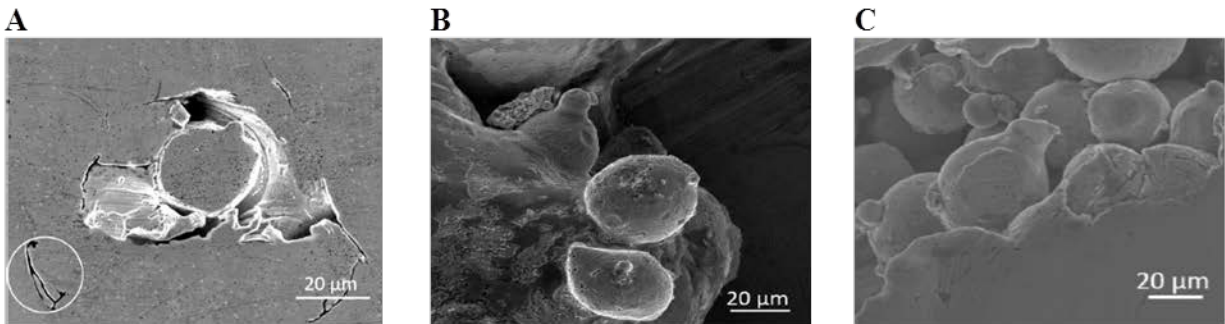


Figure 2.13: SEM images of pore morphology using (a) 195-W laser power and 1200-mm/s scan speed, (b) 95-W laser power and 389-mm/s scan speed, (c) 70-W laser power and 287-mm/s scan speed [83].

2.6. Grain Size Refinement Strengthening Via Mechanical Alloying

Several methods have been proposed to produce materials with nanostructured grains, showing remarkable structures and properties [84]. Bulk nanostructured materials (BNMs), generally defined as materials with grain sizes of less than 100 nm, exhibit high strengths relative to

typical materials of the same compositions, making them promising for structural applications. One promising means of processing BNMs is the mechanical alloying (MA) of mixed powders in high-energy ball milling [85], and the subsequent consolidation of these powders into 3D parts.

Ball milling is extensively utilized for preparing nanostructured metallic powders [86]. Grain size refinement in the powder occurs as a result of the repetitive fracturing and re-welding of the powder particles in an extremely vigorous ball mill. Following consolidation into a nanocrystalline material, the material displays extraordinary mechanical and physical features compared to conventionally processed equivalents. The ultimate grain size of BNMs is typically established by the microstructural stability in conjunction with the parametric gap utilized in the milling process [85].

2.6.1. Mechanisms of Nanostructure Formation

During milling, the powder material undergoes rigorous plastic deformation, causing grain refinement. This procedure entails five evolutionary stages within the powder particle: flattening due to plastic deformation, welding-dominance, fracturing, and the formation of equiaxed particles, arbitrary welding orientations, and the stable steady-state of the powder particles, during which there is continuous microstructural refinement, as illustrated in Fig. 2.14 [87, 88]. It is important to balance the cold-welding and fracturing processes to ensure effective mechanical alloying. The processes of fragmentation and particle coalescence occur simultaneously during ball milling [89]. During coalescence and plastic deformation, the particles become cold-welded together as others break down as a result of shear fracture, and dynamic fracture in the fragmentation process.

Fecht proposed [90] that nanocrystalline structure formation by ball-milling occurred in three major stages. First, the powder particles experienced rigorous plastic deformation. Deformation was restricted to the shear bands that formed tightly packed networks of dislocations. In the second stage, through dislocation arrangement, the grains became separated into sub-grains, split by low-angle grain boundaries. The sub-grain formation was attributed to the recombination and annihilation of dislocations and the reduction in atomic-level strain. Lastly, additional deformation caused the reduction of the sub-grain size and the reorientation of the sub-grains into grains with a large-angle misorientation.

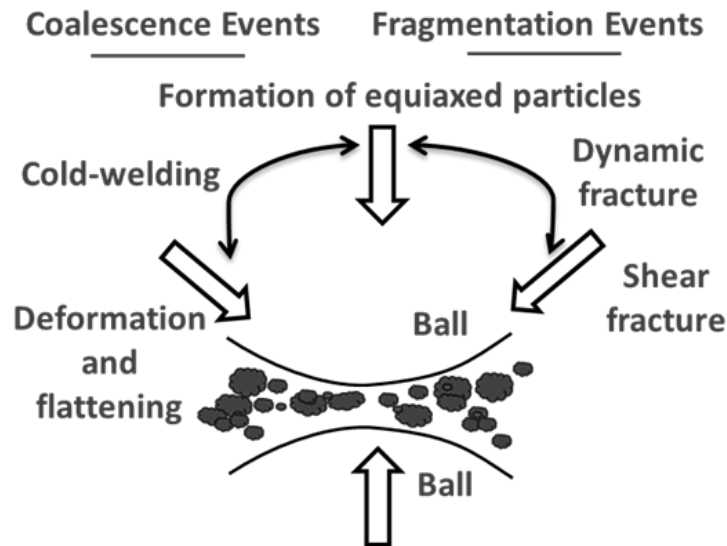


Figure 2.14: Evolutionary stages during ball milling (edited from [88]). The schematic shows the characteristic repeated fragmentation and coalescence events during MA.

As discussed above, rigorous plastic deformation during milling is a recurring procedure; the milling time dictates the overall deformation strain. All the metals and alloys display the same behaviors regarding the decrease in grain size and increase in atomic strain [91]. Microstructural homogeneity is a major factor to consider during grain refinement; to attain a microstructure with

nanoscale grains, a sufficiently long milling time is needed. Previous research [90] illustrated that this deformation is restricted to shear bands, which eventually occupy the entire sample. Therefore, it is obvious that the microstructural characteristics indicate various relative levels of deformation, rather than basic distributions of randomly oriented equiaxed grains.

As shown by the XRD results reported in previously published literature, the grain dimensions of mechanically alloyed powder particles decrease with an increase in milling time before reaching the minimum dimensions [90]. The minimum grain dimension attainable by powder milling has been attributed to a balance between the grain refinement resulting from rigorous plastic deformation and thermal recovery by the material itself [85, 90, 92]. This research has led to the following significant findings and explanations: (1) The smallest grain size is inversely related to the bulk elastic modulus or melting point; (2) The smallest grain size is directly correlated to the vital equilibrium space between two edge dislocations in face-centered cubic (FCC) metals; and (3) Inadequate experimental proof suggests that smaller grain sizes are attained at lower milling temperatures. Mohamed [93] developed a dislocation model to quantitatively describe the minimum grain size attainable through milling. The smallest acceptable grain size was controlled by the balance between the recovery rate occurring by dislocation annihilation and recombination and the strain-hardening rate introduced by dislocation generation. By balancing the rates of decrease and increase in the grain size, the minimum grain size was decreased, thereby increasing the hardness, increasing the self-diffusion activation energy, and decreasing the stacking-fault energy in the material.

2.6.2. Ball-Milling of Metal Matrix Composites (MMCs)

MMCs can also be developed by ball-milling. Milling can successfully mix reinforcing particles with the matrix phase, causing the matrix phase to surround the reinforcement particles,

removing voids between the matrix and the reinforcements, and attaining solid-state bonding between the two phases. Furthermore, the ability to evenly distribute the reinforcements and obtain a good reinforcement/matrix interface means that mechanical milling can create nanocrystalline grain structures within the metallic matrices [94, 95].

During the ball-milling of a ductile matrix/brittle reinforcement mixture, the matrix can undergo deformation, flattening, and cold-welding, similar to a monolithic metal. The presence of hard reinforcement particles promotes the fracturing procedure, which decreases the time necessary to attain an equiaxed mechanically alloyed powder [96]. The morphology of the milled composite particles influences the eventual mechanical properties of the consolidated materials. Fogagnolo et al. [97] found that the BNM processed from Al/Si₃N₄ powder and milled for 4.5 h experienced the lowest tensile elongation under extrusion; it required 45% more load than that needed to extrude the powder milled for 10 h. The elevated extrusion rate, attributed to the flake-like morphology of the powder or micro-crack irregularities, reflected the degraded ductility of the materials [97]. Therefore, an adequate milling time must be employed to attain a stable steady state and achieve an equiaxed structure in the milled powder.

The dimensional changes in the reinforcements rely on both the milling parameters and inherent aspects of the matrix and reinforcement materials. Because the feedstock materials utilized for milling form ductile–brittle systems, the reinforcement particles become embedded and trapped in the ductile matrix phase. It has been suggested that the metallic matrix phase hinders the forces acting on the reinforcements, and therefore minimizes the total energy available to fracture the reinforcements.

One benefit of mechanical milling processes as a synthesis technique for MMC powders is the even distribution of the reinforcement, which usually cannot be achieved through regular blending. Prasad et al. [98] noticed that a more homogenous distribution of the ceramic particles in composites led to their having elevated strength and increased ductility. When milling begins, the metal surfaces adhere to the reinforcements. Consequently, the reinforcement particles become captured (i.e., are cold-welded) by the matrix. Therefore, it is suggested that the accumulation of ceramic particles within the metal matrix would promote crack initiation. Such cracks would propagate via the metal matrix and fracture the metal particles. The newly fractured surfaces, with attached reinforcement particles, would then weld to other metal surfaces. The reinforcement particles, upon further milling, would become evenly distributed in the metal matrix.

The existence of hard reinforcement particles could affect the process of grain refinement within the metal matrix phase [99]. During ball milling, the reinforcement particles burst into nanoscale particles. The related improvement in the grain refinement process is deduced by a mechanism involving the interactions of dislocations with small hard particles, as well as dislocation generation caused by the disparity in thermal expansion coefficients between the reinforcement and matrix phases [99]. To summarize, the process of grain refinement is eased within the metal matrix only when the reinforcement particles are extremely small (<100 nm), either by fracturing during milling or as raw material.

2.6.3. Mechanical Behavior of Bulk-Nanostructure Metallic Materials

The elevated strength of nanostructured metallic materials can be attributed to numerous strengthening mechanisms. These mechanisms include solid-solution strengthening, grain refinement strengthening, dispersion strengthening, and precipitate hardening. The effect of grain

size d on the yield strength σ is usually expressed in terms of the Hall–Petch relation: $\sigma_{yield} = \sigma_0 + k_y d^{-\frac{1}{2}}$, where σ_0 is the intrinsic friction stress of a given material, and k_y is the Hall–Petch constant. A foundation of the Hall–Petch correlation is the threshold frictional stress level necessary for dislocation motion. This is defined as the locking factor, which causes an increase in the strength of a material with a decrease in the grain size [100].

Apart from grain refinement, ball milling typically enhances the solid solubility of solute elements, which promotes solid solution strengthening relative to that in conventional materials. Other contributions to strength involve the strong interactions of dislocations with dispersoids, commonly known as the Orowan strengthening mechanism. Along with these strengthening mechanisms, composite strengthening resulting from the existence of the hard reinforcement phase is found in nanostructured composites consolidated from milled nanocomposite powders [101].

During the ball-milling process, remarkably high dislocation densities can be introduced. Upon consolidation, the dislocation densities remain high, because the dislocations most likely stabilize through interactions with nanoscale dispersions [102-104]. The dislocation densities within dispersion-strengthened materials may be greater than those in dispersed free materials. Thus, repeated plastic deformation causes a decrease in the dislocation density to levels existing in the equilibrium condition; therefore, the flow stress is not increased, because every new dislocation loop causes dislocation annihilation over its own length, leading to work-softening behavior [103]. Work-softening can be attributed to the decreased friction stress in Hall–Petch strengthening during the unlocking of dislocations from alloying atmospheres or impurities, or during barrier breakage in dislocation or grain structures [105].

2.7. Nanomaterials in AM

The employment of nanomaterials in metal AM has great potential. AM could permit the adjustment of various material properties by presenting new possibilities in the development of nanocomposites. Nanomaterials employed in AM could include metals, carbon materials, ceramics, and semiconductor materials.

Currently, two main methods permit the integration of nanomaterials into AM builds. The first involves interrupting a print job to introduce, either manually or automatically, nanomaterials into the build. The second uses pre-mixing of the nanomaterials into the host powder before performing the build with the mixture [63].

For pre-mixed materials, in-situ particles can be created during the build. The energy of the applied laser beam is used to overcome the activation energy required to form chemical compounds from the powder components, as seen in in-situ MMCs. Alternatively, it can be used to trigger the propagation of chemical reactions in the build, as seen in a TiC-Al₂O₃ composite formed with TiO₂, Al, and C feedstock powder [106]. However, these processes can experience limitations, including clogged powder nozzles, powder aggregation, bad finish, and negatively affected build porosity. These issues demonstrate that much research remains to be done before nanomaterials can be successfully utilized in AM, especially regarding the types of nanomaterials that are compatible with certain powder types and build methods.

The addition of nanomaterials can have significant effects on the host build material or the bulk powder. For example, metal nanoparticles can decrease the sintering temperatures, increase density, decrease shrinkage, mitigate distortion, and alter conductivity. Although carbon nanomaterials, including nanotubes, graphene, and buckyballs, can significantly improve the

thermal and electrical conductivities while decreasing the density, they can also induce greater brittleness and surface roughness. Ceramic and semiconductor nanomaterials can increase the tensile strength of the build and improve the sintering process, but could also increase the brittleness of the end product. It can be seen that, while many new nanomaterials to alter material properties have been identified, much research remains to be done before AM with nanomaterials, including nanocomposites, can be optimized. Despite this uncertainty, initial research findings point to several potential benefits arising from the further development of nanomaterials in AM.

2.8. Influence of Post-Treatment

The qualities of SLM-processed parts are sometimes inferior to those of traditionally processed parts. Post-processing heat treatment can be used to enhance the mechanical properties and remove unwanted residual stresses from SLM parts. Heat treatment also modifies the microstructure, giving the material a better fatigue life and a higher resistance to creep.

Another promising post-treatment is hot isostatic pressing (HIP). In this process, the sample is subjected to a high pressure and temperature within a pressure vessel, decreasing the porosity and increasing the densification [107]. These changes generally lead to better mechanical properties.

Densification during the HIP process has been described as a three-step procedure: (1) it begins with the loose packing of powder, (2) followed by a reduction in the related porosity from the increased neck lengths at the contact points between adjacent particles and (3) a reduction in the individual pore sizes [107, 108]. The increase in the neck lengths, as well as the filling of minute openings, is achieved in each stage by the plastic deformation of the powder particles, mass

diffusion to the residual free surfaces, and power-law creep. High operating temperatures and pressures can be utilized to attain a nearly 100% relative density at temperatures lower than that would be necessary for sintering alone, as well as pressures lower than that would be necessary for cold isostatic pressing [107]. The driving force needed to attain densification is ascribed to the decrease in the surface area, and thus to the surface energy of the pores. The temperature and pressure are both important to the determination of the densification level. Because the consolidation of the milled powder typically requires the application of high temperatures for long periods, it is difficult to retain any nanoscale features. The diffusion kinetics can create coarse, microscale grains formed in the interstices between the powder and nanoscale particles [109, 110]. Therefore, HIP gives rise to an enhancement of the fracture toughness and ductility of the end material, because the coarse grains prevent crack growth [111]. However, despite attaining nearly maximum density, the HIP material may exhibit a low level of ductility [112]. This is because of the existence of preceding particle boundaries, normally carrying surface oxides, which cannot be eliminated by isostatic deformation. Thus, to fracture the preceding particle borders, shear stress must be applied to the material, which can also improve the densification.

After SLM processing, it is also important to improve the quality of the surface. Re-melting the solidified surfaces of the consolidated layers has proven to be an efficient way of performing surface smoothing, reducing porosity, and removing aggregates [113].

Chapter 3

Fabrication of TiB₂/316L Composites by Selective Laser Melting: Influence of Nanoscale Reinforcement Content, Powder Preparation Method, and Hot-Isostatic Pressing Post-Treatment

Abstract

Selective laser melting (SLM) was employed to fabricate TiB₂/316L stainless steel composites with a range of nanoscale TiB₂ contents (vol.%). First, the evolution of the constituent phases, microstructural features, and size distribution with the milling time was investigated. This research determined that the powder particles were both coarsened and refined during the early stages of milling (0–6 h), depending on the milling time. After 8 h of milling, the powders exhibited a wide size distribution but a stable spherical morphology, while the average crystallite size of the stainless-steel matrix phase significantly decreased to 11.11 nm, due to severe plastic deformation. Second, the powders obtained after 8 h of milling or mixing were processed by SLM. The resulting microstructure of the SLM-processed nanocomposites was characterized by SEM, EBSD, and TEM, while the mechanical properties were characterized using microhardness, compression, and wear tests. It was found that the microstructures and mechanical properties of the SLM-processed nanocomposites were sensitive to the TiB₂ content. The optimal TiB₂ content was determined to be 10 vol.%. Further, the TiB₂ particles were homogeneously dispersed and formed nanoscale ring-like structures along the grain boundaries. In contrast to the SLM-processed, unreinforced 316L stainless steel sample, the TiB₂/316L nanocomposites exhibited higher microhardnesses and compressive yield strengths while showing low coefficients of friction

and wear rates; this was due to the combined effects of grain refinement and grain-boundary strengthening. The hardness of the nanocomposite sample prepared from the ball-milled powder exceeded that of the samples made with the directly mixed powder, but only in the case of those with the highest TiB_2 reinforcement particle content, that is, 15 vol.%. This was a result of the finer particle sizes and the enhancement of the wetting behavior in the molten pool. Finally, a hot isostatic pressing (HIP) post-treatment was applied to some of the SLM-fabricated components in order to increase their final density. The microstructural characteristics of the HIP-subjected samples evolved with the HIP holding time from equiaxed grains to segregated regions of coalesced reinforcement particles. In addition, significant drops in the hardness and wear resistance values were observed after HIP treatment due to the high-temperature annealing effect.

3.1. Introduction

Austenitic stainless-steel alloys are known for their excellent resistance to corrosion and suitably high ductility and are therefore used in the aerospace, defense, and biomedical domains [114]. However, even though austenitic stainless steel is a desirable material, it exhibits poor mechanical properties at high temperatures, is susceptible to thermal shock, and has limited wear resistance. Strategies for solving these issues have included incorporating secondary phases such as ceramic particulates with sizes in the micron range at the matrix grain boundaries [115]. However, the results have been disappointing [116, 117], owing to the limited degree of interfacial wetting between the ceramic particulates and the metal. Basically, the large ceramic particles are prone to cracking during mechanical loading, resulting in poor ductility and the premature failure of the material [118].

Metal matrix nanocomposites (MMNCs) have recently been incorporated into the metal matrix

as nanometer-sized secondary phase dispersions [118]. Indeed, most nanostructured materials are fundamentally different from conventional polycrystalline ones and lead to improvements in parameters such as the yield strength, toughness, and hardness because of the resulting microstructural refinement [118, 119]. The use of these materials as a reinforcing secondary phase is likely to improve the performance of steel alloys with respect to engineering applications such as gas turbines, automobiles, and biomedical devices. One way to produce nanostructured materials is "mechanical alloying," which is a nonequilibrium, low-temperature, and solid-state powder processing technique [86, 120]. The process involves the repeated deformation, fracturing, and cold welding of powder particles in a high-energy ball mill.

Additive manufacturing (AM), which is based on the layer-by-layer incremental manufacturing concept, enables the rapid fabrication of three-dimensional shapes with complex geometries [2, 53, 68]. Due to the high energy density of the laser beam being used, even MMNCs may be processed by this technique [121]. The high geometrical freedom and low processing cost of the AM process enable the production of complex products that were difficult to manufacture using conventional approaches. This has the potential to lead to a real revolution in the use of MMNCs. Indeed, the AM of MMNC components represents an important direction in the field of AM research and should help fulfill future demands for novel materials with unique properties [106]. Unfortunately, the range of commercially available materials that can be applied to AM is limited; this is because the appropriate process parameter combinations for each material used need to be investigated extensively. Selective laser melting (SLM), which is an AM technology, involves the relatively complete melting of the feedstock powder and its subsequent rapid solidification [122, 123]. It is known that the nanoscale ceramic reinforcements tend to agglomerate during the casting process, owing to the large van der Waals attractive force, leading

to microstructural non-homogeneity [124]. Therefore, microstructural refinement resulting from rapid solidification during the SLM process is a potential way of preventing solute segregation and increasing the degree of particle dispersion; this can be achieved by substantially reducing the size of the reinforcing phase particles and modifying their distribution in the matrix. The setup for the SLM process, as well as the primary parameters affecting the process, their characteristics, and the bonding mechanism have been described in detail elsewhere [8, 122].

The effects of the microstructure and mechanical properties of steel alloys produced by SLM have been studied extensively [79, 125-130]. However, there have been few studies on the SLM processing of Fe-based matrix composites, although there have been several attempts to produce steel matrix composites by conventional approaches through casting or powder metallurgy. Hao et al. [131] studied the effect of the SLM processing parameters on a hydroxyapatite/316L composite for use as a material for load-bearing implants. Song et al. [132] added hard SiC particles to pure Fe powder to improve the mechanical properties of the iron matrix fabricated by SLM.

In the present study work, SLM was used to process nanostructured, TiB₂-reinforced 316L stainless steel in bulk. It has been reported that TiB₂ is a suitable discontinuous reinforcement material that exhibits thermodynamic and mechanical stability at high temperatures [133]. First, the evolution of constituent phases, microstructural features, and size distribution with milling time was investigated. Second, we focused on the effect of the nanoscale reinforcement volume content on the microstructural evolution and mechanical properties of the SLM-processed TiB₂-reinforced 316L stainless steel, including its densification level, microhardness, and microcompression, as well as wear properties at room temperature. Further, specimens were fabricated by SLM, using the obtained milled and mixed powders, and their characteristics, such

as the densification level, hardness, and wear properties were evaluated. The results of this research provide insight into the role of the initial powder characteristics in the formation of microstructures during SLM processing. Lastly, HIP-post treatment was applied to composites processed using ball-milled 15% TiB₂/316L powder to examine its influence on composite densification, microstructural evolution, and the mechanical properties. The microstructure-properties relationships of the TiB₂-reinforced 316L stainless-steel nanocomposites were established, so that nanocomposite parts with a novel nanoscale reinforcement architecture and improved performance can now be fabricated successfully. We believe that the alternative fabrication route presented in this study should significantly increase the use of TiB₂-reinforced 316L stainless-steel nanocomposites.

3.2. Experimental Procedures

3.2.1. Powder Preparation

The starting materials used were a 99.7% purity 316L stainless-steel powder with nearly spherical particles having an average diameter of 45 μm (Fig. 3.1(a)) and a 99.0% TiB₂ powder with nearly hexagonal prismatic particles, 2–12 μm in size (Fig. 3.1(b)). Four different TiB₂/316L nanocomposite systems containing 2.5, 5, 10, and 15 vol.% TiB₂ particles were prepared by ball milling the TiB₂ and 316L powders in a Pulverisette 4 ball mill (Fritsch GmbH); the ball-to-powder weight ratio was 5:1, the main disc rotational speed was 200 rpm, and the milling time was 8 h. The balls were made of stainless steel (the same material as that of the inner surface of the mill), and the milling process was performed in an Ar-protective atmosphere. There was a pause of 15 min after every one-hour cycle.

After 8 h of ball milling, the TiB_2 nanoparticles corresponding to a reinforcement concentration of 15 vol.% were homogenously dispersed around the surfaces of the 316L particles, leading to the TiB_2 /316L nanocomposite powder system exhibiting good flowability, as shown in Fig. 3.1(c). To further study the obtained composite powder, the interior structure of the ball-milled powder was investigated using transmission electron microscopy (TEM), as shown in Fig. 3.1(d). It was observed that the TiB_2 nanoparticles, which had a mean size of 45 nm, had penetrated into the matrix, and were uniformly dispersed within it. Further, the reinforcing nanoparticles formed a clear and coherent interface with the matrix. It was, therefore, concluded that the final nanocomposite feedstock powder consisted of TiB_2 nanoparticles and a 316L matrix.

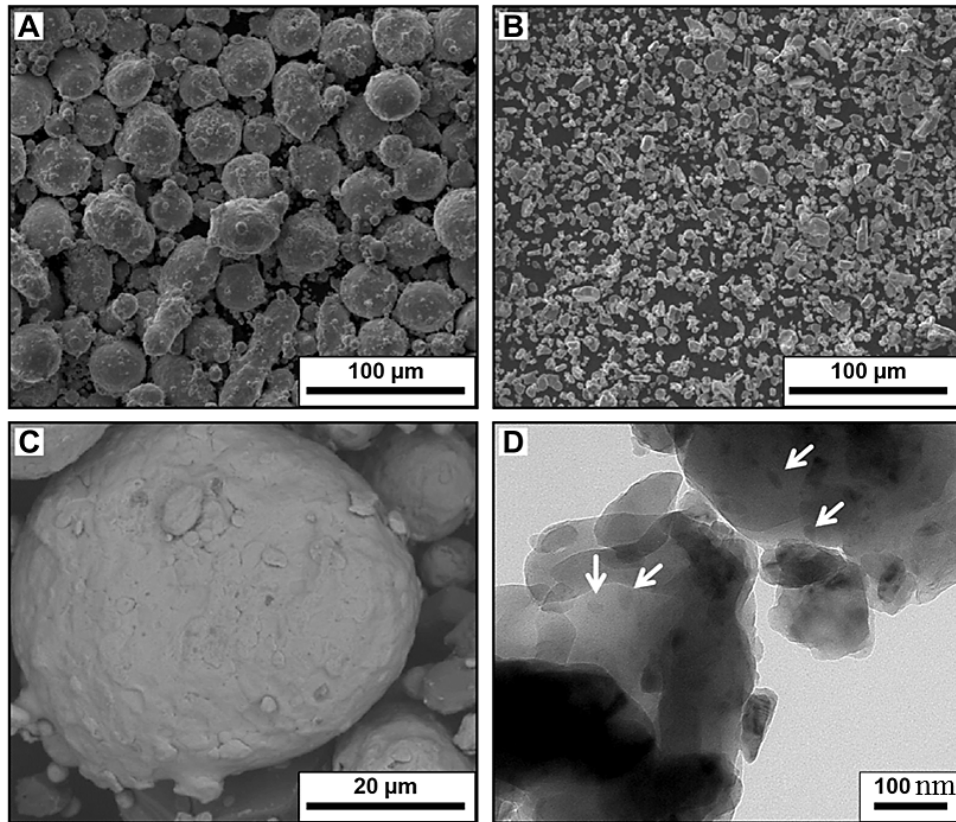


Figure 3.1: Microstructures of starting (a) 316L and (b) TiB_2 powders and (c) homogenously mixed 15 vol.% TiB_2 /316L powder. (d) TEM image of feedstock 15 vol.% TiB_2 /316L powder.

3.2.2. SLM Process and Hot-Isostatic Pressing Post-Treatment

The SLM system consisted of a fiber laser, an automatic powder-layering apparatus, an inert Ar gas protection system, and a computer system for process control. Based on a series of preliminary experiments, the SLM parameters were fixed, as follows: laser power of 100 W, spot size of 0.18 mm, hatch spacing of 0.12 mm, and a powder layer thickness of 0.05 mm. A scan speed of 250 mm/s was used to produce a pure 316L stainless-steel sample while a scan speed of 83.3 mm/s was used to produce the nanocomposite samples. Cylindrical specimens with dimensions of 8 mm × 6 mm were produced.

A standard HIP post-treatment procedure was subsequently applied to the TiB₂-containing ball milled nanocomposite containing 15 vol.% TiB₂ using a commercial service provided by Quintus Technologies, USA. Two HIP-treatment cycles were utilized:

- 1- Heating for 2 h at a temperature of 1150 °C and a pressure of 2070 bar (produced by an Ar gas flow) followed by rapid cooling to 200 °C at a rate of 100 °C/min.
- 2- Heating for 2 h at a temperature of 1150 °C and a pressure of 2070 bar (produced by an Ar gas flow) followed by rapid cooling to 900 °C at a rate of 50 °C/min. Subsequently, holding at 900 °C for 2 h followed by rapid cooling to 200 °C at a rate of 100 °C/min.

The second HIP cycle was used to study the effect of a secondary annealing treatment (i.e., longer holding time) on the composite densification, microstructure, and properties.

3.2.3. Microstructural Observation

The phases of the bulk specimens were identified through X-ray diffraction (XRD), which were performed using a PANalytical X'Pert PRO X-ray powder diffractometer with a Cu K_α radiation source at 45 kV and 40 mA; continuous scan mode was used and the scan rate was 5°/min.

Metallographic samples were prepared as per the standard procedures and were etched with Marble's reagent for 10 s. Their microstructures were analyzed using a scanning electron microscopy (SEM) system (Nova 230). A Philips CM 200 TEM system was also used to examine the internal microstructures of the nanocomposite sample with 15 vol.% TiB₂. The TEM samples were prepared using a focused ion beam (FIB). Electron backscattered diffraction (EBSD) analysis was used to study the variations in the crystal orientation, grain boundary misorientation, and texture of the nanocomposite sample with 15 vol.% TiB₂. For the EBSD analysis, the acceleration voltage of the SEM was 15 kV, while the step size was 40 nm. The EBSD data were collected using an EDAX system. To improve the statistical reliability, EBSD scans were performed at a lower magnification. Further, the data were collected at a rate of 258 fps over a scan area of 60 × 60 μm. Cleaning operations were performed on the scans, to remove any rogue points.

3.2.4. Mechanical and Wear Behaviors

The Vickers hardness was measured using an LM800AT (Leco) microhardness tester with a load of 100 g and an indentation time of 10 s; a minimum of 15 indentations were performed.

Uniaxial compression tests were performed on micropillars fabricated from the various samples. This novel approach not only provides stress-strain curves for small specimens but also limits the presence of large strain gradients [134]. Further details of this method can be found elsewhere [135-137]. Micropillars of pure 316L stainless steel and the nanocomposite samples having an average diameter of 4 μm and an aspect ratio of 1:3 were fabricated using the FIB. A FEI Nova600 Nanolab dual-beam FIB SEM operated at 30 kV was used for this purpose. The yield strengths and ductilities of the nanocomposite samples were determined by uniaxial microcompression tests performed on an MTS Nanoindenter XP at room temperature and a strain

rate of 10^{-4} s^{-1} . A diamond indenter with a flat-end tip with a diameter of $10 \text{ }\mu\text{m}$ was used for this purpose. The load-displacement data were converted into (engineering) stress-strain values. At least four pillars were tested for each condition. To attain a better understanding of the micromechanism responsible for the deformation within the areas of failure, a compressed pillar of the 15 vol.% $\text{TiB}_2/\text{316L}$ nanocomposite was FIB milled and subjected to TEM observations.

Dry sliding wear tests were performed on the SLM-processed samples using a T50 ball-on-disk tribometer at room temperature. A 3-mm-diameter 52100 bearing steel ball was used as the counterface material. A load of 3 N was applied in the tests. The friction unit was rotated at 840 rpm with a rotation radius of 2 mm for 20 min; (for section 3.3.3.2 the friction unit was slid linearly at a speed of 500 cycle/min and an amplitude of 3 mm for 20 min). The coefficient of friction (COF) was recorded during the sliding process. In the ball-on-disc configuration, the sample is mounted on a moving stage, while a known force is applied to the ball, which is held in contact with the sample surface to cause wear. The volume of material lost was measured using an ST400 white-light profilometer. The profilometer had a vertical resolution and accuracy of 8 and 80 nm, respectively, and a lateral resolution of $2 \text{ }\mu\text{m}$. The cross-sectional area of the wear track was multiplied by the circumference of the wear track to get the total volume of material removed. This volume was then divided by the load applied and the total distance traveled during the test to calculate the wear rate of the material ($\text{mm}^3/\text{N m}$). When the same test parameters are used for a number of samples, the wear rate can be used as a quantitative metric for comparing the wear resistances. The morphologies of the worn surfaces of the SLM-processed samples were observed using SEM.

3.3. Results and Discussion

3.3.1. Characterization of Feedstock Powder

3.3.1.1. Phases and Crystallite Sizes

Figure 3.2 shows typical XRD patterns for the prepared powders recorded for different milling times and powder processing methods. For every sample, sharp γ -Fe peaks were clearly detected.

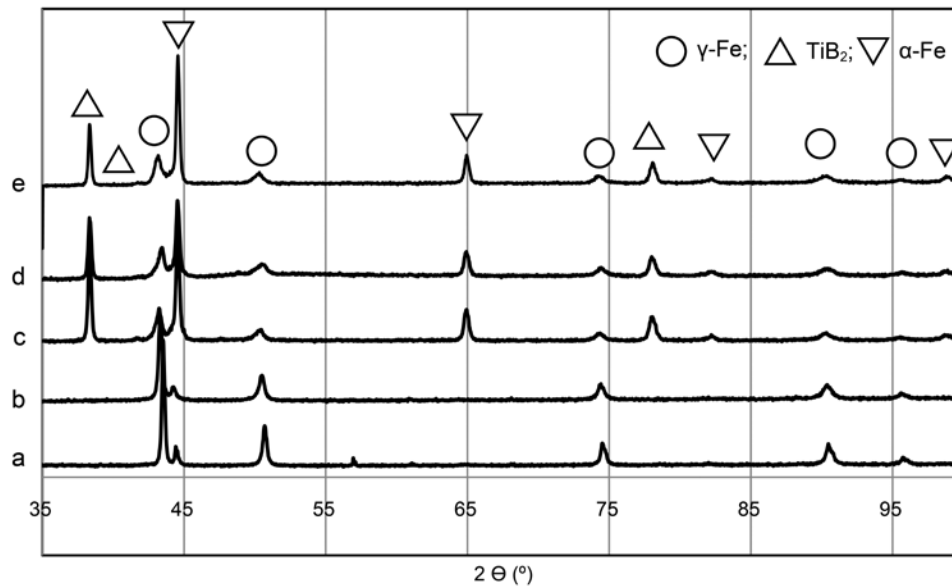


Figure 3.2: XRD patterns obtained for the 2.5% TiB_2 /316L powders (a) after 8 h of direct mixing and after milling for (b) 2, (c) 4, (d) 6, and (e) 8 h.

Note that the TiB_2 peaks were relatively weak due to the small volume fraction of 2.5 vol% TiB_2 present in the samples, and no peaks were observed after 2 h of milling time or for directly mixed powder.) Strong diffraction peaks corresponding to the TiB_2 phases were clearly detected after 4–8 h of milling. In addition, the α -Fe phase was also identified for all samples, but its intensity increased after milling for 4, 6, and 8 hours due to the severe plastic deformation that induced a phase transformation from γ -Fe to α -Fe.

Table 3.1: Variation in 2θ locations and intensities of γ -Fe diffraction peaks of 2.5% vol. TiB₂/316L nanocomposite powders with different milling times

Sample	2θ (°)	Intensity (cts)	FWHM (°)	2θ (°)	Intensity (cts)	FWHM (°)
Standard	43.583	-	-	50.792	-	-
2-h milling	43.3083	5836.18	0.2751	50.4485	1499.17	0.4678
4-h milling	43.2019	1622.20	0.6965	50.2850	611.89	0.7217
6-h milling	43.3720	1567.50	0.7747	50.4105	596.59	1.5739
8-h milling	43.1672	1564.96	0.8027	50.2109	604.42	0.7681

Table 3.1 shows the observed changes for the strongest γ -Fe phase diffraction peaks and the corresponding intensities for ball-milled powders. When the milling time was increased from 2 to 8 h, the diffraction peaks corresponding to the γ -Fe phase broadened (Fig. 3.2(e)), while their intensities decreased significantly (Table 3.1). This observation is consistent with the formation of a considerable number of small crystallites after powder milling, as well as with the distortion of the crystalline lattice due to changes in the atomic positions. In addition to peak broadening, the γ -Fe peaks were shifted to lower angles as the milling time increased from 2 to 8 h. Both the peak-broadening and peak-shifting phenomena can be attributed to the increased energy consumption during milling [86]. As a result, the degree of dislocation and compressive stress in the powder increased, leading to an unstable powder system with large lattice [138]. The powder particles did not experience any deformations or structural changes during the direct mixing process, and therefore the resulting powders produced narrower XRD peaks (Fig. 3.2a).

Figure 3.3 shows the crystallite sizes and lattice parameters calculated for the γ -Fe phase for a range of milling times. After ball milling, the crystallite sizes decreased rapidly from 44.24 to 11.52 nm during the early milling stage (2–6 h), while the corresponding lattice parameter increased from 0.3601 to 0.3625 nm. As the milling time further increased to 8 h, the crystallite

size and lattice parameter of the γ -Fe remained at a constant level of 11.11 nm and 0.3628 nm, respectively. In contrast, the material formed by direct mixing exhibited no apparent structural changes because very little energy was consumed.

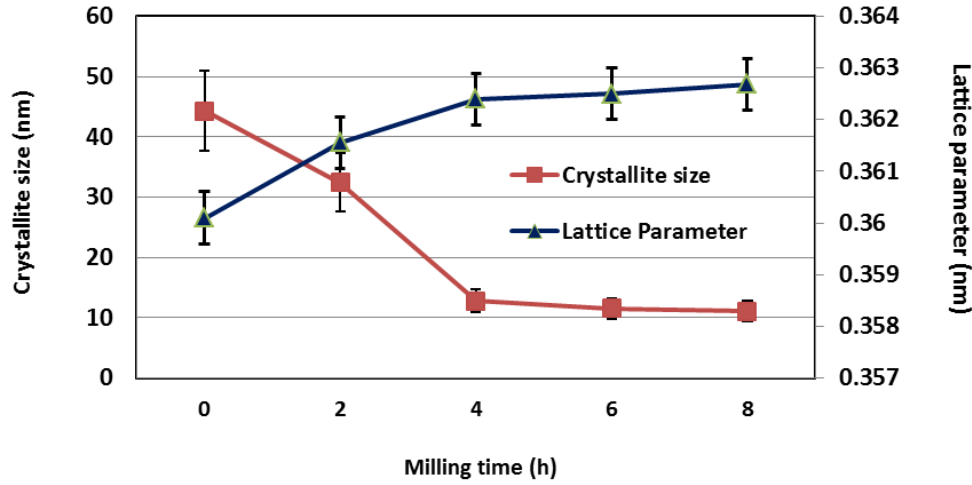


Figure 3.3: Changes in the crystallite size and lattice parameters observed for the γ -Fe phase of the 316L composite after ball milling for specific times.

The decrease in particle crystallite size during milling is generally attributed to the severe plastic deformation of the soft 316L powders, which generates crystal defects, such as point defects and dislocations [139, 140]. These crystal defects increase the strain and internal energy of the lattice. To relieve the energy of the lattice, the dislocations rearrange themselves into a lower energy state, resulting in the formation of low-angle sub-boundaries. Ma et al. [141] suggested that grain subdivision into subgrains was the main mechanism responsible for significant grain refinement. As the milling time increased, more intense deformation occurred, which in turn increased the dislocation density as well as the number of sub-grain misorientations at their boundaries. These misorientations were subsequently transformed into high-angle grain boundaries and finally into nanosized grains [142]. Hence, the presence of hard, small TiB_2

particles in a milling system significantly inhibits dislocations due to the Orowan bowing mechanism [86]. This mechanism causes an increase in the dislocation density, which accelerates the process of grain refinement. During the final milling stage (6–8 h), the lattice dislocation density saturates, and its effect on the grain refinement process becomes negligible. Consequently, the mean crystallite size of the milled powder reaches its smallest level and remains almost unchanged during this stage. Analysis of the XRD patterns supports the conclusion that TiB_2 atoms completely diffuse into the 316L lattice during 2–8 h of milling, causing an increase in the lattice parameter values.

3.3.1.2. Microstructural Evolution of MA-Processed Powders

Figure 3.4 shows SEM images describing the particle morphology and microstructural evolution of the milled powders as functions of the milling time. The variations in the average particle size and particle size distribution with the milling period are shown in Figs. 3.5 and 3.6, respectively. These three figures indicate that the duration of the applied mechanical alloying (MA) has a moderate effect on the microstructural characteristics of the milled powders, such as the particle morphology, size, and size distribution. At the beginning of the process (during the first 2 h), the particles undergo minor fracturing. During the next stage (from 2 to 4 h), the 316L powder matrix is subjected to severe plastic deformation due to its ductile nature. At this stage, the cold-welding mechanism becomes dominant, and the average particle size increases to $46.78 \pm 20.50 \mu\text{m}$. The obtained particle size distribution (D) exhibits a certain degree of uniformity, with $D_{10} = 33.71 \mu\text{m}$, $D_{50} = 42.23 \mu\text{m}$, and $D_{90} = 67.85 \mu\text{m}$ (Fig. 3.6). In addition, cold welding can be observed on the surfaces of the powder particles.

After the milling time was increased to 6 h, the deformed particles were broken into smaller pieces since the fracturing process started to prevail over the cold welding. The fractured

particles appeared slightly elongated, with some assuming oblong shapes rather than the initial spherical shapes (Fig. 3.4(c)). At this stage, the average particle size decreased slightly to $45.31 \pm 16.8 \mu\text{m}$, while the particle size distribution did not change significantly ($D_{10} = 34.1 \mu\text{m}$, $D_{50} = 42.4 \mu\text{m}$, and $D_{90} = 64.5 \mu\text{m}$; see Fig. 3.6). The powder characteristics after 6 hours of milling suggest that the number of dislocations increased due to the plastic deformation and stress concentration that occurred in the areas surrounding the reinforcement phase. The accumulated strain energy led to the initiation and extension of cracks as well as particle fracturing, which improved the homogenous distribution of the reinforcement particles.

After the milling time was increased to 8 h, the milled powder exhibited a considerable increase in size, while the majority of particles basically retained their spherical shapes (see the upper-right image of Fig. 3.4(d)). These results suggest that, during the final stage of MA, the atomic diffusion effect of the reinforcement particles increases, and the cold-welding mechanism becomes dominant again. The obtained particle size distribution ($D_{10} = 34.02 \mu\text{m}$, $D_{50} = 43.69 \mu\text{m}$, and $D_{90} = 105.4 \mu\text{m}$) becomes significantly wider (Fig. 3.6). At the applied rotational speed of 200 rpm, the centrifugal effect of the ball milling causes the reinforcement particles to disperse uniformly across the powder mixture with minimum changes in the particle morphology. In addition, the collisions between the grinding balls (characterized by high kinetic energies) and the powder particles cause the breakup of agglomerated particles. (Our intention was to mill the powders gently to maintain their relative spherical morphology, which led to better flow properties during SLM).

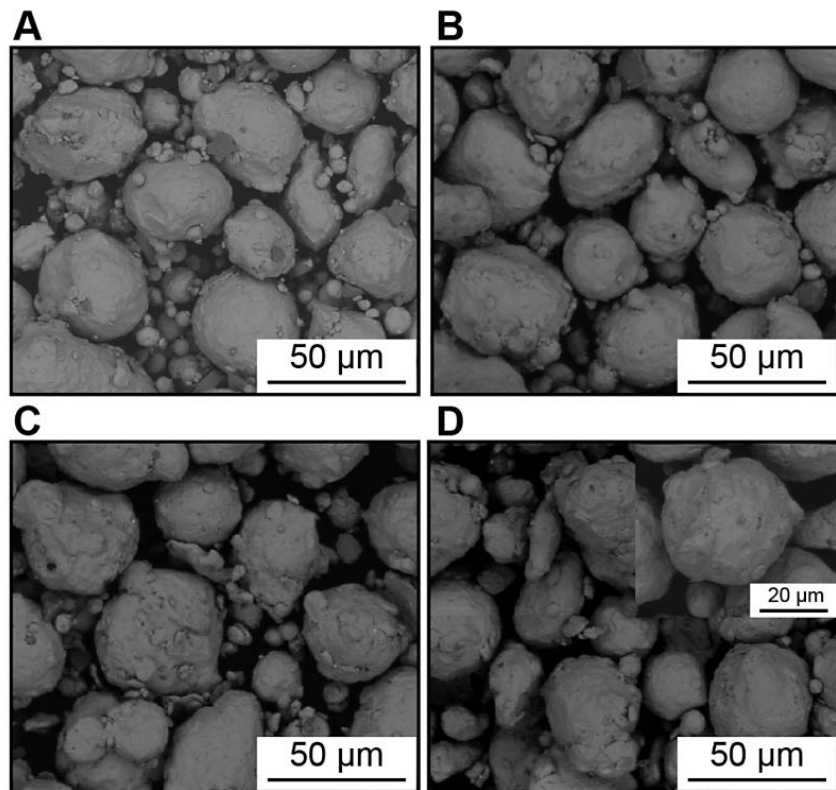


Figure 3.4: SEM images showing characteristic microstructures of milled powders after (a) 2, (b) 4, (c) 6, and (d) 8 h of milling. The inset in the upper right corner of Fig. 3.4(d) describes the particle morphology after 8 h of milling.

