



UNIVERSIDAD MICHOACANA DE SAN
NICOLÁS DE HIDALGO
INSTITUTO DE INVESTIGACIÓN EN METALURGIA Y MATERIALES



PROGRAMA DE DOCTORADO EN CIENCIAS EN METALURGIA
Y CIENCIAS DE LOS MATERIALES

EFFECT OF ADVANCED MANUFACTURING TECHNOLOGIES ON THE MICROSTRUCTURE-PROPERTY RELATIONSHIP OF 440C MARTENSITIC STAINLESS STEEL

Tesis que para obtener el grado de Doctora en Ciencias en Metalurgia
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ON THE MICROSTRUCTURE-PROPERTY RELATIONSHIP OF
440C MARTENSITIC STAINLESS STEEL

*A dissertation submitted in partial fulfilment of the requirements for the degree of
Doctor of Philosophy*

in the

Institute in Metallurgy and Materials Science
Department of Steelworks

by

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August 2024



ACKNOWLEDGEMENTS

This work was performed under the supervision of Dr. Alberto Ruiz Marines and Dr. Venkata Karthik Nadimpalli, to whom I would like to express my sincere gratitude for their support, mentoring guidance, encouragement, and valuable advice which have contributed to my academic growth.

I would like to express my deepest appreciation and warm thanks to my co-supervisor Dr. Venkata Karthik Nadimpalli and Dr. David Bue Pedersen who made this project possible. The support and guidance they provided me during this journey and my time at DTU are highly valuable. I deeply appreciate the trust they have placed in me and the amazing opportunity they have giving me.

I would like to give special thanks to Professor Marcel A. Somers for their insightful feedback and outstanding help. For giving valuable advice in the field of materials science in all the inspiring conversations we had. Their support and collaboration have been essential to the success of this project. Thanks must also be given to Emilie Valente and Thomas Dahmen for their assistance and guidance during my research stay at DTU

I wish to thank the members of my advisory committee Dr. Arnoldo Bedolla, Dr. Victor López, and Dr. Jorge Verduzco for their time, advice, and patience over the years.

I am would like to express sincere gratitude to the Universidad Michoacana de San Nicolás de Hidalgo, the National Council of Science and Technology (CONACHYT, México), and the Technical University of Denmark (DTU, Denmark) for providing financial support, which made this research possible.

Thanks to staff members Antonio Rodríguez, Simón, Jorge, Remedios, and Sayil who supported me when I needed it. Their expertise in operating the equipment was crucial to the successful completion of my experiments. Thanks go to my friends at the institute, Teresita, Heriberto, Richard, Tony, Rodrigo, Marlén, Arturo, Miranda, and Martín for giving me the strength to keep going with my hard work and for all those memorable moments we shared. To Corentin, whose faith in me, encouragement and support meant everything when I was far away from home.

Last but not least, I would like to acknowledge my parents, Alejandra and Jorge, my siblings Zao and Alexei, my lovely niece Naomi, and my nephews Ian and Lennin for their unconditional love and endurance during my PhD journey.

DEDICATION

To the loving memory of Rosa María Herrejón

TABLE OF CONTENTS

Acknowledgements	iii
Dedication.....	iv
Table of contents.....	v
List of tables	ix
List of figures	x
 RESUMEN GENERAL	 xvii
GENERAL ABSTRACT.....	xix
 CHAPTER I INTRODUCTION	 1
1.1 Overview	1
1.2 Justification	2
1.3 General and specific objectives	2
1.4 Outline of thesis	3
 CHAPTER II LITERATURE REVIEW	 5
2.1 Martensitic stainless steels.....	5
2.1.1 <i>Introduction</i>	5
2.1.2 <i>Metallurgy and alloying of martensitic stainless steels</i>	6
2.1.3 <i>Manufacturing of martensitic stainless steels</i>	7
 RESEARCH RESULTS AND DISCUSSION	 11
 CHAPTER III AN INVESTIGATION OF THE MICROSTRUCTURE EVOLUTION OF HEAT-TREATED SPRAY FORMED 440C MARTENSITIC STAINLESS STEEL	 12
Abstract	12
3.1 Introduction.....	13
3.2 Experimental details.....	14

3.2.1 Materials	14
3.2.2 Heat treatment process	14
3.2.3 Microstructural characterization	15
3.3 Results and discussion	16
3.3.1 Characterization of the as-received (AR) microstructure.....	16
3.3.2 Effect of austenitizing temperature and time on the microstructure and hardness	17
3.3.3 Effect of tempering temperature and time on the microstructure and mechanical properties	23
3.4 Conclusions.....	31
 CHAPTER IV EFFECT OF HEAT TREATMENT PROCESSES ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF SPRAY-FORMED 440C MARTENSITIC STAINLESS STEEL	32
Abstract	32
4.1 Introduction	33
4.2 Experimental details	35
4.2.1 Materials manufacturing.....	35
4.2.2 Heat treatment	35
4.2.3 Microstructural characterization	35
4.2.4 Mechanical characterization	36
4.3 Results and discussion	37
4.3.1 Microstructural characterization.....	37
4.3.2 Mechanical behavior.....	40
4.4 Conclusions	51
 CHAPTER V MICROSTRUCTURAL AND MECHANICAL CHARACTERIZATION OF SPRAY-FORMED AND CONVENTIONALLY CAST AISI 440C MARTENSITIC STAINLESS STEEL	52
Abstract	52
5.1 Introduction	53
5.2 Experimental details	54
5.2.1 Materials Manufacturing	54
5.2.2 Conventional casting (VIM).....	54