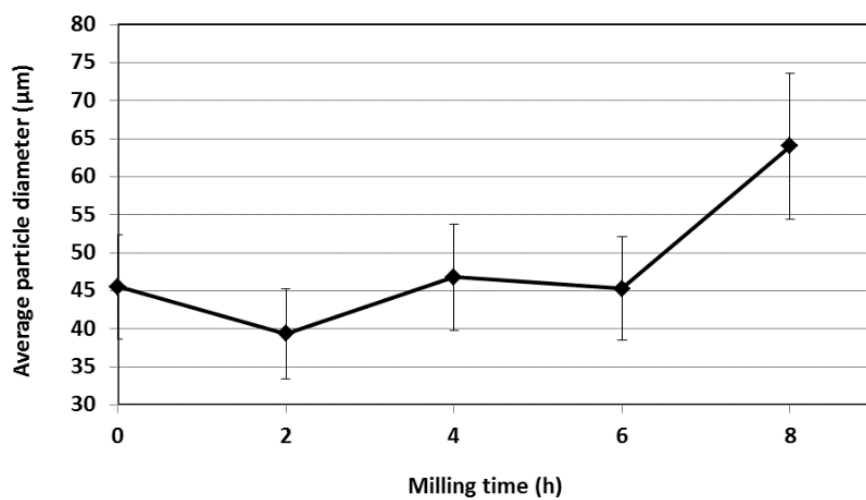


Figure 3.5: Average particle diameter plotted as function of ball-milling time.

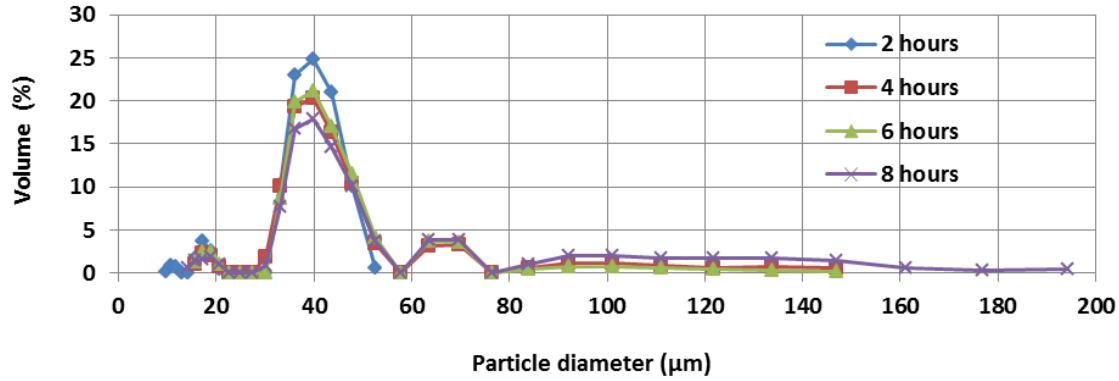


Figure 3.6: Effect of milling time on the particle size distribution for milled powders.

3.3.2. Characterization of SLM-Processed Nanocomposites: Influence of Nanoscale Reinforcement Content

3.3.2.1. XRD Analysis

Figure 3.7 shows typical XRD patterns of the SLM-processed pure 316L and nanocomposites containing reinforcements in different concentrations by volume. Strong diffraction peaks corresponding to γ -Fe were identified in the 316L sample. Furthermore, diffraction peaks related to the TiB_2 -containing phase were observed in the case of the nanocomposites; this was true for all the reinforcement concentrations. This confirmed that TiB_2 -reinforced 316L-based nanocomposites with different volume fractions of reinforcements were successfully produced by the SLM process. Further, the high cooling rate associated with the SLM process induced the appearance of the α -Fe phase. Diffraction peaks corresponding to the TiB phase were also detected in the samples, suggesting that the dissolution of TiB_2 had occurred during the SLM process. There were no significant differences between the different XRD profiles; the only difference was that the intensities of the peaks related to the reinforcements increased with the increase in the reinforcement content.

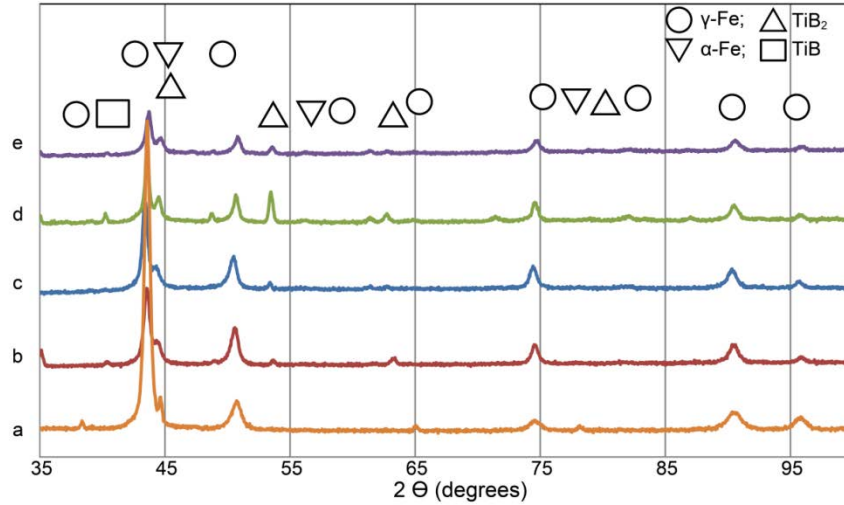


Figure 3.7: XRD spectra of SLM-processed samples of (a) pure 316L and nanocomposites with different TiB_2 reinforcement volume contents: (b) 2.5%, (c) 5%, (d) 10%, and (e) 15%.

3.3.2.2. SEM Microstructural Characterization

Figure 3.8(a) shows an SEM microstructural image of unreinforced 316L while Figs. 3.8(b), (c), (d), and (e) show the effects of the addition of TiB_2 on the microstructures of the SLM-processed samples. The unreinforced 316L sample contained equiaxed grains with an average size of around $2\ \mu\text{m}$. However, the average grain sizes of the SLM-processed unreinforced 316L and nanocomposite samples were smaller than those of the corresponding previously produced cast samples, owing to the cooling rate during the SLM process being much higher than that during the casting process. More interestingly, the nanocomposite samples contained even smaller grains; this was particularly the case for reinforcement contents of 5–15 vol.%. This was attributable to the addition of TiB_2 . The added TiB_2 nanoparticles acted as nucleation sites to assist the heterogeneous nucleation process, given the high wettability between 316L and TiB_2 [143], leading to further grain refinement. Therefore, the refinement of the 316L phase was achieved by two different refinement processes: rapid solidification and the addition of

reinforcements. A similar phenomenon was reported by Hao et al. [131] during the SLM processing of a composite of 316L and hydroxyapatite. Further, in the nanocomposite samples, novel ring-shaped structures were distributed uniformly; in these structures, a few TiB_2 nanoparticles were found to be present along the grain boundaries of the 316L matrix in a highly homogenous manner. This was probably because the TiB_2 nanoparticles bonded with each other. The degree of bonding increased with the increase in the content (vol.%) of the TiB_2 reinforcements.

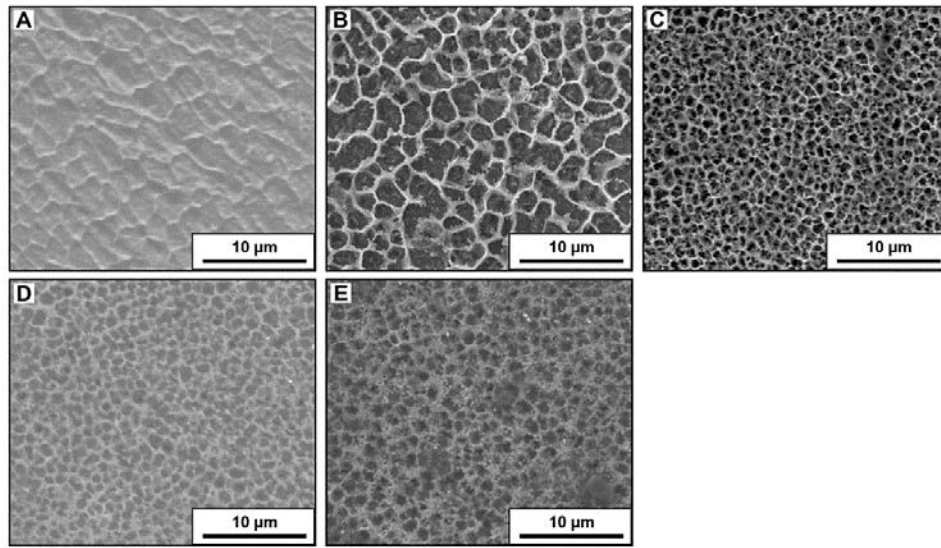


Figure 3.8: SEM images showing characteristics of etched microstructures of SLM-processed samples of (a) pure 316L and TiB_2 /316L nanocomposites with different TiB_2 reinforcement volume contents: (b) 2.5%, (c) 5%, (d) 10%, and (e) 15%.

High-magnification SEM images, shown in Fig. 3.9(a), confirmed that the nanoparticles bonded with each other coherently, resulting in the formation of continuous, well-dispersed, and refined ring-like structures with a mean thickness of 300 nm and an average internal diameter of 1.2 μm . The combined effects of the strong convection caused by rapid heating by the laser beam and the repulsive forces contributed to the formation of these homogeneously dispersed, ring-like

structures of TiB_2 reinforcements in the solidified matrix [21]. Thus, the starting concentration of the TiB_2 nanoparticles played a key role in determining the microstructural development of TiB_2 during the SLM process. The distribution density of the TiB_2 nanoparticles within the matrix increased, while their dispersion state remained uniform (Fig. 3.9(b)), with increases in the initial TiB_2 content. As the TiB_2 content was increased to 10 vol.%, the particles of the TiB_2 reinforcing phase remained nanoscale in size; however, the average thickness decreased to 170 nm and the morphology underwent further refinement (Fig. 3.9(c)). Further, even at higher reinforcement contents, regular ring-like structures of the TiB_2 reinforcements were observed. However, the average thickness of the ring-like structures increased significantly, to 490 nm, owing to the high concentration of the reinforcements (Fig. 3.9(d)). The TiB_2 reinforcing phase was tightly clustered and developed into a network, exhibiting a highly dense distribution throughout the matrix. It was confirmed that, of all the specimens subjected to SLM, that with 10 vol.% TiB_2 reinforcements exhibited the finest nanostructure.

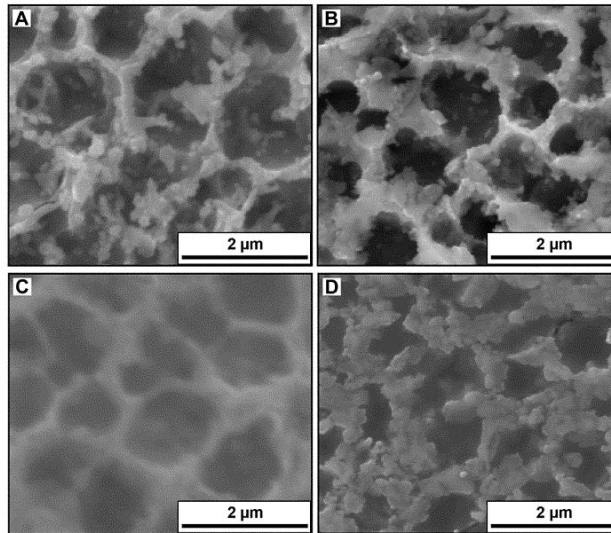


Figure 3.9: High-magnification SEM images showing characteristics of etched microstructures of TiB_2 /316L nanocomposites with different TiB_2 reinforcement contents: (a) 2.5%, (b) 5%, (c) 10%, and (d) 15%. The dispersion states of the reinforcements can be seen in the images.

The etched cross-section of the pure 316L SLM sample consisted of metallurgically bonded layers, which had a homogeneous microstructure and did not contain a significant number of interlayer pores (Fig. 3.10(a)). Further, the microstructure contained elongated grains (i.e., those with a dendritic structure), which were roughly parallel to the building orientation (see the arrow in Fig. 3.10(a)), and a region of fine, equiaxed grains with an average diameter of 1.5 μm , which were the result of rapid solidification. Conventional dendritic solidification features were not formed after the SLM process. Instead, a directional cellular microstructure, attributable to the insufficient growth of the secondary dendrite arms, was formed [144]. If there is a chemical concentration or temperature gradient in the molten pool, it may lead to the generation of a surface tension gradient and attendant Marangoni convection, making the solidification process a nonsteady-state one. Meanwhile, the rapid solidification process was kinetically limited by the crystal growth, which normally occurs in the direction of the maximum heat flow. These factors resulted in a variety of crystal orientations with localized regularity. However, after the addition of 15 vol.% TiB_2 , the cross-section showed a heterogeneous layer-wise microstructure, with continuous and refined ring-like structures also being observed (Fig. 3.10(b)).

The layer-wise microstructure, which corresponded to the cross-sections of the melted scan tracks (i.e., circular arc-shaped boundaries) was observed clearly, because alternating (x-y) melt scans were performed, as shown in Fig. 3.10(c)). The width of the melt pool was observed to vary from around 100 to 150 μm , while the average layer thickness was around 50 μm . A large number of balls, which are metallurgical defects typically associated with SLM, were formed owing to the "balling" effect (i.e., the instability of the melt pool due to thermocapillary phenomena) on the surface (see the arrows), resulting in an apparent decrease in the densification. The average relative density of the nanocomposite with 15 vol.% TiB_2 , obtained by

Archimedes' principle, was around 90.03% of that of the bulk, in contrast to that of pure 316L, which is around 97.5% of that of the bulk (the density of bulk 316L stainless steel is 7.99 g/mm^3 [114]). After the addition of 15 vol.% TiB_2 , the nanocomposite specimen was also susceptible to cracks resulting from increased residual stresses, which consisted of thermal and contraction stresses [145, 146].

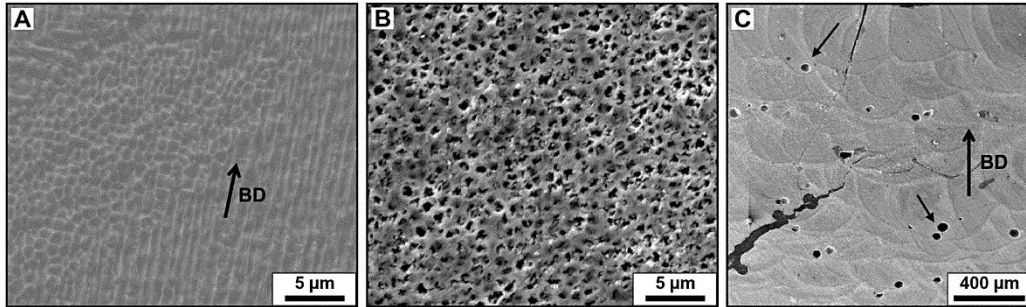


Figure 3.10: SEM images showing the characteristics of the cross-sections of the SLM-processed samples of (a) pure 316L and (b) the 15 vol.% TiB_2 /316L nanocomposite, (c) low-magnification image of the 15 vol.% TiB_2 /316L nanocomposite showing the overlapping of the melt pool and the layer-wise microstructural features along the building direction (BD); pores can be seen clearly in the image.

3.3.2.3. TEM Characterization

Figure 3.11 shows TEM images of the SLM-processed 15 vol.% TiB_2 /316L nanocomposite as well as the corresponding selected area diffraction (SAD) pattern. The TEM image confirmed the presence of submicron-sized 316L grains and the retained nanoscale TiB_2 particles. The grain size of the composite was around $0.5\text{--}1 \text{ }\mu\text{m}$ and in good agreement with the size determined from SEM observations. Distinct nanoscale TiB_2 particles, with a particle size of around 60 nm , were observed in the grain boundaries of the 316L matrix; these were formed because of the partial melting of the individual milled TiB_2 particles. The image also shows the 316L matrix

grain boundary with a metal–ceramic interface, where the 316L matrix has wetted the TiB_2 particles. Further, small spherical precipitates can be seen in the TiB_2 side of the interface (see the arrow in Fig. 3.11(a)). It is generally believed that the presence of a very thin reaction layer at the particle–matrix interface can improve the degree of interfacial bonding in metal-matrix composites. However, it was not possible to capture an image of the interfacial reaction zone between the TiB_2 nanoparticles and the 316L matrix. The fact that the 316L matrix has a high Ni content and a low C content improved the wettability [147]. Furthermore, there was no evidence of any amorphous regions anywhere within the sample. To further confirm this, we tilted the sample at those regions that we believed might be amorphous. However, the tilting of the sample resulted in changes in the contrast, suggesting crystallinity. The sample exhibited a large number of dislocations (Fig. 3.11(b)), as a result of the high solidification rate and because of the differences in the coefficients of thermal expansion of the matrix and the TiB_2 reinforcements. The dislocations arranged themselves into a low-angle configuration, and the degree of mismatch increased across the boundary (diffraction contrast between the adjacent subgrains).

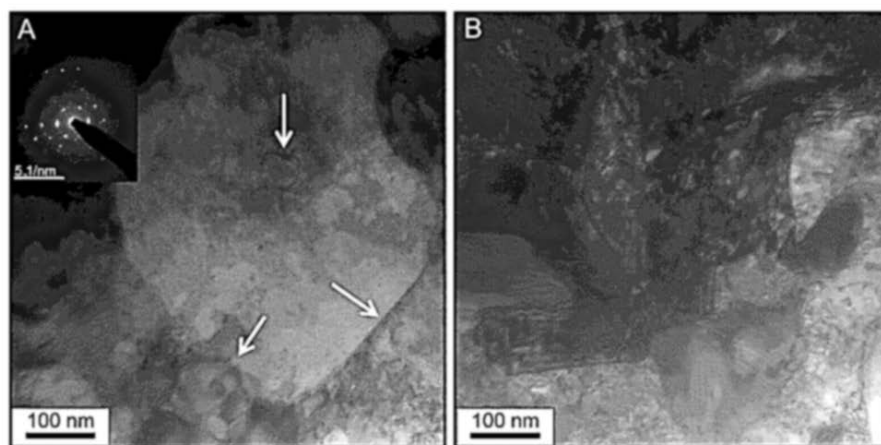


Figure 3.11: (a, b) TEM images of 15 vol.% TiB_2 /316L nanocomposite obtained in two different regions and showing spherical precipitates at the interface as well as an increase in the dislocation density of the 316L austenitic matrix.

3.3.2.4. EBSD Analysis

Figures 3.12a and 3.12b show the EBSD orientation maps corresponding to both the top and the front views of the 15 vol.% TiB₂/316L nanocomposite. The color-coded inverse pole figure is also shown. Here, the points on the sample with the [111] axis parallel to the surface normal are blue, those with the [101] axis parallel are green, and those with the [001] axis parallel are red; those with intermediate orientations are given intermediate colors (see legend in the corner of Fig. 3.12(a)). It can clearly be seen that the grains were oriented randomly and not in a preferred direction. This is evidenced by the large variety of colors that are visible. The top-view image suggests the presence of fine, equiaxed grains, which formed as a result of rapid solidification, as discussed earlier. As expected, the scanning strategy employed (i.e., “alternate-hatch” scanning) affected the directionality of the solidification process. Therefore, the front-view image suggested that the structure exhibited a bimodal grain size distribution; the region with columnar grains/epitaxial growth that formed during the solidification of the previous layer extended towards the building direction of heat conduction, as the laser scan had the same orientation. Rotating the scanning direction through 90° usually breaks up the defined columnar structure [148]. The direction of the heat flow dictates the texture evolution and, given the high total energy input and the corresponding relatively large melt pool and low thermal gradient, the variations that occur are the local process-related values. It was also noticed that the presence of non-molten particles/pores and TiB₂ nanoparticles resulted in the cessation of epitaxial growth.

Based on the misorientation angles (where the misorientation angle is the angle between the direction in which the laser was moved and the direction of columnar grain growth), three types of boundaries were identified: those from 2° to 5° (red), those from 5° to 15° (green), and those corresponding to larger angles (>15°) (blue). The low-angle (2–5°) boundaries are generally not

regarded as being grain boundaries but are assumed to be subgrain boundaries formed by dislocation rearrangement. An analysis of the misorientation angles showed that most of the grains were separated by high-angle grain boundaries, as can be seen from the grain boundary misorientation maps (Figs. 3.12(c) and 3.12(d)). This was probably due to the high scanning rate used in this study; a high scanning rate leads to the elongation of the molten pool [149]. However, it can be seen that, at the border of the tracks, small zones confined by low-angle boundaries were present.

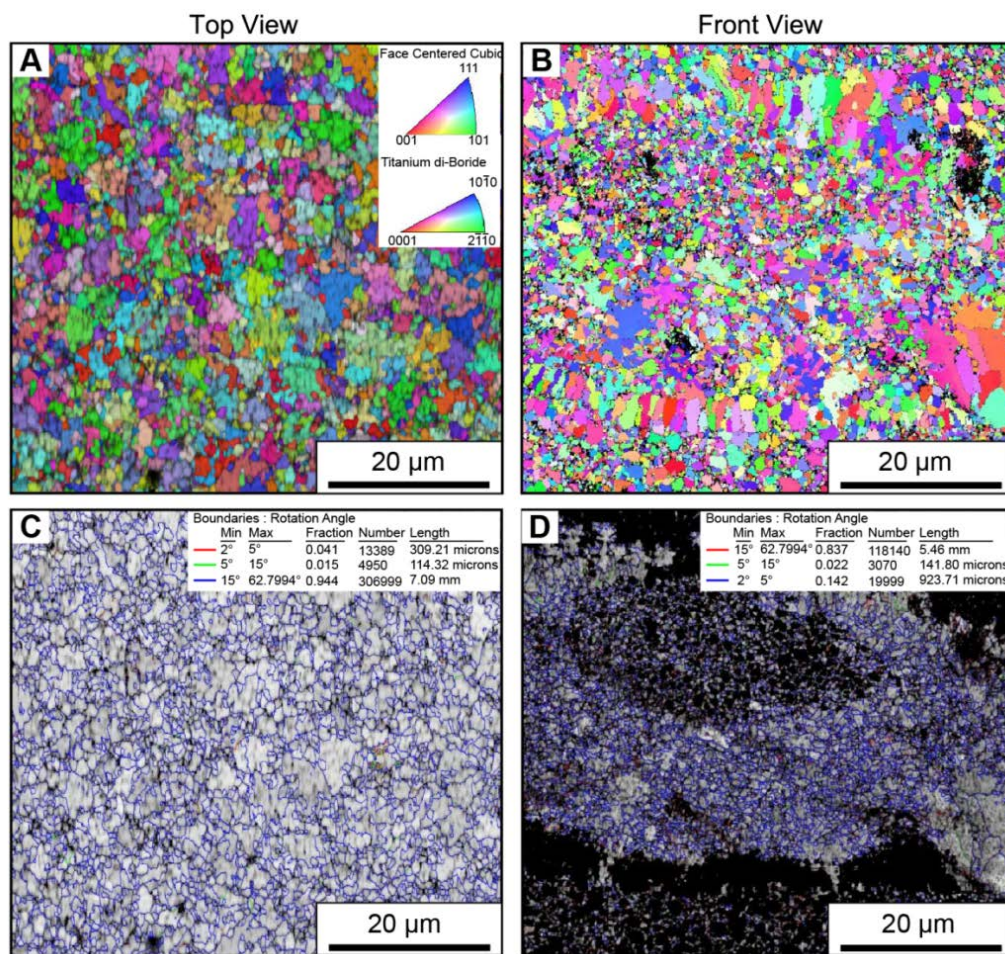


Figure 3.12: (a, b) EBSD orientation maps of the 15 vol.% TiB₂/316L nanocomposite showing both the FCC 316L and the TiB₂ phases; (c, d) grain boundary misorientation maps superimposed on an image quality map of the 316L matrix.

The pole figure and inverse pole figure maps in Fig. 3.13 show that a dominant texture component developed in the direction of grain growth because the preferred growth direction of the cubic crystals during solidification is $\langle 100 \rangle$ [150]. Further, the preferential alignment and intensity along the building direction seemed to be slightly different from those seen in the front-view image of the build. This was expected, as the same area was melted several times because of the narrow scan spacing used. Therefore, the crystallographic orientation probably deviated owing to the repeated solidification and annealing in the narrow scanned builds. However, on the whole, it was shown that the "alternate-hatch" scanning strategy (i.e., changing the scan direction by 90° between consecutive layers) resulted in a decrease in the texture along the build and the scanning directions and that this consequently minimized the anisotropic properties of such structures. This agreed with the observations reported by Boegelein et al. [151].

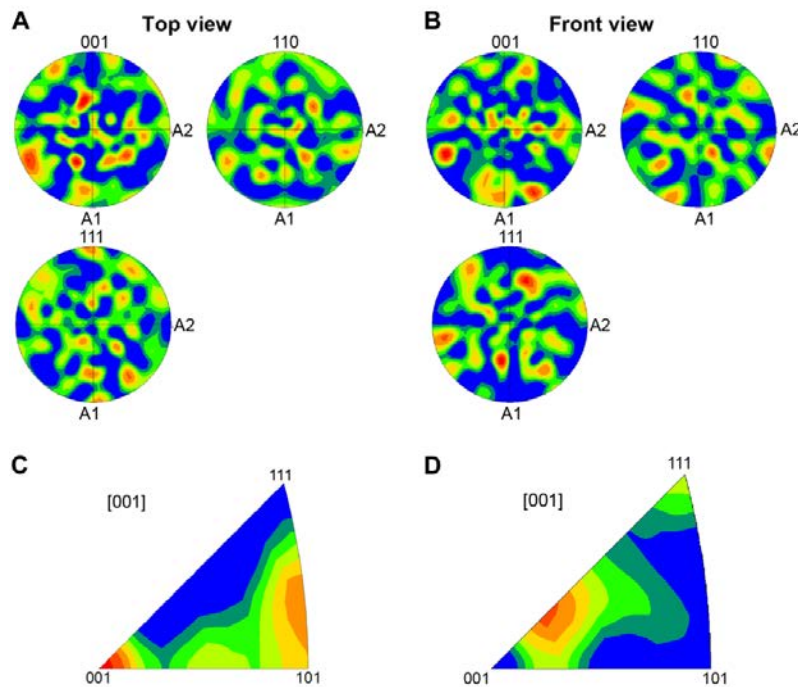


Figure 3.13: (a, b) Pole figures for γ -Fe phase; (c, d) inverse pole figures for γ -Fe phase indicating the random texture of the material.

3.3.2.5. Hardness and Wear Performance

Figure 3.14 shows the average microhardness values of the as-built TiB₂/316L samples. The microhardness of the SLM-processed unreinforced 316L under the same conditions was 210–233 HV_{0.1}. The addition of 2.5 vol.% TiB₂ resulted in a significant increase in the hardness. In addition, by further increasing the reinforcement content, the microhardness increased continuously. The incorporation of 15 vol.% TiB₂ nanoscale reinforcements within the 316L matrix resulted in an approximately three-fold increase in the microhardness to around 611 HV_{0.1}. The observed increase in the hardness can be attributed to the generation of obstacles to dislocation motion because of the increase in the dislocation density and owing to the presence of the TiB₂ nanoparticles in the matrix, as well as to the further grain refinement of the matrix. Nevertheless, with the addition of 15 vol.% TiB₂, the microhardness showed a relatively large fluctuation (i.e., a high standard deviation). The degree of densification was low after the addition of 15 vol.% TiB₂, owing to pore formation (Fig. 3.10(c)). This fact was responsible for the high variation in the hardness.

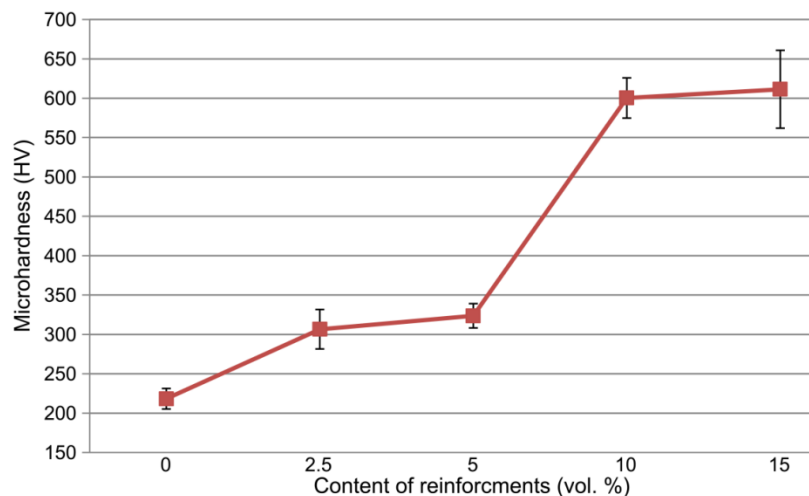


Figure 3.14: Evolution of microhardness of the nanocomposites as a function of the TiB₂ reinforcement volume content.

One of the primary aims of incorporating ceramic reinforcements into the 316L matrix is to improve its wear resistance. Table 3.2 shows the average wear rates of the pure 316L and TiB₂/316L nanocomposite samples. Figure 3.15 shows the friction coefficient of the pure 316L and TiB₂/316L nanocomposite samples. Among the samples, the pure 316L sample exhibited the highest COF and wear rate. On the other hand, the TiB₂ dispersions decreased both the COF and wear rate of all the SLM-processed samples. The worn surfaces showed parallel grooves and irregularly shaped debris, which are representative of classic abrasive wear (Figs. 3.16(a), 3.16(b), and 3.16(c)). The TiB₂ particle content was low. Hence, they split during sliding, resulting in the spalling and delamination of the worn surface.

Table 3.2: Average wear rates for pure 316L and 316L nanocomposite samples

Material	Wear rate (mm³/Nm) × 10⁻⁴
Pure 316L	9.865
316L/2.5 vol.% TiB ₂	6.276
316L/5 vol.% TiB ₂	4.489
316L/10 vol.% TiB ₂	0.744
316L/15 vol.% TiB ₂	0.046

The COFs of the samples with higher TiB₂ contents (10 and 15 vol.%) decreased sharply to 0.595 and 0.441, respectively. Further, the maximum wear rate showed a three-fold decrease, with the minimum value being 0.046×10^{-4} mm³/Nm. No decrease in the wear performance was noticed in the case of the 15 vol.% TiB₂/316L nanocomposite, though its degree of densification was poor. The decrease in the wear rate with the increase in the reinforcement volume fraction was confirmed by examining the worn surfaces. The worn surfaces of the nanocomposite samples with higher TiB₂ contents, which are shown in Figs. 3.16(d) and 3.16(e), were covered with a smooth adherent and a strain-hardened tribolayer, indicating adhesive wear. The extensive

ploughing and cutting of the matrix by the abrasive particles was prevented by the presence of large volumes of TiB_2 particles. It can be seen from the micrographs (Figs. 3.16(d) and 3.16(e)) that the reinforcing particles came on the top surfaces of the composite samples after sliding.

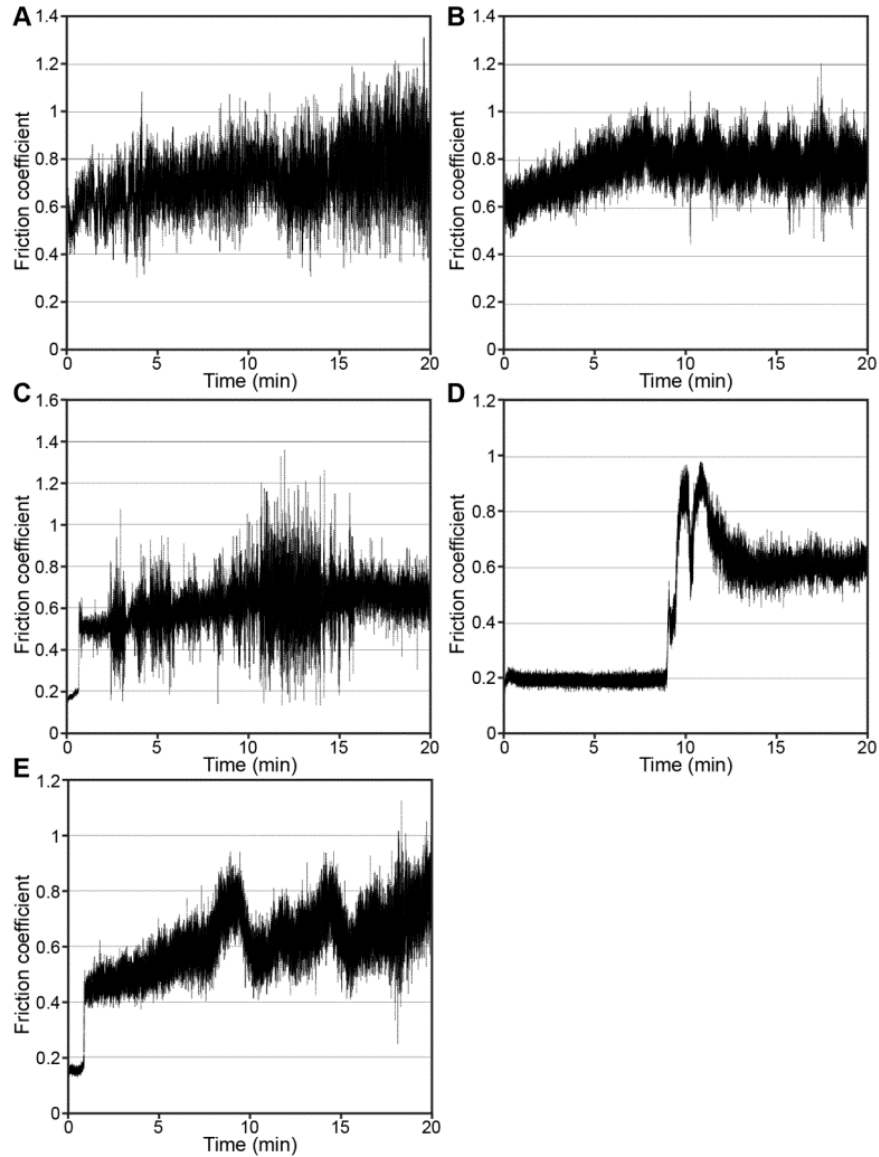


Figure 3.15: Coefficients of friction of SLM-processed (a) pure 316L sample and samples of the TiB_2 /316L nanocomposites with different TiB_2 reinforcement volume contents: (b) 2.5%, (c) 5%, (d) 10%, and (e) 15%.

Neither particle cracking nor separation of the particles from the matrix was observed. In these two cases, the uniformly dispersed nanoscale TiB_2 reinforcements exhibited a high tendency to adhere to each other, thus showing a low degree of fragmentation/breakage during sliding. Thus, the volume fraction of the reinforcing particles had a significant effect on the wear resistance. In addition to the increases in the microhardness (Fig. 3.14), a strain-hardened tribolayer formed on the worn surface, acting as a protective layer to improve the wear resistance. The improvement in the wear resistance may also be attributable to the strong interface bonding of the TiB_2 phase with the 316L matrix, such that the spalling of the particles was prevented during wear.

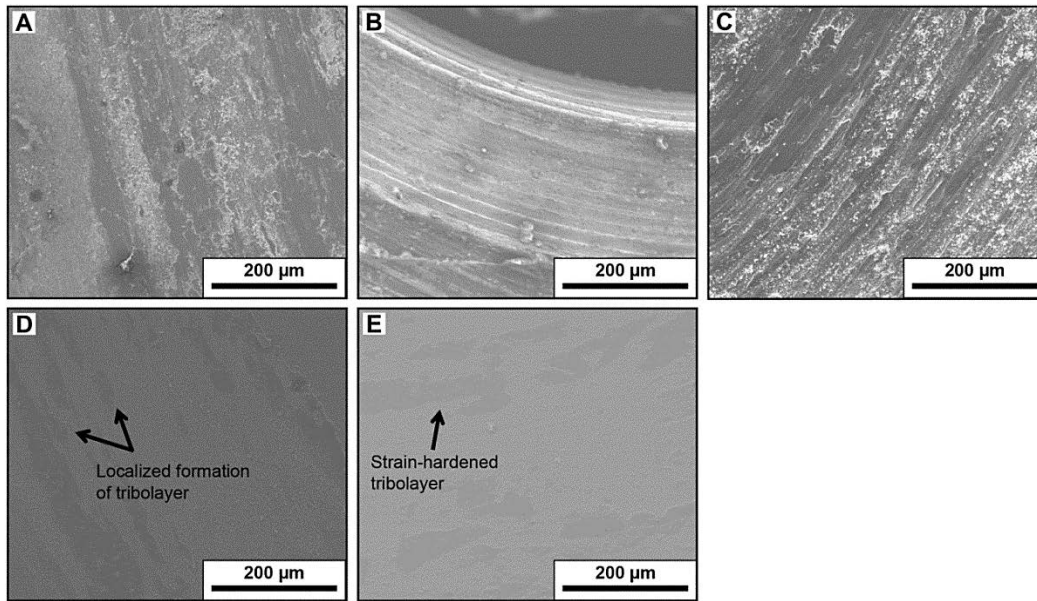


Figure 3.16: SEM images showing morphologies of worn surfaces of samples of (a) pure 316L and TiB_2 /316L nanocomposites with different TiB_2 reinforcement volume contents: (b) 2.5%, (c) 5%, (d) 10%, and (e) 15%.

3.3.2.6. Microcompression Testing

Figure 3.17 shows the compressive stress-strain curves for the compressed pillars of the TiB_2 /316L nanocomposites. For comparison purposes, pure 316L stainless steel was also tested.

For all the conditions, the stress initially increased linearly with the strain until the appearance of a small strain burst, which is regarded as being the first yield strength, since it indicates the start of detectable plasticity. The unreinforced 316L exhibited high ductility, which was evidenced by its large plasticity. With the addition of only 2.5 vol.% TiB₂, the yield strength increased by a factor of approximately two compared to that of the unreinforced base material. The yield strength and modulus of elasticity increased with the TiB₂ content (coinciding with the hardness increase). It was also noticed that although the 15 vol.% TiB₂/316L nanocomposite sample exhibited some porosity, its mechanical properties had not deteriorated; instead, it exhibited increases in both hardness and yield strength while maintaining its ductility. Nahme et al. [152] had reported a lower compressive yield strength for a TiB₂/316L composite fabricated by conventional powder metallurgy.

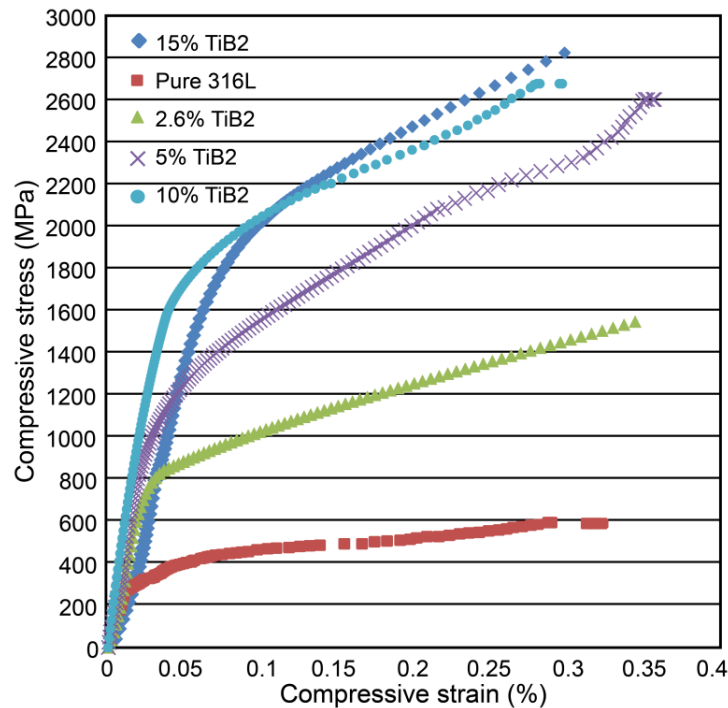


Figure 3.17: Compressive stress-strain curves of pillars of the TiB₂/316L nanocomposites.

The higher yield stress of all the SLM-processed composite samples can be attributed to the decrease in the grain size resulting from the high cooling rate during the SLM process and to the reinforcement with the TiB_2 particles. The reinforcing TiB_2 nanoparticles constrained the crystalline growth of the 316L matrix, thereby further refining the eventually solidified nanocomposites, as can be seen in the SEM images. Grain refinement significantly contributes to the strength of alloys owing to the Hall-Petch' strengthening effect. Finally, the formation of novel ring-like structures, which were observed by SEM, also improved the yield strength through grain boundary strengthening, while allowing the ductility to remain unchanged. The interconnections between the neighboring TiB_2 nanoparticles improved while the grain boundaries of the 316L matrix were strengthened. The load was effectively transferred from the 316L matrix to the stronger TiB_2 particles via the interface, resulting in an increase in strength. The prevention of the dislocation motion by the TiB_2 nanoparticles also played a significant role in increasing the yield strength.

3.3.2.7. Strengthening Mechanisms

The solidification rate corresponding to high-energy laser melting can reach values as high as 10^6 K/s [153]. This significantly restricted the effective crystal development of the TiB_2 nuclei, as there was insufficient time for grain growth to occur. This process allowed the favorable nanoscale structure of the TiB_2 reinforcing phase to be retained (Fig. 3.8). The existence of the Marangoni effect within the pool induced a liquid capillary force [53], which acted on the precipitated TiB_2 and accelerated its relocation in the melt, so as to regulate the distribution of the nanoscale TiB_2 reinforcements within the solidified matrix (Fig. 3.9). For an even higher TiB_2 content, a very high concentration gradient and solute diffusivity were established in the melt. As the TiB_2 crystals grew, there was a continuous accumulation of the solute on the

interface moving into the liquid. Gu et al. [154] reported a significant loss of the nanostructure of TiC/Ti bulk nanocomposites after SLM, suggesting that the potential effect of the rapid solidification resulting from laser processing on Ti grain refinement was weakened. However, this was not observed in the present study. One reason could be that the amounts of the TiB_2 reinforcements deposited were smaller than those in the study by Gu and coworkers [154].

A TEM image of a compressed pillar of the 15 vol.% TiB_2 /316L nanocomposite is shown in Fig. 3.18. Fine grains of approximately 100 nm in size can be seen. We also observed TiB_2 nanoparticles approximately 20–50 nm in size; these served as strong obstacles to the dislocation motion. In addition, void regions about 100 nm in size (the white regions in the images) were also observed. The diffraction patterns shown were recorded from general regions and include diffractions from several grains.

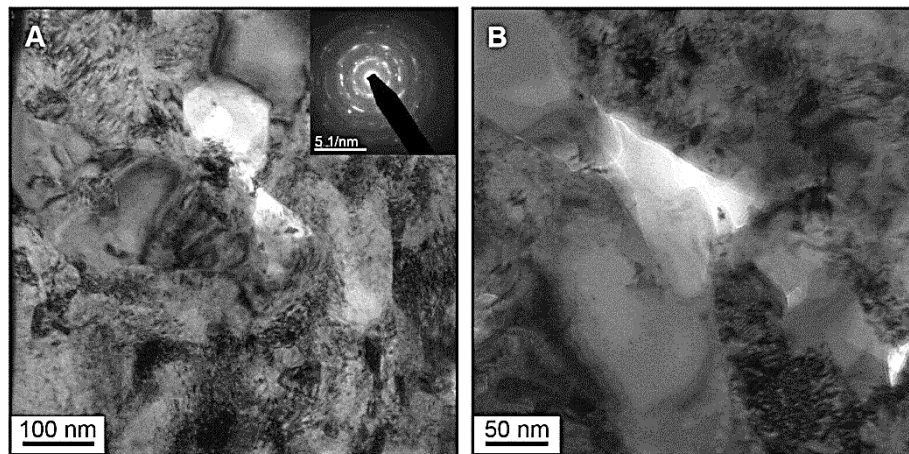


Figure 3.18: TEM image of compressed pillar of 15 vol.% TiB_2 /316L nanocomposite showing the dislocation arrangement and the nanograins: (a) low- and (b) high-magnification images.

During compression, the flow stress increased owing to the transfer of the load from the matrix to the reinforcing TiB_2 particles. As the external stress led to dislocations proliferating, the

spacing between them decreased. Hence, a higher stress was required to further deform the samples. In the nanocomposite system that was the subject of our investigation, 316L serves as the ductile phase and contributes to the plasticity, while TiB_2 is the hard phase and contributes to the strength. Further deformation would cause the TiB_2 particles to fracture and the particle/matrix interface to tear, owing to the strength being low, which would lead to the initiation and propagation of cracks until the final failure.

The major strengthening mechanisms of the 316L stainless steel samples reinforced with TiB_2 and fabricated by SLM were identified to be dispersoid (Orowan) strengthening, grain-boundary strengthening, and grain refinement induced by the rapid solidification process and the formation of heterogeneous nucleation sites by the TiB_2 particles. The individual contributions probably varied, depending on the final microstructure. The incorporation of the nanoscale TiB_2 reinforcing particles constrained the crystalline growth of the 316L matrix, thereby refining the crystal size of the solidified nanocomposites (i.e., grain refinement strengthening). Grain refinement is an efficient means of simultaneously improving both the yield strength and the ductility [155]. Another factor was grain-boundary strengthening, in which the interconnections between the neighboring TiB_2 nanoparticles improved while the grain boundaries of the 316L matrix strengthened. During mechanical loading, the strong bonding coherence between the reinforcement/matrix boundaries effectively improved load transfer because of the shear stresses at the interface, hence increasing the yield strength of the TiB_2 /316L nanocomposites. In addition, the uniform distribution of the ring-like structures of the reinforcements along the grain boundaries, attributable to the creation of Orowan loops, effectively constrained the crack propagation during plastic deformation, thus enhancing the ductility of the nanocomposites.

As the compression stress–compression strain curves clearly show, a novel feature of the

processed nanocomposites was that they retained most of their ductility even as their yield strength increased significantly. Although the high ductility of the nanocomposites can be attributed to the compression testing mode—in this mode, most of the pores close during deformation—other factors also contributed to the ductility [156]. First, the ductile nature of the 316L stainless steel matrix and the excellent interfacial bonding enhanced the overall ductility of the nanocomposites. Second, the uniform distribution of the ring-like reinforcement structures along the grain boundaries effectively improved the plasticity by delaying the propagation of cracks at the interfaces. The concentration of high stresses resulting from the formation of TiB_2 particles at the grain boundaries also helped to increase the degree of strain hardening [157]. Third, the presence of a large fraction of high-angle grain boundaries as well as the bimodal grain size distributions observed during the EBSD analyses also contributed to the ductility [158] (the ductility of metallic materials increases with an increase in the misorientation angle). The large grains with a bimodal size distribution effectively blocked and stored dislocations and hence improved the strain hardening rate [159, 160]. The high-angle grain boundaries were more effective in blocking the slip dislocations and forced the dislocations to tangle and accumulate near the boundaries. Indeed, the existence of the TiB_2 nanoparticles in the 316L matrix caused the dislocations to accumulate in their neighborhood, thus increasing the dislocation density near the interface.

3.3.3. Effect of HIP Post-Treatment

3.3.3.1. Densification Mechanism

To improve the processing of $\text{TiB}_2/316\text{L}$, it is important to understand the densification mechanisms. The mechanism for densification by laser-powder-bed AM (e.g. SLM) is a result of the almost complete melting and re-solidification of the material. The energy supplied by a

scanning laser beam is absorbed by the powder particles through both the bulk-coupling and powder-coupling mechanisms [161]. Initially, these mechanisms are activated when the laser energy is absorbed by a narrow layer of individual particles, producing a significant temperature increase, which depends on the bulk powder properties. The heat generated by the laser beam is mainly transferred towards the particle center until a local steady-state temperature is attained for the laser-irradiated area. Then, further energy absorption melts the powder and produces a molten pool.

In the ball-milled TiB_2 /316L nanocomposite, the TiB_2 nanoparticles are uniformly dispersed throughout the 316L matrix. During the initial stage of laser melting, the TiB_2 nanoparticles in the area being lasered are not entirely exposed to the laser irradiation, and therefore the laser melting is not uniform. Gu et al. [162] suggested that the dissolution of the ceramic phase with a high melting point followed the melting of the base metal. In contrast to the Gu et al. study, we believe that the ceramic TiB_2 particles are not completely melted, but instead are partially melted. When the TiB_2 nanoparticles were sufficiently wetted by the surrounding 316L liquid, they precipitated inside the laser-irradiated 316L pool, forming a desired nanostructure [162]. On the other hand, for the directly mixed composite powder, the TiB_2 particles were distributed among the 316L powder particles. Therefore, both the 316L and TiB_2 powders were simultaneously exposed directly to the laser beam. The effect of the evaporative recoil on the melt is significant in those areas exposed to the laser beam, and the resultant dynamic recoil pressure tends to exert an effective disturbance on the SLM behavior of the TiB_2 phase [163].

Figures 3.19a and 3.19b show the pore and crack formations for the 316L composite reinforced with 15 vol.% TiB_2 fabricated from the directly mixed and ball-milled powders, respectively. The deep grooves and pores were more distinct for the directly mixed powders, (upper-right image of

Fig. 3.19a), although the cracks appeared larger and more severe for the ball-milled sample. In general, cracks nucleate and propagate in the scanning overlap zone between two adjacent deposited layers. As a result, long (1–2 mm) and short (100–200 μm) cracks with different degrees of overlapping were formed. The short cracks can mainly be attributed to the boundary liquation cracking, as observed by Zhong et al. [164]. Zhao et al. [165] suggested that it was difficult to eliminate the short cracks by merely adjusting the laser processing parameters. Because the particle structure and size distribution of the ball-milled powders were more uniform than directly mixed powders, the laser beam was able to interact more uniformly with the milled powder. This resulted in a steadier melting process and a more uniform solidification process for the sample processed using milled powders.

The cracks evident in Fig. 3.19 can be understood by examining the wettability of the molten metal, which controls the densification during the SLM process. The wetting behavior and hence densification are also dependent on the applied laser energy input. The wetting of a solid by a liquid is related to the surface tensions of the solid-liquid (γ_{sl}), solid-vapor (γ_{sv}), and liquid-vapor (γ_{lv}) interfaces. Wettability of a solid can be defined by the contact angle θ , as follows [7]:

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (3.1)$$

From Eq. 3.1, we can see that the applied liquid would completely wet the solid surface as $\cos \theta \rightarrow 1$, thus favoring densification. This means lowering the contact angle θ , which is also a function of the operating temperature [166], enhancing the liquid–solid wettability, thus favoring a sufficient densification level. When $\gamma_{sl} > \gamma_{sv}$, then $\theta > 90^\circ$, and the liquid becomes spheroidized instead of wetting the solid substrate. Consequently, defects occur (porosity,

balling, cracks) when non-optimized SLM processing conditions are used. The observed phenomenon in turn affects the densification process for the SLM-produced composite powder.

Cracks are also caused by differential shrinkage, which is also a function of wetting and the optimization of the laser energy. The shrinkage rate $d(\Delta L/L_o)/dt$ during the solidification can be estimated as follows [167]:

$$\frac{d(\frac{\Delta L}{L_o})}{dt} = \frac{\Delta P W}{2R\mu} \quad (3.2)$$

where ΔP is the capillary pressure, R the grain radius, W is the liquid thickness, and μ is the liquid viscosity.

The dynamic viscosity (μ) of the melt inside the pool can be estimated using the following formula [168]:

$$\mu = \frac{16}{15} \left(\sqrt{\frac{m}{kT}} \gamma \right) \quad (3.3)$$

where m is the atomic mass, k is the Boltzmann constant, T is the temperature, and γ is the liquid surface tension. When the TiB_2 content in the molten 316L matrix increases, the viscosity and surface tension of the composite melt also increases considerably, which in turn decreases the wetting characteristics (Eq. 3.1). Therefore, when insufficient laser energy input is applied, the operating (workable) temperature is low, which in turn increases the melt viscosity, according to Eq. (3.3). The SLM process induces a sharp thermal gradient across the surface between the center and the edge of the melt pool, leading to a surface tension gradient and the Marangoni convection process [169]. The Marangoni flow, combined with low wettability, causes the melt to spheroidize instead of spreading outwards over the underlying surface [70]. At the same time,

the shrinkage rate increases during solidification, which produces thermal stress in the solidified samples. Therefore, cracking in SLM samples processed using either mixed or milled powder arises from differential shrinkage and limited wettability, which is related mainly to the non-optimized processing conditions.

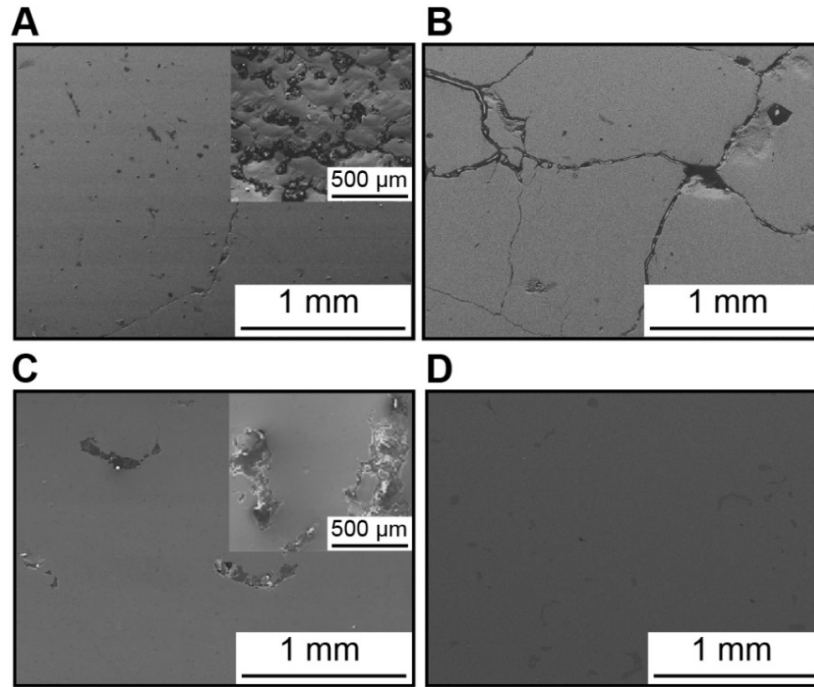


Figure 3.19: Low-magnification SEM images showing un-etched characteristic morphologies of SLM-processed 316L composites reinforced with 15 vol.% TiB_2 (a) before HIP treatment and using directly mixed powder (b) before HIP treatment and using ball-milled powder (c) HIP-1 and (d) HIP-2 treatment cycles.

Even when the nanocomposites contain cracks, subsequent HIP treatment can alleviate those cracks. Figures 3.19c–d show the unetched cross-sectional microstructures of the 316L nanocomposite reinforced with 15 vol.% of TiB_2 (using ball-milled feedstock powder) after HIP treatment. After the first HIP cycle (HIP–1), several original small pores remain visible, while

additional larger pores appear (Fig. 3.19c). Tamas-Williams et al. [170] suggested that pore formation during heat treatment can be correlated with the pore locations in the original structure. Since Ar gas cannot escape from the material bulk during HIP, the resulting high internal gas pressure constitutes a driving force for pore regrowth. However, the internal porosity and the number of interconnected pores were substantially reduced after the HIP-2 cycle with the longer hold time, even though there were still some very fine open pores (Fig. 3.19d).

Both the applied high pressure at elevated temperatures and longer hold times during the HIP-2 treatment effectively compressed the material, increasing its density. The relative density (with an initial value of 91.5%) of the nanocomposite increased to around 97.8% after HIP-1 and then to around 99.5% during HIP-2. Longer HIP treatment times are known to increase the diffusion rate and binding strength between particles, leading to almost complete densification (Fig. 3.19d). Therefore, the data presented in this work indicates that HIP treatment can effectively reduce the porosity of SLM-fabricated components under non-optimized processing conditions.

In addition to the improvement in the densification after subjecting the nanocomposites to HIP treatment, the microstructures changed significantly. Figures 3.20a and b show the etched cross-sectional microstructures of the nanocomposite after the HIP-1 treatment. For comparison, the etched microstructures for the HIP-2 treated specimen are depicted in Figs. 3.20c and d. Since the HIP treatment was conducted above the recrystallization temperature of the 316L matrix, major changes in the composite microstructure occurred, thus increasing its homogeneity. Although equiaxed grains can still be observed during HIP-1, there was significant grain coarsening (Fig. 3.20b), in comparison with the nanocomposite sample before the application of HIP. It is interesting to note that the pinning effect of the TiB_2 phase does not lead to grain growth inhibition. Dadbakhsh et al. [171] suggested that, at high HIP treatment temperatures, the

diffusion of some elements results in the coexistence between the stable and equilibrium phases, which in turn produces a more homogenized material. However, the fine TiB_2 particles tend to coalesce, such that the ring-like structures are no longer visible after the application of HIP-2 treatment (Fig. 3.20(c)). This results in the coarsening and segregation of the TiB_2 particles, transforming the matrix appearance from a smooth, uniform distribution of fine TiB_2 particles to the one characterized by severely coalesced nanoparticles and segregation. Thus, the microstructural features of the HIP-treated samples evolve with an increase in the HIP holding time, from coarse equiaxed grains to regions containing a segregated TiB_2 phase. This phenomenon originates from the significant plastic deformation at high temperatures and longer holding times during the application of HIP, thus enhancing the recrystallization process and promoting grain growth.

Interestingly, the TiB_2 phase in the SLM-processed nanocomposite after the application of the HIP-2 process, (see the dashed circles in the upper-right corner of Fig. 3.20(d)) exhibits a very similar morphology to the initial TiB_2 particle morphology prior to SLM (Fig. 3.1(b)). We regard this as being direct evidence for only partial melting of the TiB_2 phase during SLM, and evidence of only partial melting even after the application of HIP.

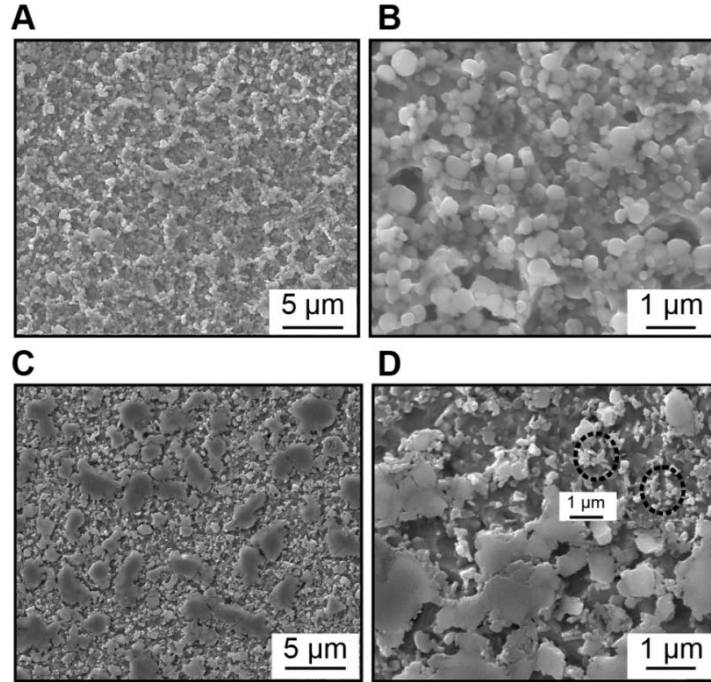


Figure 3.20: SEM images showing characteristic morphologies of etched SLM-processed nanocomposites after (a, b) HIP-1 and (c, d) HIP-2 treatments.

3.3.3.2. Hardness and Wear Behavior

The effects of the powder handling method, reinforcement volume content, and HIP treatment on the hardness of nanocomposites produced by SLM are shown in Fig. 3.21. As discussed in section 3.3.2.5, the Vickers hardness of a TiB_2 /316L nanocomposite is much higher than that of the unreinforced 316L matrix (almost $215 \text{ HV}_{0.1}$) due to the homogeneous incorporation of TiB_2 reinforcing particles. With the addition of only 2.5 vol.% TiB_2 , the composite hardness values increased, with no differences being observed in the hardness of the directly mixed and ball-milled samples. Therefore, we can conclude that the obtained samples did not exhibit any enhanced properties when the corresponding powders were prepared via ball milling with a low reinforcement content. However, when 15 vol.% TiB_2 was added to the 316L matrix, the

subsequent ball milling resulted in higher hardness values, relative to direct mixing, suggesting that the particle refinement of TiB_2 leads to an improvement in the hardness, as theoretically modeled earlier by the Zener equation [172].

Unfortunately, both HIP cycles resulted in a significant drop in the material hardness. Although some increase in the relative density and binding strength was observed (which usually enhances the mechanical properties of a material), the microstructure coarsening caused by the high temperature and annealing effects of the treatment process resulted in a reduction in the hardness. The reduction in the hardness due to the grain coarsening was overcome by extending the hold time in the HIP-2 cycle. Longer treatment times at an elevated temperature and pressure closed most of the voids, and enhanced the diffusion kinetics, to the point where the HIP-2 sample reached nearly full density. Therefore, in the case of $\text{TiB}_2/316\text{L}$ nanocomposites, the porosity reduction certainly contributes to increasing the hardness. The standard deviation of the hardness is larger before the application of HIP and decreases after the HIP, indicating that the microstructure was homogenized.

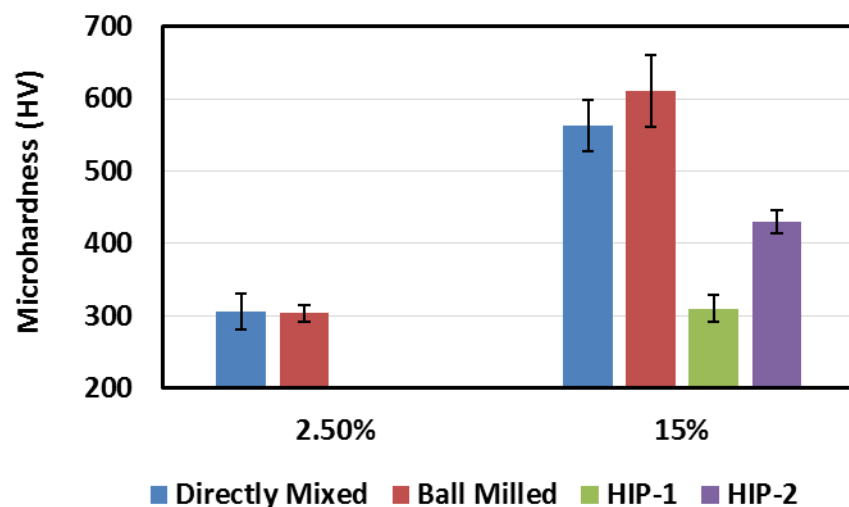


Figure 3.21: Average microhardness of SLM-processed $\text{TiB}_2/316\text{L}$ composites parts.

Figure 3.22 shows the wear rates and coefficients of friction (COF) for the SLM-processed 15 vol.% TiB₂/316L composite before and after HIP treatment. Ball-milled 15 vol.% TiB₂/316L powder, fabricated by SLM, exhibited an average COF of 0.161 and a wear rate of $0.00193 \times 10^{-4} \text{ mm}^3/\text{Nm}$. On the other hand, samples fabricated similarly, but with powders that were directly mixed instead of being ball milled, exhibited slightly higher COF and wear rate values.

To determine why the COF and wear rate values were higher for directly mixed powders than for ball-milled powders, the morphologies and microstructures of the worn surfaces were examined using SEM, as shown in Fig. 3.23. In both cases, the worn surfaces were relatively comparable, and contained large areas of a smooth strain-hardened tribolayer with no local signs of surface plowing or fracturing (Fig. 3.23(a-b)). A morphological analysis of the worn surfaces revealed the presence of shallow grooves, free of any loose abrasive fragments, which further indicated the high wear resistance of the SLM-processed samples (Fig. 3.23(a-b)). Unfortunately, examination of the microstructure and morphology did not reveal the reason for the increase in the COF and wear rate values of the directly mixed powders, relative to the ball-milled powders.

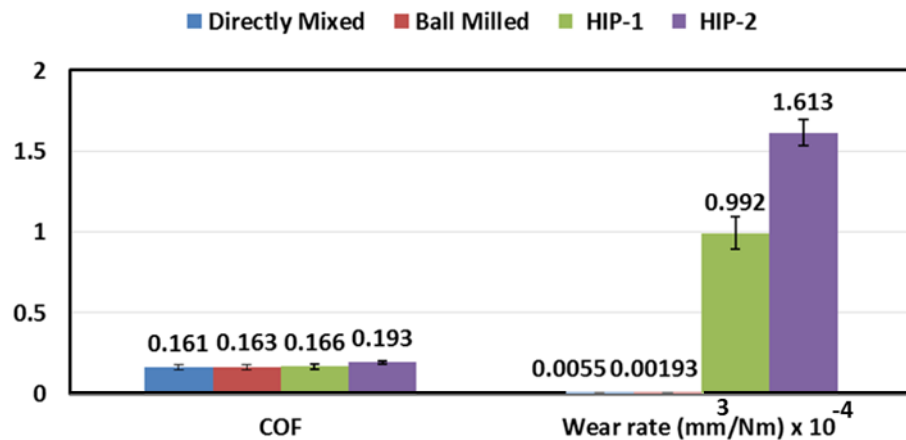


Figure 3.22: Coefficient of friction and wear rate obtained for SLM-processed 15 vol.% TiB₂/316L composites.

We believe that several fundamental mechanisms contributed to the improved composite wear performance of the ball-milled powders fabricated by SLM. First, the density of the SLM samples is one factor that significantly affects their wear resistance, since porosity is deleterious to wear. Second, nanostructured TiB₂ reinforcements improved the hardness (Fig. 3.21), thereby increasing the wear resistance of a composite. The homogeneously dispersed reinforcing TiB₂ nanoparticles within the matrix exhibit low interfacial stress values, so they cannot be easily split during sliding wear testing [173]. These hard TiB₂ particles tend to protrude from the worn surface inside the matrix when subjected to shear stress, causing a dislocation motion that acts as a strengthening mechanism. Hence, the surface layer becomes strain-hardened [174], thus improving the wear resistance of the composite. The coarse TiB₂ particles associated with directly milled powders are easily fragmented during sliding, leading to slightly lower wear resistance (Fig. 3.22). On the other hand, the refined TiB₂ nanoparticles associated with ball-milled powders are not easily fragmented during sliding. They exhibit a strong tendency to adhere to each other and become strain-hardened, which improves the material wear resistance.

After HIP treatment, both the COF and wear rate values of the composite samples sharply increased, owing to the grain coarsening and corresponding coalesced regions of TiB₂ reinforcing particles, although the densities were improved (Fig. 3.19)). After the HIP-1 and HIP-2 cycles, the composite wear rates increased slightly to 0.992×10^{-4} and 1.613×10^{-4} mm³/Nm, respectively. At the HIP-1 condition, the wear surface appears non-homogeneous, comprising regions that contain both the strain-hardened tribolayers and concentrations of coalesced reinforcing nanoparticles. The worn surface was typically rough and loose, consisting of deep, parallel grooves and granular wear debris, suggesting that the specimen experienced severe abrasive wear, which in turn led to a relatively high wear rate. Under the HIP-2 condition,

although some granular wear debris was detected, the worn surface was found to be much more disrupted and consisted of large coalesced TiB_2 nanoparticle concentrations.

This data suggests a probable transition from adhesion (Fig. 3.23a, b) to an abrasion or micro-plowing (Fig. 3.23c, d) wear mechanism, which may explain the observed spalling of a tribolayer and the related increase in the wear rate. Meanwhile, the TiB_2 nanoparticles tend to concentrate into clusters, resulting in microstructural non-homogeneity (Fig. 3.23d). The nanoparticle concentrates are prone to fracturing and/or cracking because of the stress concentration during sliding. The presence of irregularly shaped fragments in the micrographs reveals that localized deformation and delamination of the worn surface have occurred. When the cracks eventually connect to each other, debris is formed and splits away from the worn surface, thus increasing the wear rate.

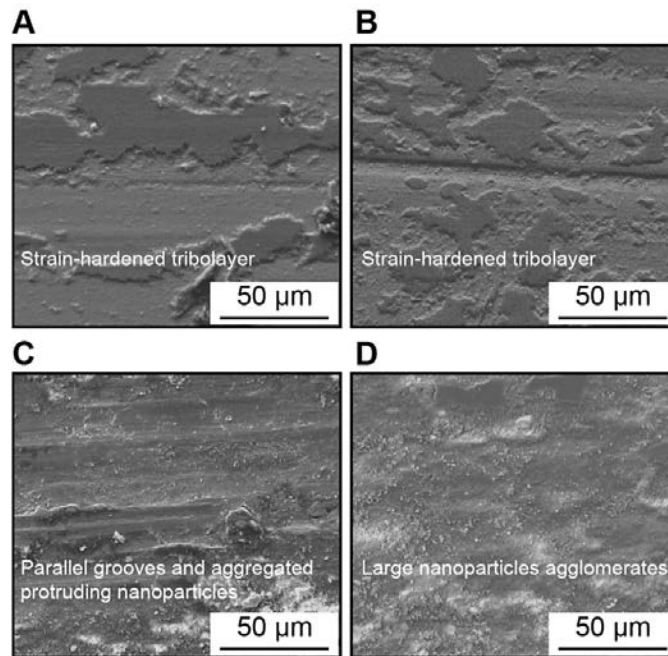


Figure 3.23: SEM images showing morphologies of the worn surfaces of the 316L composite reinforced with 15% TiB_2 (a) before HIP treatment and using directly mixed powder (b) before HIP treatment and using ball-milled powder and (c) after HIP-1 (d) after HIP-2.

3.4. Conclusions

Understanding the relationships between TiB₂/316L composite powder processing, SLM processing, microstructures, and mechanical properties is key to satisfying the demands for new applications. This research investigated the effects of TiB₂/316L powder preparation, SLM processing, and the application of HIP on the microstructural evolution and mechanical properties of microscale and nanoscale composites. Based on the results obtained in this study, we can draw the following conclusions:

1. The average crystallite size of the 316L matrix powder continually decreased with an increase in the ball milling time, due to the generation of dislocations and other lattice defects, reaching a constant value of 11.11 nm after 8 h of milling.
2. The milled powder particles experienced both cold-welding and fracturing during the early milling stages (0–6 h). After 6–8 h of milling, the composite particles were significantly coarsened and characterized by a wider size distribution ($D_{10} = 34.02 \mu\text{m}$, $D_{50} = 43.69 \mu\text{m}$, and $D_{90} = 105.4 \mu\text{m}$), while maintaining roughly spherical shapes.
3. The microstructural and mechanical properties of the SLM-processed TiB₂/316L nanocomposite samples were sensitive to the initial TiB₂ nanoparticle content. In the case of the optimal TiB₂ content, which was found to be 10 vol.%, the homogeneously dispersed TiB₂ reinforcements formed nanoscale structures with an average ring thickness of 170 nm. The addition of the TiB₂ ceramic reinforcements in the SLM-processed samples improved the compressive yield strength, hardness, and wear resistance. Further, the nanocomposite samples exhibited a good combination of compression yield strength and ductility during the microcompression tests. Although the 15 vol.% TiB₂/316L nanocomposite exhibited some

porosity, it also exhibited a remarkably high wear resistance. A wear resistance 10 times higher than that of unreinforced 316L stainless steel and a very low wear rate was achieved.

4. The densification behavior of the composite was a function of the powder preparation method. The deep grooves and pores were more distinct for the directly mixed powders, because the ball milling creates a more uniform distribution of particles. As a result, the laser was able to densify the ball-milled powder more consistently, although the cracks appeared to be larger and were more severe for the ball-milled sample.

5. Although powder preparation techniques (directly mixed vs. ball milled) did not affect the hardness values of the SLM-processed 316L composites with 2.5 vol.% TiB_2 , a 15 vol.% TiB_2 reinforcing particle content led to higher hardness values for those samples formed from the ball-milled powder. Therefore, direct mixing is preferable at low reinforcement concentrations, since the corresponding SLM process would require less time for densification. The ball-milled powders are more suitable at higher reinforcement volumes. The use of longer mixing periods combined with higher fractions of TiB_2 reinforcement might lead to a deeper understanding of the complexity of the system.

6. The HIP post-treatment was found to be effective for eliminating major cracks and pores in SLM-fabricated components under non-optimized conditions. The use of high temperatures and a holding time during the application of HIP led to more severe plastic deformation and the recrystallization of the composite powders. As the HIP holding time increased, the microstructural characteristics evolved such that the equiaxed grains were transformed into agglomerated nanoparticles. As a result, the hardness and wear resistance of the composite decreased.

Chapter 4

Selective Laser Melting of TiC/316L Nanocomposites: Influence of Starting TiC Particle Size and Volume Content

Abstract

Selective laser melting (SLM) was utilized to process TiC/316L nanocomposite parts with different starting TiC particle sizes and volume contents. The influence of the starting TiC particle size and volume content on the constitutional phases, microstructural features, and mechanical properties of the SLM-processed nanocomposite parts was investigated. The densification behavior was controlled by both the starting TiC content and the particle size; the densification level was enhanced with the use of fine starting TiC particles owing to the improvement of the reinforcement–matrix wettability. In general, by increasing the volume content of the TiC, the hardness increased and the coefficient of friction (COF) and wear rate decreased owing to the combined effects of grain refinement and grain-boundary strengthening. However, in contrast to the starting coarse TiC particles, the SLM-part processed with the starting fine TiC particles shows better wear resistance, in particular at a 10–15% TiC content, owing to improved TiC dispersion throughout the matrix and increased density.

4.1. Introduction

Laser-based additive manufacturing (AM), an inspiring manufacturing technology, enables quick fabrication of three-dimensional metallic components in a layer-by-layer manner, according to computer aided design (CAD) data [4, 175, 176]. Normally, the above-mentioned components with complex shapes are not easy to attain through conventional processing methods. Selective laser melting (SLM), a powder-bed-based AM process, can be used to create bulk-form parts from the starting loose metallic powder of the desired components [123, 177]. Parts with a nearly

full density and complex geometries can be fabricated using the SLM process through the selective melting and rapid solidification of the powder layers with a high-energy laser beam [121, 178].

In recent years, there has been an increasing demand among various industries for metal matrix composites (MMCs) owing to their high strength and stiffness and their outstanding wear resistance [179]. MMCs are typically processed by casting or powder metallurgy; however, there are major problems associated with these conventional processing routes. For example, these processes can be complex and time consuming, they require expensive casting molds, and they may result in an undesirable coarse grain structure. The limited particle-matrix interfacial bonding resulting from the low working temperature used during conventional processing may further decrease the mechanical properties of the parts produced [180]. In addition, it is difficult to achieve uniform distribution of nanoscale reinforcement throughout MMCs because significant Van der Waals attractive forces can lead to microstructural inhomogeneity [124]. The use of a high-density fiber laser beam [181] in the SLM process causes an increase in temperature in the laser-induced molten pool with a small melting pool and a rapid cooling rate [53]. These unique metallurgical phenomena are beneficial for obtaining refined microstructures with improved properties [53]. The use of SLM can aid in overcoming the uncontrolled agglomeration of nanoparticles that results in microstructural inhomogeneity and even in the disappearance of existing favorable nanostructures [115, 117]. All of these advantages make SLM a novel candidate process for fabricating metal matrix nanocomposites because SLM can shorten the processing cycle and reduce costs, has high design flexibility, and can produce parts with superior performance.

Thus far, the SLM process has been successfully used to fabricate 316L stainless steel [79, 128, 182-184]. At the present time, industries have a great need for high-performance engineering materials; however, the relatively low mechanical strength and poor tribological/wear performance of this steel has limited its applications [185, 186]. Austenitic 316L stainless steel matrix composites (SMCs), with the combined favorable properties of the ductile matrix phase and the harder reinforcing phase, have received considerable research attention [133]. Among the various types of particulate reinforcement, TiC is one of the best and is most commonly used with steel matrices owing to its low density, superior corrosion resistance, high hardness, and thermodynamic and thermal stability in iron alloys [187-190]. The hardness and wear resistance of the composites depend on various microstructural parameters such as the reinforcement volume fraction and size, distribution of embedded particles, and interfacial bonding between the matrix and reinforcement. If no defects exist, an increase in the volume fractions of the reinforcement leads to an increase in the density, hardness, and elastic modulus of the composite (rule of mixtures) [191].

A promising method for fabricating nanocomposite powders is mechanical alloying via ball milling, which is a non-equilibrium, low-temperature, and solid-state powder processing technique, owing to its powerful, relatively cheap, and easy operation [192]. This method can accommodate a wide range of reinforcement volume contents with uniform distribution of the embedded particles. During high-energy ball milling, the powder particles undergo repeated deformation, cold welding, and fracturing. Therefore, the grain size is significantly refined during the milling process, resulting in enhancement of the mechanical properties.

A thorough review of the literature shows that few studies of SLM processing of SMC parts have been performed, although there have been several attempts to fabricate SMCs via conventional

approaches such as casting or powder metallurgy. Hao et al. [131] studied the effect of the SLM processing parameters of a hydroxyapatite/316L composite for load-bearing implants. However, understanding the specific contribution of the starting TiC particles (sizes and volume contents) to the microstructural evolution, including the densification level, of SLM-processed SMC parts plays a fundamental role in determining the material properties, but this contribution remains unclear. In the present study, TiC/316L nanocomposite powder systems with different starting TiC particle sizes and volume contents were fabricated via SLM. The variations in the constitutional phases, densification level, microstructural features, and mechanical properties using the microhardness and wear testing were investigated. We believe that as the current work concentrates on an alternative fabrication route, it would significantly contribute to the widespread use of the SLM technique in the future.

4.2. Experimental Procedures

4.2.1. Powder Feedstock

The matrix alloy used in this study is commercially available 99.7% purity gas-atomized 316L stainless steel powder with a nearly spherical shape and a mean particle size of 45 μm (Fig. 4.1a). The reinforcement was TiC powder with two different particle sizes, that is, coarse TiC powder (99.9% purity) with a mean particle size of 1 μm (Fig. 4.1b) and fine TiC powder (99+% purity) with a mean particle size of 50 nm (Fig. 4.1c). Four different TiC/316L nanocomposite systems containing 2.5, 5, 10, and 15 vol.% TiC particles were prepared with two different starting TiC particle sizes by ball milling the component powders. The mixing process was performed in a Fritsch Pulverisette 4 vario-planetary mill using a ball-to-powder weight ratio of 5:1, a main-disk rotation speed of 200 rpm, and a mixing time of 8 h. To avert excessive temperature accumulation during ball milling, a 15-min interval followed each hour of ball

milling. After ball milling, the nanocomposite powder had flattened and transformed to an angular structure, with uniform TiC reinforcement embedment into the 316L matrix (Figs. 4.1d and 4.1e).

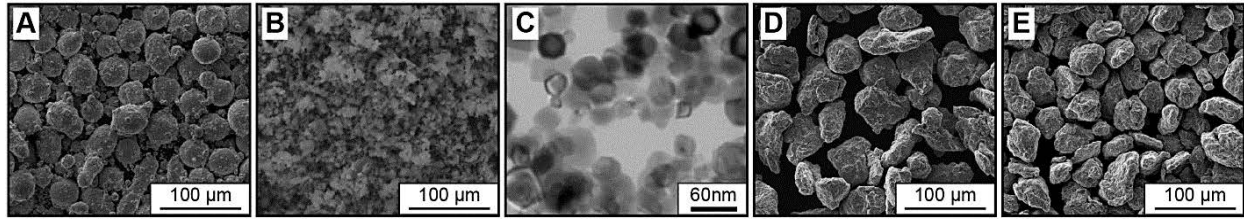


Figure 4.1: Microstructures of the starting materials. (a) 316L stainless steel powder; (b) microscale TiC; (c) nanoscale TiC. Ball-milled 316L feedstock nanocomposite powder with the starting (d) microscale TiC; (e) nanoscale TiC.

4.2.2. SLM Process

The SLM apparatus mainly consisted of a fiber laser, automatic powder spreading system, inert Ar gas protection system, and a computer system for process control. Before the SLM process, a steel substrate was fixed on the building platform and leveled. The building chamber was sealed and filled with Ar gas. Then, the TiC/316L nanocomposite powders were uniformly spread on the substrate using the automatic powder spreading system until a layer thickness of 50 μm was obtained. An alternate X–Y direction laser scan strategy between consecutive layers was applied, and the hatch spacing between the neighboring scan tracks was 50 μm. The laser power was maintained at 100 W with a scan speed of 250 mm/s. Cylindrical samples with dimensions of 8 mm × 8 mm × 6 mm were fabricated via SLM.

4.2.3. Microstructural Characterization

Phase identification of the SLM-processed samples was performed using a PANalytical X'Pert PRO X-ray Powder Diffractometer with Cu K α radiation at 45 kV and 40 mA, using a continuous scan mode at 5°/min. The densification level of the SLM parts was estimated using Archimedes' principle. The specimens for the metallographic examination were ground and polished according to standard procedures. The polished specimens were etched with Marble's reagent for 10 s. The high-resolution microstructures were characterized using a 230 Nova scanning electron microscope (SEM). In addition, a Philips 420 transmission electron microscope (TEM) at 120 kV was used to examine the internal microstructure of the 15% vol. TiC/ 316L samples. The TEM samples were prepared via focused-ion beam (FIB) milling.

4.2.4. Hardness and Wear Performance

The Vickers hardness of the SLM-processed samples was measured using a microhardness tester (Leco, LM800AT) at a load of 200 g and an indentation time of 10 s for a minimum of 15 indentations. The wear performance of the samples were estimated using dry sliding wear tests conducted in an HT-500 ball-on-disk tribometer in air at room temperature. All of the materials were ground and polished prior to wear testing to obtain a uniform surface finish. The counterforce material was a 52100 steel ball with a diameter of 3 mm. The friction unit was rotated using a test load of 3 N at a speed of 840 rpm for 20 min, with a rotation radius of 2 mm. The coefficient of friction (COF) of the specimens was recorded automatically during the wear tests. The wear volumes V of the specimens were estimated using an ST400 white light profilometer. The wear rate w was then calculated as follows: $w = \frac{V}{FL}$ (mm³/Nm), where F is the contact load and L is the total sliding distance. The worn surface morphologies were observed using SEM.

4.3. Results

4.3.1. Phases

Figures 4.2 and 4.3 shows the typical XRD patterns of the SLM-processed nanocomposite samples with different volumes of coarse and fine TiC particles, respectively. Strong diffraction peaks of the austenitic stainless steel corresponding to γ -Fe, as well as diffraction peaks for the TiC phase for all the reinforcement volumes were observed for all samples. This confirms the formation of TiC-reinforced 316L nanocomposites after SLM using different reinforcement volume fractions. In addition, the high cooling rate associated with the SLM process leads to the formation of the α -Fe phase. Axen et al. [193] reported that the presence of ceramic reinforcements, which have a much lower coefficient of thermal expansion than iron alloys, introduces a tensile stress into the matrix of the composite, which ultimately increases the martensitic transformation. No significant differences in the XRD patterns are found when comparing Figs. 4.2a and 4.2d except that there is a difference in the peak intensities due to the difference in the amount of the reinforcement embedded in the 316L matrix. The peak intensities of the reinforcements increase while the γ -Fe/ α -Fe peaks decrease with increasing reinforcement content. It was also noted that owing to the sufficient protection of the sealed building chamber filled with Ar gas, the oxidation phenomenon during SLM was remarkably restricted, and the diffraction peaks for oxides were not detected in the SLM-processed parts.

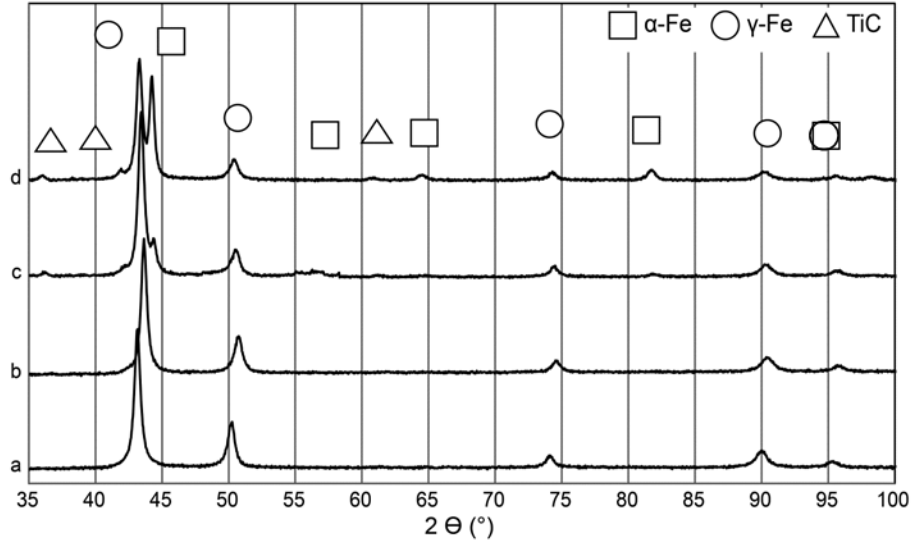


Figure 4.2: XRD spectra of the 316L SLM-processed nanocomposites reinforced with coarse starting TiC reinforcements with volumes of (a) 2.5%, (b) 5%, (c) 10%, (d) 15%.

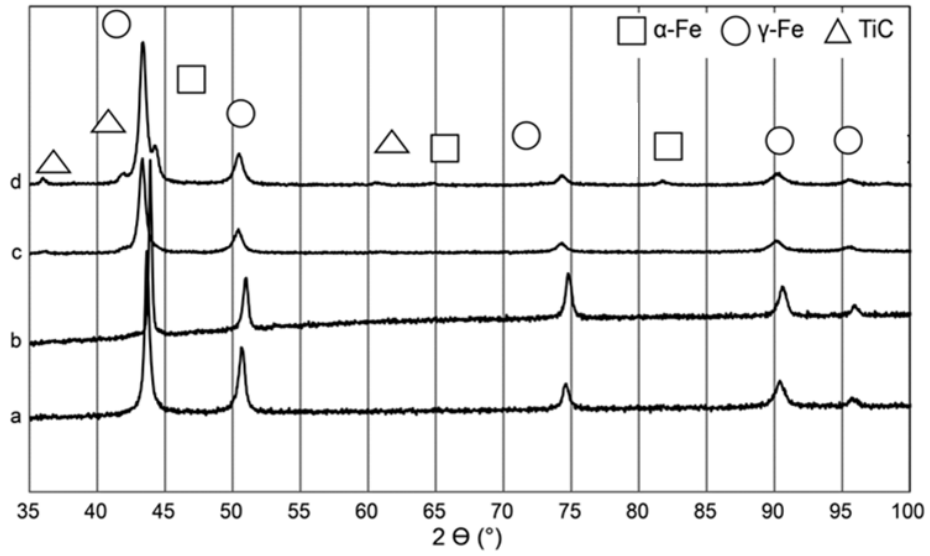


Figure 4.3: XRD spectra of the 316L SLM-processed nanocomposites reinforced with fine starting TiC reinforcements with volumes of (a) 2.5%, (b) 5%, (c) 10%, (d) 15%.

Table 4.1 lists the variations in the 2θ values and intensities of the detected γ -Fe peaks in the SLM-processed nanocomposites with different starting 15 vol.% TiC particle sizes. The 2θ

values of the standard γ -Fe phase (standard $2\theta = 43.583^\circ$ and 50.792°) are also listed for reference. In general, the tensile and thermal stresses that developed during SLM processing led to a shift of the peaks to 2θ values that were lower than the standard values. According to Bragg's law [140], the smaller 2θ values indicate a larger interplanar crystal distance of the corresponding crystal planes, implying distortion of the crystal lattices of the stainless steel matrix caused by the laser-induced non-equilibrium metallurgical process. Typically, the existence of defects, mainly residual stress and unmelted TiC particles, is responsible for variations in the interplanar crystal distance. Furthermore, a close comparison revealed that the full-width at half maximum (FWHM) of the strongest detected diffraction γ -Fe peaks in the SLM-processed parts with fine TiC particles was considerably larger than that of the γ -Fe peaks in the SLM-processed parts with coarse TiC particles. The opposite was observed for the intensity level. According to Scherrer's formula [140], the increase in the FWHM indicated that the crystalline size of the 316L matrix decreased. Therefore, an SMC part with a significantly refined crystal structure was produced from the fine TiC powder systems via SLM.

Table 4.1: Variation of 2θ locations and intensities of the γ -Fe diffraction peaks in SLM-processed nanocomposites with different starting 15% vol. TiC particle sizes

Sample	2θ ($^\circ$)	Intensity (counts)	FWHM (rad)	2θ ($^\circ$)	Intensity (counts)	FWHM (rad)
Standard	43.583	-	-	50.792	-	-
$D_{50} = 1 \mu\text{m}$	43.3182	8720.03	0.4811	50.4143	1739.37	0.7960
$D_{50} = 50 \text{ nm}$	43.2624	7052.73	0.5251	50.3578	1148.87	0.8419

4.3.2. Effects of Starting TiC Size and Volume Content on Densification Behavior

The SEM micrographs of the polished top surfaces of the SLM-processed nanocomposites using coarse and fine starting TiC particles with different volume contents are shown in Fig. 4.4, and the corresponding quantified relative densities are shown in Fig. 4.5. At a relatively low reinforcement content for both starting particle sizes, the surface of the SLM-processed parts was fairly dense and smooth; only minor micro-sized pores were formed, suggesting that the nanocomposite powders were almost melted and that particle–particle metallurgical bonding occurred. This result also suggests that the energy density of the delivered laser beam is sufficient such that the nanocomposite system with a relatively high-absorbed energy can possess a stable molten pool. The slight porosity (less than 100 μm) observed is probably associated with typical casting defects, mainly shrinkage and gas trapped/inclusions within the melt pool or evolved from the powder during consolidation owing to the directional liquidus/solidus transition near the center of the walls, because it often appears at the former scan line.