5.2.3 Heat treatment	55
5.2.4 Microstructural characterization	55
5.2.5 Mechanical characterization	56
5.3 Results and discussion	56
5.3.1 Characterization of initial microstructures	57
5.3.2 Characterization of heat-treated microstructures	61
X-ray diffraction.....	61
Energy dispersive spectroscopy	64
Scanning electron microscopy	66
Electron backscatter diffraction.....	70
5.3.3 Mechanical properties.....	72
Hardness	72
Tensile and compressive testing.....	74
5.4 Conclusions	78
 CHAPTER VI COMPARISON OF WEAR PROPERTIES OF 440C TOOL STEEL FABRICATED BY SPRAY-FORMING AND CONVENTIONAL CASTING	79
Abstract	79
6.1 Introduction	80
6.2 Experimental procedure	81
6.2.1 Materials and methods.....	81
6.2.2 Wear testing	82
6.3 Results and discussion	83
6.3.1 Microstructural characterization	83
6.3.2 Carbide size, morphology, and distribution after tempering.....	87
6.3.3 Wear behavior of tempered CC and SF alloys.....	90
6.4 Conclusions	105
 CHAPTER VII THE POTENTIAL OF DIRECTED ENERGY DEPOSITION IN THE MANUFACTURING OF HIGH-PERFORMANCE 440C STAINLESS STEEL	106
Abstract	106

7.1 Introduction	107
7.2 Experimental details	109
7.2.1 <i>Material manufacturing techniques</i>	109
7.2.2 <i>Heat treatment</i>	109
7.2.3 <i>Microstructural characterization</i>	109
7.2.4 <i>Mechanical evaluation</i>	110
7.3 Results and discussion	111
7.3.1 <i>Microstructural characterization</i>	111
7.3.2 <i>Mechanical characterization</i>	113
<i>Hardness</i>	113
<i>Tensile tests</i>	114
<i>Compression test</i>	121
7.4 Conclusions	129
 CHAPTER VIII SUMMARY AND CONCLUDING REMARKS.....	130
 REFERENCES	131

LIST OF TABLES

Table 2.1	Alpha and gamma-forming elements [1]	6
Table 2.2	Carbide and non-carbide forming elements [2]	7
Table 3.1	Chemical composition of spray formed 440C martensitic SS (wt.%)	14
Table 3.2	SEM-EDS data of carbides in the sample austenitized at 1050 °C for 1 h.....	26
Table 4.1	Nominal chemical composition (wt. %) of the spray-formed 440C MSS as determined by optical emission spectroscopy.....	35
Table 4.2	SEM-EDS data of carbides in the sample austenitized at 1050 °C for 1 h.....	39
Table 4.3	Best fitting of Hollomon exponents n and constant K values of samples tempered for 0.5 h at a temperature of 350 °C and intercritical treatment	45
Table 4.4	Estimated compressive strength from the indentation hardness and real data obtained from compression tests.....	49
Table 4.5	Effect of different heat treatments on the mechanical and elastic properties of SF 440C MSS. All the samples were tempered for 0.5 h at 350 °C	50
Table 5.1	Mean chemical composition (wt. %) of the two applied steels	54
Table 5.2	Quantitative EDS analysis of carbides and matrix	60
Table 5.3	Quantitative EDS analysis of carbides and matrix in Figure 6(a, a')	66
Table 5.4	Effect of tempering temperature on the mechanical and elastic properties of conventional cast and SF 440C MSS. All the samples were austenitized at 1050 °C for 1 h.....	77
Table 6.1	Mean chemical composition (wt. %) of the two steels	81
Table 6.2	Quantitative EDS analysis of the worn surface	87
Table 6.3	Microstructural features comparison of phases	90
Table 6.4	Mean CoF, volume loss, wear rate, and hardness values of the SF an CC samples	94
Table 6.5	Quantitative EDS analysis of the worn surface	97
Table 7.1	Nominal chemical composition (wt. %) of 440C MSS produced through both routes as determined by optical emission spectroscopy	109
Table 7.2	EDS point analysis of oxides in the as-printed horizontal specimen.....	118

LIST OF FIGURES

Figure 2.1	Conventional manufacturing process of tool steels	7
Figure 2.2	Spray forming process illustration	9
Figure 2.3	Representative scheme of two of the most common additive manufacturing technologies in the production of metals a) DED and b) L-PBF [3]	10
Figure 3.1	(a) Secondary electron SEM micrograph of SF 440C in the AR condition, (b) XRD diffractogram in which characteristic peaks are identified, (c) phase map, and (d) IPFZ map of the ferrite phase and carbide particles.....	17
Figure 3.2	(a) Prior austenite grain size as a function of austenitizing temperature and time. (b) Normal distribution of grain size in sample austenitized at 1050 °C for 1 h.....	18
Figure 3.3	XRD pattern of the as-quenched samples austenitized at different temperatures for (a) 0.5 h, and (b) 1 h. (c) Pattern indexation of sample austenitized at 1050 °C for 1 h. (d) Retained austenite content in the as-quenched samples as a function of the austenitizing temperature and time	19
Figure 3.4	SEM micrographs of AISI 440C after austenitizing at (a) 1000, (c) 1050, and (e) 1100 °C for 0.5 h and (b) 1000, (d) 1050, and (f) 1100 °C for 1 h.....	20
Figure 3.5	EBSD phase map (a) overall microstructure of the sample austenitized at 1050 °C for 1 h and comparison of the as-quenched samples austenitized at (b) 1050 °C for 1 h and (c) 1100 °C for 1 h	22
Figure 3.6	(a) Hardness values of the as-quenched AISI 440C SS as a function of austenitizing temperature and time. Peak deconvolution of the second martensite reflection in sample austenitized for 1 h at (b) 1050 °C and (c) 1100 °C	23
Figure 3.7	SEM/BSE micrographs showing the microstructure of the as-tempered AISI 440C SS for 0.5 h at (a) 150, (d) 350 (g) 550, 1 h at (b) 150, (e) 350, (h) 550, and 2 h at (c) 150, (f) 350 (i) 550	24
Figure 3.8	XRD patterns for the 440C MSS tempered samples as a function of temperature and time.....	25
Figure 3.9	(a) SEM image of the sample cryo treated and tempered for 0.5 h at 350 °C, (b) EDS spectra of particle 6 in (a), and (c-f) EDS mapping composition.....	26