A close examination revealed that large, irregularly shaped pores (i.e., keyhole pores) with sizes greater than 140 μm appeared on the nanocomposite samples with higher amounts of reinforcements. Their formation can be attributed to rapid solidification of the melt without complete filling of gaps with molten pools [194, 195]. These pores are formed because of the instability of the melting pool and non-linear solidification, that is, various regions with different melting and solidifying behaviors. With an increase in the reinforcement content, the surface tension and Marangoni flow gradient from the center to the periphery of the molten pool increase. This leads to instability of the melting pool as well as the formation of many tiny droplets that splash from the liquid front as a result of the decrease in the liquid's surface energy at a short length scale. The instability of the liquid and the thermocapillary forces usually

increase as the reinforcement of the contents increases. When the liquid flows from the periphery to the molten pool center, the direction of the liquid flow is changed from outward to inward [71]. The resultant radically inward liquid flow forces the liquid to spheroidize when it comes close to the laser beam center, thereby increasing the tendency of formation of relatively large pores. In this situation, both the surface tension and viscosity of the molten pool are fairly large and the pool melt flow may be significantly disordered, resulting in the heterogeneous dispersion of heat and a mass transfer. As a result, the melting instability and the balling effect are considerably increased, leading to the moderately low densification level in the solidified scan tracks.

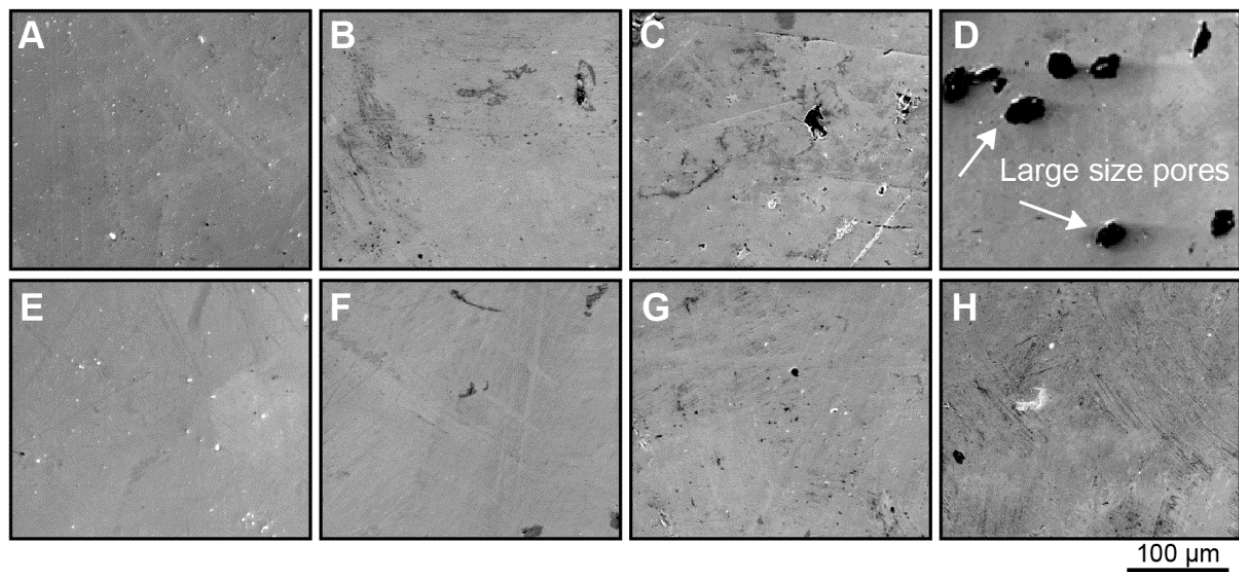


Figure 4.4: SEM images showing surface morphology and densification level of SLM-processed 316L nanocomposites reinforced with TiC particles at various volume reinforcements and size: coarse TiC (a) 2.5%, (b) 5%, (c) 10%, (d) 15%; fine TiC (e) 2.5%, (f) 5%, (g) 10%, (h) 15%.

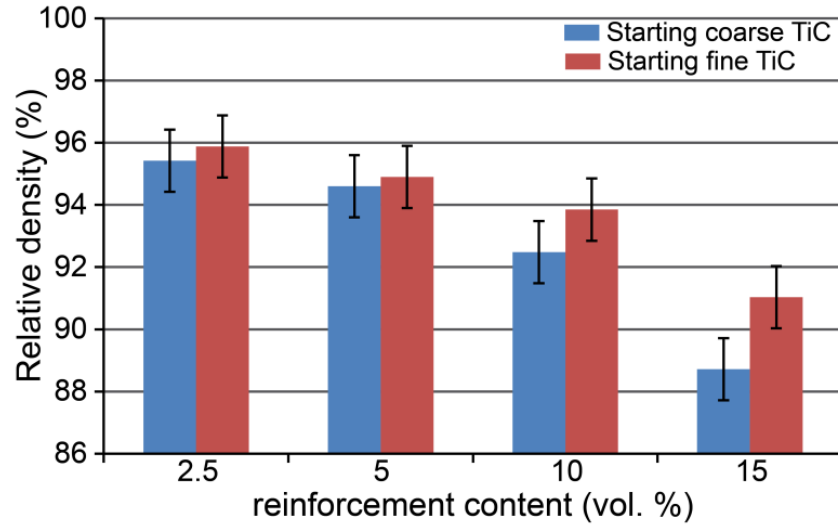


Figure 4.5: Densification levels of SLM-processed parts.

A careful comparison showed that the porosity in general was lower for the fine TiC particles than for the coarse ones, particularly after reinforcement with 10–15 vol.% TiC particles, although the processing parameters in this study were similar for all nanocomposite systems. When fine TiC particles were used, the amount and size of the pores on the SLM-processed nanocomposite samples were smaller. The surface melting temperature decreases with a decrease in the particle size (i.e., melting-point depression phenomenon). Therefore, a liquid phase can easily be formed at lower temperatures as bonding between particles occurs. This results in a higher density and less porosity. In addition, although both reinforcements undergo milling, their distribution and fluctuation in size are different. Fine starting TiC particles result in narrow particle size distributions, which explain the difference in density. For coarse starting TiC particles, when the uneven powder layer undergoes laser melting, the solidification front or laser-scanned front of a flowing molten pool tends to be easily interrupted, becomes discontinuous, and produces irregularly shaped pores between the irregular and uneven SLM layers. This

reduces the reinforcement or matrix wettability as well as the coherence of the resultant interfacial bonding owing to the fairly low specific surface area of the coarse TiC particles. As a result, the property of limited wetting in SLM attributed to coarse TiC particles is a major factor in the reduction of the densification of SLM-processed SMC parts (Fig. 4.4d).

4.3.3. Microstructural Observation Using SEM

Figures 4.6 and 4.7 illustrate the effects of the starting TiC particle size and volume content on the microstructural development of the SLM-processed nanocomposites. Figure 4.6a shows the region of continuous equiaxed fine grains and the other regions comprised of cellular dendrite grain structures that grow along the center of the melt pool (in the direction of the increasing temperature gradient). The rate of cooling of the melting pool during the SLM process is normally dependent and is correlated with the thermal gradients in the laser scan direction and the build direction [148, 196]. The complete growth of the dendrite structure is limited by the high rate of solidification [144]. However, a fine microstructure is formed at the core of the melting pool and begins to coarsen as it moves away from the center line until it reaches the heat-affected zone (HAZ) located at the border.

The higher magnification insets are shown in the upper-left corner of 4.6(a) and 4.6(b) to show additional details. The TiC reinforcing phase bonded with each other to form a continuous ring-like structure with a relatively uniform dispersion throughout the matrix. This is particularly important for improving the various mechanical properties of the SLM-processed nanocomposites. As the TiC reinforcement volume content increased, continuous distributions of the network of ring-like structures formed as a result of the increased concentration of TiC nanoparticles. It is interesting to note that the nanocomposite possessed finer grains after the

addition of 5 vol.% TiC particles, which may be attributed to the fact that the TiC particles normally function as nucleation sites in assisting heterogeneous nucleation as a result of the good wettability for nucleation of the 316L steel on TiC [143]. This leads to further refinement of the grains. A similar observation during SLM processing of the hydroxyapatite composite and 316L was reported by Hao et al. [131]. The refinement in grain size was found to be in a good agreement with the extremely broad XRD diffraction peaks observed.

Both nanocomposite systems show strong similarities in their morphology but have differently sized TiC particles. The average thickness of the ring-like structure was smaller for the samples fabricated with fine starting TiC particles than for those with coarse starting TiC particles. Regarding the fine starting TiC particles, the improved wettability of the 316L melt and the TiC particles obtained contribute to the formation of coherent particle or matrix interfaces. The refined TiC particles were dispersed uniformly throughout the matrix, showing a homogeneous nanocomposite structure (Fig. 4.7). In general, because of the significantly high solidification rate, 10^3 – 10^7 K/s [53], the TiC particles did not undergo coarsening and retained a favorable nanostructure. Figure 4.8 shows the EDS elemental maps for all of the samples to further elucidate the structures; here, the distribution of elements reveals both the 316L stainless steel phase and the TiC phase. The EDS analyses were performed at a low magnification (500×) to improve the statistical reliability of the data. It is clear that TiC phase, represented by Ti and C, was uniformly dispersed. Combined with the XRD results, the elemental analysis confirmed that 316L/ TiC nanocomposites with different TiC content were successfully produced by SLM.

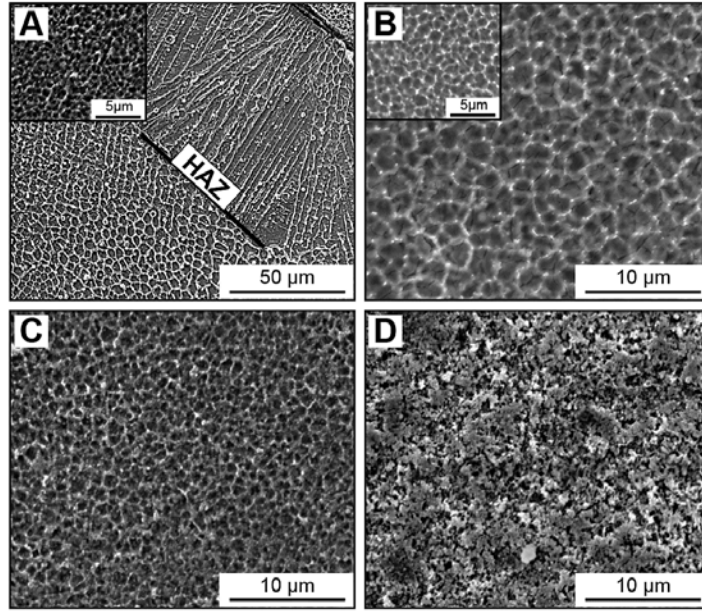


Figure 4.6: SEM images showing characteristics of SLM-processed coarse starting TiC/316L nanocomposites at various volume reinforcements: (b) 2.5%, (c) 5%, (d) 10%, (e) 15%.

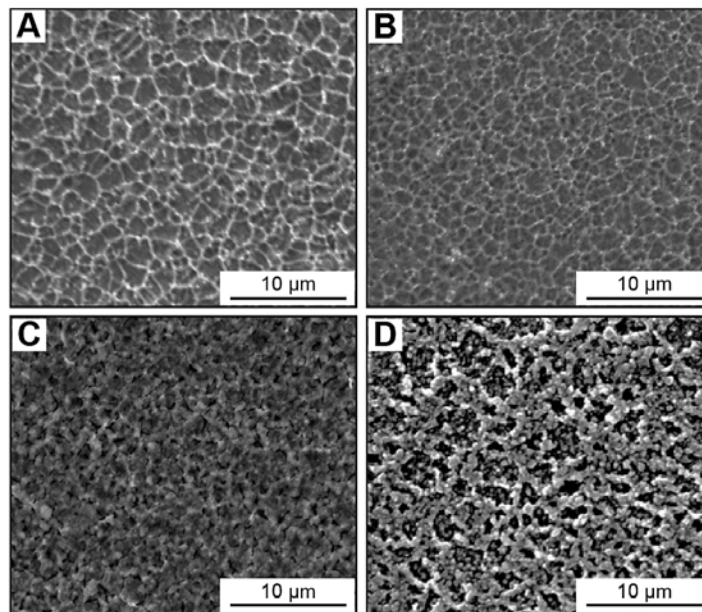


Figure 4.7: SEM images showing characteristics of SLM-processed fine starting TiC/316L nanocomposites at various volume reinforcements: (b) 2.5%, (c) 5%, (d) 10%, (e) 15%.

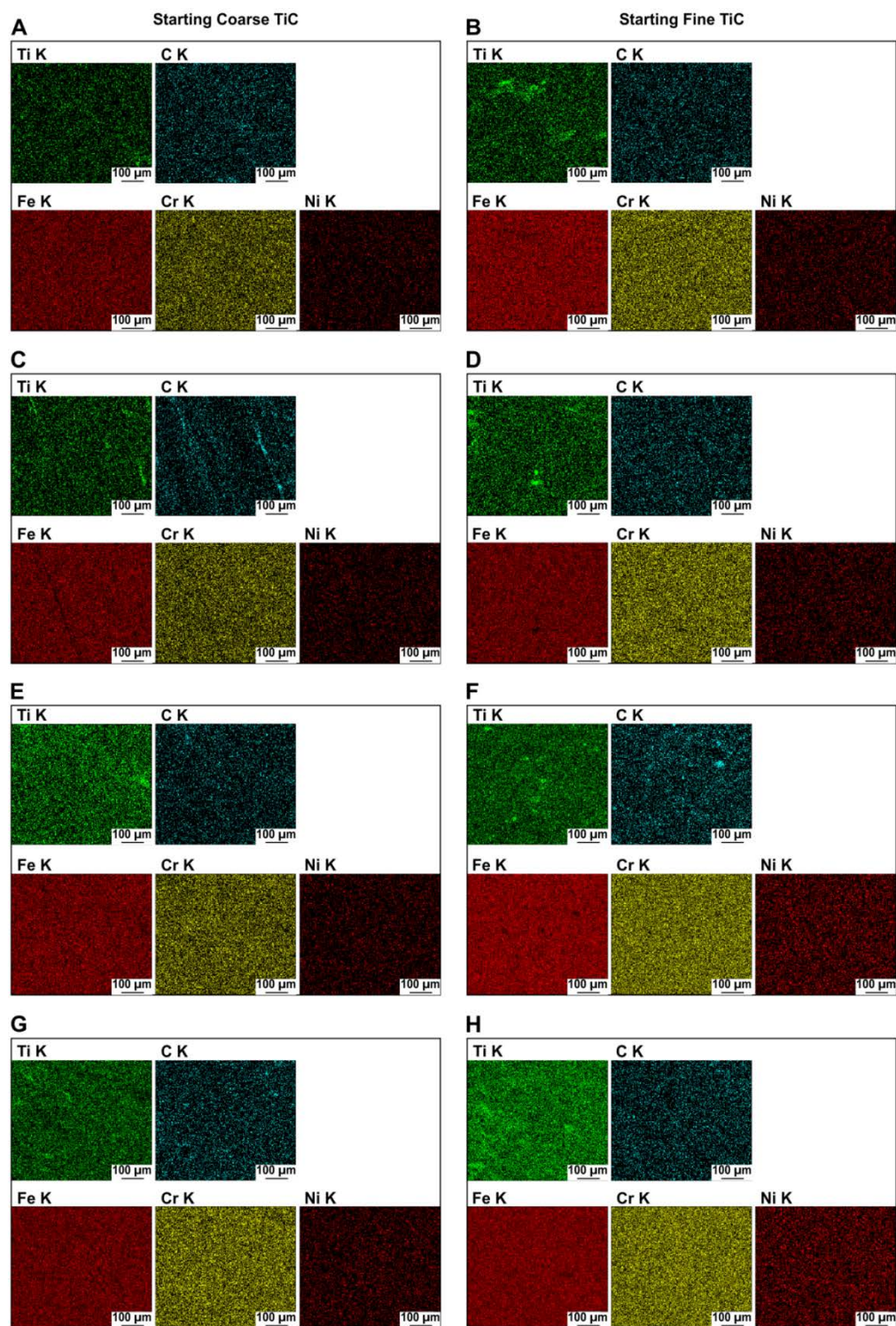


Figure 4.8: EDS elemental mapping showing distribution of major elements in the produced 316L stainless steel nanocomposites samples with: (a, b) 2.5% TiC; (c, d) 5% TiC; (e, f) 10% TiC; (g, h) 15% TiC.

4.3.4. Microstructural Observation Using TEM

Figure 4.9 shows the TEM images of the SLM-processed 15% vol. TiC/ 316L nanocomposites and the corresponding selected area diffraction (SAD) patterns. Both TEM images confirm the presence of sub-micron-sized 316L grains and retained nano-scale and round TiC particles. The grain size of the nanocomposite was in the range of $\sim 0.5\text{--}1\text{ }\mu\text{m}$. The formation of nano-scale particles with a size of $\sim 200\text{ nm}$ in the 316L matrix gains is generally attributed to the partial melting of the milled TiC particles (Fig. 4.9a). This observation is consistent with the SEM results. When fine starting TiC particles were used, the distribution and morphology after SLM were narrower and more round than those when coarse starting TiC particles were used (Fig. 4.9b).

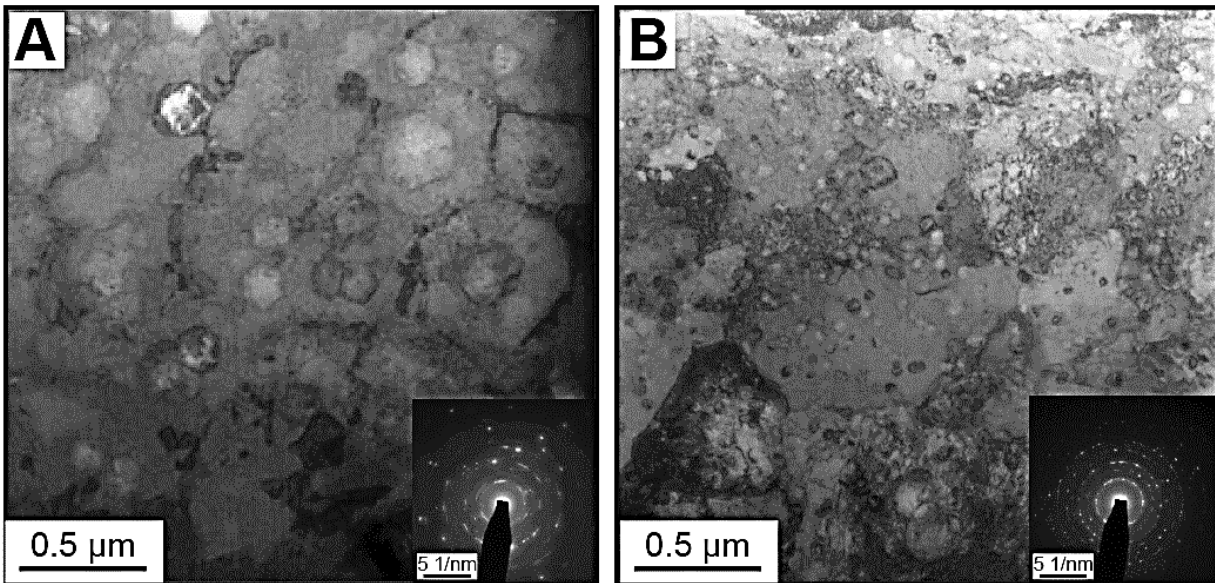


Figure 4.9: TEM images for 316L reinforced with the starting (a) coarse TiC, (b) fine TiC nanocomposite, revealing spherical precipitates at the interface and in increased dislocation density in the 316L matrix.

The TEM images reveal that the 316L matrix grain boundary has a metal–ceramic interface where the 316L matrix has wet the TiC reinforcements, and spherical precipitates have formed on the TiC side of the interface. This wetting improves the interfacial bonding throughout the metallic matrix composite. Nevertheless, no interfacial area was observed between the TiC nanoparticles and 316L matrix. The excessive Ni content and low C content of the 316L matrix boosts wettability (work involving adhesion increases). There was no evidence of any amorphous parts. To verify this, we tilted the sample believed to be amorphous, as slanting in certain parts reveals any contrast transform, which usually suggests crystallinity. The sample exhibited a high level of dislocations caused by the high solidification rate and also by the dissimilarities in the thermal coefficient between the TiC reinforcements and the 316L matrix. The amount of dislocation is affected by the particle size, particle volume fraction, and matrix strength [197].

4.3.5. Microhardness and Wear Performance

Figure 4.10 shows the effect of the starting TiC particle size and volume content on the microhardness of the SLM-processed nanocomposite. In general, the microhardness of the SLM-processed nanocomposite is associated with the densification level and reinforcement volume content. The microhardness of the fabricated nanocomposites was higher than that of the unreinforced 316L parts fabricated via SLM (maximum value $\sim 215 \text{ HV}_{0.2}$). The microstructures of the SLM-processed parts were critically refined, thereby maximizing the hardness values as a result of extremely fast heating and cooling. The TiC reinforcing particles that were uniformly distributed along the grain boundaries of the matrix also contribute to increasing the hardness values (grain boundary strengthening). The presence of the α -Fe/martensite phase after SLM processing resulted in a further increase in the overall hardness of the nanocomposites [198]. In

Chapter 3, we reported higher hardness values after SLM processing of 316L stainless steel nanocomposites reinforced with TiB_2 in comparison to those reinforced with TiC . The difference in hardness values are attributed to the higher energy density applied in earlier work and possibly the complex hexagonal structure of TiB_2 that possess higher hardness [199]. However, we reported a slight increase in the hardness value after SLM processing of TiC -reinforced H13 steel relative to the unreinforced H13 steel [200]. One possible explanation for this phenomenon is that 316L matrix is initially soft, in contrast to H13 steel, and hence reinforcement can lead to a remarkable increase in hardness. Unlike the hardness values obtained with low volume contents, which showed a small standard deviation, the microhardness values of the SMC part with 15 vol.% coarse TiC particles showed a relatively large fluctuation. This variability is because of the relatively low density of the SLM-processed SMC part caused by the presence of pores, particularly small pores (less than 5 μm), which are mostly underneath the indentations during the microhardness test. Hence, the interfacial bonding in the reinforcement matrix may weaken, further reducing the microhardness of the SMC part.

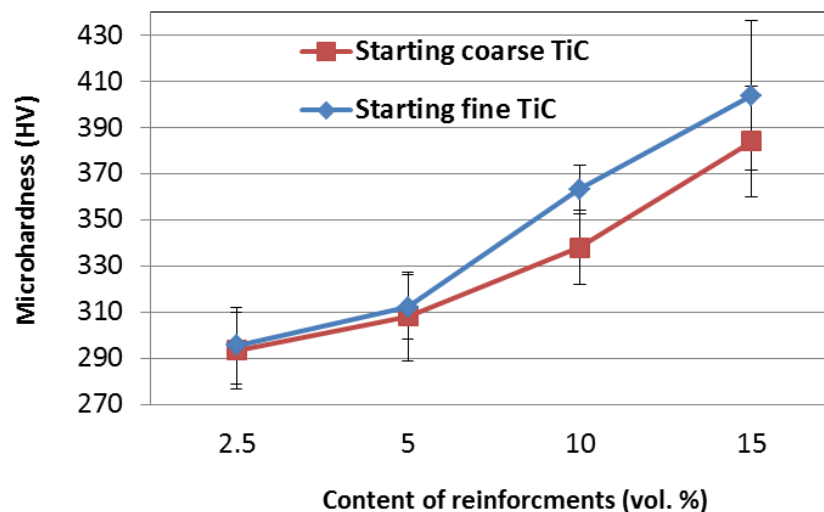


Figure 4.10: Influence of the starting particle sizes and volume contents of the TiC particle on the variation of microhardness of SLM-processed nanocomposites.

No significant differences were observed in the hardness values between the coarse and fine starting TiC particles; they both tended to increase with increasing TiC content. However, a slight increase was observed for the fine TiC particles with 10 and 15 vol.% TiC. For the SLM-processed SMC part using fine starting TiC particles, the mean microhardness increased markedly to $\sim 403 \text{ HV}_{0.2}$, which is attributed to the enhanced densification level and coherent particulate/matrix interfacial bonding. Furthermore, as the TiC particles are refined, the grain size of the 316L matrix decreases and, accordingly, the grain refinement strengthening effect becomes more significant. It has been also reported that the larger the carbide particles, the harder the dissolution, and thus, the softer the matrix [201]. Owing to the influence of grain refinement as well as grain boundary strengthening, the hardness of the SLM-processed SMC part with fine TiC particles is considerably improved, demonstrating no less than 40% improvement of the SLM-processed unreinforced 316L.

Table 4.2: Average coefficient of friction (COF) and wear rate of the 316L nanocomposites parts

Sample	Average COF	Wear rate (mm^3/Nm) $\times 10^{-4}$
316L-2.5% TiC (coarse)	0.738	9.696
316L-5% TiC (coarse)	0.714	8.573
316L-10% TiC (coarse)	0.670	7.338
316L-15% TiC (coarse)	0.698	3.555
316L-2.5% TiC (fine)	0.716	9.431
316L-5% TiC (fine)	0.713	7.770
316L-10% TiC (fine)	0.649	4.304
316L-15% TiC (fine)	0.691	3.106

Table 4.2 indicates the effect of the starting TiC particle sizes on the COF and wear rate of the SLM-processed nanocomposites. To determine the main microstructure associated with the tribological properties and the corresponding wear mechanisms associated with the SLM-processed SMC areas, the morphologies associated with the worn surfaces were studied, as shown in Figs. 4.11 and 4.12.

It is apparent that both nanocomposite systems experience a lower weight loss when the amount of reinforcement increases. For a low reinforcement content, the mechanism of abrasive wear is dominant. In general, the enhanced hardness values contribute to improvement of the wear performance of the SLM-processed nanocomposites; the performances increased with increasing TiC volume content. Galgali et al. [202, 203] reported that the wear properties of TiC-reinforced cast iron composites depend on both the amount of reinforcement content and graphite present. The material loss is due to the removal of material chips that are located in the 316L matrix as a result of microcutting in the rough debris. As long as the TiC reinforcements stay in the 316L matrix during the wear test, the wear resistance in the composite increases with increasing volume content. No breaking and splitting of particles in the matrix was observed. Hence, the volume content of the reinforcements is quite effective for enhancing the wear resistance. By increasing the reinforcement volume content, the matrix will be protected by a higher amount of reinforcements, and the wear morphology changes to a strain-hardened tribolayer (Fig. 4.12d).

For the nanocomposites reinforced with fine starting TiC particles, the average COFs and wear rate were generally lower than those of the samples produced with coarse starting TiC particles, although both starting TiC particles resulted in increasing wear resistance with increasing TiC volume content. The micrographs show that grooves are formed parallel to one another in the sliding direction (Fig. 4.11a). In general, deep and broad grooves are formed when coarse

starting TiC particles are used, while shallow and narrow grooves are formed when fine starting TiC particles are used. This is because the fine TiC particles restrict large plastic deformation of the surface material or flow of the matrix during sliding. Figure 10c shows that the worn surfaces are covered with compacted wear debris. The amount of compacted debris increases when fine starting TiC particles are used (Fig. 4.12c). At the same time, owing to increased grain refinement effects (Figs. 4.6 and 4.7), severe plastic deformation of the nanocomposite samples occurs on the worn surface and a strain-hardened tribolayer is formed, which shields the actual 316L matrix through additional plowing and spalling (Figs. 4.12c and 4.12d). Consequently, the removal of material through sliding is restricted and the wear performance is enhanced, implying the change of the wear mechanism from abrasion to adhesion of the strain-hardened tribolayer. It is thus reasonable to conclude that by using fine starting TiC particles, the actual wear performance of the SLM-processed nanocomposites will improve gradually.

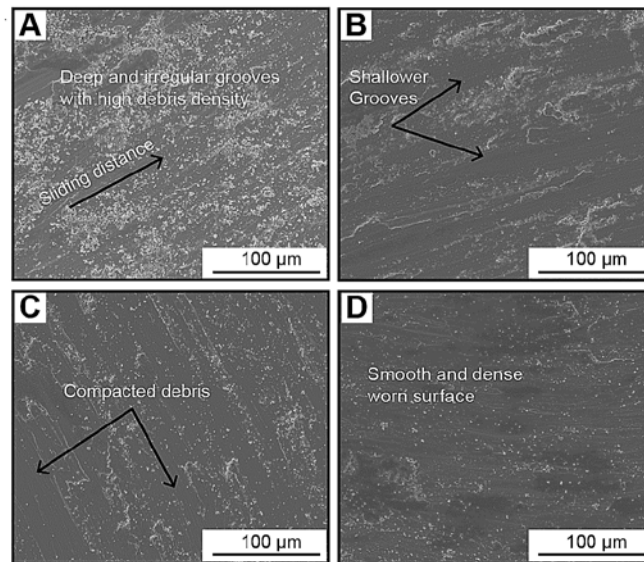


Figure 4.11: SEM images showing the worn morphologies of 316L/TiC nanocomposites using the coarse starting TiC particles with different volume contents: (a) 2.5%; (b) 5%; (c) 10%; and (d) 15%.

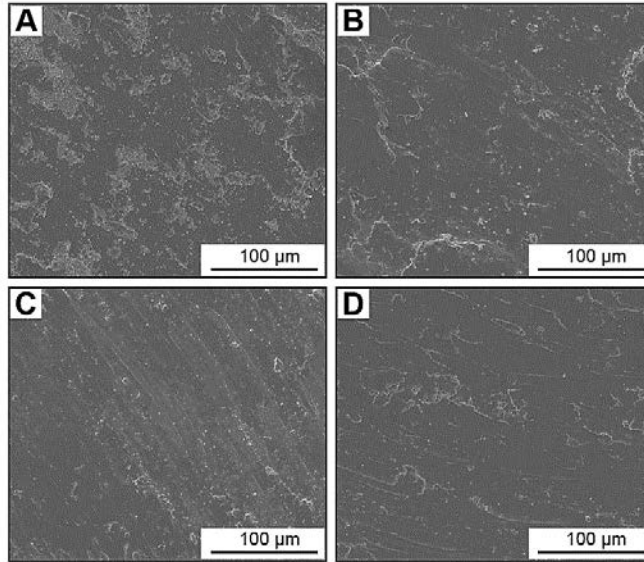


Figure 4.12: SEM images showing the worn morphologies of 316L/TiC nanocomposites using the fine starting TiC particles with different volume contents: (a) 2.5%; (b) 5%; (c) 10%; and (d) 15%.

4.4. Discussion

In this section, the relationship between the densification, microstructure, and wear performance will be established. The observations in the present work suggest that changes in the reinforcement size distribution and the particle volume fraction have a strong effect on the microstructure, densification, hardness, and wear resistance of the nanocomposites.

The nanocomposites reinforced with coarse TiC particles showed a lower wear resistance than that of the nanocomposites reinforced with fine TiC particles. Greater spalling occurs in the wear process with the coarse reinforcements. During SLM, the rearrangement rate of the starting fine TiC reinforcing particles is enhanced, leading to a better distribution of the TiC particles within the matrix and a better densification level of the SLM-processed parts. The decrease in particle size improves the surface contact that exists between the particles and steel matrix, ultimately

resulting in proper melting and solidification [204]. A recent study by Chang et al. [64] on the effect of starting particle size distribution on SLM shows that a higher relative density can be obtained with a smaller particle size distribution and a proper reinforcement volume fraction. Similar to our own observations, El-Kady et al. [205] showed that as the amount of SiC particles increased, the densification of the composite decreased. They also reported that increasing the amount and reducing the size of SiC particles promoted high hardness in the Al matrix composite. Axen et al. [193] reported that during the wear test, coarse ceramic particles are more easily pulled out from a hard matrix than fine reinforcements owing to the minimal deformation of the martensitic microstructure during the wear test, which causes the fine particles to remain inlaid in the matrix for a longer time than coarse particles. It is not easy for the evenly homogenously distributed ultrafine TiC nanoparticles to become fragmented in the course of the sliding wear test; nonetheless, there is a high tendency of the particles to stick to one another owing to minor interfacial stresses of the nanoscale reinforcing phase in the matrix [173]. The worn surface exhibits severe plastic deformation below the recrystallization temperature. A hardened sliding layer composed of substantially refined grains is formed on the wear surface, which improves the wear resistance. As a result, an inadequate laser energy density input leads to an occurrence of porosity and thus, further optimization of the SLM processing parameters is required.

The interparticle spacing λ between the reinforcements plays a major role in the wear resistance of the composite materials; it is affected by both the reinforcement particle size d and the volume fraction f , as shown by the formula below [206]:

$$\lambda \propto \frac{d}{\sqrt{f}} \quad (4.1)$$

The improved wear resistance that occurs with an increase in the TiC content is related to the decrease in λ . This leads to the formation of smooth worn surfaces with no significant grooves. The value of λ corresponding to a small volume content is considerably larger in composites reinforced with coarse TiC particles than in those reinforced with fine TiC particles. Axen et al. [193] proposed a standard for obtaining the optimum level of wear resistance in particle-reinforced steel matrix composites, which expressed as $\lambda < D_g < d$, where D_g is the groove size. Pagounis et al. [207] reported that the wear resistance is enhanced when the particle size is decreased and the reinforcement content is increased, if $\lambda/D_g < 1$. The wear resistance has a strong relationship with the hardness values, porosity, and distribution of reinforcements. The worn surface was considerably abrasive with the coarse TiC and low reinforcement content consisting of deep and irregular grooves that displayed the plastic deformation and plowing of the worn surface. Owing to the weak particle/matrix interfacial bonding, coarse TiC particles protrude and separate from the worn surface under applied shearing stress of the load. However, using the starting fine reinforcements, the spalling and plowing of the worn surface decreased. The grooves on the worn surface became shallower and developed smooth edges with low quantities of wear debris and a relatively small particle size. The compacted worn surface with fine TiC particles shows no significant material spalling or debris (Fig. 4.12d). The worn surface has relatively shallow grooves that are unconstrained from almost any loosened abrasive fragments, leading to a high wear resistance. The fine TiC starting particles result in a better densification level; therefore, the impact of plowing is debilitated, resulting in a smooth, worn surface (Figs. 4.12c and 4.12d).

4.5. Conclusions

SLM was utilized to process TiC/316L nanocomposite parts with different volume contents and sizes of the starting TiC particles. The main conclusions of the present study, which might be helpful for other laser-powder-based AM technologies and for different nanocomposite materials, are as follows:

- (1) The densification behavior was controlled by both the starting reinforcement content and the particle size. The densification level of the SLM-processed SMC parts was improved with the use of fine starting TiC particles. Owing to the presence of coarse TiC particles with a limited liquid–solid wettability, the laser-scanned tracks/layers were interrupted and discontinuous, resulting in a relatively low densification level of the SLM-processed parts. A sufficiently high densification level of the bulk was obtained for the SLM-processed parts with fine TiC particles, owing to the enhancement of the reinforcement/matrix wettability.
- (2) The TEM results show that a fine dispersion of TiC particles was retained in the SLM-processed nanocomposite parts.
- (3) With increasing TiC volume content, the microhardness and wear performance were remarkably enhanced, particularly with fine starting TiC particles, owing to the improvement of the densification level and microstructural homogeneity. These enhancements were observed with a low amount of spalling during wear testing.

Chapter 5

Scanning Strategies for Texture and Anisotropy Tailoring During Selective Laser Melting of TiC/316L Nanocomposites

Abstract

In this study, the SLM process was used to fabricate cylindrical-shaped components from 316L stainless steel reinforced with 15% TiC nanoparticles by employing various laser scanning methods. A deep relationship between the SLM process and the microstructure and properties of the resulting component has been established to understand the influence of scanning strategy on the solidification microstructure and texture, which were investigated using scanning electron microscopy, electron backscattered diffraction, X-ray diffraction. It is suggested that the resulting bimodal grain structure can be related to the heat flowing from the solidifying melt pool. Relatively strong fibrous <100> textures along the building and scanning directions could be transformed into weak cubic ones, and the mechanical properties of the produced components can be made relatively isotropic by rotating the scanning vector inside or between the created layers by 90°. The obtained results indicate that the utilized laser-scanning strategies allowed tailoring of the densification level, solidification microstructure, crystallographic texture and anisotropy of the fabricated parts. Hence, SLM can be successfully used for manufacturing 316L stainless steel nanocomposite parts with a high densification and controllable texture.

5.1. Introduction

316L stainless steel is a known ductile biocompatible material, which exhibits superior corrosion resistance properties [208]. However, it is also characterized by low hardness and poor wear

resistance, which ultimately limit its usage in potential applications [185, 186]. On the other hand, TiC is a lightweight biocompatible ceramic material, which is highly resistant to wear and can endure temperatures greater than 1000 °C [199, 209]. However, TiC is not as soft as 316L stainless steel, which makes its machining very challenging. This problem can be potentially solved by fabricating composites containing both the 316L and TiC materials, which would combine the high strength of ceramic TiC with the softness of 316L stainless steel, and thus possibly have a great potential for widespread use in the medical, automotive, and aerospace industries.

Additive manufacturing (AM) represents a key enabling technology, which can shorten the product development cycle and decrease its manufacturing costs. It belongs to a class of advanced technologies, which can directly use three-dimensional computer aided design data to automatically fabricate multifunctional parts in a layer-by-layer manner [176]. Owing to the large number of the geometrical degrees of freedom during layer-by-layer addition, parts with extremely complex shapes and geometrical features (which are difficult to produce using conventional manufacturing techniques) can be fabricated [210]. Selective laser melting (SLM) is a new and very promising AM technique for fabricating components with complex shapes via selective melting of metal powder and subsequent rapid solidification (the detailed information about the SLM process, including the experimental setup, main technological parameters, and its advantages, disadvantages, and practical applications can be found elsewhere [68, 178, 211-213]). Currently, SLM has only been used to process a few commonly used metals and metal alloys, and its potential (in terms of material versatility) has not been fully explored yet.

Owing to the high energy density of the fiber lasers, high-performance functional components of metal matrix composites can be fabricated using this technique; this would be of particular interest to the industry. The high cooling rate (as high as 10^5 K/s), which can be achieved during the SLM process, and the highly nonequilibrium nature of the process favors the production of bulk materials with a very fine microstructure and superior mechanical properties [5, 53]. Further, this novel processing method is capable of preventing particle aggregation and homogenizes the reinforcement particles across the entire metal matrix [121, 214], something that is very difficult to achieve during conventional manufacturing [117]. Owing to the above-mentioned advantages, the processing of (nano) composite materials by SLM could lead to a real breakthrough with respect to the applicability of these materials. However, the stability and behavior of the melt pool formed during SLM determine the porosity and mechanical properties of the fabricated nanocomposite components. Therefore, a better understanding of the process is necessary to deal with the challenges mentioned.

Previously published studies [75, 128, 131, 149, 182, 183, 214-216] suggest that the stainless steel parts produced by SLM exhibit a solidification structure consisting of very fine equiaxed and/or elongated grains with the crystallographic orientation depending on the shape of the obtained crystallization isotherms and epitaxial growth mechanism. In addition, the laser beam movement through the multiple layers of the resulting melt pool and subsequent rapid cooling produce parts composed of columnar and parallel elongated grains with a controlled texture, which depends on the overall heat flow direction/thermal gradient [6]. However, the microstructure and mechanical properties of SLM-fabricated parts are significantly affected by various SLM parameters such as speed, power, and thickness of the utilized laser beam as well as the building orientation of a fabricated part. The layer-by-layer addition process and high thermal

energy gradient of the SLM laser beam lead to preferential crystal growth via directional solidification, while the utilized laser beam scanning path can significantly affect heat input and dissipation during SLM and thus the resulting microstructural evolution [217]. Thus, selecting a proper SLM laser scanning strategy can produce sharp single-component textures or more uniformly distributed crystal orientations [148, 218, 219]. As a result, varying the SLM building orientation can lead to different degrees of densification as well as microstructure and texture variations and, hence, different mechanical properties of the produced specimens (in other words, the utilized scanning strategy during SLM determine the anisotropy of the mechanical properties of the fabricated components). Geiger et al. [220] demonstrated that the texture and elastic anisotropy of IN738LC alloy can be tailored along the building direction by using different scanning strategies in the course of the build-up process. In addition, low material porosity and crack density can be achieved by adjusting SLM scanning parameters [221], while SLM laser remelting can be considered a promising method for enhancing the surface quality and reducing its porosity [222-225]. The latter is capable of removing surface contaminants, breaking down oxide films, and forming a clean solid–liquid interface at the atomic level, which ensures heterogeneous growth of epitaxial grains [70]. Carter et al. [226] showed that employing the “island scan strategy” strongly affects the resulting grain structure (characterized by repeating patterns) as well as the cracking behavior of the fabricated parts. Aboulkhair et al. [227] described the porosity minimization of AlSi₁₀Mg components by optimizing the SLM scanning strategy at a maximum laser power of 100 W; they also discussed the effects of the utilized scanning strategy on the basic microstructure of the fabricated metal components. The accumulation of residual stress is inevitable during SLM, but it can be controlled by selecting a proper building strategy [79].

In Chapter 4, we investigated the effects of the TiC content and particle size on the microstructure and mechanical properties of the resulting 316L stainless steel nanocomposites. However, the correlation between the processing-microstructure-properties of SLM-fabricated 316L stainless steel nanocomposite components, their mechanical properties, and the optimum densification level has not been studied yet. In this work, a nanocomposite consisting of 316L stainless steel reinforced with 15 vol.% TiC nanoparticles was produced by SLM using four different laser scanning strategies. The effects of the scanning method on the solidification microstructure and texture of the obtained specimens were investigated by scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and X-ray diffraction (XRD) techniques. The anisotropy of the mechanical properties of the produced components was also analyzed based on their microstructure and crystallographic texture. The obtained results indicate that tailoring the degree of densification, microstructure, crystallographic texture, and mechanical properties of the fabricated components can be achieved by varying the SLM scanning strategy.

5.2. Experimental Procedures

5.2.1. Fabrication of Test Specimens

Gas-atomized 316L stainless steel powder, consisting of spherical particles of 45 μm size, was used as the matrix material, while the reinforcement particles with a mean size of 2–12 μm were made of TiC. Nanocomposite powders were prepared via mechanical alloying inside a high-energy planetary ball mill (Pulverisette 4 Vario). 316L stainless steel powder was mixed with 15 vol.% of TiC powder and milled for 8 h (the utilized procedure and the related parameters have been described in Chapter 4).

Laser melting was performed in Ar atmosphere, and the resulting samples were built on the top of a solid carbon steel plate. All processing parameters were the same for all samples, and the details of the processing parameters have also been discussed previously in Chapter 4.

In order to study the effect of the laser path on the resulting material structure, the following four different scanning strategies/building orientations have been implemented:

- I. Alternate hatches, single pass of the laser beam.
- II. Alternate hatches, two passes of the laser beam.
- III. Unidirectional hatches, two passes of the laser beam.
- IV. Cross hatches, single pass of the laser beam.

Figure 5.1 illustrates the scanning methods used during sample fabrication. In the scanning mode corresponding to unidirectional hatches, the laser beam always started from the same specimen side, while during alternate hatch scanning, the laser beam moved across the specimen surface in a zigzag manner. In addition, the effects produced during cross-hatching between successive layers and material remelting (which was observed when each layer was scanned twice before adding a new powder layer) were investigated as well. As a result, cylindrical specimens with diameters of 8 mm and heights of 6 mm were produced.

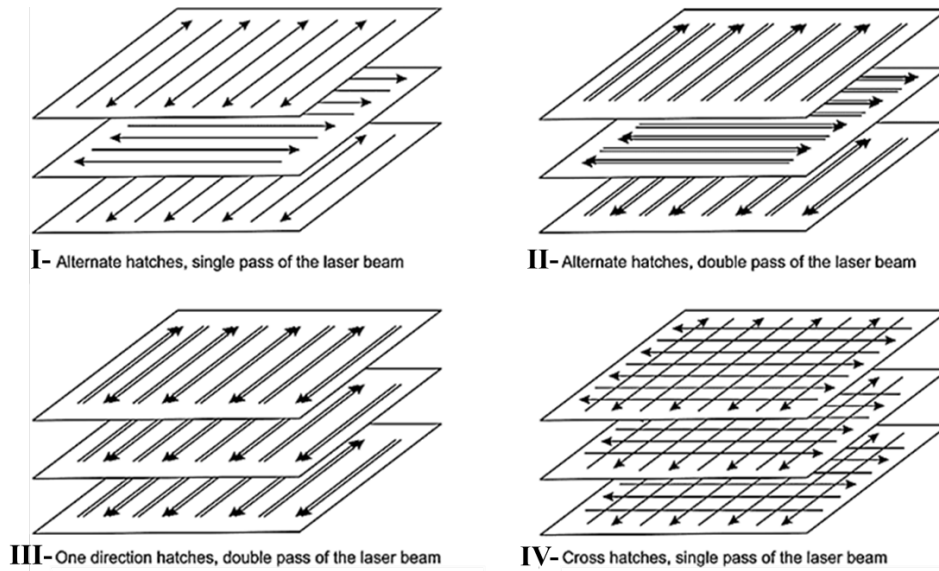


Figure 5.1: An overview of the four scanning methodologies used in this study.