Figure 3.10	Effect of tempering temperature and time on the hardness of the as-quenched samples at 1050 °C for 1 h.....	28
Figure 3.11	Stress-strain curves for the SF 440C MSS quenched at 1050 °C for 1 h and tempered at different temperatures. Effect of (a) tempering temperature, (b) tempering time, and (c) double tempering cycle on tensile elastic-plastic behavior of SF 440C MSS	29
Figure 3.12	(a) Fracture surface of the as-tempered sample for 0.5 h at 150 °C. (b) SEM/BSE image of intergranular cracks produced during tensile tests on the sample tempered at 150 °C for 0.5 h.....	30
Figure 4.1	SEM images of samples subjected to different heat treatments (a) austenitizing at 1050 °C, (b) austenitizing at 1100 °C, (c) austenitizing at 1125 °C, and (d) Q-IQ at 1200 and 900 °C. All the samples were tempered at 350 °C for 0.5 h	38
Figure 4.2	(a) SEM/BSE image of the sample tempered for 0.5 h at 350 °C, (b-f) EDS maps of the sample indicating K_{α} radiation	39
Figure 4.3	(a) X-ray diffractograms of samples austenitized at different temperatures and tempered at 350 °C for 0.5 h. (b) Volume fractions of the present phases, as determined by Rietveld refinement.....	40
Figure 4.4	(a) Hardness comparison as a function of Q-T ^P , and Q-IQ-T heat treatment processes, (b) strain-stress curves of the as-tempered samples for the different heat treatment conditions and the as-sprayed sample (AR)	41
Figure 4.5	Fracture surface of tensile samples at (a-d) macroscopic and (a'-d') microscopic levels at (a) 1050 °C, (b) 1100 °C, (c) 1125 °C, and (d) Q-IQ-T. All the samples were tempered at 350 °C for 0.5 h	43
Figure 4.6	SEM/BSE images of intergranular cracks after tensile testing on sample austenitized at 1050 °C for 1 h (a) longitudinal section and (b) high magnification image of crack within the carbide	44
Figure 4.7	(a) Hollomon plot of the plastic regime for the different heat treatments and (b) strain hardening rates as a function of the true plastic strain for the different heat treatment conditions.....	45

Figure 4.8	EBSD phase map comparison of samples austenitized at 1050 °C for 1 h (a) before and (b) after tensile testing, austenitized at 1100 °C for 1 h (c) before and (d) after tensile testing, Q-IQ-T samples (e) before and (f) after tensile testing47
Figure 4.9	(a) XRD pattern comparison of samples after tensile testing for the different heat treatments. (b) retained austenite content, as determined by Eq. (4.1), before and after straining in dependence on the austenitizing temperature.....48
Figure 4.10	Stress-displacement curves for the samples austenitized at 1050 °C for 1 h and tempered for 0.5 h at (a) 350 and (b) 450 °C49
Figure 5.1	Thermodynamic prediction of (a) phase equilibrium diagram showing the volume fraction of the phases and (b) equilibrium carbon and chromium content in austenite as a function of temperature.....57
Figure 5.2	SEM representative microstructures of 440C MSS (a-c) as-cast and (e-g) as-sprayed58
Figure 5.3	(a) XRD diffractograms of as-cast and as-sprayed materials; insert shows magnification to identify carbides. (b) EBSD phase map of the as-cast steel. (c) Volume fractions of the phases that compose the materials59
Figure 5.4	SEM/BSE detailed images of (a) as-cast and (b) as-sprayed samples.....60
Figure 5.5	XRD diffractograms of the (a) as-cast and heat-treated (quenched and tempered) conventional cast material and (b) as-sprayed and heat-treated (quenched and tempered) SF steel.....62
Figure 5.6	Comparison of carbide volume fractions after austenitizing for 1 h at 1050 °C and subsequent tempering for 0.5 h at 350 °C for (a) cast and (b) SF material. The volume fractions were determined by Rietveld refinement of the corresponding X-ray diffractograms.....63
Figure 5.7	Middle: {200/002} and {211/112} line profiles of spray formed 440C in austenitized and quenched condition. The data was fitted with two Voigt profiles (bottom) yielding the residual in the top part of the graph64
Figure 5.8	SEM/BSE images of (a) as-cast and (a') spray-formed steel. EDS element mapping of (b-d) as-cast and (b'-d') spray-formed specimens. Locations in (a) and (a') correspond to the spot analysis in Table 3. Specimens were austenitized at 1050 °C for 1 h and tempered at 350 °C for 0.5 h.....65