5.2.2. Material Characterizations

The fabricated samples were sectioned, ground, and polished using conventional metallographic procedures. Relative densities of the produced specimens were measured by the Archimedes method (their average values were calculated using the data obtained for three replicates of the same specimen type and theoretical density of the studied material equal to 7.3355 g/mm^3).

The XRD measurements were performed on polished cross-sections parallel and vertical to the building layers of the samples (i.e., the top and side views of the samples) using a Jordan Valley D1 diffractometer with $\text{Cu K}\alpha_1$ radiation, produced by a laboratory-made tube source under double-axis diffraction conditions. The obtained diffraction patterns were recorded at 2θ values ranging between 35° and 120° and a step size of 0.02° to calculate the TiC volume fractions and texture coefficient.

The resulting TiC volume fractions were calculated using the following equation:

$$TiC\% = \frac{1}{1 + \frac{C_{Ferrite}}{C_{TiC}} + \frac{C_{Austenite}}{C_{TiC}}} \quad (5.1)$$

where C denotes the volume fraction.

The degree of texture in the γ -Fe phase can be quantified using the texture coefficient T_c obtained from the XRD measurements in accordance with the following formula [228]:

$$\frac{C_{\alpha 1}}{C_{\alpha 2}} = \frac{\frac{1}{n_{\alpha 1}} \sum_0^{n_{\alpha 1}} \left(\frac{I_{\alpha 1}}{R_{\alpha 1}} \right)}{\frac{1}{n_{\alpha 2}} \sum_0^{n_{\alpha 2}} \left(\frac{I_{\alpha 2}}{R_{\alpha 2}} \right)} \quad (5.2)$$

Where

$$R \sim \left(\frac{1}{v^6} \right) \left[|F|^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \right] e^{-2M} \quad (5.3)$$

Here I is the measured integrated peak intensity, C is the volume fraction, N is the number of reflection considered, v is the lattice constant, F is the structure factor, p is the multiplicity factor, θ is the Bragg angle, and M is the temperature factor. For randomly distributed materials (corresponding to that of isotropic materials), the magnitude of T_c is close to unity; it departs from unity when the (hkl) plane assumes a preferred orientation (corresponding to that of anisotropic materials) [229].

The resulting microstructures were examined with a Nova 230 SEM instrument at an acceleration voltage of 15 kV. Prior to SEM observations, the samples were etched with Marble's Reagent for 10 s. The obtained microstructures and textures were also characterized using an EBSD analysis performed on an EDAX system (the step size utilized during all EBSD scans was

equal to 0.4 μm). The average confidence index of the conducted measurements was approximately 0.70. In order to improve the statistical reliability of the obtained EBSD data, the corresponding scans were performed at low magnifications.

Vickers microhardness tests were performed at an applied load of 200 g using a Leco microindentation hardness tester (model LM800AT); a minimum of 15 indentations were produced for each sample.

5.3. Results

5.3.1. Morphologies of As-Deposited Specimens and Densification Behavior

Figures 5.2a and b show the low-magnification side-view images of the sample microstructures obtained by SLM scanning methods I and III after etching (the corresponding relative densities are listed in Table 5.1). The individual scan tracks and cross-sections of the melt pools represented by half-cylinders/crescents can be clearly observed in Fig. 5.2. According to Fig. 5.2a, the width of the individual scan tracks/grains was approximately equal to the length of the hatch spacing (around 120 μm). The widths of the obtained melt pools varied from 110 ± 10 to 170 ± 15 μm and were higher than the layer thickness (50 μm). Furthermore, these melt pools were not always continuous, owing to the variations in their depths and shapes. The laser track overlaps, which occurred during SLM, caused each melted track to bond with the adjacent tracks. Several solidified zones were characterized by curved edges and contained unmelted particles (see the image depicted in the upper-right corner of Fig. 5.2a).

The obtained results indicate that the SLM building orientation has a significant effect on the specimen density. In general, when the scanning direction is rotated by 90°, the laser beam is oriented perpendicularly to the direction of the previously deposited layer, which results in

changes in the heat dissipation for that layer as well as in the direction of the total temperature gradient [217]. The described phenomenon increases the density of the fabricated specimen and bonding strength between the deposited layers. Deep melt pools were produced at the starting/final points of the scan tracks, and pore formation was observed along the scanning direction after several scans. It can be assumed that the obtained keyhole melt pools were created due to heat accumulation at the specified points of the scan paths. Since the temperature evolution at the starting/final points is transient in character, the produced keyhole pools become unstable and easily collapse to form larger pores.

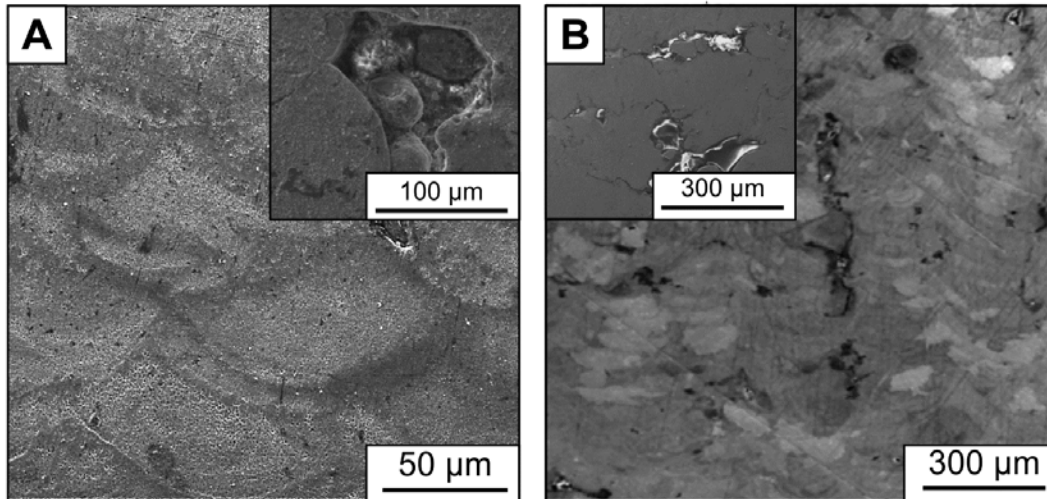


Figure 5.2: SEM images of the TiC/316L nanocomposites processed by SLM scanning methods (a) I and (III). The obtained data demonstrate an overlap between the melt pool and the individual layer microstructural features (such as pores and cracks) along the building direction.

However, the remelting process (by performing double laser scanning) produces more uniform and smoother layers and efficiently reduces the number of pores formed between the neighboring melt pools at the scan track edges. When the double-pass scanning method was used, the voids between the adjacent laser tracks mostly disappeared, and higher-density specimens with a

smooth and defect-free surface were produced (see Table 5.1; the potential effect of laser remelting on the densification level and surface roughness of the SLM fabricated samples has been investigated previously [222, 230]). As a result, the flowability and rheological properties of the obtained melt were enhanced during double scanning. Hence, the density of molten 316L alloy reinforced with TiC particles was sufficiently high, leading to more homogeneous and efficient mass and heat transfer inside the pool. However, the density of the sample obtained by scanning method IV was still higher than that of the sample produced by scanning method II because the cross-hatch scanning technique used during fabrication of sample IV, which resulted in more irregular scan tracks, appears to have compensated for the pore formation process, thus lowering the number of pores and increasing the relative density of the obtained specimen.

Table 5.1: Relative densities of the 15 vol.% TiC/316L nanocomposite samples obtained by various SLM scanning methods.

Scanning method			
I	II	III	IV
92.48%	96.04%	86.91%	96.40%

5.3.2. Microstructural Evolution

Figures 5.3 and 5.4 show the high-magnification side-view and top-view images of the nanocomposite samples respectively fabricated by different SLM scanning methods. The observed grain structures were clearly affected by the geometry of the melting pool, since both the heat flow and grain growth occurred perpendicularly to the liquidus/solidus interface, leading to the morphology observed.

According to the results presented in Figs. 5.3 and 5.4, the resulting solidification morphology was highly correlated with the chosen SLM building strategy. In general, the microstructure of the SLM-fabricated components is characterized by discontinuous columnar grains/dendrites, whose orientation is determined by the heat flow direction, which in turn depends on the laser beam movement. The observed dendrites contained a distinct columnar structure aligned along the building direction (similar to the directionally solidified microstructures). Furthermore, a comparison of the images depicted in Figs. 5.3a and b revealed that the dendrite size was significantly affected by laser remelting during double scanning, which caused the formation of finer dendrites as compared to those depicted in Fig. 5.3a. During the second laser pass, the laser beam was focused on the already solidified material, whereas during the first pass it was focused only on the powder particles. Thus, during the second pass, a smaller amount of the laser energy was absorbed, and the produced heat was removed more quickly. As a result, the average size of the melt pools obtained after the second pass was smaller, while some parts of the material structure created after the first scan were retained in the final product. A larger number of particle interfaces broke during the second pass, and a greater amount of the pore defects was eliminated (Table 5.1). The presence of pores impedes the recrystallization process due to the pinning of the required dislocations and boundaries [231]; therefore, the reduction in porosity observed during the second laser pass produces dendrites with a finer structure.

The samples fabricated by double unidirectional hatch scanning (method III) exhibited two solidification modes (corresponding to cellular dendrites mixed with equiaxed grains), while for the specimens produced by cross-hatch scanning (method IV), the resulting solidification microstructure mainly consisted of fine equiaxed grains with sizes below 1 μm , regardless of the view direction (Figs. 5.3d and 5.4d).

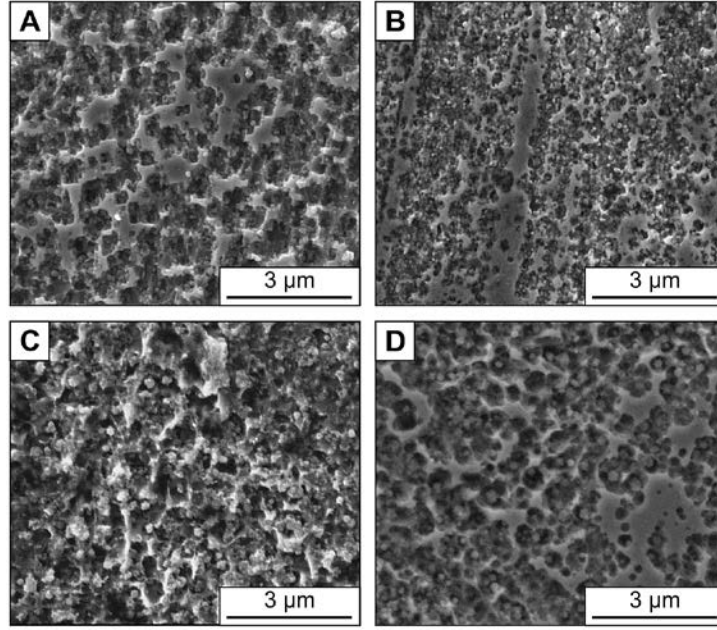


Figure 5.3: High-magnification SEM images of the 15 vol.% TiC/316L nanocomposite sample cross-sections obtained by SLM scanning methods (a) I, (b) II, (c) III, and (d) IV.

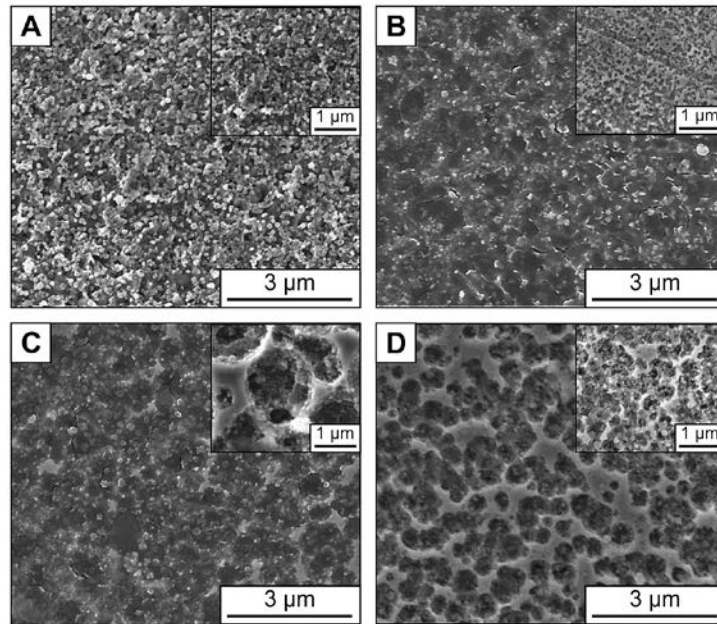


Figure 5.4: High-magnification SEM images of the top sides of the 15 vol.% TiC/316L nanocomposite samples obtained by SLM scanning methods (a) I, (b) II, (c) III, and (d) IV.

For all the SLM-processed samples, TiC nanoparticles were present both at and within the columnar dendrites/grain boundaries (Figs. 5.3 and 5.4). The observed segregation of TiC particles most likely occurred because of the high SLM solidification rate and use of different scanning methods; the TiC volume content measured by XRD, as described in section 5.2.2, for the sample tops and sides are listed in Table 5.2. The formation of intense vortex flows inside the molten pool causes a relative increase in the concentration of heavy particulates between the adjacent vortices [149]. Chemical inhomogeneity can affect the resulting concentration profile, while constitutional supercooling of the grown cells may cause changes in the solidification mode and, thus, variations in the TiC content. When different scanning methods are used, the TiC phase ultimately agglomerates, resulting in heavy particle concentrations greater than 15 vol.%. On the other hand, short interaction times and high conductive heat transfer rates lead to the formation of very small volume of TiC. During double laser scanning, the processed material is heated to a relatively high temperature (due to the larger amount of supplied heat), and its larger fraction is exposed to this temperature for a longer period. Thus, the volume of the produced TiC phase can be controlled by varying the supplied amount of energy, which can be achieved by selecting a proper scanning method. Further investigations of this phenomenon will be conducted in future studies.

Table 5.2: TiC volume contents determined by XRD for the 15 vol.% TiC/316L nanocomposite samples, which were obtained by various SLM scanning methods.

Scanning #	Top view	Side view
I	12.7±0.3%	14±1%
II	14.8±0.7%	19.7±1.5%
III	14.5±0.2%	14.3±0.1%
IV	12.2±0.5%	21.7±0.3%

5.3.3. EBSD Analysis

5.3.3.1. EBSD Orientation Maps

Figure 5.5 shows the EBSD orientation maps corresponding to both the top and the side views of the nanocomposites produced by different scanning methods (various colors correspond to the combinations of the Euler angles and grain orientations measured for the crystal lattice; thus, similar colors represent grains with the same crystallographic orientation). For the crystals with a cubic structure, columnar grains preferentially grow along the energetically favorable $\langle 100 \rangle$ crystal direction [232]. The directions of the heat flow and cooling during the solidification process determine the textural evolution, which occurs at a high total amount of supplied energy, large resulting melt pool, and low thermal gradient; the observed variations are caused by the local process-related parameters. For example, when the laser beam was moving from the left to the right, the produced grains were slanted to the right, suggesting that the direction of the local heat transfer played a major role in determining grain orientation.

Both the top and side views of the nanocomposite samples contain elongated columnar grain structures as well as fine equiaxed grains (note that the columnar grains do not extend into the adjacent layers unlike in previous published studies [148, 233]). During SLM, there is no nucleation barrier to solidification; therefore, the produced grains with crystallographic orientations identical to those of previously solidified grains can grow epitaxially [221]. This is the reason for the elongated grains observed in the side and front views of all the samples. Several grain axes were larger than the thickness of the utilized powder layer (50 μm), while the width of each columnar grain was approximately 5 μm , which was much lower than the diameter of the laser beam (75 μm). The columnar centerline spacing was set to approximately 150 μm in order to maintain the hatch distance of 125 μm . In general, the presence of unmolten particles,

pores, and TiC nanoparticles in the produced samples as well as the rotation of the scanning direction disrupted the defined columnar/epitaxial growth structure and make individual laser tracks undistinguishable [148]. This observation was similar to the results previously reported in the literature [148, 200, 214, 233].

In particular, the samples produced by using scanning methods I and II exhibited a bimodal grain structure, which was represented by the large areas of elongated columnar grains adjacent to the regions containing fine grains. These fine grains (observed at the borders of scan edges) exhibited a small degree of elongation perpendicular to the building direction, indicating variations in the heat flow direction during material solidification. In contrast, in the regions located at a distance from the laser track centerline, small freshly nucleated grains with different growth directions could be observed (see Fig. 5.5f). Thus, it can be suggested that the formation of bimodal grain structures is related to the heat transfer from the solidifying melt pool. As a result, the produced bimodal grain structure translates into a bimodal texture inside the material (the red areas correspond to the elongated grains of the strong $\langle 001 \rangle$ texture, in contrast to the normal texture of the remaining sample material). However, most of the formed grains exhibited a random orientation, as evidenced by various colors on the corresponding EBSD images. In addition, the grain growth direction became even more random when the scanning direction between each layer was rotated by 90° since the columnar directional microstructure was fragmented by the induced complex thermal field.

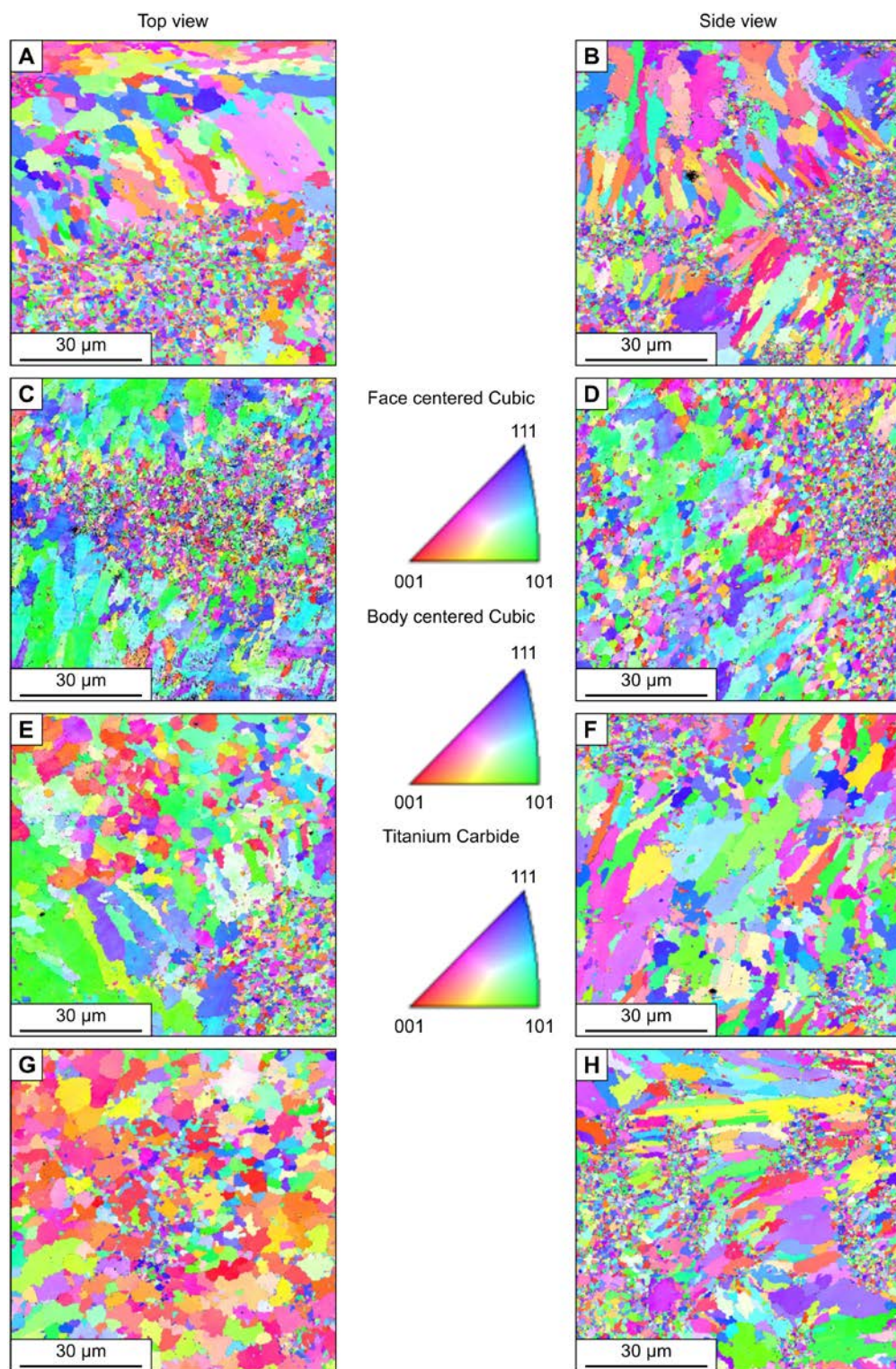


Figure 5.5: EBSD orientation maps of the 15 vol.% TiC/316L nanocomposite samples, which were obtained by scanning methods (a, b) I, (c, d) II, (e, f) III, and (g, h) IV.

A comparison of the EBSD orientation maps depicted in Figs. 5.5a and b with those displayed in Figs. 5.5c and d, respectively, revealed the differences between the corresponding grain sizes and scan track patterns. The grain size obtained after double laser scanning was relatively smaller than that observed after single scanning (these results were consistent with the SEM observations discussed earlier). The double-scanning method affects the microstructure of the previously deposited layers, which means that the second scan not only remelts some parts of the previous tracks, but also affects lower layers, initiating thermally activated diffusion processes such as phase transformation and grain growth. During double-pass scanning, the directions of the heat flow and the related thermal gradient become more complex; as a result, the produced grains become less elongated, while the crystal growth occurs more randomly, leading to the formation of a larger number of finer grains.

The use of the third scanning method resulted in a relatively more homogenous structure, as compared to the other scanning methods, since the laser path direction was rotated by 180°. For the samples processed by the unidirectional hatch scanning method, larger areas with elongated columnar grains were obtained (see Figs. 5.5e and f), in contrast to the grains with a bimodal distribution, which were observed for the samples produced by other scanning methods. Thus, it can be concluded that when SLM scanning method III is utilized, grain solidification nominally occurs perpendicularly to the building direction, which corresponds to the primary heat flow path. However, the obtained EBSD results demonstrate a slight skew in the crystallographic orientation with respect to the building direction, owing to the sample heating during SLM processing because of the laser beam movement.

For all the processed samples, equiaxed and fine grains/ cells can be observed in the fabricated specimens as a result of the high thermal gradient. In SLM, the top part of the solidified melt

pool is remelted during the scanning of the next layer, which leads to the disappearance of these grains from the composite structure. As a result, only the equiaxed grains of the last scanned layer are retained. In addition, the specimen top view contains grains that are parallel to the scanning direction. Small grains ($< 2 \mu\text{m}$) of different colors can be found around the melt pool borders, while between the border and the centerline, the average grain size reaches $6 \mu\text{m}$ (see the green–blue color areas on the corresponding EBSD images).

5.3.3.2. EBSD Misorientation Angles

The described microstructural analysis revealed that the observed elongated grains grew at a certain angle with respect to the laser movement direction, which is usually called the misorientation angle. The majority of the grains observed via EBSD could be characterized by high-angle grain boundaries containing misorientation angles (see Fig. 5.6) since the SLM process involved layer-by-layer material addition. The high energy of the laser beam causes the previous layers to remelt partially or fully each time a new layer is created, which in turn leads to material recrystallization and the formation of high-angle grain boundaries. During double scanning, the remelting time increases; as a result, the recrystallization time and number of high-angle grain boundaries increase as well. However, small zones confined by the low-angle boundaries can be observed at the laser track borders for all the samples (the corresponding misorientation angles are equal to $2\text{--}5^\circ$ or $5\text{--}15^\circ$).

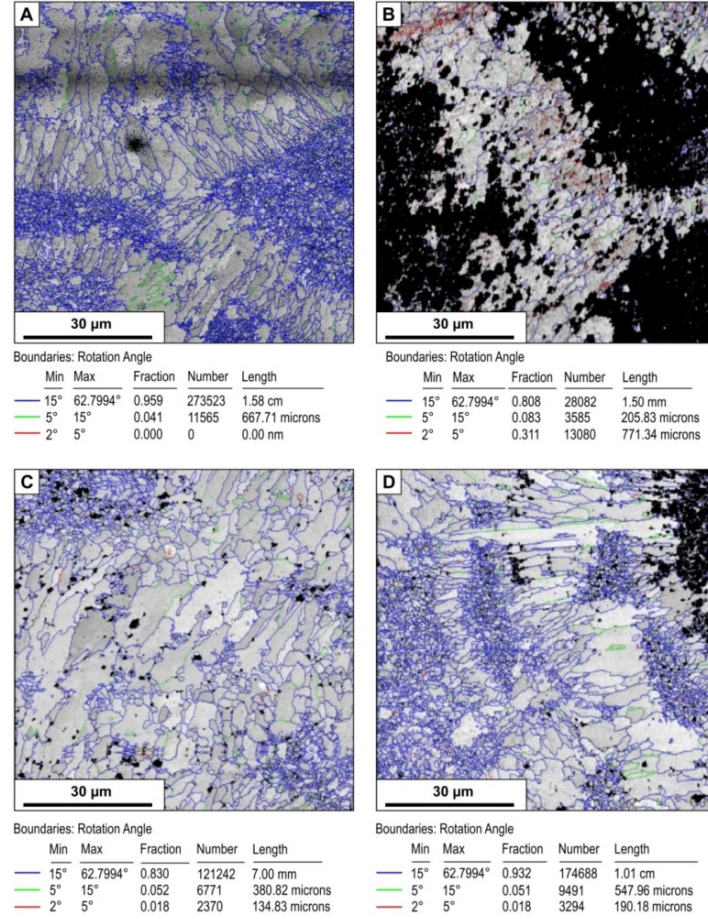


Figure 5.6: Grain boundary misorientation maps superimposed on the image quality maps of the FCC 316L matrix, which was obtained by scanning methods (a, b) I, (c, d) II, (e, f) III, and (g, h) IV.

5.3.4. Texture Development

5.3.4.1. Texture Coefficients Derived From the XRD Analysis

The directional solidification of the melt pool discussed previously caused the formation of specific textures. Table 5.3 lists the texture coefficients obtained from the sharpest peak of the γ -Fe phase corresponding to the (200) plane using different SLM scanning methods. When scanning methods I and IV are utilized, the resulting texture coefficients tend to approach unity.

After single laser pass between consecutive layers, the scanning/solidification direction was rotated by 90° (which corresponded to alternate hatching or cross-hatching scanning); hence, a reduction in the degree of the crystallographic texture along the building and scanning directions was observed, which minimized the anisotropy of the produced components [233]. Thus, it can be concluded that the utilized scanning methods did not affect the crystallographic texture of the SLM fabricated specimens. The texture coefficients obtained for sample I (0.97 for the top view and 0.95 for the side view) were close to unity as compared to those calculated for sample III (1.16 for the top view and 0.70 for the side view). Similarly, the texture coefficient obtained for sample IV exhibited values close to unity, which was typical for isotropic behavior. On the other hand, double laser scanning performed during fabrication of sample II resulted in a large deviation from unity, which characterized anisotropic behavior.

Table 5.3: Texture coefficients T_c derived from the XRD data for the 15 vol.% TiC/316L nanocomposite samples, which were obtained by various SLM scanning methods.

Scanning #	Top view (200)	Side view (200)
I	0.97	0.95
II	0.72	0.88
III	1.16	0.70
IV	1.03	0.98

5.3.4.2. Pole Figures Derived From the EBSD Analysis

Local crystallographic textures of the SLM-processed nanocomposites were also investigated based on the countered pole densities represented by the pole figures derived from the EBSD analyses, as shown in Fig. 5.7.

When scanning method I was utilized, a part of the melted and resolidified material contributed to texture reduction, which in turn caused a large spread in the grain and crystal orientations. When the scanning direction was rotated by 90° between the subsequent layers during buildup, the degree of the (100) fiber-like texture along the scanning direction was lowered significantly, and the texture pattern was replaced with a weaker (100) cubic structure along the building direction and, to a lesser extent, along the scanning direction during both the first and the second scans. However, the (100) pole figure depicted in Fig. 5.7b shows that the high-intensity zone was elongated along the scanning direction, suggesting that the melt pool formed during the first scan still produced a greater structural effect than the pool formed during the second scan, owing to the difference in their sizes.

For all samples, the obtained colored crystal orientation maps indicated that one of the $\langle 001 \rangle$ axes of the formed crystals were predominantly aligned parallel to the building direction. Hence, it can be concluded that the thermal gradient direction during solidification of the molten layers determines their primary orientation. In addition, the secondary preferred crystallographic orientation can be controlled during SLM, since the $\langle 001 \rangle$ crystal axis is preferentially aligned parallel to the laser scan direction, as illustrated by the observed color variations with respect to the testing direction. As a result, a single-component cubic texture is formed when scanning methods I and IV are used. A comparison of the domains produced after using scanning methods I and II reveals the increase in the texture strength with structure height. The exposure time per layer decreased after the formation of domain 1, which resulted in a different value of thermal gradient and thus produced a change in the degree of the layer epitaxial growth and the related texture strength. When scanning method I was used, the resulting texture was not perfectly symmetric with respect to the laser scanning directions (this was true for both the parallel and

vertical ones). The $\langle 100 \rangle$ direction was more oriented along the specimen length (scanning direction) than along its thickness (building direction), which most likely occurred due to the scanning length and asymmetric thermal gradient at the sample end (similar observations were reported by Geiger et al. [220]).

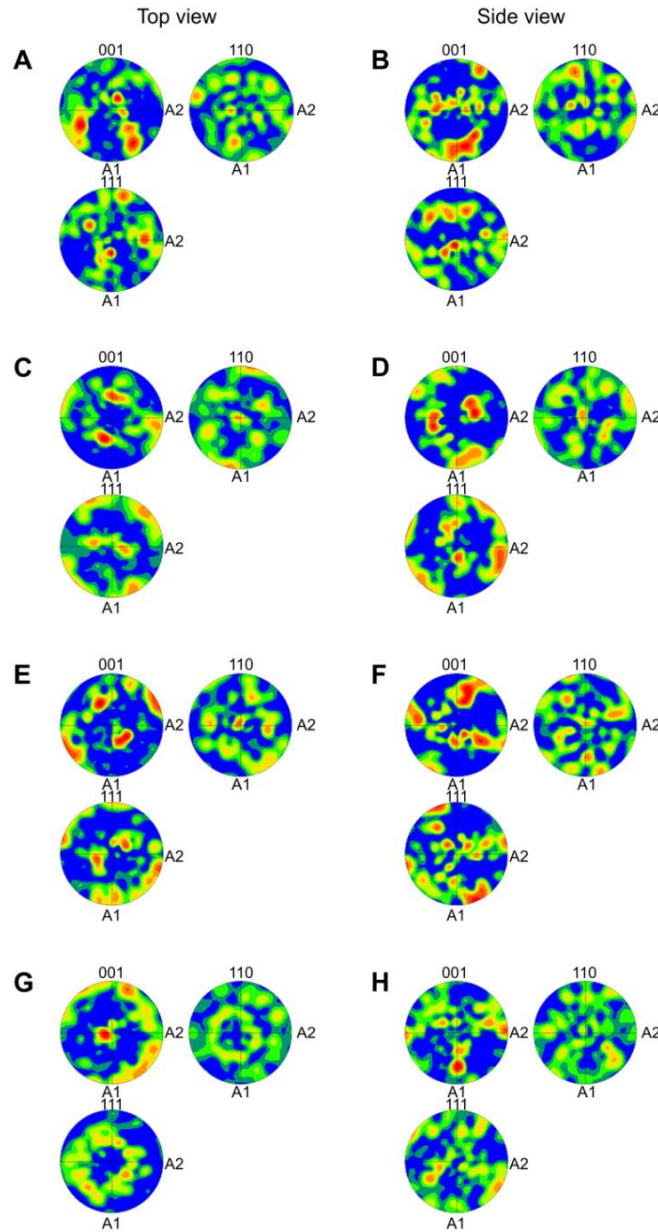


Figure 5.7: Pole figures obtained for the FCC 316L matrix, which was produced by scanning methods (a, b) I, (c, d) II, (e, f) III, (g, h) and IV.

When the unidirectional hatch scanning method was employed, the (011) $\langle 100 \rangle$ texture was observed on the outermost surface normal to the building direction (Fig. 5.7c). The (011) plane was mostly parallel to the consolidated surface, while the $\langle 100 \rangle$ direction was oriented along the scan track direction (similar results were reported in a previous study [233]). Nevertheless, according to the side view parallel to the building direction, the $\langle 100 \rangle$ fiber-like texture along the scanning direction was strong, while the preference for the (011) plane was much weaker (see Fig. 5.7e). When a sample was scanned using long vectors, and the scanning direction was not rotated by 90° , the (100) texture was strong along the scanning direction, and a weaker (110) texture was observed along the building direction (as indicated by the corresponding pole figures depicted in Figs. 5.7e and f). Thus, the low intensities observed for the remaining pole figures suggest the presence of a fiber-like texture.

5.3.5. Mechanical Properties

The Vickers hardness values measured for the nanocomposite sample tested from top and side surfaces are shown in Fig. 5.8 (the microhardness of the SLM-processed unreinforced 316L sample was 210–233 HV_{0.1}). The fine dispersion of TiC particles in the 316L matrix resulted in a hardness increase for all produced samples, which could primarily be attributed to the grain boundary strengthening and grain refinement as well as to the presence of the α -Fe phase [234].

In general, the building orientation has a considerable effect on the specimen hardness. Indeed, the degrees of porosity, grain refinement (described by the Hall-Petch relation), and homogeneity of the particle distribution (greater homogeneity results in higher dispersion strengthening) play significant roles in determining the mechanical properties of the SLM products. Some differences in the hardness values obtained for the sample tops and sides were observed except for the samples produced using scanning method I and IV, which resulted in a relatively isotropic

material. The single-pass alternate hatch scanning method produced materials with a lower degree of anisotropy, which is consistent with the results of earlier studies [200]. Furthermore, the double-pass scanning method produced specimens characterized by larger hardness values because of the additional grain refinement of the fabricated nanocomposite, greater homogeneity of the particle distribution, and density increase (despite the distinct difference in the values obtained for the sample top and side, which suggested that the produced nanocomposite exhibited a high level of anisotropy). Finally, the observed large hardness values could also be attributed to the texture formation and microstructural effects, including morphology, size, and distribution of TiC nanoparticles.

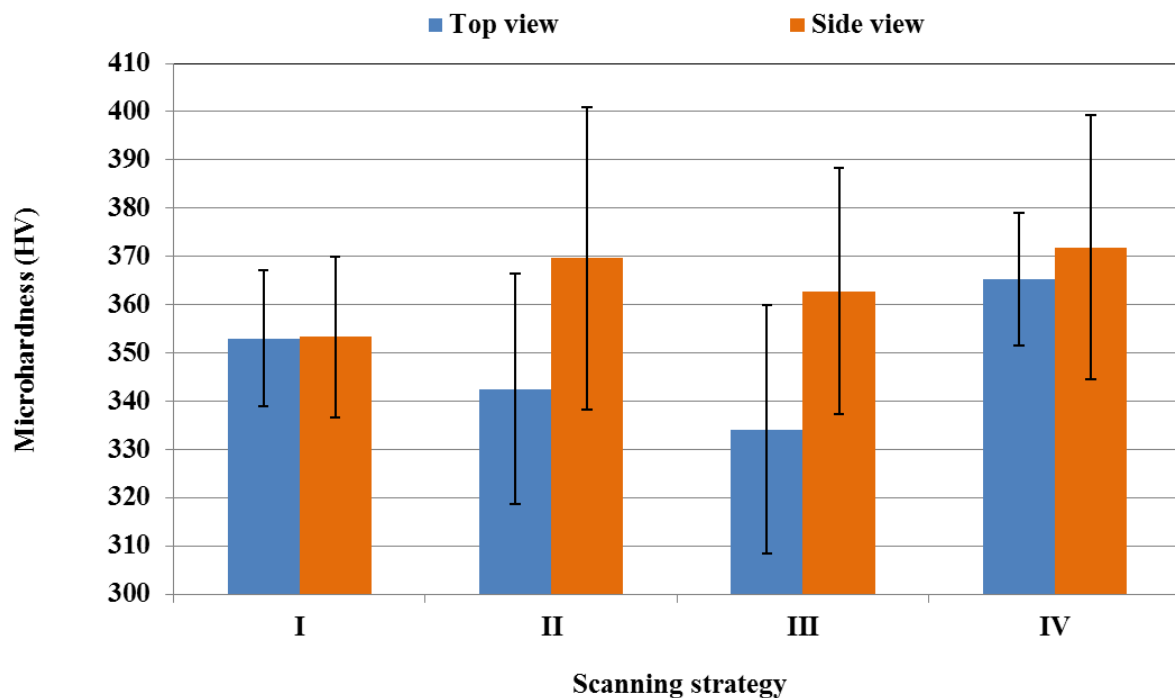


Figure 5.8: Effect of the scanning strategy on the hardness of the obtained SLM nanocomposite samples.

5.4. Discussion

5.4.1. Densification Behavior

The effect of scan overlapping on the formation of consecutive melt pools and the related densification process is described in Fig. 5.9. Although the layer thickness was identical in both cases, a very small overlap area was observed in Fig. 5.9a. To obtain good metallic bonding, the currently scanned track must remelt a portion of the previously scanned layer. In this case, layers are created partially from the supplied powder and partially due to remelting of the previously formed layer, improving the bonding between particle-particle and between layer-layer. As a result, the selected scanning method has a significant effect on the overall solidification direction (including texture variations).

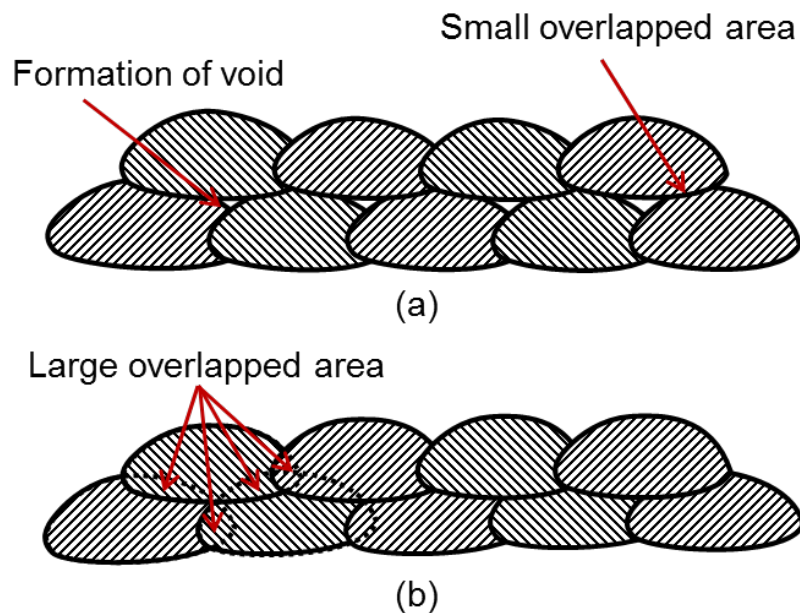


Figure 5.9: The influence of overlap factor and the type of scanning method on the appearance of consecutive melt pools: (a) small overlapped area that result in poor bonding between the two adjacent layers (i.e., lower densification) and (b) large overlapped area that result in good bonding between the two adjacent layers (i.e., higher densification).

The results obtained in this work also revealed that it was possible to minimize specimen porosity by using a carefully controlled laser scanning strategy. A number of previous studies have suggested that laser remelting after the deposition of each layer improves its degree of densification, increases surface roughness, refines columnar microstructure, and limits the formation of microstructural defects (even at a low laser energy density) [222, 230, 235]. Partial remelting ensures high-density of the SLM-fabricated specimens, since it eliminates surface contaminants, removes any oxide films, and produces a clean solid-liquid interface at the atomic level, which allows heterogeneous development of epitaxial grains. However, the low porosity observed in the proximity of the laser scan line was most likely related either to the directional liquidus shrinkage or gas inclusion, or the formation of keyholes, because it was also observed repeatedly for the previous scan lines [236].

5.4.2. Crystallographic and Morphological Textures

The microstructures of the fabricated nanocomposites were largely typical of those seen in the case of the SLM process and were influenced by the melt-pool geometry. The obtained EBSD results showed that the produced nanocomposite samples viewed from both the top and side views contain elongated columnar grain structures that grew epitaxially along the centerline of the melt pool as well as fine equiaxed grains. The small newly nucleated equiaxed grain zone could be observed at a distance from the centerline [36]. This equiaxed zone contains fresh randomly oriented grains, which are usually formed at a low temperature in the presence of inoculating agents (TiC). Small grains or dendrites inside a chill zone may also be removed by the strong convection flow observed in the beginning of the solidification process, which leads to the formation of heterogeneous nucleation sites for future equiaxed grains. The produced

equiaxed grains eventually become randomly oriented, thus completing the columnar growth process.

The scanning method, involving beam rotation from one layer to the next, resulted in the introduction of two grain directions, one of which was parallel to the building direction, and the other one was skewed at an angle of 15–30°. Thijs et al. [221] reported that elongated grains mostly grew parallel to each other at a tilt angle of 19° with respect to the building direction when a unidirectional scan vector was used. The areas around the produced columnar grains exhibited a fine microstructure because of the multifaceted cross-directional heat extraction. For example, the newly nucleated grains appeared to be columnar; however, they were very short and thin, which suggested that the morphology and number of the newly formed columnar grains could be modified via double scanning. Ultimately, the obtained crystals exhibited random orientations in the single axis region, which resulted in the rotationally symmetric preferred orientations characterized by a fiber texture.

The grain fineness and solidification process are dependent on the growth rate (R) and thermal gradient (G) [36]. The latter parameter corresponds to the temperature difference measured over a certain distance dx (dT/dx) and varies with time as well as with the location inside the melt pool. The growth rate, R , depends on the speed of the moving heat source, v , and the angle between the moving source direction and the growth direction of the solidifying material. Under steady-state conditions, the magnitude of R is equal to the product of v and the cosine of Θ (as has been assumed for simplicity in this work). The G/R ratio determines the stability of the solidification front and hence the resulting solidification mode. Thus, as its magnitude changes from a high value to a low one, planar, cellular, columnar dendritic, and equiaxed dendritic

structures are sequentially formed. The $G \times R$ value determines the fineness of the structure (the higher is its magnitude, the finer is the structure). It also determines the cooling rate and, therefore, the solute diffusion length of the solid phases, which are formed during solidification [222].

Another aspect is related to constitutional supercooling. Since the ratio G/R measured at the centerline is small when the degree of constitutional supercooling before the solidification front is high, an equiaxed grain structure is formed, owing to the existence of a relatively long supercooled zone. As a result, only centerlines (equiaxed grain bands) without any visible fusion lines, which might be related to the partial remelting during the next laser scan, can be observed. The difference in the grain sizes of samples I and II originated from the difference in the numbers of laser passes and, therefore, the Q value (heat input per unit area). At a higher value of Q , which corresponds to a lower value of G (temperature gradient, $^{\circ}\text{C}/\text{cm}$), the magnitude of R (growth rate, cm/s) is equal to the laser speed (v), which is a constant. Thus, the $G \times R$ value calculated for sample I would be lower. The lower is the $G \times R$ value, the coarser are the grains. Owing to the movement of the heat source, the measured thermal gradients and growth rates varied across the melt pool. The highest values were observed at the centerline of the melt pool, which decreased along the direction towards the border of the scan track. The measured growth rate even reached zero at the melt pool border, where the laser movement direction was perpendicular to the direction of the heat transfer. The variations in the magnitudes of G and R significantly affected the solidification mode and degree of fineness for the obtained structures. However, since the values of G and R were varied equally in a similar manner, no significant changes in the solidification mode were expected.

The observed anisotropy of the mechanical properties of the produced specimens is correlated not with their microstructure or grain shapes, but with the texture formation. The side and top of the sample fabricated by scanning methods II, or III were characterized by distinct mechanical properties (the specimen fabricated using SLM scanning method II exhibited the sharpest texture and thus the highest degree of anisotropy).

One important factor, which is responsible for the deterioration of the mechanical properties of SLM-processed samples, corresponds to residual porosity. The greater the density of a material, the stronger is its structure. In addition, fine TiC particles were added to the melt to serve as preexisting surfaces for heterogeneous nucleation, which led to further grain refinement [70] and enhancement of the material mechanical properties due to the increase in the grain boundary area (through the Hall-Petch effect). Grain precincts and grain atomic defects frequently act as locations for heterogeneous nucleation in the fresh phase during the initial stage, which also plays a critical role in the strengthening mechanism.

The resulting texture is also affected by the direction of the laser scanning path. It was found that regardless of the direction characteristics of the scanning process, the latter considerably affected texture formation, owing to the difference in the melt pool sizes and specimen dimensions. When the scanning direction was rotated by 90° , the degree of texture was reduced significantly, and a weak cubic phase was formed along the building direction. Furthermore, the degree of morphological texture increased after partial remelting, since the majority of the elongated grains were oriented along the building direction. Indeed, double scanning produces partially disordered orientations since significant heat diffusion occurs from the top building layer.

Finally, it can be concluded that texture development entirely depends on the actual scanning directions and is not affected by the utilized substrate or SLM materials beneath the existing deposition layer. The use of sophisticated scanning strategies can simplify the process of texture tailoring. Thus, the anisotropic behavior, which is observed in the course of building complex parts, is most likely related to different texture gradients along the three dimensions. The ideal alignment, in which the $\langle 001 \rangle$ plane would be parallel to the building direction, could not be tailored since it was observed for all the four utilized scanning methods.

5.4.3. Additional Remarks

By understanding the factors that affect the solidification process in different specimen regions, it is possible to produce samples with different microstructures. For example, it is possible to grow only equiaxed grains and thus develop materials with isotropic properties through effective grain refinement or inoculation. Alternatively, the degree of solidification could be controlled to ensure the growth of columnar grains and hence produce materials, which exhibited anisotropic behavior. However, the choice of the scanning strategy may be limited by the geometry of the fabricated components. For example, when the specimen cross-section is large, the time between each laser pass is much greater than that for the cylindrical samples fabricated in this study. In contrast, for a thin cross-section, the time for each laser pass may be significantly reduced to produce a band heating effect. Ideally the optimal scan strategy should be determined on a layer-by-layer basis by taking into account specimen's geometry and adjusting the laser power and scan speed parameters to allow microstructure tailoring and thus make the fabricated component suitable for its intended application. However, such an optimization would require a detailed thermal modeling of the entire SLM process.

5.5. Conclusions

The presented results highlight the capabilities of SLM to process metal matrix nanocomposites using various scanning strategies. Material addition in a layer-by-layer manner and intense directional cooling during the SLM process lead to the formation of a unique solidification structure. The orientation of the produced elongated grains depends on the local heat transfer conditions, which are determined by the utilized scanning method. Owing to the partial remelting of the previously scanned adjacent laser tracks, both the morphological and crystallographic textures were developed. The obtained results revealed that the laser scanning strategy used during SLM determined the geometry of the formed crystallographic and morphological textures as well as the densification degree of the SLM-processed nanocomposites and hence the anisotropy of their mechanical properties. In addition, it has been shown qualitatively that the resulting crystallographic texture is the primary reason for the large differences in the hardness values measured for the tops and sides of the fabricated components. The final TiC volume content was also significantly affected by the scanning strategy employed.

Owing to the controlled nucleation and growth on proper selection of the scanning method, the SLM-produced samples may possess a columnar grain structure, an equiaxed structure, or a mixture of those. It was also found that rotating the scanning direction by 90° inside a layer or between the layers (utilized in scanning methods I and IV) allowed production of isotropic materials. Therefore, the results obtained in this study indicate that the selection of a proper SLM scanning method can produce desired morphological and crystallographic textures of the SLM-processed parts with either anisotropic or isotropic properties.

Chapter 6

Densification Behavior, Microstructural Evolution, and Mechanical Properties of TiC/316L Nanocomposites Fabricated by Selective Laser

Melting

Abstract

Here we investigate the influence of the volumetric laser energy density (η) induced by selective laser melting (SLM) on the phase evolution, densification behavior, microstructure evolution, and mechanical properties of TiC/316L stainless steel nanocomposite parts. Correlations between the SLM processing parameters and the microstructures, mechanical properties, and metallurgical mechanisms of the fabricated parts were established. High scan speeds (low η values), created disordered liquid solidification fronts, with parts containing large balling and long pore chains defects due to low liquid viscosity and highly unstable melt flow behavior caused by densification-limiting Marangoni convection. Conversely, low scan speeds (high η values) improved densification, but induced fine spherical pores and thermal microcracks due to increased liquid lifetime and thermal stress. A maximum densification of 98.23% was achieved for samples processed at η of 300 J/mm³. The microstructural features and mechanical properties of SLM-processed nanocomposites were sensitive to the applied η . On increasing η , the dispersion state of nanoscale TiC was changed. The increase in η enhances the Marangoni flow intensification and the attendant capillary force intensity, preventing TiC aggregation and promoting a uniform dispersion in the solidified matrix. With increasing η , however, the TiC particle size increases, whereby some of the nanoparticles lose their initial standard nanostructure owing to the significant thermal accumulation within the molten pool. The samples

processed at an η of 67 J/mm³ showed the most refined microstructure as it was exposed to the highest cooling rate, which in turn exhibited a higher compressive yield strength compared to samples processed at an η of 300 J/mm³. We also observed an intensification of the <100> crystallographic texture with increasing η . Nanocomposites processed under optimum process conditions showed the lowest wear rate and an adherent and plastically smeared tribolayer was formed on the worn surface.

6.1. Introduction

Laser-based additive manufacturing (AM) is developing rapidly as an advanced material processing technology [123, 176, 178]. In contrast to conventional “top-down” machining processes that remove material, AM is a “bottom-up” process that relies on material addition, producing parts from a feedstock through layer-by-layer shaping and consolidation. This allows the fabrication of many complex configurations using a computer-controlled laser beam source [237, 238]. AM processes, including the versatile selective laser melting (SLM), offer many advantages, including net-shape component fabrication directly from computer-aided design (CAD) models with high degrees of processing flexibility, and better material utilization rates [239, 240]. SLM can be used with metal powders to produce metallic components with complex shapes [53, 241] that cannot be achieved cost-effectively using conventional processes, such as casting, forging, or powder metallurgy. The flexibility of feedstock materials combined with high-energy fiber lasers, which exhibit high absorption ratios for metals [242], allow the net-shape fabrication of metal matrix composite (MMC) components with superior performance [121]. However, the full potential of SLM regarding material versatility has not yet been thoroughly investigated.

316L stainless steel is a widely used alloy for structural (e.g., aerospace and automotive), surgical tools and medical equipment applications due to its superior corrosion resistance, high ductility, and biocompatibility. However, 316L shows poor wear resistance and reduced mechanical performance at high temperatures, preventing its use in high-temperature and high-pressure applications [185, 186]. The performance of 316L can be improved by dispersing nanoscale hard ceramic reinforcements within the 316L matrix to produce a nanocomposite. Such ceramic reinforcements can improve the mechanical properties of the alloy composite by providing high specific moduli, hardness, and wear resistance [189, 234, 243, 244]. However, when using traditional manufacturing methods, such as casting or classical powder metallurgy, it is difficult to fabricate high-density nanocomposites without excessive grain growth. In such nanoscale MMCs, the nonhomogeneous dispersion of nanoparticles in the metal matrix, caused by the enhanced van der Waals kinetics of aggregation, could promote the formation of coarsened clusters or the disappearance of the original nanostructure [245], thereby degrading the mechanical properties. Therefore, it is necessary to develop a new method for processing nanocomposites with minimum coarsening of the nanoscale reinforcements and uniform reinforcement distribution in the matrix.

During SLM, molten materials experience non-equilibrium solidification because of the rapid heating and cooling of the laser-irradiated zone. The cooling rate in SLM can reach 10^5 K/s [246], while that in casting processes is approximately 10–70 K/s [247]. The solidification of the relatively small molten pool over a large metallic bed at a high cooling rate can create fine microstructures and lead to the homogenous dispersion of alloying elements in SLM-processed parts [53]. For these reasons, SLM may be appropriate for producing finely structured and well-dispersed MMCs. Producing nanocomposite components by SLM could generate new technological opportunities in high-value markets such as the aerospace industry for high-

temperature applications and could open new avenues for research. During industrial manufacturing, SLM could contribute to reducing lead times and costs, increasing processing capability, and permitting the fabrication of complex freeform geometries (i.e., near-net shape manufacturing technology with minimum machining) directly from CAD models. However, significant processing challenges still need to be overcome.

During SLM, thermal energy is repeatedly applied to the feedstock and hence the energy density affects the microstructure and properties of the fabricated parts. Furthermore, the SLM process is affected by molten-pool instability and process-induced defects, such as pores and lack of fusion, undesirable microstructures, and long processing times [248]. The high degree of shrinkage during the liquid–solid transformation creates considerable residual stresses and cracks in SLM-processed components. Moreover, melt instability may cause balling, or the spheroidization of the molten pool liquid (another common solidification defect in SLM) [249], which ultimately lowers the final density of the fabricated components.

The occurrence of such problems may relate to the stability, configuration, and thermal behavior of the molten pool during SLM [53, 250]. SLM processing parameters (spot size, laser power, scanning speed/laser exposure time, and layer thickness) and powder material properties (particle size, morphology, thermal conductivity, and liquid surface tension) largely determine the metallurgical nature of the molten pool and therefore the final microstructure and mechanical properties of the SLM-processed component.

Thijs et al. [233] suggested that the key parameters for microstructural evolution in the SLM process are the thermal gradient during cooling and the direction of heat flow in the molten pool. Ma et al. [251] indicated that homogeneous and more refined microstructures were obtained

using higher scanning speeds in direct laser fabrication because of the faster solidification rates. Simchi [252] demonstrated that densification in iron-based powders depended greatly on the processing parameters, including laser power, scan rate, layer thickness, and scan line spacing. Elsewhere, Simchi [253] showed that increased laser energy densities produced higher temperatures in the molten pools of iron-based powders, which in turn facilitated liquid pore filling. Kruth et al. [254] found that decreased scan speeds when processing 316L formed irregular molten pools, causing increased grain sizes and large pores. Gu and Shen [255] studied the balling behavior of SLM-fabricated 316L, demonstrating that the density could be optimized by controlling the processing parameters. Cherry et al. [256] investigated the kinetics of the balling phenomenon by varying the processing parameters to reduce balling in 316L components. Wang et al. [75] concluded that the applied laser energy density determines both the grain size and final density, which in turn affect the mechanical properties of the part. Ahmadi et al. [257], proposed a computational method to elucidate the relationship between the processing, microstructure, and properties, with emphasis on the grain size and melt pool in SLM-processed 316L samples.

The addition of ceramic nanoparticles to the 316L matrix may promote a different consolidation mechanism and microstructure from those previously reported in investigations of pure 316L, because of differences in the multiple modes of heat, mass, and momentum transfer, and chemical reactions during SLM [214]. The complex metallurgical phenomena involved in SLM, as discussed above, necessitate an investigation of the role of the laser energy density in the SLM process and the changes in microstructure and properties for a range of processing parameters. Hao et al. [131] demonstrated the feasibility of producing hydroxyapatite/316L composite parts by SLM, in which the additive imparted biocompatibility to the stainless steel composite. In Chapters 3 and 4, we discuss the fabrication of the 316L nanocomposite SLM parts reinforced with TiB_2 or

TiC, respectively, and reported improvements in the mechanical and tribological properties of 316L MMCs.

To the best of our knowledge, no previous study has comprehensively investigated the relationships between the processing conditions and the densification, microstructural evolution, and mechanical properties of SLM-processed TiC/316L nanocomposites. The objective of this study is to establish the relationships between SLM processing conditions and the resulting microstructural characteristics and mechanical properties of TiC/316L nanoscale MMCs to enable the reliable fabrication of nanocomposite parts with superior performance. TiC was selected as the reinforcing material due to its high hardness, good wettability, and thermodynamic stability with a steel matrix [244]. The crystal phases, densification behavior, and microstructural evolution of nanocomposite parts produced using a range of different SLM energy densities were studied here and the resulting mechanical properties of the parts were evaluated. The results may also provide a theoretical basis applicable to other laser-based processing techniques.

6.2. Experimental Procedures

6.2.1. Powder Preparation and SLM Processing

Gas-atomized 316L stainless steel powder (powder supplier: MTT Technologies GmbH) was used as the matrix material. The 316L powder had the particle size distributions of $d_{10} = 30.24 \mu\text{m}$, $d_{50} = 40.80 \mu\text{m}$, and $d_{90} = 56.25 \mu\text{m}$. The reinforcement material was nearly spherical TiC particles with an average size of 50 nm (powder supplier: US Research Nanomaterials, Inc.). The TiC/316L nanocomposite powder, containing 15 vol.% TiC was milled in a Pulverisette 4 vario-planetary mill using a ball-to-powder weight ratio of 5:1 and disk rotation speed of 200 rpm for 8

h. After ball-milling, the TiC nanoparticles were homogenously dispersed over the 316L particle surfaces, promoting favorable flowability (Figs. 6.1a and 6.1b).

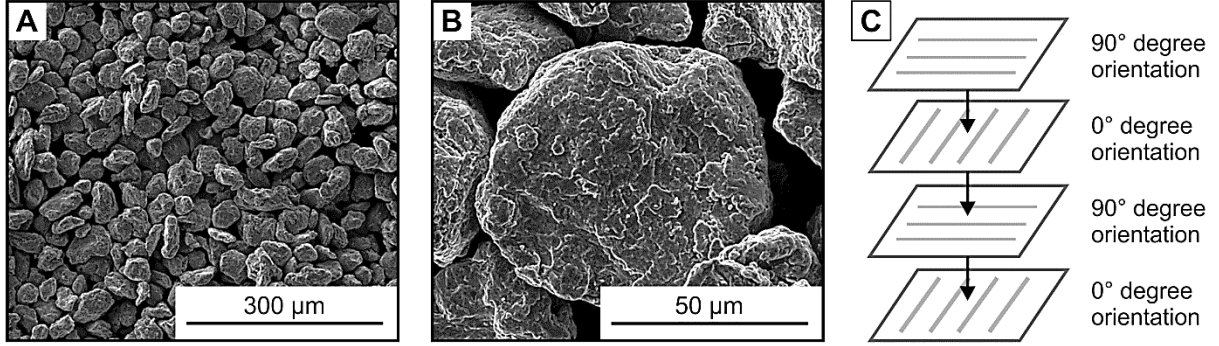


Figure 6.1: (a, b) TiC/316L nanocomposite feedstock after 8 h of milling, (c) “alternate-hatches” method of scanning.

The SLM system consisted of a fiber laser, automatic powder-layering apparatus, argon gas protection system to avoid material oxidation under high-temperature processing, and computer-based process control panel. The layering system deposited a powder layer with a thickness of 50 μm (d) on a carbon steel substrate. A constant laser power (P) of 100 W and spot size of 180 μm were maintained. Each layer was scanned once using an alternate-hatching scanning pattern with a hatch spacing (h) of 120 μm and a 90° rotation applied between consecutive layers, as shown in Fig. 6.1c. Higher final densities of SLM parts have been reported using this scanning method [254]. To vary the processing conditions, scan speeds (v) of 250, 133, 83, and 55.6 mm/s were selected in the SLM control program, corresponding to volumetric energy densities (η) of 67, 125, 200, and 300 J/mm³, as calculated using [258]:

$$\eta = \frac{P}{v h d} \quad (6.1)$$

Such processing conditions were used to assess the effect of laser energy input on the properties of the powder layer being processed. According to Eq. 6.1, η can be enhanced by increasing P or decreasing v , h , or d . Bulk cylindrical specimens of 10 mm diameter and 8 mm height were produced.

6.2.2. Microstructural Characterization

Phase analysis by X-ray diffraction (XRD) was performed using a PANalytical X'Pert PRO X-ray powder diffractometer with Cu K_{α} radiation at 40 kV and 40 mA in continuous-scan mode at $5^{\circ}/\text{min}$ over the 2θ range of $35\text{--}100^{\circ}$. The relative densities of the SLM-processed specimens were determined based on Archimedes principle. Specimens for metallographic assessments were prepared in accordance with standard practices, and etched using a Marble's Reagent for 10 s. The microstructures of the SLM-processed nanocomposite samples were examined from both top and side views using a Nano 230 scanning electron microscope (SEM). An FEI T12 transmission electron microscope (TEM) at 120 kV was used to examine the internal microstructures of the fabricated nanocomposites. The TEM samples were prepared via focused-ion beam (FIB) milling. Prior to electron backscatter diffraction (EBSD) characterization, the samples were polished with $0.25\text{ }\mu\text{m}$ diamond paste for 8 h. EBSD was used to study variations in the crystal orientation, grain boundary misorientation, and texture of the nanocomposites using both surface and cross-sectional imaging. An energy-dispersive X-ray spectroscopy (EDS) system with a primary energy of 20 kV and a step size of 40 nm was used to collect the EBSD scans, which were performed at a lower magnification to improve the statistical reliability of the data.

6.2.3. Mechanical and Tribological Properties

A Leco LM800AT micro-hardness tester was used for measuring the Vickers hardness values at a load of 0.2 kg and an indentation period of 10 s. Dry rotary wear tests were performed according to the ASTM G99 standard using a T50 ball-on-disk tribometer in air at room temperature. The specimen surfaces were ground and polished prior to wear testing to ensure identical surface roughness values. The counterface material was a 3-mm-diameter 52100 chrome steel ball, applied with a test load of 3 N. The friction unit was rotated at 840 rpm for 20 min and a fixed rotation radius of 2 mm. A ST 400 light profilometer with a vertical resolution of 8 nm, accuracy of 80 nm, and lateral resolution of 2 μm was used to measure the volume of materials lost (V). The wear rate (W) of the samples was then determined by: $W=V/(F L)$ ($\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$), where F is the contact load and L the total sliding distance.

The mechanical properties of the samples were also evaluated by uniaxial micro-compression tests of micro-pillars using an MTS Nanoindenter XP at room temperature and a strain rate of 10^{-4} s^{-1} . For such tests, micro-pillars were fabricated by FIB milling at 30 kV (FEI Nova600 Nanolab Dual-Beam FIBSEM); the pillars had an average diameter of 4 μm and an aspect ratio of 1:3. In the compression tests, a modified diamond indenter tip geometry, with a flat-end tip diameter of 10 μm , was used within a nanoindenter to probe the microscale mechanical behavior of the fabricated micro-pillars. Further details regarding this testing method can be found elsewhere [61, 135-137, 259]. At least four pillars were tested under each condition.

6.3. Results and Discussion

6.3.1. Phase Analysis

XRD spectra of TiC/316L nanocomposite parts processed using various SLM processing conditions are presented in Fig. 6.2. Strong diffraction peaks corresponding to the austenitic/ γ -Fe phase from the 316L steel were identified for all SLM-processed samples. In contrast to the results reported by Wang et al. [75], the high cooling rate associated with SLM processing forms the ferrite/ α -Fe phase. TiC peaks were observed for all samples, indicating the successful formation of TiC-reinforced 316L for all applied η values. In general, the TiC peaks were significantly broader and weaker in intensity than the 316L peaks, suggesting the formation of refined TiC crystallites and increased lattice defect concentrations in the SLM parts. Similar observations were reported in our previous work [234].

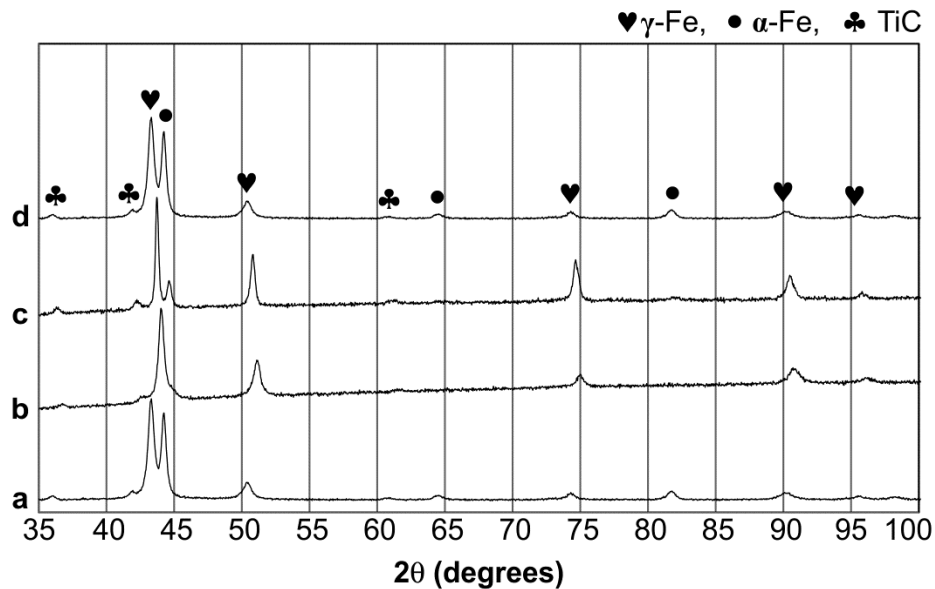


Figure 6.2: XRD spectra of SLM-processed TiC/316L parts produced using various laser energy densities (η): (a) 67 J/mm³; (b) 125 J/mm³; (c) 200 J/mm³; (d) 300 J/mm³.

Table 6.1 shows the changes in the 2θ locations for γ -Fe peaks with varying SLM energy densities. The standard diffraction peaks for the γ -Fe phase are located at $2\theta = 43.583^\circ$ and 50.792° . At the low v of 55.6 mm/s and corresponding high η of 300 J/mm³, the 2θ locations of the γ -Fe phase diffraction peaks were relatively close to those of the standard phase. As the applied v increased above 83 mm/s, the locations of the γ -Fe diffraction peaks shifted to higher 2θ values. At the highest v of 250 mm/s, the diffraction peaks for the γ -Fe phase broadened dramatically according to the measured full-width-at-half-maximum (FWHM). Scherrer's equation indicates the formation of refined crystallites in the TiC/316L nanocomposite under this SLM processing condition.

Table 6.1: Variation of 2θ locations and intensities of the γ -Fe diffraction peaks in SLM-processed nanocomposites with various applied energy densities

Sample	2θ location ($^\circ$)	Intensity (cts)	FWHM (rad)	2θ location ($^\circ$)	Intensity (cts)	FWHM (rad)
Standard	43.583			50.792		
67 J/mm³	43.2624	7052.73	0.5251	50.3578	1148.87	0.8419
125 J/mm³	43.3945	3319.69	0.4974	50.4142	1643.33	0.5508
200 J/mm³	43.6922	8111.84	0.2314	50.7568	3586.59	0.3942
300 J/mm³	43.6179	7727.91	0.2762	50.6550	2704.34	0.4934

With increased input laser energy density, the 2θ locations of the γ -Fe phase peaks in SLM-processed parts shifted to either lower or higher angles relative to the standard γ -Fe peaks. Decreased 2θ values indicate increased distances between adjacent lattice planes according to Bragg's law [260], attributed to the lattice distortion caused by laser-induced thermal stress and the distribution of TiC reinforcement particles in the matrix.

6.3.2. Densification Behavior

Figure 6.3 presents micrographs showing the strong effect of the applied laser scanning speed, and thus η , on the development of several types of laser-induced defects, such as porosity in terms of size and shape of pores, balling, and hot cracking; the relative density of the produced nanocomposites increased with increasing η .

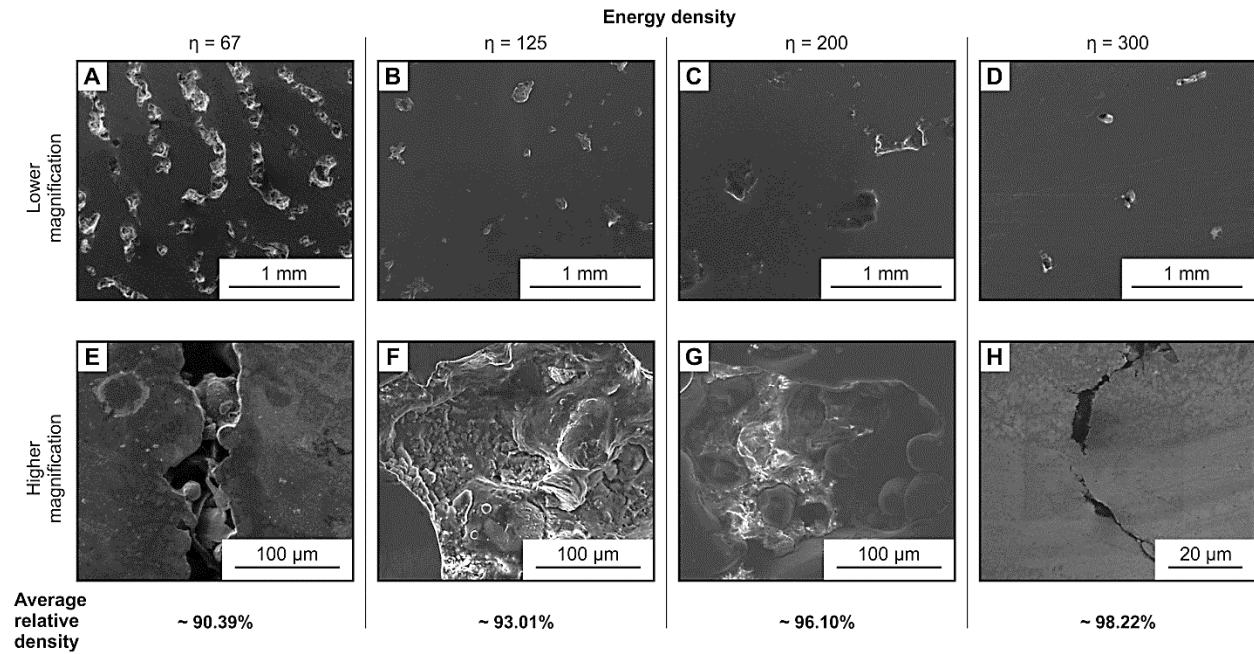


Figure 6.3: SEM micrographs showing the effect of processing laser energy density (η) on sample porosity. The above two rows of micrographs show the variations in the microstructure and porosity with the applied laser energy density. The bottom row quantifies the relative densities as a function of the laser energy density.

At $\eta = 67$, the sample reached its peak porosity (a relative density of 90.39%), with elongated pores, and clusters of microscale balls. The pores were irregular in shape, uniformly dispersed, and interconnected with a defined orientation along the surface. Notably, the majority of pores occurred in the layer boundaries, indicating that a low laser energy input may cause delamination

and the formation of horizontal cracks in the SLM specimen (Fig. 6.3e). This pore network comprised large cavities filled with loosely packed particles with an average diameter of 25 μm , including some residual unmelted feedstock particles, which resulted in the low density. Such features are attributed to the short dwell-time of the laser spot (low energy input) combined with the low penetration of the laser into the powder layer, leading to a relatively small and low temperature molten pool. In turn, these characteristics resulted in insufficient melting of the powder and melt flow instability (i.e., solidification before adequate metallurgical bonding), which reduced the contact area between the molten pool, metal powder, and substrate. Such behavior was also reported in earlier studies [238, 261]. In addition, the repeated rapid laser heating followed by high cooling rates resulted in the development of large internal thermal stresses in these areas, which promoted solid-state cracking. All of these mechanisms produced defects as a result of insufficient energy input, reducing the final relative density.

At lower η ($\leq 200 \text{ J/mm}^3$), the liquid solidification front was relatively disordered, producing interrupted scan tracks. A small number of balls also occurred between adjacent laser tracks (as indicated by the arrows in Fig. 6.3e, Fig. 6.3f). The balling effect causes inter-track pores between discontinuous scan tracks as the current layer is processed. In layer-by-layer SLM processing, balling prevents uniform deposition of fresh powder on the previously processed layers and promotes porosity due to poor interlayer bonding. At higher scan speeds, the balling phenomenon may arise from the large temperature difference between the powder melt layer and adjacent layers, which could cause melted particles to rapidly merge into larger droplets due to surface tension. The reduced heat transfer due to the addition of TiC to the 316L powder exacerbates this problem. Small liquid droplets splash from thin, discontinuous track surfaces, owing to the reduced surface energy of the liquid at short length scales. This results in the

development of numerous micrometer-scale spherical splashes around the surface that result in balls. Our observations of the balling phenomena and melt instability agree well with other studies [249, 255]. Klocke et al. [262] found that low laser powers and high scanning speeds could eliminate balling; however, partially melted parts were observed.

When η was increased to 300 J/mm^3 , the parts showed no significant pores or balling defects and the relative density increased to 98.22%, which was the maximum densification obtained in this study. Clear and ordered liquid solidification was observed, resulting in stable and continuous molten scan tracks with superior metallurgical bonding between adjacent layers compared to the lower η conditions. However, such a high energy input resulted in the formation of some fine spherical pores and thermal cracks, which prevented the parts from reaching complete densification. Garibaldi et al. [237] suggested that at high energy inputs, conduction mode welding is replaced by key-hole welding (which occurs during strong or unstable interactions between the laser and the melt pool) and is associated with surface vaporization of the feedstock material, resulting in gas bubbles that can remain trapped inside the melt pool during solidification. Substantial accumulated residual thermal stresses occur in SLM-processed parts during solidification, resulting in cracks. The principal formation mechanism of residual stresses in SLM parts is the shrinkage of the cooling molten top layer by thermal contraction being prevented by the previously processed solidified layers. Zhu et al. [263] showed that the thermal shrinkage of metals during laser melting increased with increasing laser power or decreasing scan speed. The formation of micro-scale hot cracks is attributed to the interruption of the liquid film at grain boundaries by tensile stresses during solidification [164]. A previous report [80] used both experimental and theoretical approaches to show that, in an SLM-processed part, tensile stresses form at the top and bottom surfaces of the part, with the intermediate area

subjected to compressive stress. Therefore, microcracks from tensile stress are generally located between two adjacent layers.

Fischer et al. [161] showed that the maximum increase in temperature within a laser-induced melt pool is given by:

$$\Delta T_{max} = \frac{2A\eta}{k} \left(\sqrt{\frac{k_{th} \tau_p}{\pi}} \right) \quad (6.2)$$

where A is the laser absorptivity, k the thermal conductivity, k_{th} the heat diffusivity, and τ_p the duration of laser irradiation. Higher η values result in a higher amount of the laser energy being converted into a temperature increase. A higher temperature produces sufficient heat transfer within the melt pool to enhance the binding of particles and promote densification.

The wettability between the TiC ceramic particles and the 316L matrix also affects the densification behavior of SLM-processed nanocomposite parts. For a system of reactive wetting of liquid metals on a ceramic phase, the equilibrium contact angle θ_{eq} can be approximated as [264]:

$$\cos \theta_{eq} = \frac{(\gamma_{sv} - \gamma_{sl})}{\gamma_{lv}} \quad (6.3)$$

where γ_{sl} , γ_{sv} , and γ_{lv} are the surface tensions of the solid–liquid, solid–vapor, and liquid–vapor interfaces, respectively.

The densification of the melt in SLM is controlled by the viscosity μ , which is strongly dependent on the operating temperature T, which can be calculated for a system of unreinforced 316L by [168]:

$$\mu = \frac{16}{15} \left(\sqrt{\frac{m}{kT}} \gamma \right) \quad (6.4)$$

where m is the atomic mass, k is Boltzmann's constant, and γ is the liquid surface tension of the steel.

At lower v values, the dwell-time of the laser beam on the powder increases, which increases the temperature of the melt pool (determined by the energy applied to the material; Eq. (6.2)), thereby decreasing the surface tension and viscosity (Eq. (6.4)). In contrast, the TiC particles in the 316L matrix increase μ significantly, which in turn reduces the melt flow and the overall rheological performance of the composite melt. Clearly, increasing the applied η increases T and decreases μ and γ_{sl} , which in turn decreases θ_{eq} (Eq. (6.3)). The wettability of the liquid metal is thereby enhanced, favoring the consolidation and densification of the SLM-processed MMC. Higher operating temperatures allow the formation of sufficient low viscosity liquid metal, resulting in sufficient fluidity to improve the metallurgical bonding between neighboring layers. A low v also maintains sufficient liquid-phase metal for a longer period, promoting metal flow and backfilling of shrinkage voids between dendrites [252]. However, high v causes greater convexity in the molten pool, i.e., a much higher wetting angle exists between the liquid and solid phases. This is ascribed to the increased μ at increased v . The dominant solid phase ultimately hinders molten pool flow, spreading, and wetting. For low η , incomplete melting combined with unfavorable wetting characteristics promoted balling, as demonstrated by Simchi and Pohl [265].

At high η , a sharp temperature gradient is developed between the center and edge of the molten pool by the applied Gaussian heat source of the laser. The temperature gradient increases the surface tension gradient in the melting pool and the consequent Marangoni convection [252]. The formation of convective streams in the pool increases the magnitude of the thermocapillary forces

(and their extent of penetration into the sample), causing liquid instability [71]. At higher v (low η values), Marangoni convection and liquid capillary instability both increase. The combined effects of Marangoni flow and poor melt flowability at high μ cause the melt to flow radially inward toward the melt pool center, instead of spreading on the underlying surface [214, 266]. The radial flow causes the liquid to spheroidize toward the center of the laser beam area, thereby promoting the formation of coarsened balls of solidified material (Fig. 6.3e) and the elongation of pores at layer interfaces. When multilayer processing is performed by increasing v while holding other parameters (laser power, scan interval, and layer thickness) constant, the melt pool is not large enough to completely fill gaps, thus increasing the porosity. In addition, previous layers are insufficiently remelted and do not bond well with the new layer (e.g., the poorly melted particles observed in Fig. 6.3e). Therefore, in SLM, the flow and wetting characteristics of the molten pool must be carefully controlled to obtain the desired structure.

6.3.3. Microstructure and Texture

6.3.3.1. Effects of the Applied η on the Distribution State of TiC

The microstructures of the SLM-processed TiC/316L parts produced at different η are shown in Fig. 6.4. The TiC nanoparticles have smaller grain sizes and a higher melting point than those of 316L stainless steel. They remain partially melted as impurity phases and act as nucleation sites for the molten stainless steel, facilitating heterogeneous nucleation and consequently causing further refinements [267]. All the different η values applied during SLM in this study were not sufficient to completely melt TiC because of its high melting point [214]. This is apparent from the TiC particles retaining their starting spherical morphology after SLM. However, the dispersion states of TiC are significantly influenced by the applied η . At low η , the TiC nanoparticles tend to aggregate into clusters, forming microscale agglomerates of

several nanoparticles formed in the matrix, as shown in Figs. 6.4a, 6.4e. As the applied η is increased to 125 J/mm^3 , the distribution of TiC reinforcing particles is improved, in which the TiC nanoparticles bonded with each other, forming continuous novel ring-like structures (Fig. 6.4b). High-magnification image, however, shows the presence of some nonhomogeneous TiC agglomerates in the matrix (Fig. 6.4f). When η is increased further to 200 J/mm^3 , the TiC reinforcements are uniformly and homogeneously distributed throughout the matrix (Fig. 6.4c) with no visible aggregation of TiC nanoparticles within the SLM-processed part, even when observed under high magnification (Fig. 6.4g); however, the grain size is increased markedly. At the highest η of 300 J/mm^3 , the TiC reinforcements remain uniformly distributed (Fig. 6.4d). Clearly, the development of the nanoscale TiC microstructure during SLM is sensitive to the applied η . In summary, at $\eta \geq 125$, the dispersion state of the TiC reinforcement is enhanced (i.e., uniform and homogeneously distributed in the matrix) but at the expense of obtaining comparatively coarse grain formation. Microstructural analysis (Fig. 6.4) demonstrates the ability to tailor the microstructure by using SLM processes with different η values: on decreasing the laser scan speed, and thus the degree of undercooling and solidification rate, SLM-processed MMC components with increasingly coarse microstructures were obtained.

The Marangoni convection within the molten pool, generated by the high temperature and surface tension [268, 269], induces a liquid capillary force that causes the rearrangement of TiC reinforcements. According to Arafune and Hirata [270], the intensity of Marangoni flow can be evaluated using the dimensionless Marangoni number (M_a):

$$M_a = \frac{\Delta\sigma L}{\mu v_k} \quad (6.5)$$

where $\Delta\sigma$ is the surface tension difference of Marangoni flow, L the length of the free surface, μ the dynamic viscosity, and ν_k the kinematic viscosity. The high temperature in the SLM process induced by the use of high η causes a sharp decrease in μ , which intensifies the Marangoni flow and turbulence within the melt pool as well as the resulting magnitude of the capillary force (see Eq. 6.5). This, in turn, increases the rate of nanoscale TiC rearrangement in the melt, preventing TiC aggregation and promoting a uniform dispersion in the solidified matrix (Figs. 6.4c and 6.4d).

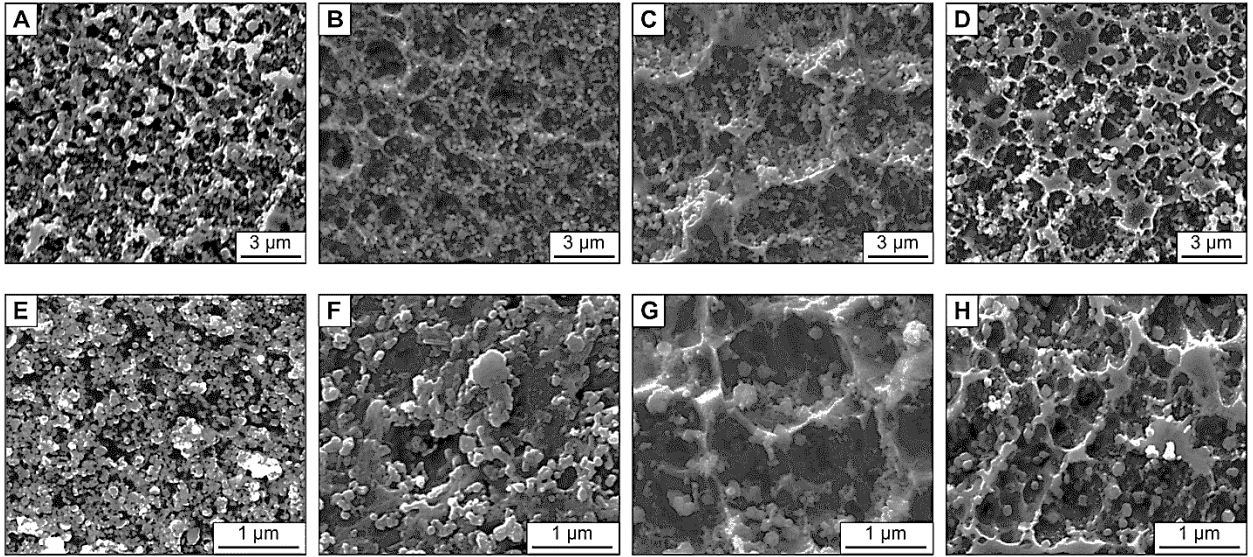


Figure 6.4: High-magnification SEM images showing the evolution dispersion states of nanoscale TiC reinforcement in SLM-processed TiC/316L nanocomposites at various applied laser energy densities (η): (a,e) $\eta = 67 \text{ J/mm}^3$; (b,f) $\eta = 125 \text{ J/mm}^3$; (c,g) $\eta = 200 \text{ J/mm}^3$; (d,h) $\eta = 300 \text{ J/mm}^3$.

Figure 6.5 schematically demonstrates simple mechanisms for varying the distribution states of TiC nanoparticles by decreasing the laser scan speed while keeping other processing parameters constant. In the laser-induced molten pool comprising TiC-reinforced and 316L melt particles

developed by SLM, a sharp temperature gradient was formed between the edge and center of the molten pool. This produces a surface tension gradient and the consequential Marangoni flow, which, in turn, induces a liquid flow for capillary forces [252]. Whenever capillary forces act on the TiC nanoparticles, a torque is generated around the particles because of the particle center misalignment [253]. The current torque leads to the rotation of the TiC nanoparticles within the pool, offering a likelihood of rearranging its distribution. It is known that the size of the temperature gradient determines the strength of capillary forces [251]. Moreover, an inadequate laser energy input seems to weaken both the SLM temperature gradient and the attendant capillary force intensity, which, in turn, is inadequate to reshuffle the TiC nanoparticles within the molten pool. Indeed, at a relatively high scan speed and resultant low η , it increases the solidification rate of the liquid front in the molten pool; therefore, there is a considerably short time for the thermal Marangoni flow to rearrange the TiC nanoparticles. As a result, the TiC reinforcing particle distribution state is significantly non-uniform because of the formation of some clusters of reinforcing particles at a comparatively low η of 67 J/mm³ (Fig. 6.5a).

When η is increased by decreasing the scanning speed, the rate of rearrangement of TiC reinforcing nanoparticles inside the molten pool increases because of Marangoni flow intensification (Eq. 6.5). The torque force constantly drives the TiC nanoparticles, which congregate around the core of the Marangoni flow pattern, forming a TiC ring-like structure. Meanwhile, repulsive forces tend to occur between the TiC reinforcing particles whenever an adequate quantity of 316L melt develops within the molten pool [254]. Although the converging flow pushes the TiC nanoparticles toward the center, the collective impacts of the repulsion forces and Marangoni flow develops a ring-like structure in the solidified matrix whenever an adequately high η (≥ 200 J/mm³) is applied. Under this condition, good wetting of TiC by the

liquid alloy enhanced the TiC dispersion state. Nonetheless, when η is increased excessively to 300 J/mm^3 , the TiC reinforcement ring structure shows obvious coarsening (Fig. 6.4d) because of the considerable thermal accumulation within the molten pool as well as the consequent grain growth and the large increase in TiC particle size.

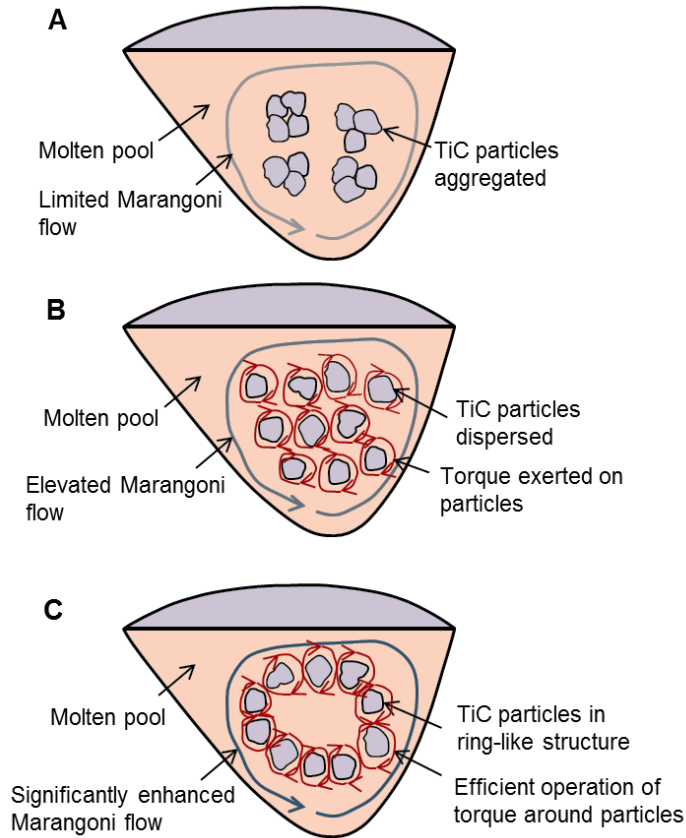


Figure 6.5: Schematic of the movement mechanisms of TiC nanoparticles in the melt pool under various scanning speeds: (a) high scan speed; (b) moderate scan speed; (c) low scan speed.

6.3.3.2. Effects of the Applied η on the TiC Particle Size

In addition to the influence of the applied η on the TiC dispersion state within the matrix, the applied η also affects the evolution of the nanoscale TiC particle size by changing the undercooling degree and the resulting solidification rate. Figure 6.6a and b show TEM

micrographs of the nanocomposites fabricated under low and high η and show whether the applied η affects the TiC particle size. At high scan speeds, η is low, which increases the solidification rate of the liquid front within the molten pool, causing large temperature gradients within the pool and high degrees of undercooling of the melt. Typically, the time available before solidification is insufficient for TiC grain growth, leading to the favorable formation of refined TiC nanostructures (Fig. 6.6a). By examining the TEM image (Fig. 6.6a), we can confirm that the TiC nanoparticles relatively maintain their initial refined size of ~ 60 nm.