Figure 5.9	Metallic composition of (a) light carbides and (b) dark carbides in the heat-treated conventional cast and spray-formed materials after austenitizing at 1050 °C for 1 h and tempering at 350 °C for 0.5 h.....	66
Figure 5.10	SEM/BSE (inserts) micrographs of heat-treated cast 440C MSS (a) after austenitizing at 1050 °C for 1 h and tempering for 0.5 h at 150, 250, 350, 450, and 550 °C in (b) to (f), respectively	67
Figure 5.11	SEM micrographs of heat-treated SF 440C MSS (a) after austenitizing at 1050 °C for 1 h and after tempering for 0.5 h at 150, 250, 350, 450, and 550 °C in (b) to (f), respectively	69
Figure 5.12	Secondary electron images of conventional cast steel tempered for 0.5 h at (a) 350 °C and (b) 450 °C. SF material tempered for 0.5 h at (c) 350 °C and (d) 450 °C..	70
Figure 5.13	EBSD phase map comparison of heat-treated (a) cast and (b) spray-formed specimens. EBSD orientation maps showing microstructure in the (c) cast and (d) spray-formed specimens. The samples were OQ from an austenitizing temperature of 1050 °C and tempered at 350 °C for 0.5 h	71
Figure 5.14	Hardness comparison of the tempered-partitioned cast and spray-formed materials	74
Figure 5.15	Tensile stress-strain curves comparison of CC and SF samples (a) as-cast and as-sprayed conditions. After austenitizing at 1050 °C for 1 h and tempering at (b) 150, (c) 250, (d) 350, (e) 450, and (f) 550 °C	75
Figure 5.16	Stress-displacement curves for the specimens austenitized at 1050 °C for 1 h and tempered at 350 °C for 0.5 h (a) CC and (b) SF condition	76
Figure 6.1	XRD patterns of the two materials for the tempering temperatures of (a) 350 and (b) 450 °C, in which the presence of the phases that conform the steel are seen ..	83
Figure 6.2	SEM/BSE micrographs of specimens after tempering at 350 °C (a) SF and (b) cast; and their respective particle size distributions of eutectic carbides. Carbide area distribution of (c) SF and (d) CC materials	84
Figure 6.3	SEM/BSE images of the two materials showing different phases for the tempering temperatures of 350 and 450 °C	85

Figure 6.4	SEM micrographs showing details of the phases and their respective EDS microanalysis	86
Figure 6.5	High-magnification SEM images showing the presence of chromium-rich carbides within the martensitic matrix and at the interdendritic zones	88
Figure 6.6	Carbide particle analysis: carbide area, aspect ratio, and nearest neighbor distance (NND) between carbides.....	89
Figure 6.7	Friction coefficient as a function of time for the tempered SF and cast materials. (a) First test and (b) second test.....	91
Figure 6.8	3D images of the digitalized wear tracks under different conditions, obtained by the profilometer after the tests	92
Figure 6.9	(a) Track width, (b) track depth, (c) microhardness, and (d) wear rate, of tempered materials after the dry sliding wear test	93
Figure 6.10	SEM images showing the appearance of the worn surfaces of the different samples	95
Figure 6.11	SEM/BSE micrographs of the worn surface showing the details of the particles that formed during the wear test and the corresponding EDS microanalysis	96
Figure 6.12	EDS-maps of the worn surface showing the matrix (Fe), carbides (Cr), oxide (O), and the atomic composition of the oxides.....	98
Figure 6.13	EDS mapping of the counter-body (Al_2O_3 ball) after testing the CC 450 °C specimen	99
Figure 6.14	EDS mapping of the debris after testing the CC 450 °C specimen	100
Figure 6.15	Cross-section SEM images of the worn surface of each sample	101
Figure 6.16	EBSD analysis of the SF sample tempered at 350 °C. Pole figure of (a) martensitic matrix and (b) worn subsurface. (c) Grain average misorientation and (d) Kernel average misorientation of the worn cross-section surface. (e-f) Grain average misorientation, and Kernel misorientation distributions, respectively	103
Figure 6.17	EBSD analysis of the SF sample tempered at 350 °C. Pole figure of (a) martensitic matrix and (b) worn subsurface. (c) Grain average misorientation and (d) Kernel average misorientation of the worn cross-section surface. (e-f) Grain average misorientation, and Kernel misorientation distributions, respectively	104

Figure 7.1	OM/SEM images of the microstructure of the 440C MSS. (a-c) detail structure at the interface between two deposits. (d) Macrography of the as-deposited steel. (e-f). Top and bottom layers, respectively	111
Figure 7.2	EBSD orientation maps of the AP (a) horizontal and (d) vertical samples. Grain average misorientation of (b) horizontal and (e) vertical samples. Kernel average misorientation of (c) horizontal and (f) vertical samples.....	112
Figure 7.3	Vickers micro-hardness (a) horizontal as-printed and heat-treated and (b) vertical as-printed and heat-treated samples	114
Figure 7.4	Stress-strain tension curves for DED AISI 440C steel as a function of printing direction (a-b) as-printed and (c-d) heat treated	115
Figure 7.5	Fractographies of the horizontal DED tensile fractured samples (a-c) AP and (d-f) HT samples	117
Figure 7.6	EDS mapping images of the fracture surface of the as-printed horizontal specimen	118
Figure 7.7	EBSD analysis results of the AP DED steel after tensile testing: (a-b) Phase distribution in the horizontal and vertical specimens respectively. (c-d) Orientation maps colored according to the inverse pole figure in the horizontal and vertical specimens respectively. (e-f) Pole figure and inverse pole figure in the horizontal and vertical specimens respectively.....	120
Figure 7.8	Grain average misorientation distribution of AP DED specimen after tensile testing, (a) horizontal and (b) vertical building directions. Kernel average misorientation distribution of AP DED specimen after tensile testing, (c) horizontal and (d) vertical building directions	120
Figure 7.9	Vickers hardness map below the fracture surface after the tensile test (a) Horizontal-AP and (b) vertical-AP.....	121
Figure 7.10	(a) Stress-displacement curves for horizontal and vertical DED 440C AP and HT samples.....	122
Figure 7.11	Surface fracture of HT vertical sample after failure	123
Figure 7.12	EBSD analysis results of the AP DED steel after compression test: (a-b) Phase distribution in the horizontal and vertical specimens respectively. (c-d) Orientation maps colored according to the inverse pole figure in the horizontal and vertical	

	specimens respectively. (e-f) Pole figure and inverse pole figure in the horizontal and vertical specimens respectively.....	124
Figure 7.13	Grain average misorientation distribution of AP DED specimen after tensile testing, (a) horizontal and (b) vertical building directions. Kernel average misorientation distribution of AP DED specimen after tensile testing, (c) horizontal and (d) vertical building directions	125
Figure 7.14	Frequency distribution of grain average misorientation for the (a) horizontal and (b) vertical samples. Kernel average misorientation frequency distribution of (c) horizontal and (d) vertical samples. Misorientation frequency distribution of (e) horizontal and (f) vertical samples.....	126
Figure 7.15	XRD diffractograms of the AISI 440C DED as-printed and after compression samples in the (a) horizontal and (b) vertical building directions	128