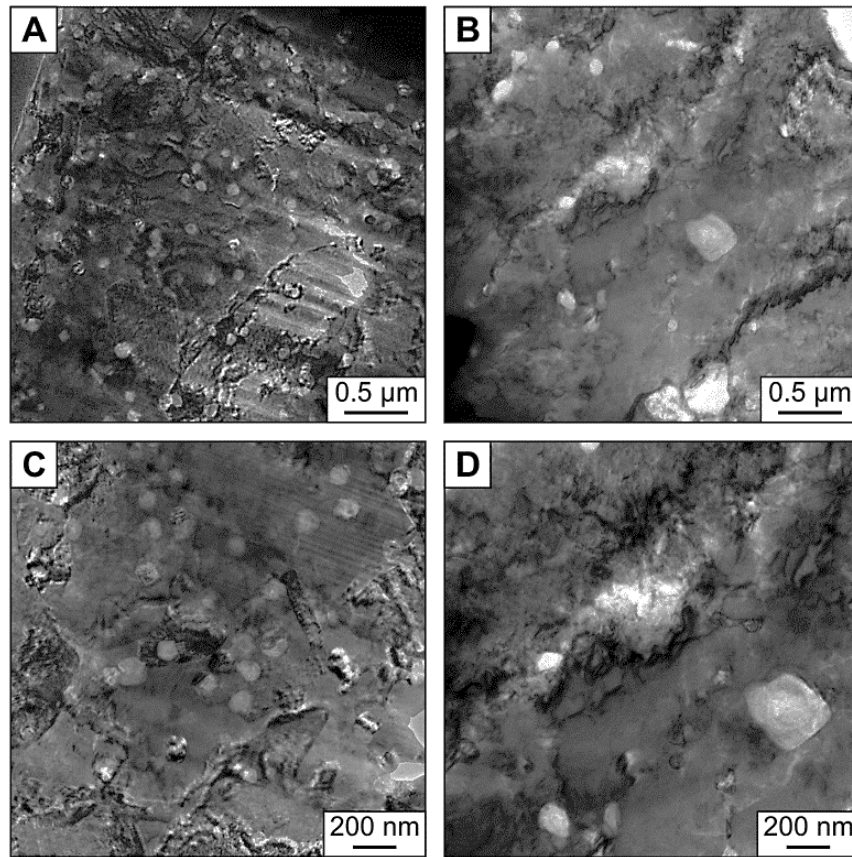


Figure 6.6: TEM images showing the TiC particle size of SLM-processed TiC/316L nanocomposites obtained at (a, c) $\eta = 67 \text{ J/mm}^3$; (b, d) $\eta = 300 \text{ J/mm}^3$. Notice the size of the nearly spherical TiC particles at the interface as well as an increase in the dislocation density of the 316L austenitic matrix.

At the lowest scan speeds in this study, on the other hand, η is high; hence, the temperature in the molten pool increases, resulting in significant thermal accumulation within the molten pool. Because of the ensuing rapid temperature increase, heat conduction through the substrate is avoided. The longer molten time and the slower cooling rate significantly enhance the activity of grains within the TiC nanoparticles in the molten pool, allowing grain growth for some of the TiC particles. The statistical results show that some of the TiC particles in the fabricated nanocomposite with η of 300 J/mm^3 become very coarse and lose their initial standard nanostructure, reaching a value of $200 \text{ }\mu\text{m}$ (Fig. 6.6d). Apart from this, the matrix of the composite shows an increased dislocation density (Fig. 6.6d). The Orowan bypassing of hard fine particles by dislocations, which contributes to composite strengthening, is clearly revealed by the TEM image (Fig. 6.6d). It is known that the grain boundaries and particle/matrix interfaces are major sources of dislocations because of the large differences in thermal expansion coefficient between TiC and 316L. At higher η , particles are more homogeneously distributed, creating a larger number of particle-matrix interfaces. Under these conditions, all particle clusters are broken, further increasing the number of such interfaces. At higher energy densities, more grain boundaries are available, increasing the total number of dislocation sources.

6.3.3.3. Microstructural Examination by EBSD

The EBSD orientation image maps, as shown in Fig. 6.7, qualitatively describe the morphology and size of the grains as a function of the energy density. The inverse pole figure (IPF) shown in the middle of the Fig. 6.7 illustrates the relationship between the colors used in the EBSD maps and the crystal orientations in the SLM-processed samples. The laser energy density determines the size of the molten pool; longer periods of focused laser irradiation result in larger and deeper

molten pools (compared to shorter irradiation times). Pools formed during a previous scan may also experience partial re-melting. Repeating the scanning process causes the formation of well-aligned periodic melt pools. Therefore, the applied energy density significantly affects the grain size and orientation of SLM-processed parts.

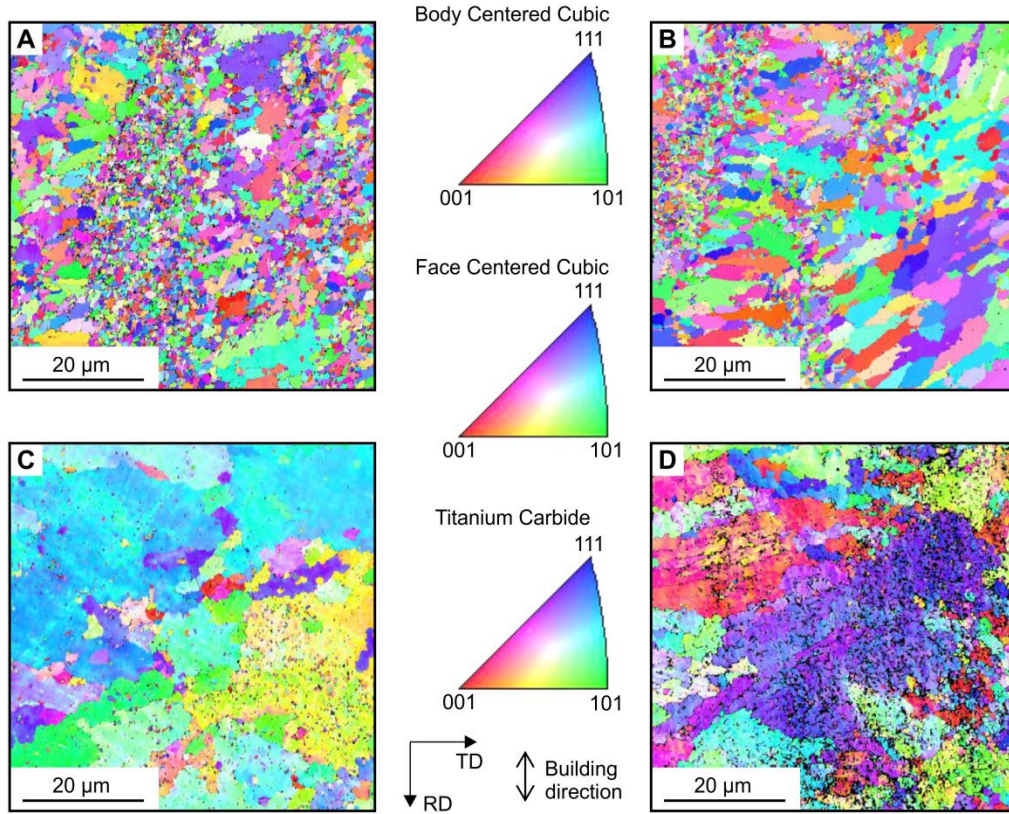


Figure 6.7: EBSD orientation maps of SLM-processed TiC/316L nanocomposite parts produced using different laser energy densities (η): (a) 67 J/mm^3 ; (b) 125 J/mm^3 ; (c) 200 J/mm^3 ; (d) 300 J/mm^3 .

Figure 6.7a shows a decrease in the area of the red regions in the EBSD map and an increase in the area of the green regions compared to Fig. 6.7c, indicating a weakening of the (001) orientation and a strengthening of the (100) orientation in the nanocomposite samples. Along the

building direction (BD), the preferential $\langle 001 \rangle$ orientation is predominant and appears well ordered at lower η values. However, the crystallographic orientation appears partially disordered at higher η values because of the repeated partial melting and solidification caused by heat diffusion from the top building layer. The heat flux is maximum normal to the fusion line; hence, cellular dendrites would theoretically grow perpendicular to the melt pool boundary. However, here we observed cellular dendrites growing in different directions as their orientation is influenced the crystal structure in addition to the heat flux direction.

The sample processed using $\eta = 67 \text{ J/mm}^3$ showed a mostly equiaxed morphology and a very fine grain size, which is attributed to the rapid cooling rate. A clear increase in grain size was observed for the sample processed using a higher η of 125 J/mm^3 . This is again due to the higher energy density producing a larger melt pool, resulting in a lower thermal gradient and cooling rate of the melt pool and subsequent coarsening of the microstructure. A further increase in the energy density resulted in the grain size reaching a relatively stable plateau. The laser input has the ability to create a stable melt pool at a high temperature; the grain size will not depend on scan speed in this case, which results in a similar trend.

Niendorf et al. [271] suggested that high energy inputs could tailor the microstructures of SLM materials by inducing the growth of large columnar grains with distinct orientations. However, microstructural refinement is directly correlated to η and the resulting cooling rates. The thermal gradient (G), solidification rate (R), and cooling rate ($T = G \times R$) determine the fineness of the grains [272]. Higher T values (i.e., for lower η or higher scanning speeds) create finer microstructures. Since the SLM process generates extremely high cooling rates of $\sim 10^6 \text{ K/s}$, very fine microstructures can be achieved in SLM-processed nanocomposites. However, using a higher η /lower scanning speed can reduce the cooling rate, resulting in grain growth.

The cooling rate of the molten pool in the laser engineered net shaping (LENS) process is also applicable to SLM processing and can be given as follows [273]:

$$\frac{\Delta T}{\Delta t} = \frac{\alpha_{\lambda} Q \sqrt{V}}{d^2 \sqrt{2\rho c k d}} \quad (6.6)$$

where $\frac{\Delta T}{\Delta t}$ is the cooling rate of the molten pool, α_{λ} is the absorptivity at the laser wavelength λ , k is the thermal conductivity, ρ is the density of the metal, c is the specific heat, Q is the laser power, V is the scanning velocity of the laser beam, and d is the diameter of the molten pool. Hence, it can be seen that the applied energy density plays a major role in controlling the cooling rate of the molten pool, which is proportional to the square root of the scanning velocity. Hence, the grain size and orientation of SLM-processed nanocomposites (and subsequent mechanical properties) can be tailored by varying the applied energy density.

6.3.3.4. Texture Development

The directional solidification in the SLM molten pool creates a crystallographic texture, in addition to the morphological texture described in section 6.3.3.1. Figures 6.8a and 6.8b show the pole figures of the γ -Fe phase when processed at low and high energy densities, respectively, considering the side view of the specimens. The pole figures quantify the texture intensities for the three crystallographic direction groups $\langle 001 \rangle$, $\langle 101 \rangle$, and $\langle 111 \rangle$. 316L stainless steel has a cubic structure; hence, the evolution of epitaxial growth in the (001) texture parallel to the building direction is favored [233]. The general texture of both samples was a complex composite cluster of textures (edge-on-cube and fiber textures), which resulted in anisotropic behavior, as predicted by Tayon et al. [274]. The fiber texture in both samples was a result of grains oriented parallel to the heat flow direction; the predominant direction of

heat flow was from the melt pool to the substrate as this had the maximum temperature gradient. However, more importantly, the maximum texture intensity was found to increase with increasing total energy input; the sample processed using an energy density of 300 J/mm^3 showed almost fourfold the maximum value as that of the sample processed using 67 J/mm^3 . This was due to a larger amount of partial remelting when a higher energy density was applied, which in turn enhanced the smoothness of the deposited layers. This suggests that increasing the laser energy density increased the texture intensity.

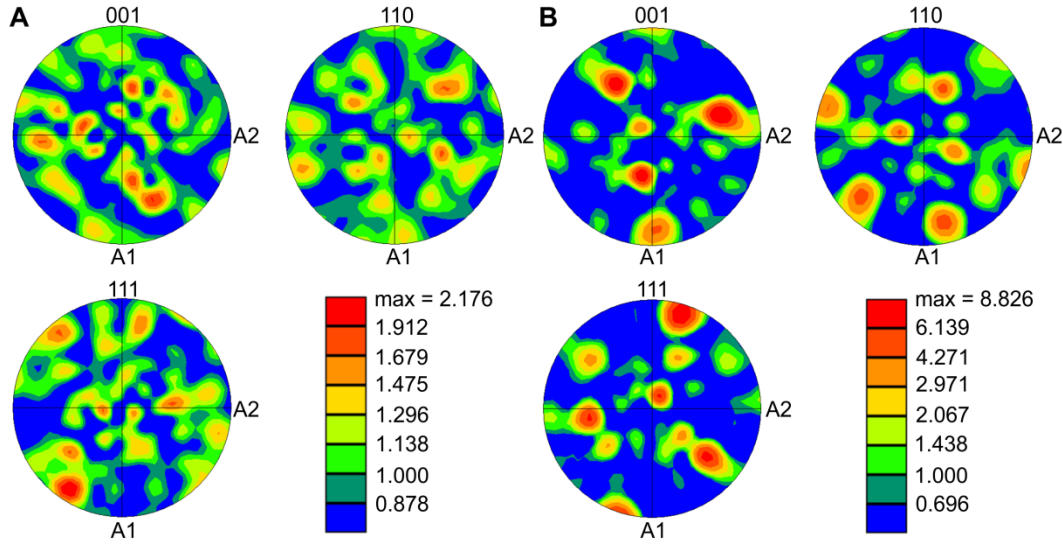


Figure 6.8: Pole figures of the γ -Fe phase in the SLM-processed TiC/316L parts produced using different laser energy densities (η): (a) 67 J/mm^3 ; (b) 300 J/mm^3 . Notice that the maximum texture intensity of the SLM sample processed at 300 J/mm^3 was almost fourfold that of the sample processed at 67 J/mm^3 .

A low-energy-density laser with a larger cooling rate results in a relatively weakly textured fine-grained structure, so more nuclei are developed which grow in random directions. However, high-energy-density lasers trigger the elongation of columnar grains with high aspect ratios

parallel to the building direction. The direction of heat flow determines texture evolution; when high energy inputs create relatively large molten pools with low thermal gradients, the variations in values related to local conditions, i.e., G and R , are less pronounced [233]. These results demonstrate that the crystallographic textures of 316L nanocomposites can be tailored by manipulating the SLM processing parameters.

6.3.4. Mechanical Properties

6.3.4.1. Microhardness and Wear Performance

Figure 6.9 depicts the effect of the applied energy density on the microhardness values measured on the polished cross-sections of SLM-processed TiC/316L parts. The incorporation of TiC particles into the 316L matrix (average hardness of 316L ~ 215 HV_{0.1}) indeed showed increase in the hardness values, irrespective of the applied η . The hardness is influenced by variations in heating and cooling rates at various energy densities. The hardest samples were obtained at the highest scanning speed and lowest energy density (67 J/mm^3). The increased hardness is associated with the increased microstructural fineness, per the Hall-Petch relation, as observed in EBSD imaging (Fig. 6.7a). Above the energy density of 67 J/mm^3 , a sharp reduction in hardness occurs because of the increase in the grain size.

Examination of Fig. 6.9 shows that SLM processing at higher energy densities causes two opposing effects on the hardness values of the processed parts. The reduced scanning speed improves layer melting, which improves binding between the molten particles, creating higher densification, reduced porosity, and hence better mechanical properties. At lower scanning speeds and higher energy densities, the melting pool is enlarged and the thermal gradient reduced, causing lower thermal and residual stresses, which decrease the hardness of the

sample. The higher temperature of the melt pool and the lower cooling rate also increase the grain size because of the longer melt time, which reduces hardness per the Hall-Petch relation. However, the homogenous distribution of TiC particles throughout the matrix enhances the hardness.

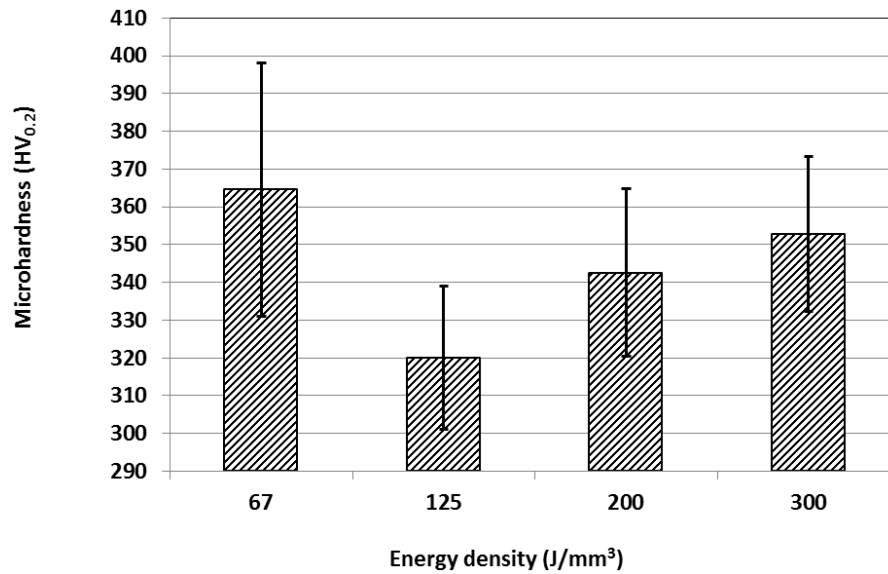


Figure 6.9: Effects of the applied laser energy densities (η) of SLM-processed TiC/316L nanocomposite parts on microhardness.

Furthermore, the grain refinement caused by rapid solidification after laser melting favors increased hardness. Song et al. [126] proposed that the high mechanical strength of SLM-processed specimens was related to grain fineness and high dislocation densities resulting from high cooling rates, while Abe et al. [275] suggested that high porosities caused low ductility in SLM samples. These reports demonstrate the competition within the SLM component between layer melting and grain size growth. In some cases, therefore, the microhardness values of SLM nanocomposites increase with increased laser energy input. At lower energy densities,

grain coarsening causes decreased hardness, but the increased relative density obtained at higher energy densities can increase hardness.

Figure 6.10 shows variations in the average wear rate values of the SLM-processed TiC/316L nanocomposites parts. The values do not always have a direct relation with the hardness of the nanocomposite. The samples processed using the highest scanning speed and lower η exhibit the highest wear rates of $3.106 \times 10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, attributable to the limited densification level and pore formation relative to that of the other samples. At this low η , the TiC nanoparticles form clusters within the metal matrix, causing poor microstructural homogeneity. The pores and nanoparticle aggregates are both prone to cracking under stress concentrations during sliding. This forms debris, which separates from the wear surface when the expanded cracks become connected, resulting in significant increases in the wear rate.

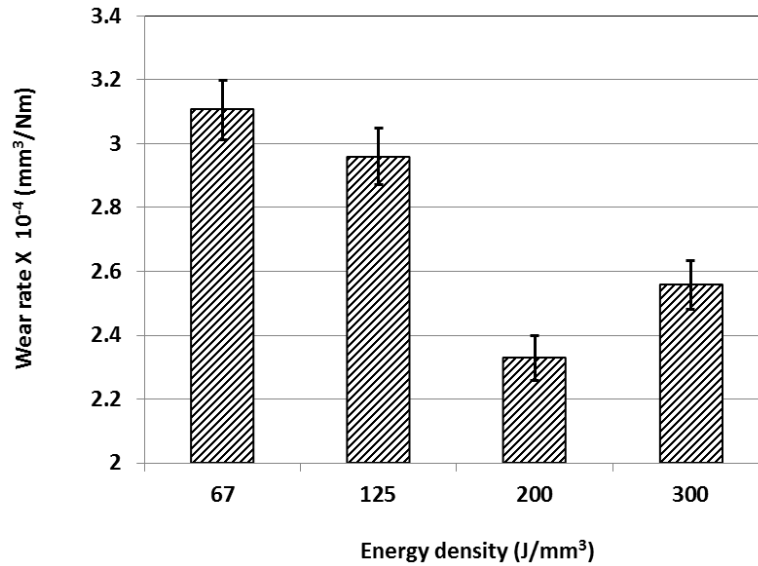


Figure 6.10: Effect of the applied laser energy densities (η) of SLM-processed TiC/316L nanocomposite parts on average wear rate.

Detailed SEM studies of the worn surfaces of the tested samples are shown in Fig. 6.11. At low η , the wear surface is disrupted, comprising deep parallel grooves from abrasion wear, large-sized agglomerates, and some ultrafine nanoscale particles. The presence of irregular fragments at the groove edges reveal severe local deformation, delamination, and surface plowing during sliding.

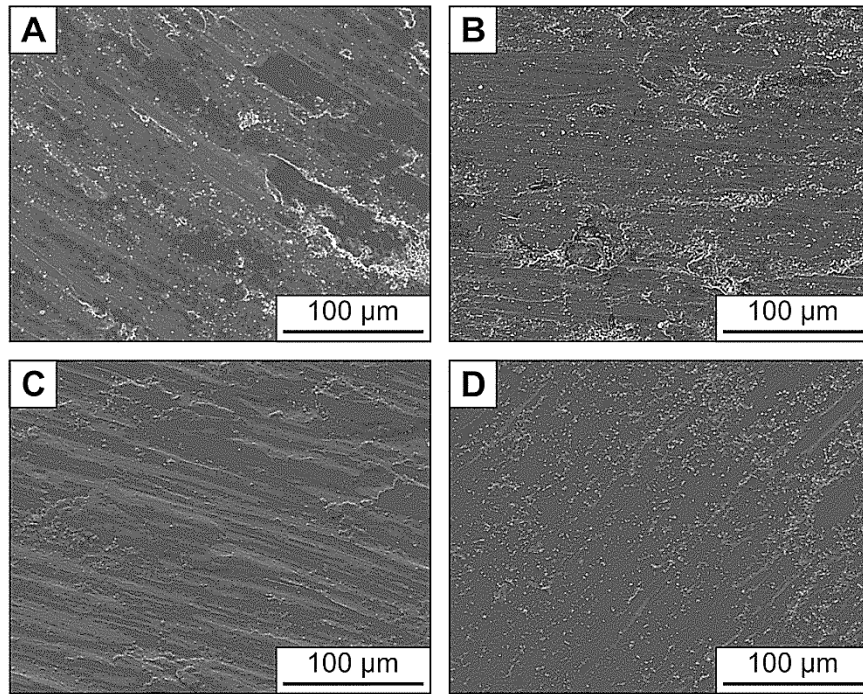


Figure 6.11: SEM images showing typical morphologies of the worn surfaces of TiC/316L parts processed at (a) $\eta = 67 \text{ J/mm}^3$, (b) $\eta = 125 \text{ J/mm}^3$, (c) $\eta = 200 \text{ J/mm}^3$, and (d) $\eta = 300 \text{ J/mm}^3$.

On increasing η to 125 J/mm^3 , some abrasive fragments remain on the worn surface but no agglomerates of nanoparticles are visible in the matrix (Fig. 6.11b). The worn surface shows much shallower grooves with localized deep portions, free of any loose abrasive fragments. This is accompanied by an attendant wear rate of $2.959 \times 10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ (Fig. 6.10).

For $\eta = 200 \text{ J/mm}^3$, the worn surface of the SLM-processed sample becomes smooth with reinforcing nanoparticles embedded in the adhesive tribolayer. An adherent and strain-hardened tribolayer completely covers the worn surface of the sample. The lowest wear rate of $2.328 \times 10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ (Fig. 6.10) are obtained in this sample.

The TiC/316L nanocomposite part produced at optimum η demonstrates superior wear performance. It is reasonable to suggest that, since the TiC reinforcement is homogeneously dispersed in the SLM-processed part, material removal during the sliding tests by abrasion changes to tribolayer adhesion. This transition is expected to reduce the wear rate in the sliding tests. This transition to tribolayer formation is attributed to the uniform distribution of nanoscale TiC reinforcements with lower interfacial stresses in the matrix, preventing nanocomposite breakage during sliding [118]. Because of the improvement in densification and increased hardness of this sample, the protective tribolayer is easily smeared plastically on the worn surface [174]. The proposed transition from material removal to tribolayer adhesion supports the reduced wear rate during sliding.

When η is increased further to 300 J/mm^3 , although some localized tribolayer formation is observed on the worn surface, it shows severe spalling and delamination. Deep parallel grooves form on the worn surface, which also shows the appearance of irregularly shaped debris and plowing after sliding. The wear mechanism, in this instance, is micro-plowing, rather than adhesion. Some large-sized reinforcing particles are observed at groove edges on the worn surface. The obtained average wear rate of $2.558 \times 10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ (Fig. 6.10) are slightly higher than those of the sample processed at 200 J/mm^3 . The severe localized plowing of the surface during sliding caused a slight increase in the wear rate attributed to the coarse microstructure, which split during sliding.

Under the proper η , the nanoscale TiC reinforcements are uniformly distributed in the matrix (Figs. 6.4c and 6.4g). During sliding wear, the homogeneously dispersed ultrafine TiC particles stick together, driven by small reinforcement/matrix interfacial stresses. Friction on the surface causes plastic deformation, which produces a strain-hardened layer of refined TiC nanoparticles on the wear surface (Fig. 6.11c), improving the wear properties. At higher η , although the densification level is maintained, TiC loses its nanostructure during SLM (Fig. 6.6b). The coarsened TiC particles are thus prone to spalling and splitting under sliding. The plowing action between the TiC particles and 316L matrix occurs with tangential force, producing the deep grooves on the surface that suggest limited wear performance (Fig. 6.11d).

6.3.4.2. Micro-Compression Properties

Figure 6.12 shows the engineering stress–strain curves of the compressed micro-pillars. The as-fabricated stainless steel processed using an energy density of 67 J/mm^3 exhibited a higher compressive yield strength compared to that of the sample processed at 300 J/mm^3 . This difference in strength is consistent with the two materials having different relative densities (Fig. 6.3) and microstructures (Fig. 6.4). The improved high yield strength is attributed to the fine microstructure (Hall–Petch relation); a high dislocation density and large residual stresses resulting from the rapid solidification could also play a role. The enhanced strengths of the SLM-fabricated TiC/316L nanocomposites are attributed to various strengthening mechanisms imparted by the TiC particulates: (1) no wetting problems, so loads are shared by the retained reinforcements; (2) dislocation pinning by TiC particles; (3) grain boundary strengthening. These mechanisms fall within elemental-addition and rapid-solidification strength refinement behavior. Notably, the compressed pillars exhibited high ductility due to the highly ductile nature of the

austenitic 316L matrix and the excellent interfacial metallurgical bonding that retains the overall ductility in the composite.

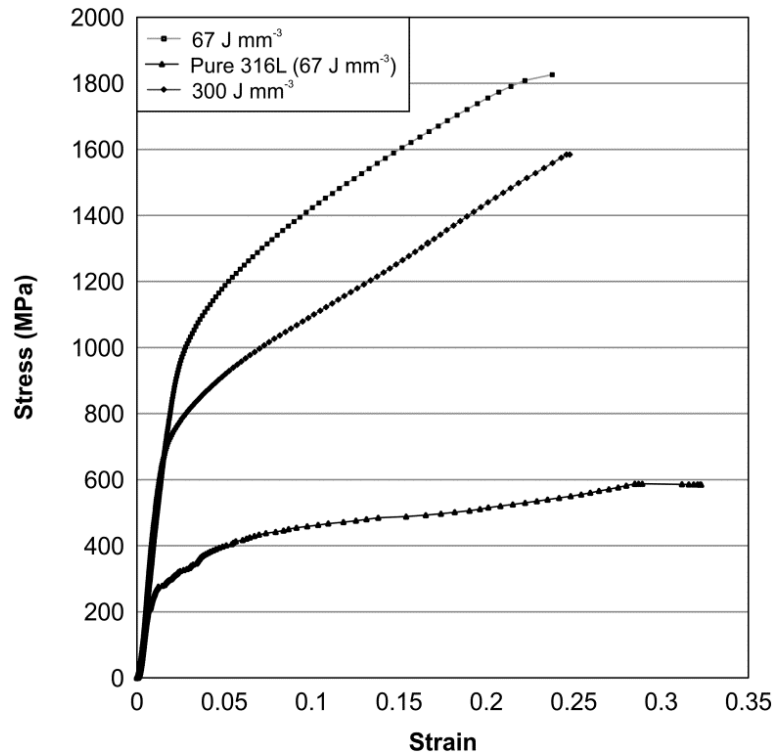


Figure 6.12: Microcompression stress-strain curves of unreinforced 316L stainless steel and nanocomposite pillars.

6.4. Conclusions

The investigation of the phase constituents, densification behavior, microstructural evolution, and mechanical properties of TiC/316L nanocomposite parts produced using SLM demonstrated that this method is suitable for fabricating such materials within a wide range of processing conditions. The following conclusions were obtained from this study:

1. The final relative density of SLM-processed TiC/316L parts depended on the applied scan speed and the corresponding energy density. All porosity, balling, and cracking defects were

related to the selection of inappropriate laser processing parameters, which in turn lowered the density of the nanocomposites. Using a low η of 67 J/mm³ produced a disordered liquid solidification front resulting in large pores and balling defects from enhanced liquid instability due to Marangoni convection. Using a high η of 300 J/mm³ resulted in maximum densification, although some fine porosity and thermal cracking were observed due to low liquid viscosity, the liquid phase existing for a long period, and high thermal stresses. Variations in the thermo-kinetics and thermo-capillary characteristics within the molten pool, such as the viscosity, wettability, and liquid–solid rheological properties, all influenced the densification behavior.

2. The distribution state and particle size of nanoscale TiC reinforcement in a 316L matrix could be tailored by regulating the laser energy density used during SLM. In this study, increasing η from 67 to 300 J/mm³ homogenizes the dispersion of nanoscale TiC reinforcing particles from agglomerates, while causing significant coarsening of the TiC particle size and the partial disappearance of the reinforcement nanostructure.
3. The grain orientations and crystallographic textures of SLM-processed components can be tailored by controlling the applied energy density (which affects the grain size due to variations in the thermal history and degree of cooling of the molten pool). The microstructures of the SLM-processed nanocomposites showed significant coarsening with decreased laser scan speed, caused by the decreased kinetic cooling rate. Our results also showed that increasing the applied energy density intensified the crystallographic textures.
4. Both microhardness and wear rate were influenced by the densification degree, the grain coarsening due to lower cooling rate, and the size and dispersion state of TiC particles in the matrix. The nanocomposites processed under optimum process conditions ($\eta = 200$

J/mm³) showed the lowest wear rate of $2.328 \times 10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$. An adherent and plastically smeared tribolayer was formed on the worn surface.

5. The compressive yield strength obtained for the sample processed using η of 67 J/mm³ was higher than that obtained for the sample processed using η of 300 J/mm³ because of grain refinement, despite the lower density of the former. Ductility was high for all samples owing to the soft nature of the austenitic 316L matrix and good interfacial metallurgical bonding.
6. These findings could provide the basis for optimizing the energy densities used in fabricating 316L nanocomposite components (using SLM or other laser-based materials processing technologies) in order to achieve materials with particular grain structures and mechanical properties for various applications.

Chapter 7

In-Situ Formation of Novel TiC-Particle-Reinforced 316L Stainless Steel

Bulk-Form Composites by Selective Laser Melting

Abstract

A 316L-Ti-graphite powder mixture was ball-milled for 4 h and subsequently processed by the additive manufacturing process of selective laser melting (SLM). TiC particles were formed in situ within the 316L stainless steel matrix through a laser-induced reaction via a nucleation-growth mechanism from the melt. The mechanisms underlying the formation of the TiC particles by SLM were elucidated. The effects of the applied laser energy density (η) on the densification, microstructure, and mechanical properties of the SLM-processed parts were investigated. It showed that the TiC phase was completely formed at energy densities higher than 67 J/mm^3 . Sub-stoichiometric TiC_{1-x} was formed as a result of the fast cooling rate, which prevented carbon atoms from diffusing completely into the TiC crystal lattice. Scanning electron microscopy images showed that TiC particles were uniformly distributed within the 316L matrix after processing; the specimens underwent grain coarsening with the decrease in the cooling rate that is controlled by the scanning speed. The composite sample processed using low η suffer from porosity and limited densification due to poor wettability characteristics. An optimum densification of 98.88% was obtained at η of 300 J/mm^3 . The microhardness and wear resistance were both influenced by the densification level and grain size of the matrix. The wear tests revealed that the TiC/316L composites processed using η of 100 J/mm^3 possessed the lowest wear rate of $1.31 \times 10^{-4} \text{ mm}^3/\text{Nm}$. The worn surface indicated that the high wear resistance was due to the formation of adherent and strain-hardened tribolayer.

7.1. Introduction

316L stainless steel alloys are of great use in industry because they possess superior ductility and excellent corrosion resistance. However, the applicability of these alloys is hindered by their limited strength and wear resistance at both ambient and high temperatures [185, 186, 276]. To overcome this problem, 316L alloys can be strengthened by dispersing hard and fine ceramic particles uniformly within the alloy matrix [244, 277]. Among the various ceramics used to reinforce steel alloys, TiC is particularly attractive for its excellent properties such as a high melting temperature (~ 3430 K), high hardness (2859–3200 HV), high Young's modulus (~ 440 GPa), low density (~ 4.93 g/cm³), good corrosion resistance, and high chemical stability at elevated temperatures [147, 187, 204]. The resulting increase in strength of the alloys is due to the dispersed particles decreasing dislocation movements within the alloy matrix. These metal matrix composite (MMC) materials exhibit superior physical and mechanical properties, such as high thermal stability, fatigue strength, and wear resistance, making them suitable for applications in the automotive, aerospace, and biomedical industries [179].

7.1.1. Ex-Situ vs. In-Situ MMCs

In most cases, reinforcing powders are directly added to the metal matrix to create ex-situ composites. However, in such composites, the interface between the reinforcing particles and the metal matrix is often a source of weakness because of the difference in thermal expansion coefficients of the matrix and reinforcement. When ceramic particulates are incorporated by ex-situ processes, thin oxide layers are formed on the surfaces of the particulates. These oxide layers affect the quality of particulate bonding with the metal matrix and may cause cracks that can propagate from the interface into the matrix [115, 278-280].

To overcome these problems, several attempts have been made to develop in-situ-formed MMCs, in which the reinforcements are synthesized through a chemical reaction among the starting elemental materials themselves [281]. In-situ composites require fewer processing steps, since the reinforcement materials are formed during intermediate steps. In contrast with ex-situ composites, the ceramic reinforcements formed during in-situ processing are finer, more thermodynamically stable, and more uniform in size distribution in the metal matrix [118, 282-284]. As a result, the reinforcement-matrix interface within in-situ MMCs is generally cleaner and more compatible because it does not undergo gas adsorption or oxidation, promoting stronger interfacial bonding and improved mechanical properties in the final products. The composite matrix is generally strong enough to transfer stress to the reinforcement phases, increasing the bulk strength [285, 286]. As a result, the in-situ MMCs often show better service properties.

7.1.2. Fabrication of MMC Components by Conventional Methods vs. Additive Manufacturing

Bulk-form MMCs with in-situ-formed reinforcements are commonly processed by conventional manufacturing methods such as powder metallurgy [287] or casting [288]. However, the high melting points of MMCs can impair the production of full-density components. Indeed, in conventional manufacturing processes, issues such as gas entrapment, limited interfacial wetting characteristics between metals and ceramic particles, agglomerations of the reinforcement phases within the matrix, and interfacial microcracking arise regularly. In addition, these processes require expensive single-purpose equipment, such as molds and dies, which hinders the application of MMCs in small-volume manufacturing or components with complex shapes. The preprocessing and post-processing steps of conventional manufacturing processes also increase the lead time and

the cost for fabrication. Therefore, it is important to find a new processing method for fabricating complex-shaped MMCs parts to deal with these problems.

Recently, the use of laser-based additive manufacturing (AM) to consolidate metal powders into three-dimensional shapes of unlimited complexity has attracted attention for industrial production. Selective laser melting (SLM) is a newly developed AM technique that allows the building of parts in a layer-by-layer manner, using a moving laser beam that selectively fuses and consolidates thin layers of a loose powder [68, 289, 290]. The SLM process affords high flexibility in materials selection and can be used to produce complex-shaped parts from MMC materials [131, 154], which is difficult to accomplish using conventional methods. The SLM process produces in-situ MMCs after almost completely melting the starting materials, which causes an in-situ reaction [291, 292] involving multiple modes of heat, mass, and momentum transfer via the laser scanning process [293]. The highly nonequilibrium nature of laser processing in SLM allows the possibility of creating unique fine microstructures [53]. However, for in-situ-synthesized composites, the prediction and control of the formation of in-situ phases and microstructures remains difficult during SLM. The energy density of the laser used may directly affect the densification level, microstructure, and mechanical properties of the in-situ-fabricated composites; therefore, it is essential to understand and successfully manipulate the laser energy during the SLM process.

7.1.3. Present State of Knowledge in Laser Processing of In-Situ MMCs and Outline of the Chapter

The fabrication of novel in-situ MMCs via laser processing has been demonstrated previously. Choi and Mazumder [294] used laser cladding to synthesize in-situ Fe-Cr-C-W composites in order to produce a novel wear-resistant material. The composition and volume fraction of carbides in the composite were controlled by adjusting the preheating temperature, power density, and

scanning speed during the laser melting process. Borkar et al. [295] laser-deposited TiC-reinforced Ni-matrix composites in situ and reported improvements in the tribological properties of the composites. Zhong et al. [296] produced in-situ TiC particles reinforcing a NiAl intermetallic matrix by laser metal deposition. Gu et al. [297] developed in-situ TiC particle-reinforced Ti–Al matrix composites by mechanical alloying (MA) and reported on SLM behavior. Gu et al., in another study [291], were able to produce bulk-form TiC/Ti₅Si₃ in-situ composites by SLM of SiC/Ti as-milled powder using various applied energy densities. They showed that the applied energy density played a major role in controlling the microstructural features as well the densification and mechanical properties of the SLM-processed composites. Lu et al. [298] produced TiC in situ in a Cu matrix by SLM using a CO₂ laser. All of these studies showed the feasibility of producing in-situ TiC particles to reinforce various metal and intermetallic matrices to provide elevated performance. However, as far as the author knows, there exists no published research on in-situ TiC- reinforced 316L matrix by SLM. The microstructure and mechanical properties are largely dependent on the processing parameters (i.e., variation in the thermal history and melting pool size leads to variation in the final microstructure and mechanical properties of the produced components). It is therefore important to investigate the SLM processing parameters and the metallurgical mechanism involved in order to produce TiC-reinforced 316L composites with high densification and optimum properties.

In this study, we examined the feasibility of synthesizing TiC particles from pure Ti and pure C in situ as reinforcements for a 316L stainless steel matrix. The feedstock powders obtained after 4 h of ball-milling were processed by SLM. The TiC particles were synthesized by a direct reaction between elemental Ti and graphitic C powders during SLM, and the changes in the densification degree, phases, microstructure, and mechanical properties of the components produced using

different laser energy densities were studied. We proposed a mechanism to explain the synthesis formation of the TiC particles within the 316L matrix by SLM. We believe that the in-situ fabrication of MMCs by the alternative route of AM is a promising method to produce cheaper components that fulfill the increasing demand for high performance with their superior properties.

7.2. Experimental Procedures

7.2.1. Powder Preparation

The starting powder materials used (powder supplier: Atlantic Equipment Engineers) were the following: water-atomized 99.9% purity 316L powder with irregularly shaped particles of $\sim 44\ \mu\text{m}$ in size (Fig. 7.1a), 99% purity Ti powder (99% Ti, $< 0.038\ \text{Ni}$, $< 0.0033\ \text{Al}$, $< 0.029\ \text{C}$, $< 0.002\ \text{Mo}$, $< 0.05\ \text{Fe}$, $< 0.029\ \text{Si}$) with polygonal particles of $\sim 10\ \mu\text{m}$ in size (Fig. 7.1b), and 99.95% purity graphite powder with a mean particle size of $2\text{--}12\ \mu\text{m}$ (Fig. 7.1c). A mixture of 90 vol.% 316L, 8 vol.% Ti, and 2 vol.% graphite powders (94.7 wt.% 316L, 4.8 wt.% Ti, 0.5 wt.% C) was ball-milled in nitrogen for 4 h using a Pulverisette 6 planetary high-energy ball mill. The milling conditions and parameters used are listed in Table 7.1.

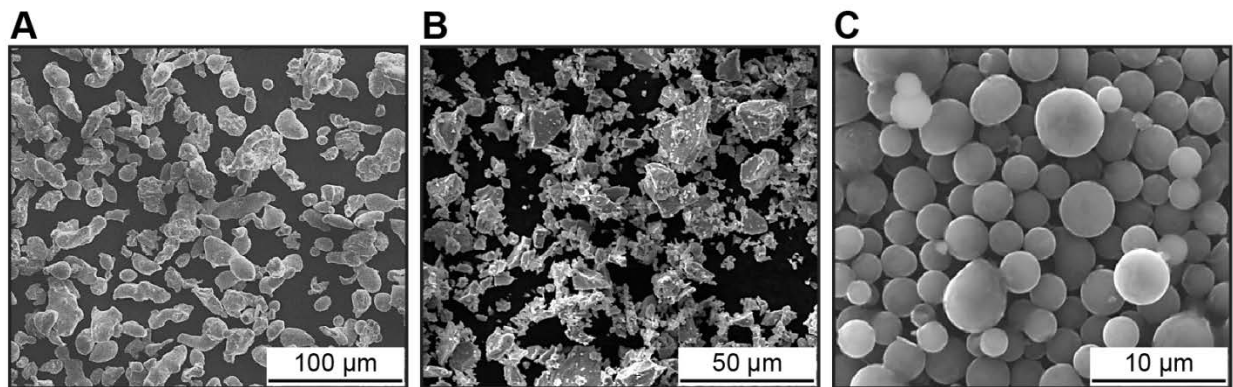


Figure 7.1: SEM images of (a) 316L stainless steel powder; (b) Ti powder; (c) graphite powder.

Table 7.1: Milling conditions used for powder preparation

Material of milling vessel	Eagle PSF-12; 4.8” outer diameter × 10” long
Grinding ball material	440C stainless steel
Ball size	1/4”
Rotation speed of main disc	82 rpm
Ball-to-powder weight ratio	9:1
Milling time	4 h
Milling environment	Nitrogen
Milling mode	2 h ball milling followed by 10 min interval

7.2.2. SLM Processing

The milled powder was used as feedstock and processed using the SLM parameters (model name: MCP HEK REALIZER II) listed in Table 7.2. The scanning was performed in an alternate-hatching pattern using a power (P) of 100 W. This means each layer was scanned once, before the scanning laser was rotated by 90° and scanning the second layer. A powder layer thickness (d) of 50 μm and hatch distance (h) of 120 μm were applied. The scan speed (v) was varied periodically to 250, 166.7, 83, and 55.6 mm/s using the SLM control program in order to change the laser energy density. The volumetric energy densities η were determined using the following expression [258]: $\eta = \frac{P}{vhd}$. (7.1)

Table 7.2: SLM processing parameters

Power	Layer thickness	Spot size	Hatch spacing	Atmosphere
100 W	50 μm	0.18 mm	0.12 mm	Argon

Four different volumetric energy densities of 67, 100, 200, and 300 J/mm³ were used to determine the laser energy delivered to the powder layer being processed. The specimens produced were cylinders with dimensions of 8 mm × 10 mm.

7.2.3. Microstructural Characterization

The phases of the feedstock powders and the SLM-processed parts were identified using X-ray diffraction (XRD) analysis using a PANalytical X'Pert PRO diffractometer. Cu K_α radiation was applied at 40 kV and 40 mA in the continuous scan mode. In order to improve the accuracy of the measurements, all the scans were performed at a low scan speed of 1.156 °/min. The densities of the SLM-processed specimens were measured using the Archimedes principle. The SLM-processed samples were cut, ground, and polished using standard metallographic procedures and then etched with Marble's Reagent for 10 s to prepare them for metallographic examination. The microstructures of the SLM-processed composite specimens were examined using a Nova 230 scanning electron microscopy (SEM) system.

7.2.4. Mechanical Properties

A LECO microhardness tester (LM800AT) was used to measure the Vickers hardness values of the specimens. The load used was 200 g, while the indentation time was 10 s. Dry-sliding wear tests were performed on the specimens using a HT-500 ball-on-desk tribometer at room temperature. The surfaces of all specimens were ground and polished prior to the wear tests. A high-carbon chrome (GCr15) steel ball bearing with a diameter of 3 mm was used as the counterface material, and the test load applied was 3 N. The friction unit was rotated at 560 rpm for 20 min with a rotation radius of 2 mm. The wear volume (V) was determined using a profilometer, and the corresponding wear rate (w) was calculated using the formula $w = \frac{V}{FL}$, where F is the contact

load and L the sliding distance [299]. Finally, SEM was used to study the morphologies of the worn surfaces of the SLM-processed specimens.