RESUMEN GENERAL

Los aceros martensíticos son aleaciones base Fe-Cr-C, capaces de ser endurecidos y revenidos debido a su alto contenido de carbono. Se utilizan comúnmente en ciertas herramientas manuales o accesorios mecánicos para cortar, conformar, formar y troquelar materiales ya sea a temperaturas ordinarias o elevadas. Los aceros inoxidable martensíticos también se utilizan en una amplia variedad de otras aplicaciones donde se requiere resistencia al desgaste, tenacidad y otras propiedades para un desempeño óptimo. Existen dos métodos de fabricación convencionales populares para fabricar aceros inoxidable martensítico. El primero es la fundición, que típicamente incluye refundición por escoria electrificada (ESR), refundición por arco al vacío (VAR) y posteriormente forjado y tratamiento térmico. Los procesos de fundición requieren varios pasos en la cadena de procesos antes de lograr el material de partida deseado para aceros grado herramienta (palanquilla/lingote). El segundo método se llama formación por pulverización (SF), un proceso de atomización por pulverización térmica para fabricar lingotes metálicos de alta calidad. La efectividad del proceso SF proviene principalmente de las altas tasas de solidificación durante el proceso de deposición, lo que permite obtener productos semiacabados de alta calidad con una microestructura fina libre de defectos relacionados con la segregación macroscópica, tal como ocurre en los materiales fabricados por medio de fundición convencional. Se sabe que los aceros formados por pulverización tienen un rendimiento significativamente mejor que los aceros fabricados por fundición debido a la microestructura de grano fino y la distribución homogénea de precipitados. Durante el proceso SF, junto con el lingote, se produce una cierta cantidad de partículas metálicas que solidifican sin ser depositadas en el lingote. El excedente de polvo está formado por pequeñas partículas esféricas que o bien fallan en alcanzar el lingote formado por pulverización o rebotan del lingote caliente ya que ya se han solidificado. Dicho polvo se acumula en el fondo del equipo SF y ha sido considerado históricamente como material de desecho que se debe refundir. Sin embargo, la fina distribución del tamaño de partícula (0-200 μm) y la forma esférica hacen que el polvo sea bastante adecuado para la manufactura aditiva (AM). La manufactura aditiva, comúnmente conocida como impresión 3D, es un proceso de fabricación capa por capa que funciona convirtiendo un modelo digital en un componente físico. El proceso es controlado por computadora y permite la creación de componentes 3D funcionales. La manufactura aditiva de componentes metálicos ofrece varias ventajas sobre las metodologías de fabricación

convencional, principalmente la mayor libertad de diseño, lo cual permite diseñar de acuerdo a la función en lugar de diseñar para la manufactura. El desarrollo e implementación de la manufactura aditiva de componentes funcionales metálicos ha aumentado considerablemente en los últimos años, ganando terreno en diversas industrias, incluidos los sectores aeroespacial, automotriz, médico, de defensa y energético. Existen varias tecnologías enfocadas en sistemas de manufactura aditiva metálicos, sin embargo, las técnicas más adecuadas utilizadas son la fusión láser de cama de polvo (L-PBF) y la deposición por energía directa (DED), ambas basadas en materia prima en forma de polvo tal como el que se encuentra disponible del proceso SF. El uso de polvo reciclado para implementarse en manufactura aditiva también crea una economía circular que mejora la sostenibilidad de toda la cadena de procesos de fabricación. Si bien varios artículos en la literatura exploran los parámetros del proceso y el rendimiento de las piezas fabricadas aditivamente, la investigación está relativamente poco explorada para los aceros inoxidables martensíticos fabricados aditivamente. Por lo tanto, la presente investigación comparó la relación proceso-estructura-propiedad para el acero inoxidable martensítico 440C (MSS) fabricado mediante tecnologías de fabricación convencionales y aditivas. Para este propósito, se estudiaron la microestructura y las propiedades mecánicas en las condiciones de fabricación y tratamiento térmico. Además, se prepararon y analizaron muestras de aceros inoxidables martensíticos convencionales y aditivamente manufacturados en términos de propiedades macroestructurales como dureza Vickers, resistencia a la tracción, resistencia a la compresión y resistencia al desgaste. También se realizó una caracterización microestructural utilizando difracción de rayos X (XRD), microscopía electrónica de barrido (SEM), difracción electrónica de retrodispersión (EBSD) y espectroscopia de energía dispersiva (EDS). También se discute un análisis detallado del rendimiento del acero inoxidable martensítico 440C fabricado aditivamente en función de sus propiedades microestructurales para desarrollar una mejor comprensión de la correlación proceso-estructura-propiedades.