7.3. Results and Discussion

7.3.1. Densification Behavior

Figure 7.2 shows the variation in the relative density of the fabricated composites as a function of the applied energy density. The micrographs in Fig. 7.2 present the effects of the laser energy density input on porosity and pore morphology. Clearly, the applied energy density has a major influence on the densification. The results showed that samples obtained with laser energy input $\eta \leq 200 \text{ J/mm}^3$ are characterized by large pores of irregular shape. Increasing the energy input to 300 J/mm^3 promotes reduction of the irregular pores while spherical minor pores are retained. Nevertheless, the sample processed using 300 J/mm^3 exhibited the highest densification.

The cross-sectional microstructures of the components fabricated at 67 J/mm^3 contained significant unmelted particle clusters, and many interconnected pores and cavities of $\sim 20 \mu\text{m}$ on average were formed. It is possible that with a combination of low milling time and low applied energy density, that the particles became agglomerated. Lu et al. [298] suggested that the graphite powder generated during the SLM process vaporizes; the graphite also burns away under the high-energy laser before it reacts fully with Ti, contributing to the high porosity. When η was increased to $100\text{--}200 \text{ J/mm}^3$, slight improvement in densification was observed; the densification level was increased from $\sim 93.12\%$ to $\sim 94.22\%$.

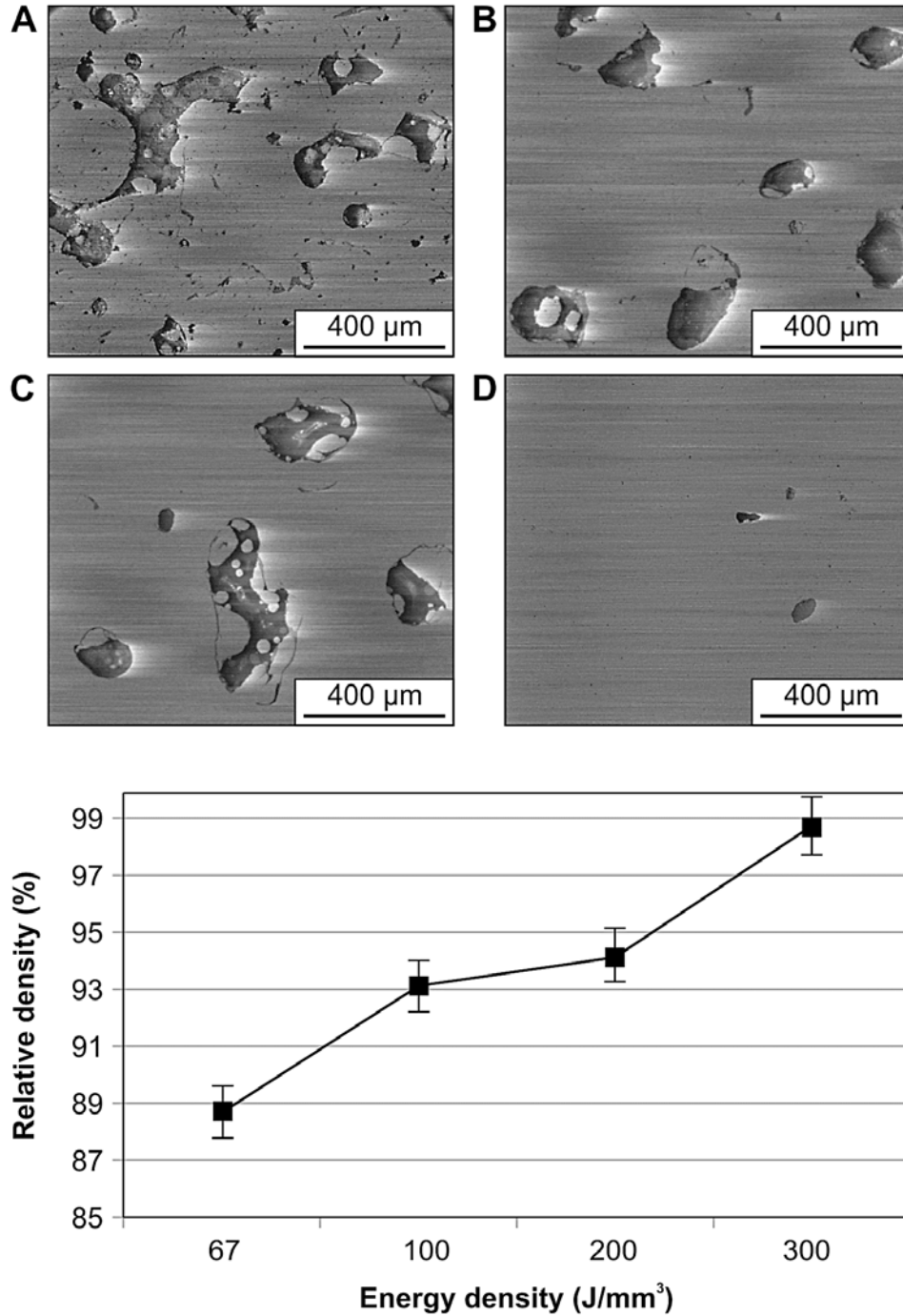


Figure 7.2: Influence of the energy density on the relative density of SLM-processed composites. (a) 67 J/mm³, (b) 100 J/mm³, (c) 200 J/mm³, (d) 300 J/mm³. The top panel shows low-magnification micrographs of different SLM samples, with relative density against laser energy density input shown in the bottom panel.

During SLM processing, in general, the densification level of the fabricated components is determined by the wettability of the precipitated TiC phase on the residual Ti–C–316L liquid phase. Porosity arises from the poor wettability of 316L with the in-situ-formed TiC. For a reactive wetting system of liquid metals on ceramic phase, the wettability is predominated by the formation of ceramic phase during processing. The equilibrium contact θ_{eq} angle can be approximately written as [7]:

$$\cos \theta_{eq} = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (7.2)$$

where γ_{sl} , γ_{sv} , and γ_{lv} are the surface tensions of the solid-liquid, solid-vapor, and liquid-vapor interfaces, respectively. Thus, liquid-solid wettability can be enhanced by lowering the contact angle, favoring sufficient consolidation of the composite system during SLM.

The dynamic viscosity (μ) of the molten pool can be defined by [168]:

$$\mu = \frac{16}{15} \left(\sqrt{\frac{m}{kT}} \gamma \right) \quad (7.3)$$

where m is the atomic mass, k is the Boltzmann constant, T is the temperature, and γ is the liquid surface tension.

As a considerably high η is applied during SLM, the resultant higher T and lower γ_{sl} both result in a decrease in μ , according to Eq. 7.3. Therefore, when the applied laser energy is relatively low, the melt viscosity increases, while the wetting characteristics deteriorate. The dynamic viscosity must be low enough so that the melt can be well-spread on the previously processed powder layer to prevent balling phenomena and other defects. In addition, the SLM process induces a sharp thermal gradient across the surface between the center and the edge of the melt pool,

leading to a surface tension gradient as well as the Marangoni convection process [169]. The Marangoni flow combined with low wettability causes the melt to spheroidize instead of spreading outwards on the underlying surface [70]. As well, shrinkage rate increases during solidification, and hence, a large amount of thermal stresses tend to develop in the solidified samples. Detailed processing maps are necessary in order to predict and control the as-built microstructure and optimize the properties of the bulk composite.

7.3.2. Phase Prevalence

Figure 7.3 shows the XRD pattern of the starting feedstock powder and SLM-processed composite parts formed using various applied energy densities. Strong diffraction peaks indexed to γ -Fe and α -Fe, corresponding to 316L, are seen clearly; very small peaks of Ti were also observed for the feedstock powder (Fig. 7.3a). The disappearance of C-related peaks after 4 h of milling is attributed primarily to the low amount of C in the initial powder mixture; a similar observation was made by Wu et al. [300]. The brittle C can be easily crushed during milling; the resulting small fragments would be trapped in the Ti or 316L powders, which may also hinder detection [301]. In addition, the mass X-ray absorption coefficient for Cu K_{α} radiation by C is very small; this causes great difficulty in detecting C by XRD, especially if it is present as small fragments trapped in Ti or 316L particles.

After processing using low energy density (67 J/mm^3), diffraction peaks indicating the initial presence of Ti remain present, suggesting that the applied energy density is insufficient to complete TiC formation (Fig. 7.3b). The low peak intensity of TiC phase is primarily due to the low amount of the initial Ti and C elements.

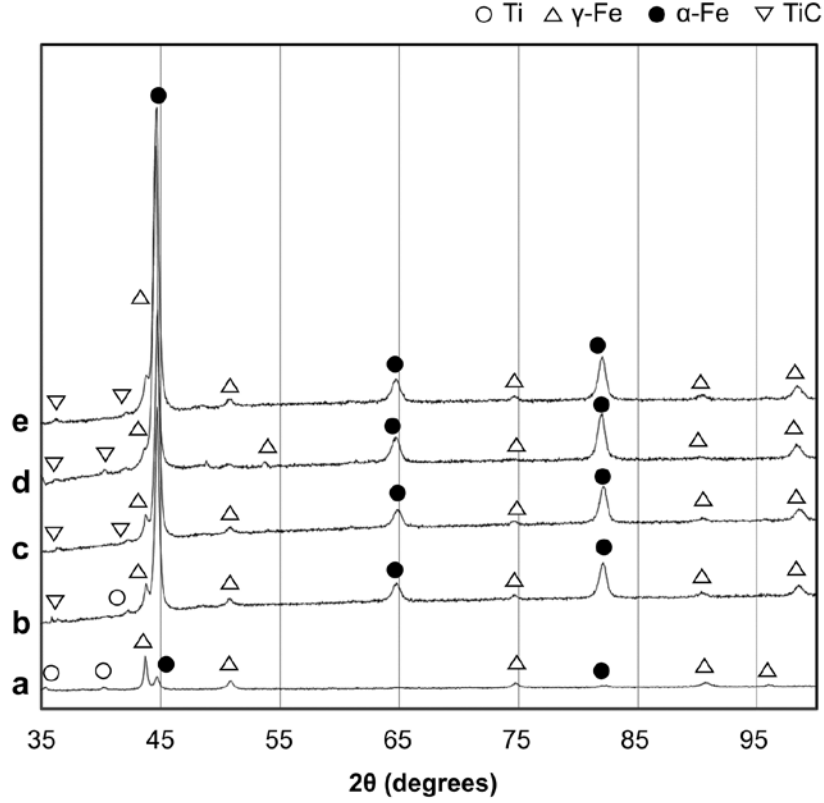


Figure 7.3: XRD patterns of the (a) starting feedstock powder and SLM-processed samples at various energy densities (η): (b) 67 J/mm^3 ; (c) 100 J/mm^3 ; (d) 200 J/mm^3 ; and (e) 300 J/mm^3 .

With decreases in the scanning speed and therefore increases in the energy density, the interaction time or energy input per unit time between the laser beam and milled powder increases, as does the energy input per unit length and the temperature of the SLM molten pool. This means that sufficient time and energy are provided to accomplish the reaction between the precursor elements, leading to the presence of complete TiC formation and absence of any secondary reaction as indicated by the XRD peaks (Figs. 7.3c, 7.3d, and 7.3e).

Notably, some incompletely reacted carbides are still present (not shown here) after processing with the lowest energy density $\eta \leq 67 \text{ J/mm}^3$. This phenomenon is eliminated when the scanning speed is

decreased. This is because there is sufficient time for the reaction between C and Ti elements to complete. Therefore, some residual Ti-indexed peaks occur when the powder is processed at a higher scanning speed and low energy density of $\eta \leq 67 \text{ J/mm}^3$. Similar behavior has been reported by Yang et al. [302] during the in-situ processing of TiC by laser cladding. However, when using a higher energy density in the SLM process ($\eta \geq 100 \text{ J/mm}^3$), the diffraction peaks related to the elemental Ti and C phases disappear completely, indicating that the in situ reaction was completed. Ti and C appear to have reacted within the molten 316L pool and form a TiC phase. Therefore, we can conclude that the energy density of the laser used during the SLM process can also be used to control the types and prevalence of phases in the final product. Furthermore, the diffraction patterns contain no peaks corresponding to Ni-Ti phases either, suggesting that no reaction occurs between the Ni and Ti during the SLM processing. The synthesis of the TiC phase is described further in section 7.3.4.

7.3.3. Microstructural Evolution

Figures 7.4 and 7.5 shows post-etching metallographic images of the samples that were SLM-processed using different energy densities. In general, the 316L matrix exhibits a ring-like structure with fine and well-bonded TiC particles that are homogeneously and uniformly dispersed along the grain boundaries and within the grain of the 316L matrix when it is formed. During the solidification process, the impurities are pushed to the grain boundaries. This explains why the presence of these phases is especially high in these regions. The results of the XRD analyses (Fig. 7.3) and SEM micrographs (Fig. 7.4) confirm the presence of reinforcing TiC particles in the SLM-processed samples.

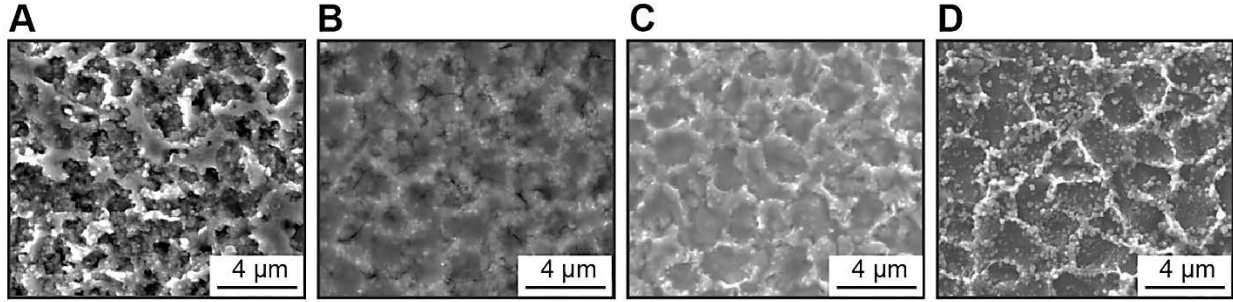


Figure 7.4: SEM images showing characteristics of etched microstructures of SLM-processed parts at various applied energy densities. (a) 67 J/mm³, (b) 100 J/mm³, (c) 200 J/mm³, (d) 300 J/mm³.

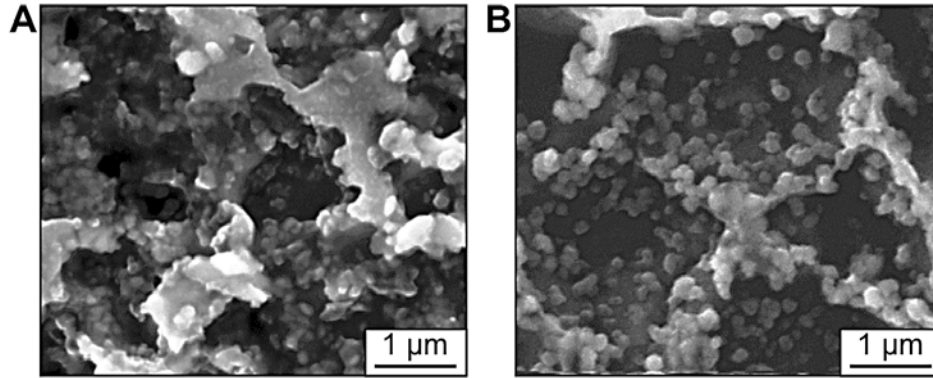


Figure 7.5: SEM images showing high-magnification characteristics of etched microstructures of SLM-processed parts processed using energy density of (a) 67 J/mm³, (b) 300 J/mm³.

Further, the composites show increased grain coarsening with increases in the applied energy density. This is as a direct result of the decrease in the cooling rate (i.e., the decrease in the scan speed results in a decrease in the cooling rate). Wang et al. [303] used welding models (which assumed nucleation is complete and that grain growth is controlled by diffusion) to quantify the effect of the directed energy deposition processing conditions on grain size. The grain growth rate in the heat affected zone (HAZ) at a given temperature T can be described as:

$$g^2 = k_1 \alpha \tau \exp\left(-\frac{Q}{R T_p}\right) + g_0^2 \quad (7.4)$$

where g_0 is the initial grain size, T_p is the peak temperature, and α and τ are defined as:

$$\alpha = \sqrt{\frac{2\pi RT_p}{Q}} \quad \text{and} \quad \tau = \frac{q/v}{2\pi\lambda e} \frac{1}{T_p - T_0} \quad (7.5)$$

where q/v is the linear heat input, q is the laser power, v is the laser scanning speed, λ is the thermal conductivity, T_0 is the preheat temperature, and τ is the time to heat from T_0 to T_p .

The above equations showed that increasing temperature, with a linear heat input, resulted in the growth of larger grains.

The SEM images indicate that the composites formed using higher energy density exhibited enhanced TiC distribution state in the matrix relative to the composites formed using the lower energy input. The reinforcing TiC particles are spherical and less than 100 nm in size (Fig. 7.5b). The in-situ reaction is typically exothermic and a higher temperature results in better wetting characteristics (relative to ex-situ composites). The rapid cooling during the SLM process restricts subsequent particle growth.

For samples processed at the lower energy density of 67 J/mm³, the TiC does not completely form, and an inhomogeneous microstructure is obtained (Fig. 7.5a). Because of the high viscosity and resultant poor flowability of the melt, the arrangement rate of the in situ formed TiC particles in the molten pool is restricted. Notably, during the low-energy-density input, significant microscale segregation of the elements is seen, creating a non-uniform elemental distribution and indicating the incomplete formation of a single TiC material and the presence of unprocessed Ti and/or C powders, supporting the observations from XRD analysis. Wu and Chen [304] indicated that there is a critical beam scanning speed, corresponding to the transition of trapping to pushing of reinforcing particles by the advancing solid/liquid interface. Trapping leads to a

uniform distribution of particles, while pushing leads to non-uniform distribution of particles. Accordingly, the particles segregation can be controlled by optimizing the SLM parameters.

7.3.4. Synthesis of TiC Particles by SLM

In this section we propose a mechanism for the formation of TiC–316L composites by the SLM processing of Ti–C–316L mixture powders. In the SLM process, the energy gained by the powder can be controlled by the applied laser scanning speed, which affects the temperature gradient [79]. When using a high scanning speed and the resultant low energy density, the obtainable SLM temperature is low, which significantly decreases the diffusion velocities of Ti and C in the melt. When a laser is scanned over the powder layer, the powder absorbs energy through both bulk and powder coupling [161]. Localized short-duration (< 4 ms) thermal cycles develop [293], causing rapid heating in the powder particles. The large amount of energy delivered by the fiber laser increases the temperature of the particles, causing the complete reaction of elemental Ti and C in the starting mixture with no residue.

The reaction between Ti and C to form TiC is characterized by a high activation energy and high heat of reaction. This reaction occurs readily to form the final products as the reaction is very exothermic. The probable reaction for the formation of TiC and the accompanying changes in the enthalpy and Gibbs free energy can be considered to correspond to two temperature ranges as shown below [298]:



When $T < 1,939$ K,

$$\Delta H = -184,571.8 + 5.042T - (2.425 \times 10^{-3}T^2) - (1.958 \times 10^6/T) \quad (7.7a)$$

$$\Delta G^\circ = -184,571.8 + 41.382T - 5.042T \ln T + (2.425 \times 10^{-3}T^2) - (9.79 \times 10^5/T) \quad (7.7b)$$

and when $T \geq 1,939$ K,

$$\Delta H = -160,311.5 + 24.79T - (2.732 \times 10^{-3} T^2) - (1.862 \times 10^6/T) \quad (7.8a)$$

$$\Delta G^\circ = -160,311.5 - 186.97T - 24.79T \ln T + (2.732 \times 10^{-3} T^2) - (9.31 \times 10^5/T) \quad (7.8b)$$

That ΔG° is always negative in the equations shown above indicates the high probability of TiC formation.

The TiC reinforcing particles can be formed in situ by a direct reaction between powders of elemental Ti and graphite. Since Ti reacts with many materials at high temperatures, in-situ-formed reinforcing particles containing Ti can be obtained readily. For instance, Lu et al. [298] were able to form TiC in situ in a Cu matrix fabricated by SLM. They reported that the change in the temperature by reaction heat was 3,210 K. Since a CO₂ laser does not generate enough heat to melt Cu, the melting occurs by the heat conducted from Ti and that generated by TiC formation. However, in the Al-Ti-C system, in-situ TiC formation occurs at the lower temperature of approximately 1,191 K. During laser melting, however, the temperatures attained are much higher, which favors TiC formation.

Figure 7.6 illustrates the formation mechanism of the TiC–316L composite during SLM at an energy density sufficient to form the TiC. During the line-by-line laser scanning, the feedstock powders (Fig. 7.6a) are heated rapidly from the high-energy absorbed. Consequently, the 316L and Ti phases melt once the operating temperature exceeds the melting point of ~1,667 °C. In the laser melt pool, once the degree of wetting of the molten Ti is sufficiently high, Ti and C react exothermically due to the exothermic nature of the material system as well as the high temperature driven by the high-energy density that induce the reaction (Fig. 7.6b). Akhtar et al. [188] suggested that during the solid-liquid reaction, the nucleation of the TiC occurs via Ti diffusing into C and

precipitating out as TiC (above 1130 °C). When the laser beam moves away from the melt pool, the molten composite system solidifies rapidly. Indeed, the solubility decreases as the temperature decreases, and many fine embryos form from the liquid via the mutual impact effect among the Ti and C elements. The embryos will act as the heterogeneous nucleation sites of TiC to accelerate the nucleation of TiC particles under the rapid solidification. C atoms preferentially combine with Ti in the melt pool to form a high-temperature TiC phase with a melting point of 3,480 K, causing the precipitation initiation of TiC phase (Fig. 7.6c). In the meantime, the TiC precipitates or solid nuclei of TiC grow successively by grain-boundary diffusion to form in situ TiC phase-reinforced 316L stainless steel composite (Fig. 7.6d). The cooling rate during the SLM process can approach 10^6 K/s [305]; therefore, the reinforcing TiC particles have limited time for grain growth and hence retaining its refined size within the 316L matrix after solidification and forming a ring-like microstructure (Fig. 7.4). Indeed, the presence of a steep temperature gradient and chemical concentration gradient at the solid-liquid interface generate variation in the surface tension between the center and edge of the molten pool [71]. The surface tension gradient will induce the Marangoni convection from a region of low surface tension to a region of high surface tension, thereby inducing thermocapillary forces exerted on the particles by the liquid [266]. The rearrangement rate of the TiC particles is thus enhanced, leading to a homogenous distribution of the TiC particles.

The peaks for TiC phase are at slightly higher 2θ angles than those of the standard material, implying a non-stoichiometry; thus, a decrease of the lattice parameter is deduced for the TiC phase. The sub-stoichiometric TiC formation and the lattice parameters for the SLM-processed samples at $\eta \geq 100$ J/mm³ were estimated by XRD and tabulated in Table 7.3 (the sample processed at $\eta = 67$ J/mm³ showed incomplete TiC formation). The lattice parameter of the in-

situ-formed TiC using $\eta = 100 \text{ J/mm}^3$ was estimated to be $4.267 \text{ \AA}$ (the stoichiometric TiC with an FCC crystal structure has a lattice parameter of $4.311 \text{ \AA}$). Therefore, non-stoichiometric TiC_{1-x} , was formed. According to Capaldi and Wood [306], the lattice parameter for $\text{TiC}_{0.55}$ was shown to be $4.283 \text{ \AA}$. Therefore, the value of x for the sub-stoichiometric TiC formed is greater than 0.55.

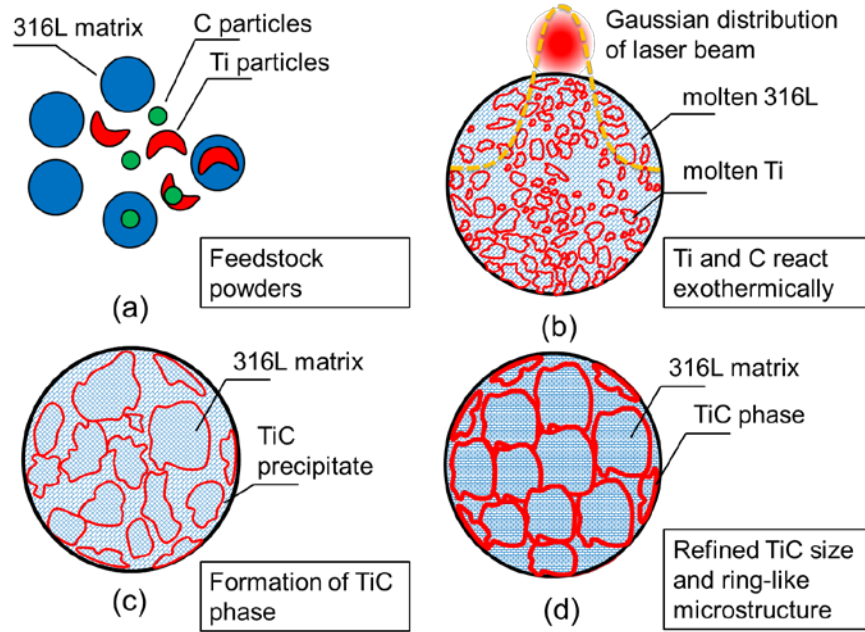


Figure 7.6: Schematic of formation mechanism of TiC–316L in situ composite by SLM.

Table 7.3: Changes in sub-stoichiometric and the lattice parameters of TiC_{1-x} with various applied energy density

$\eta \text{ (J/mm}^3\text{)}$	Sub-stoichiometric TiC_{1-x}	Lattice parameters ($\text{\AA}$)
100	0.82	4.267
200	0.90	4.287
300	0.98	4.294

The lattice constant of TiC_{1-x} of SLM-processed specimens with higher energy density has been evaluated to determine whether η affects the stoichiometry and lattice parameters of TiC. The

lattice parameters of the sub-stoichiometric TiC of SLM-processed samples using $\eta = 200$ or 300 J/mm^3 were 4.287 and 4.294 Å, respectively. The general increase in the lattice parameter of TiC_{1-x} , to form near-equilibrium TiC_{1-x} is because the increase in η leads to an increase in the processing temperature and the prolonged presence of liquid phase, which assists the diffusion of C atoms into the Ti lattice (i.e., more free C may react with Ti). The structure of stoichiometric compound TiC consists of an FCC lattice, in which carbon atoms are inserted inside the octahedral interstices; up to 72% of interstitial carbon sites can remain vacant. The possible cause of lattice contraction could be a high vacancy content inside the TiC lattice due to carbon vacancies generated from the fast solidification and stabilized by the subsequent cooling [307]. Due to the short laser melting time, carbon atoms have insufficient time to diffuse into the TiC_{1-x} lattice to form stoichiometric TiC. The formation of sub-stoichiometric TiC is not uncommon as TiC has an extremely wide range of homogeneity [308]. Brodtkin et al. [309] indicated the formation of $\text{TiC}_{0.5}$ as an intermediate phase when a starting powder composition of 4:1 is applied.

7.3.5. Hardness

Figure 7.7 shows the microhardness values of the SLM-processed samples, measured at the cross-sectional surface of specimens processed at different energy densities. For all SLM-processed composite samples, the microhardness values obtained are much higher than unreinforced 316L, which has an average microhardness of $\sim 215 \text{ HV}_{0.1}$, obtained from our previous study (see Chapter 3). The formation of $\text{TiC}_{<1}$ may prove to be useful despite it being softer than stoichiometric TiC [310]. The increase in the hardness values of the composites is attributed to combined effect of grain refinement strengthening (Hall–Petch relation) and grain boundary strengthening (i.e., homogenous distribution of TiC reinforcements within the matrix).

In our previous study [234], we produced a 316L ex-situ nanocomposite of moderate hardness ($\sim 338 \text{ HV}_{0.2}$) containing 10 vol.% TiC by 8 h of milling. In contrast, in this study, using the same applied η of 67 J/mm^3 , we produced a similar composite with only 4 h of milling and with higher hardness values. This is because in situ formed reinforcements have refined size and a relatively clean and strong interface with the matrix [311], hence yielding a higher hardness.

When η is increased from 67 to 100 J/mm^3 , no significant difference in hardness values was observed. However, a further increase in the energy density to 200 J/mm^3 causes the microhardness to decrease sharply to $\sim 313 \text{ HV}_{0.2}$. This is attributed to microstructural coarsening, as was observed in the SEM images. A further increase in η to 300 J/mm^3 sharply increases the microhardness as a result of significant improvement in densification. The enhancement in wettability of TiC by the molten 316L matrix improved the mechanical properties of the component. This result suggests that hardness values were influenced by both the densification degrees as well as the microstructure.

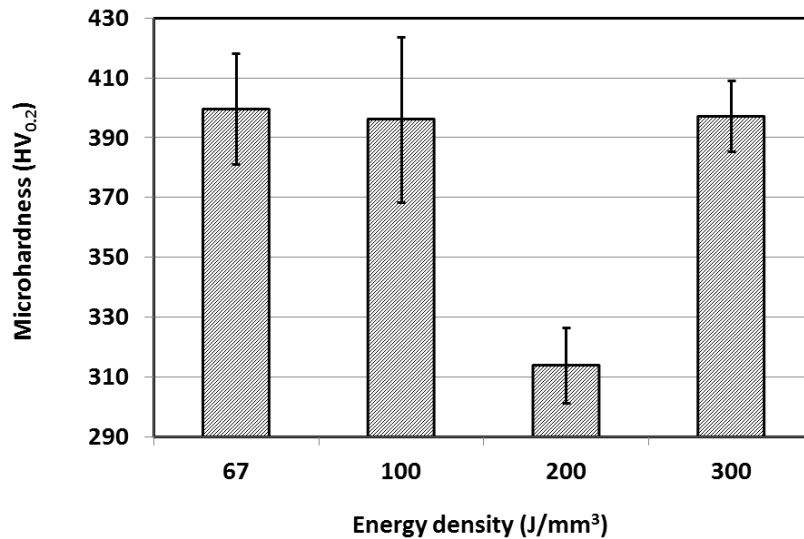


Figure 7.7: Influence of the energy density on the variation in microhardness of SLM-processed nanocomposites.

7.3.6. Wear Rate and Morphology

The differences in the wear rates of the various SLM-processed parts are shown in Fig. 7.8. Compared to the wear rate of unreinforced 316L matrix, calculated in our previous study, the wear rate of the TiC/316L parts demonstrate superior improvements in the wear resistance irrespective of the applied η . Nevertheless, the η magnitude affects the wear performance. In most cases, the change in the wear rate with laser energy is the opposite of that in the microhardness with laser energy. The TiC/316L parts prepared using a moderate η value of 100 J/mm³ exhibit superior wear performance (Fig. 7.8). This is attributed to the homogeneous dispersion of ultrafine submicron-scale TiC particles in the steel matrix and the improved densification, as well as the microstructural refinements relative to other parameter combinations (Fig. 7.8). In comparison, the parts fabricated using a high η value (300 J/mm³) show increased wear rates related to the coarse microstructure, although the densification level was improved.

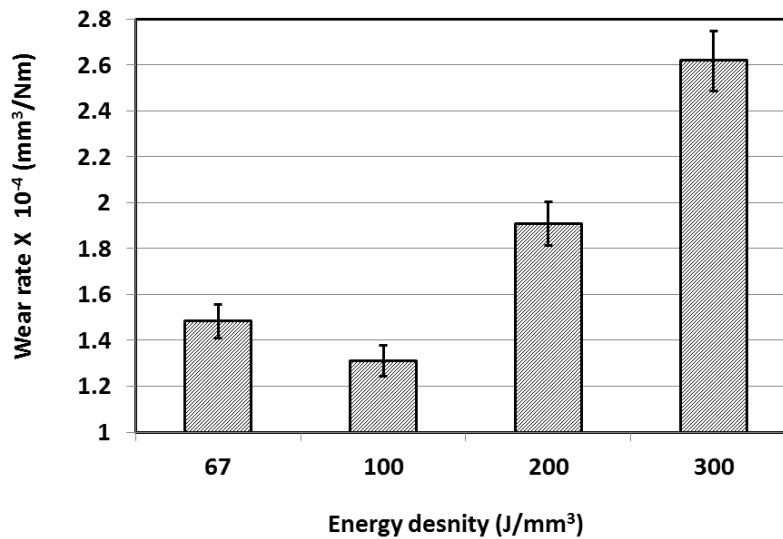


Figure 7.8: Influence of the energy density on the variation in wear rate of SLM-processed nanocomposites.

The characteristic morphologies of the worn surfaces of the test specimens are shown in Fig. 7.9, highlighting the microstructural features that generate the wear properties. When the lowest η value (67 J/mm^3) is used, parallel grooves are formed on the worn surface of the corresponding SLM-processed part, indicating abrasive wear (Fig. 7.9a). The worn surface is rough, porous, and scattered with loose wear debris. The wear rate is high because of the severe local plowing of the surface during the sliding test (Fig. 7.9a). Notably, lower degrees of densification (Fig. 7.2) are correlated to increased wear rates in the SLM-processed samples. With an increased η of 100 J/mm^3 , a dominant adhesive tribolayer forms, smoothing and densifying the worn surface and resulting in shallower grooves (Fig. 7.9b). A continuous strain-hardened tribolayer adhered to the worn surface is also formed at the further increased η of 200 J/mm^3 . Neither significant plowing nor fracturing is observed in this specimen, and no protruding particles are formed on the worn surface. This suggests that, as the laser energy density is increased, the mechanism of material removal during sliding changes from abrasion to the adhesion of the tribolayer. With the increase in η , the in-situ reaction in the molten pool becomes more efficient, and all TiC in the reaction system is completed. Therefore, the plowing effect of the TiC particles, which exhibit excellent bonding with the matrix, on the testing surface is decreased, with the worn surface showing shallower grooves with fewer protruding particles. The in-situ-formed homogeneous and refined reinforcing TiC particles do not split readily during sliding, but show a marked tendency to adhere together and undergo strain-hardening, thereby forming a tribolayer over the entire surface that enhances the wear resistance. This transition reduces the wear rate of the SLM-processed parts, as shown in Fig. 7.8. For the SLM-processed parts formed at the highest η value of 300 J/mm^3 , the worn surface consists of a severely fragmented tribolayer, with a large amount of entrapped debris (Fig. 7.9d). This is consistent with the higher wear rate (Fig. 7.8). A close

comparison of the fine-grained components formed at 67 J/mm^3 (Fig. 7.9a) with the coarse-grained components formed at 300 J/mm^3 (Fig. 7.9d) suggests that, at higher laser energy densities, the microstructure becomes coarser; this damages the tribolayer and increases the extent of spalling, thereby increasing the wear rate. The poor densification, thermal cracking, and high degree of coarsening of the microstructure may cause the spalling of the tribolayer, the formation of broader parallel grooves, and the collection of debris of aggregated small-sized particles on the worn surface. For composites produced at an even higher η value, the increased energy input and resulting increase in the SLM temperature cause coarser microstructure, resulting in decreased composite hardness. As a result, the slider penetrates the test surface deeply, as well as causing extensive plastic deformation of the surface and the loss of a significant amount of material. This, in turn, degraded the wear resistance.

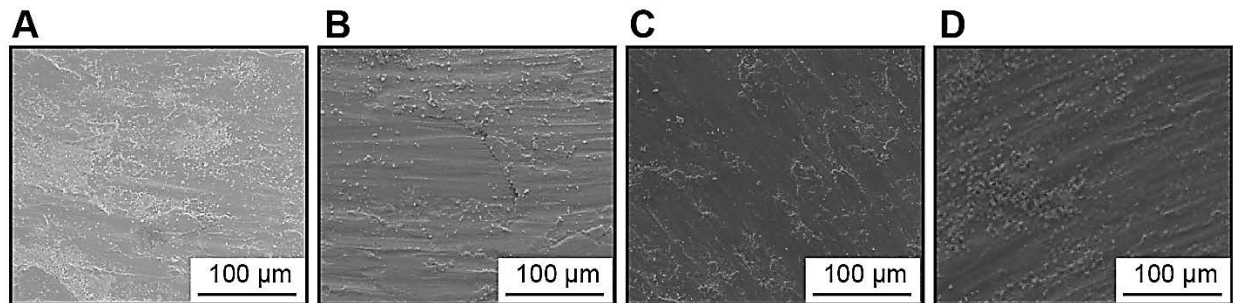


Figure 7.9: Influence of the energy density on the variation of worn morphologies of SLM-processed composite components with various applied energy densities. (a) 67 J/mm^3 , (b) 100 J/mm^3 , (c) 200 J/mm^3 , (d) 300 J/mm^3 .

A close examination of the constituent phases, microstructural characteristics, and densification properties of the 316L-based composites formed at low energy densities shows that the low hardness and poor wear performance observed are attributable to the following factors: (i) low densification rate by the formation of residual pores and (ii) an inhomogeneous reinforcing

structure caused by the incomplete in-situ chemical synthesis reaction, resulting in residual TiC particles. In contrast, the parts processed at high energy densities with higher densification rates show lower wear properties because of the microstructural coarsening and the formation of microscopic interfacial shrinkage-related pores.

7.4. Conclusions

The results of this study suggest that it is feasible to synthesize reinforcing TiC particles in 316L stainless steel by SLM in situ by carrying out the reaction $\text{Ti} + \text{C} \rightarrow \text{TiC}$ in the molten pool. The main conclusions of the study are the following:

- (1) The SLM of the as-prepared Ti-C-316L mixture powders successfully produced TiC/316L composite parts. The formation of in-situ TiC particles by SLM was achieved via a nucleation-growth mechanism. The SLM-processed components showed refined microstructures with submicron reinforcing particles. However, the laser energy input during the SLM process was crucial in determining the microstructural features of the in-situ-formed TiC/316L bulk composite. Higher energy densities of the laser resulted in coarser composite microstructures.
- (2) The densification level of the composite parts depended on the laser energy density used. The use of a low energy density resulted in low densification. Densification approaching ~98.88% of the theoretical density was achieved using a laser energy density of 300 J/mm^3 .
- (3) Both the microhardness, and wear rate were influenced by the densification level and microstructural coarsening. The microhardness decreased sharply when η was increased from 67 to 200 J/mm^3 (from ~399 to 313 $\text{HV}_{0.2}$) because of the grain coarsening caused by the

lower cooling rate; however, it increased when η was increased to 300 J/mm^3 ($\sim 397 \text{ HV}_{0.2}$) because of the density improvements.

- (4) The optimum low wear rate of $1.31 \times 10^{-4} \text{ mm}^3/(\text{Nm})$ under the optimal condition (100 J/mm^3) during the wear tests of TiC/316L composite parts was caused by the formation of an adherent strain-hardened tribolayer.

Chapter 8

Conclusion and Outlook

8.1. Current Research Accomplishments

To date, only a few metallic materials (e.g., steels, superalloys, and light alloys) have been processed successfully by SLM for commercial use in various applications. An enlarged range of processable materials would further extend the field by expanding the applicability of AM and thereby rendering SLM more sustainable, allowing the customized manufacture of complex, net-shaped, and end-useable parts. SLM offers an ideal platform for developing completely new and useful products for several applications. The additive construction of components enables a wide range of geometric variations, as well as internal structural variations. However, the processability of a material is governed by the flowability and rheological characteristics of the molten material.

In the present study, 316L stainless-steel nanocomposites were successfully synthesized via ball-milling and subsequently processed by SLM. The newly developed nanocomposites showed promise as candidate materials for structural and biomedical applications, with outstanding mechanical properties and tribological behaviors. Systematic and comprehensive studies were performed, starting with a demonstration of the effect of varying the reinforcement content on the mechanical properties of the microstructures and the tribological performance of the composites. The influence of the processing parameters, such as the scanning strategy and energy density input on these qualities was investigated. Finally, the feasibility of creating in-situ TiC-reinforced 316L composites by SLM was investigated.

The microstructure and mechanical properties were predominantly affected by the thermal gradients and cooling rates, which depended on the given process parameters. The high strength achieved was mainly attributed to a combination of grain refinement strengthening and grain boundary strengthening mechanisms: each enhanced the strength of the composite by providing obstacles to the dislocation movement. The ceramic nanoparticles pinned the grain boundaries, thereby restricting grain growth.

The remarkable effect of ceramic reinforcement on the compressive strength and hardness of the nanocomposite was demonstrated. From micro-compression testing of the nanocomposite, the compressive yield strength of around 2,000 MPa was measured for the 15% vol. TiB_2 -316L nanocomposite, which was five times higher than that of the pure 316L alloy. The hardness of the TiB_2 -316L was increased three-fold relative to that of the pure 316L. The hardening effect of the TiC reinforcement was lower than that of TiB_2 .

Various energy density levels were obtained by varying the laser scanning speed while keeping the other processing parameters constant. Various experiments as well as analyses were performed on the as-built specimens to determine the influence of energy density, a key factor in the SLM process, on the microstructures and densification of the as-built parts. The samples showed significantly different levels of porosities, with a maximum relative density of 98.3%. Decreased scan speeds led to increases in the composite grain size.

The industrial application of SLM to metal matrix composite (MMC) parts will require increased build rates and extensions of the laboratory setup. Appropriate process control will subsequently permit further engineering applications.

8.2. Recommendations for Future Work: Ongoing Research Activities and Re-Invention Issues, Opportunities, and Strategies

The AM of nanocomposites is still in its infancy and hence there is much uncharacterized behavior that occurs during fabrication. It is predicted that the range of commercially available metallic materials processable by SLM will grow. According to Shellabear and Nyrhilä [312], expansion will occur as follows:

- (i) More material types per existing class, such as nickel-based super-alloys and different stainless steels.
- (ii) New classes of materials, such as hard metals, precious metals, ceramics, completely new alloys, and tailored composites.
- (iii) Customer-specific materials.

The number as well as the types of material developments may be limited by the availability, cost, and technical issues affecting the development of resources. Several materials are difficult to weld, such as nickel superalloy and Ti–Al composites. SLM may allow the investigation and application of such highly desirable materials. It is expected that development will focus significantly on the tailoring of materials as SLM becomes more established. Such tailored materials may rely on completely new formulations or on different conventional materials.

The amalgamation of distinctive materials of a highly nonequilibrium metallurgical nature, and the incremental manufacturing philosophy of laser processing provides an advantageous technique for the concurrent development of complex configurations, new materials, and exceptional mechanical and microstructural features using laser-based AM technology. SLM has demonstrated high competence in the production of intricately shaped functional metals and

alloys, as well as (nano) composites, which cannot be readily produced by traditional manufacturing methods. The development of high-performance parts from new materials using AM is likely to benefit from the technologies developed for SLM, especially regarding the use of amorphous materials, nanostructured materials, particle-reinforced MMCs, and in-situ composite materials. The features of SLM processes for new materials must be characterized, including process control and optimization, material design and preparation, mechanical properties, microstructural characterization, while promoting the understanding of physical as well as chemical metallurgy. Thus, a core approach for sustainable improvements via the AM of high-performance metallic parts would emphasize the relationships among the designed material, the microstructure, the mechanical properties, and the tailored process. This would facilitate the effective production of new SLM-processed parts with novel microstructural features and enhanced mechanical performance.

While AM technology has great potential, many considerable and essential issues linked to laser-based AM remain unresolved, mostly in the following three areas:

- (1) Theory and scientific understanding, such as physics-based procedures and simulations thereof, comprising both materials and phase transformation under non-equilibrium laser interaction, materials kinetics, thermodynamic behaviors, and process–material–property modeling optimization.
- (2) Technical and material advances, regarding special metallic biomaterials, novel multi-phase AM-produced materials, AM procedures and process improvements, and AM devices and equipment.

(3) Application and functionality, such as function-oriented innovative design, lightweight structures, new procedures and technologies for micro- and nanofabrication systems, new high-performance applications of AM in the automotive and aerospace domains, assessment techniques, and functional requirements.

Because AM remains relatively new, the establishment of AM processing databases and standards is necessary. Thus, AM processing data for different metallic systems must be collected. Coupled with the design of feedstock material and preparation optimization, the final optimal and detailed AM processing parameters must be determined experimentally to determine a material–process database for each system. This would permit the accurate and easy control of the AM processing of feedstock materials for various industrial applications.

A theoretical understanding of the metallurgical mechanisms and microstructural developments underlying SLM fabrication is necessary for progress. The fundamental chemical and physical features of the process must be established to provide a solid theoretical basis for the AM procedures. Theoretical simulations and modeling of the microscopic fluid flows during laser-based AM must also be performed. Research into the metallurgical thermodynamics of the melt in the nonequilibrium molten pool created by SLM is of particular significance, as it will address fluid flow, mass transfer, crystal nucleation, and grain growth, thereby facilitating the design and customization of the microstructure in accordance with the local performance needs of users.

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