Palabras clave: Acero Inoxidable Martensítico AISI 440C, Tratamiento Térmico, Formación por Pulverización, Deposición por Energía Directa, Fundición por Inducción al Vacío

GENERAL ABSTRACT

Martensitic stainless steels are Fe-Cr-C based alloys, capable of being hardened and tempered due to their high carbon content. They are commonly used in certain hand tools or mechanical fixtures for cutting, shaping, forming, and blanking materials at either ordinary or elevated temperatures. Martensitic stainless steels are also used in a wide variety of other applications where resistance to wear, strength, toughness, and other properties are selected for optimum performance. Two popular conventional manufacturing methods exist for manufacturing martensitic stainless steel. The first is casting, which typically involves electro-slag remelting (ESR), vacuum arc remelting (VAR) and further forging and heat treatment. Casting methods require several steps in the process chain before reaching the desired tool steel feedstock (billet/ingot material). The second method is called spray forming (SF), a thermal spray atomization process for making high-quality metal ingots. The SF process's effectiveness stems primarily from the high rates of crystallization of the melt enabling high-quality semi-finished products with a fine-grained structure that is free of macroscopic segregation-related defects, as occurs in materials manufactured from large as-cast ingots. Spray formed steels are known to perform significantly better than cast steels due to the fine grain structure and precipitate distribution. During the SF process, together with the ingot, a certain amount of overspray powder is produced. The overspray powder is formed from small spherical powder particles that either miss the spray formed ingot or bounce off from the hot ingot since they have already solidified. The overspray powder that collects at the bottom of the S.F. plant has historically been regarded as scrap material that has to be remelted. However, the fine particle size distribution (0-200 μm) and the spherical shape make the powder quite suitable for additive manufacturing (AM). Additive manufacturing, commonly known as 3D printing is a layer-by-layer manufacturing process that works by converting a digital model into a physical component. The computer-controlled process allows the creation of functional 3D components. Metal AM offers several advantages over traditional manufacturing methodologies, primarily the increased design freedom that allows design for function instead of design for manufacturing. The development and implementation of metal AM for functional components has considerably increased over the last years, gaining ground in various industries, including aerospace, automotive, medical, defense, and energy sectors. There are various technologies focused on metal AM systems, however, the most

suitable techniques used for metallic materials are laser powder bed fusion (L-PBF) and directed energy deposition (DED), both based on powder feedstock such as the powder available from the SF process. The use of recycled overspray powder for AM also creates a circular economy that improves the sustainability of the entire manufacturing process chain. While several papers in the literature explore process parameters and performance of additively manufactured parts, the research is relatively under-explored for additive manufacturing MSS steels. The current research thus compared the process-structure-property relations for 440C martensitic stainless steel (MSS) manufactured by conventional and additive manufacturing technologies. For this purpose, microstructure and mechanical properties were studied in the as-manufactured and heat-treated conditions. Further, samples of both conventional and AM MSS steels were prepared and analyzed in terms of macrostructural properties such as Vickers hardness, tensile strength, compressive strength, and wear resistance. Microstructure characterization was also performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and energy dispersive spectroscopy (EDS). A detailed analysis of the performance of the additive manufactured 440C MSS as a function of their microstructural properties is also discussed to develop a better understanding of the process-structure-property correlation.

Keywords: AISI 440C MSS, Heat Treatment, Spray-forming, Direct Energy Deposition, Vacuum Induction Melting

CHAPTER I

INTRODUCTION

1.1 Overview

Early tool steel history shows that the development of these alloys was intimately related to the evolution of iron and steel until understanding the correlations among carbon content, alloy composition, and processing came gradually in the 19th century. In the early modern tool steels, simple plain carbon steels used to be employed as tool steels; however, by the early 20th century, a new generation of complex highly alloyed tool steels was developed. Since then, tool steels have long been considered a very special group of alloys that ensures possession of exceptional time-dependent properties such as tensile/compressive strength, creep coefficient, and shrinkage [4].

Manufacturing is essential for both economic growth and improvements in the quality of life. Manufacturing techniques can be classified as either conventional or advanced processes [5]. The most common conventional processes used in the manufacturing of tool steels are casting and spray forming. Casting typically involves secondary melting processes namely VAR and ESR, which are performed to achieve finer microstructures. Moreover, postprocessing of the components such as hot forming is also needed [6]. Because of its inherent simplicity, spray forming has become a good manufacturing alternative since it requires considerably fewer processing steps than the conventional casting and powder metallurgy processes, and provides fine-grained microstructures with high structural homogeneity [7].

As an emerging technology, additive manufacturing can fulfill the industry's growing demands to produce high-quality components in an energy/efficient way. The main advantage of additive manufacturing over traditional manufacturing techniques is its ability to produce complex geometric shapes with high precision directly from 3D model data [8]. AM technologies can also produce components without the need to include fabrication and postprocessing, which are time-consuming, difficult, and costly processes [9, 10]. Different methods have been developed to meet the demands of the process. Laser bed powder fusion (L-BPF) and direct energy deposition (DED) are the most widely used techniques for producing tool steels. Even when the processing of

martensitic stainless steels through AM technologies is challenging, these types of steels are emerging materials in AM processing techniques [11].

1.2 Justification

The use of AM in manufacturing tool steels and stainless steel has increased in the last few years due to its various benefits. To take advantage of this technique, further study of the process-structure-properties relationship of the manufactured components is essential. A comprehensive understanding of these areas would enable better control of the AM processes and the quality of the final products. Although significant progress has been made in AM tool steels and martensitic stainless steels, many obstacles still need to be overcome. The main obstacle for AM components lies in ensuring specific physical and microstructural requirements that are difficult to achieve considering the complexity of the process and the steel itself.

Even though many studies have analyzed the unique microstructural properties of additively manufactured steels in comparison to conventionally processed steels, there is a lack of overview on how such features will potentially result in advanced properties, to build functional components. Therefore, a better understanding of the processing and characterization of AM tool steels is needed, to determine property impacts on component quality and performance to achieve this functionality in a predictive and reproductive way, which also will enable better use in industrial applications. Additionally, the use of overspray powder generated during conventional manufacturing processes such as spray forming is excellent for AM. This enables a 1:1 material compatibility between the spray formed ingots and the AM powders, allowing a better comparison of the effects of the AM process, as opposed to conventional manufacturing.

1.3 General and specific objectives

The thesis aims to determine the process-structure-properties relationship of conventionally manufactured (casting and spray forming) and additively manufactured 440C martensitic stainless steel. The results of this research aim to allow researchers and manufacturing industries to produce high-performance materials sustainably and cost-effectively.

- Characterize the microstructural and mechanical properties of conventionally and advanced manufactured specimens.
- Analyze the effect of heat treatment on the microstructural and physical properties of conventionally and advanced manufactured specimens.
- Determine the AM process parameters that result in the optimal properties of the components.
- Evaluate the quality of conventionally and advanced produced specimens.
- Compare the process-structure-property relation of the manufactured specimens through the different techniques.

1.4 Outline of thesis

The research work below attempts to provide a better understanding of the process-structure properties of 440C martensitic stainless steel (MSS) manufactured by conventional casting, spray forming, and additive manufacturing direct energy deposition technologies. This dissertation is structured in six interconnected chapters designed as potential publishable articles in peer-reviewed journals. Each chapter is proposed upon the previous one, to progressively disclose the relationship between the processing methods in the performance of the steel. Chapter III takes the spray-formed steel as a reference to determine the optimal austenitizing and tempering heat treatment parameters that lead to better properties of the steel. Chapter IV explores the potential of implementing different heat treatment processes for tailoring the microstructure and mechanical properties of spray-formed 440C MSS (already published [12]). It presents the influence of different heat treatment stages on the resulting microstructure and its subsequent impact on mechanical properties like hardness, toughness, and yield strength. Chapter V compares in detail the microstructures of conventionally cast and spray formed 440C martensitic stainless steel to identify the microstructural features including grain size, carbide distribution, and phase fractions, that influence the mechanical properties of the steel. In Chapter VI, the focus shifts toward wear performance by comparing the friction coefficient, specific wear rate, and wear debris, i.a. of conventionally cast and spray-formed 440C martensitic stainless steel. The correlation between the microstructural features identified in Chapter V is deeply analyzed to provide a valuable understanding of the wear mechanisms at play. Chapter VII delves into the effect of the direct

energy deposition technique on the process-structure-properties relationship of 440C martensitic stainless steel. This chapter focuses on analyzing the non-conventional unique microstructure that results from the direct energy deposition process and its influence on the mechanical behavior of the steel. Finally, chapter VIII brings the entire research journey together, by providing a comprehensive analysis of the insights from all preceding chapters in this dissertation including general conclusions. Additionally, this chapter identifies potential limitations and proposes future research directions to further advance the understanding of performance optimization of this type of material.

CHAPTER II

LITERATURE REVIEW

2.1 Martensitic stainless steels

2.1.1 Introduction

Martensitic stainless steels (MSS) are iron-chromium-carbon-based alloys that are martensitic in the hardened condition. These steels are ferromagnetic and have moderate corrosion resistance compared to other stainless steels. The lower content of chromium makes them less expensive and suitable for mild ambient conditions that require high strength and corrosion resistance. Some of the historical applications include cutlery, ball bearings, springs, valves, and turbine equipment. The 410 MSS was the basic grade invented by Harry Brearley in 1913. Since then, its progression has led to other grades with additional alloying elements [13].

The above definition points out three main aspects to consider when referring to MSS steels. The first aspect regards the fact that MSS can be classified into three grades based on their chemical composition. All three types contain high chromium and a combination of alloying elements that allows the steel to obtain an almost fully martensitic structure with some amounts of retained austenite and an excess of carbides after quenching from elevated austenitizing temperatures. Because martensitic stainless steels are more sensitive to heat treatment than other steels, the implementation of appropriate heat treatment parameters is a determining factor in achieving their full potential [6, 14]. The second element of the definition has to do with the different manufacturing methodologies employed in the production of steel. Since MSS annual production represents only 2% of the total amount of other steel production per year, it means that its manufacturing methods could be different from other large volume produced steels due to the requirements of its high manufacturing standards to achieve the required superior properties [6, 14]. Finally, the third part of the definition refers to the final application: used to make tools for cutting, forming, or otherwise shaping the material into a part or component adapted to a definite purpose at either ordinary or elevated temperatures [15]. Despite this definition, MSSs are also used in a very wide variety of non-tool applications as a result of the excellent properties they offer,

in addition to all possible combinations that can be obtained by considering the steel grade, manufacturing methodology, heat treatment conditions, and mechanical design [6].

2.1.2 Metallurgy and alloying of martensitic stainless steels

The equilibrium microstructure of MSS at room temperature is a mixture of ferrite and carbide, while at high temperatures the equilibrium structure is almost fully austenitic. After austenitizing and quenching, the fast-cooling rate leads to the formation of the non-equilibrium phase of martensite. MSS should meet the following characteristics: have at least 10.5 wt.% of chromium for good corrosion resistance and should be austenitized, which is something challenging to achieve. To ensure these criteria are met, martensite in steels containing more than 10.5 wt.% of chromium, should necessarily add gamma-forming elements such as carbon, nitrogen, nickel, and manganese to expand the chromium levels and temperatures at which full austenitization can occur [13, 16].

Alloying elements are added to MSSs to improve physical and mechanical properties at either high or low temperatures [17]. The combination of alloying elements and heat treatment plays an important role in physical and mechanical properties. For instance, gamma-forming elements, except for cobalt, depress the martensite start and finish temperatures. This restricts the amount of alloying elements that can be added and limits the corrosion resistance of the steel [16]. Also, the effect of a single element can be seriously altered by the presence of other elements. Thus, their interaction has to be considered [2]. Alloying elements have a strong influence on annealed steels since they promote solid-solution hardening of ferrite, increase the fraction of carbide particles in the matrix, produce strengthening by dispersion hardening, and change the nature of carbide phases [1]. According to the effect on the matrix, steel alloying elements can be divided into two main categories: austenite stabilizers and ferrite stabilizers, as shown in Table 2.1 [1, 2].

Table 2.1 Alpha and gamma-forming elements [1].

Alpha-forming elements (ferrite)			Gamma-forming elements (austenite)	
Chromium	Tungsten	Columbium	Manganese	Copper
Molybdenum	Titanium	Tantalum	Nickel	Cobalt
Vanadium	Zirconium	Silicon	Nitrogen	Carbon

There are also two major categories in which steel alloying elements can be divided according to their interaction with carbon, as listed in Table 2.2. The effect of every single element is summarized below.

Table 2.2 Carbide and non-carbide forming elements [2].

Carbide-forming elements			Non-carbide-forming elements	
Manganese	Chromium	Molybdenum	Nickel	Copper
Tungsten	Vanadium	Niobium	Cobalt	Silicon
Titanium	Zirconium	---	Phosphorus	Aluminum

2.1.3 Manufacturing of martensitic stainless steels

In general, tool steels are manufactured by traditional methods including casting, powder metallurgy, spray-forming, and advanced manufacturing techniques such as additive manufacturing. A summary of typical manufacturing practices is presented below, along with their benefits and drawbacks.

Casting is one of the most common methods used in the production of MSS steels (Figure 2.1). For this process, a wide variety of manufacturing equipment and techniques are employed and no universal practice is followed; however, most tool steels are processed using either electric arc furnace (EAF) or vacuum induction melting (VIM) techniques [6, 18]. In recent years the interest in new melting, remelting, and casting vacuum techniques has increased mainly as a result of the necessity to produce alloys containing different amounts of reactive elements. These elements tend to form oxides which have a deleterious effect on the mechanical properties of the material [19].

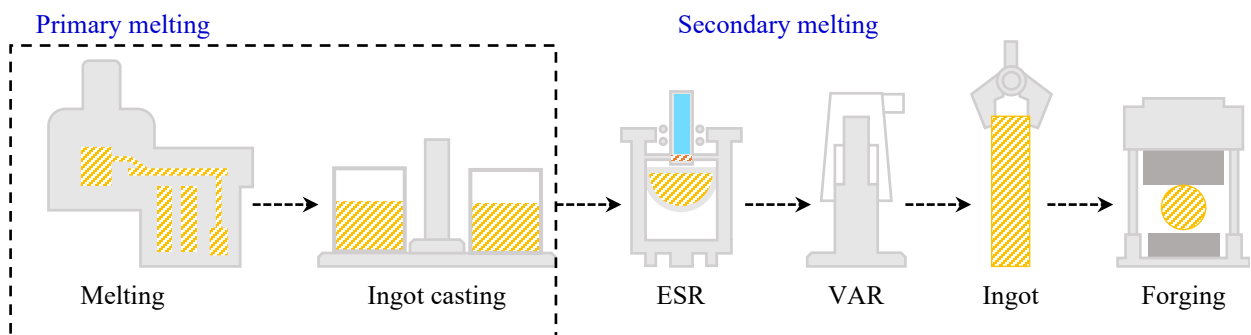


Figure 2.1 Conventional manufacturing process of tool steels.

Vacuum induction melting (VIM) is an established and tested method in the production of liquid metal. This process has been specially designed for complex alloys that must be melted under an inert gas atmosphere, and its major advantage resides in the mass transport through continuous stirring, which helps to have homogeneity and control over the alloy composition [20, 21]. Other benefits derived from this process are a high degree of flexibility, temperature control, low loss of alloying elements by oxidation, control over alloy composition, and good melt cleanliness. The abovementioned constitute the most relevant metallurgical and production reasons for using VIM, despite that it is a relatively costly process as compared with other primary melting techniques [20, 22]. On the other hand, the two main drawbacks of the process are the possible reaction between the molten alloy and the refractory, and the lack of control during solidification.

With the increasing demands of the industry, near-final-shaped components with minimal to no additional processing have been the goal in materials manufacturing. The main motivation for developing new processing technologies is to achieve high production rates combined with superior product performance and waste reduction, which leads to a decrease in manufacturing costs [23]. The spray forming or the Osprey process has proved to be a promising technology with the potential to meet the demands of the industry regarding the development and improvement of tool steels [7]. Nowadays, spray forming (SF) is an established advanced casting technique that closes the gap between conventional casting processes and methods employed in powder metallurgy (PM) [24]. In the spray forming process (Figure 2.2), liquid metal is continuously gas atomized by nitrogen or argon to produce small alloy droplets ranging from 10 to 500 μm in diameter. These droplets that reach velocities up to 100 ms^{-1} are deposited into a rotating spray-formed substrate before full solidification. During the trajectories, the metal droplets are cooled at rates between 100-100000 $\text{K}\cdot\text{s}^{-1}$ and solidification continues until a solid deposit is built up [25]. With this technique, the obtained microstructure shows an absence of dendritic morphologies, low levels of macro segregation, high levels of homogeneity, and fine equiaxed grain size from 10 to 50 μm [24-26]. The main advantage of the spray-forming process is the potential capability to manufacture complex alloys that are difficult to produce by conventional processes in considerably fewer processing steps [25]. The drawbacks of SF include porosity (achieved density from 95 to 99 %) that requires further hot working, and material losses due to atomized droplets that do not impact the formed billet [23, 25].

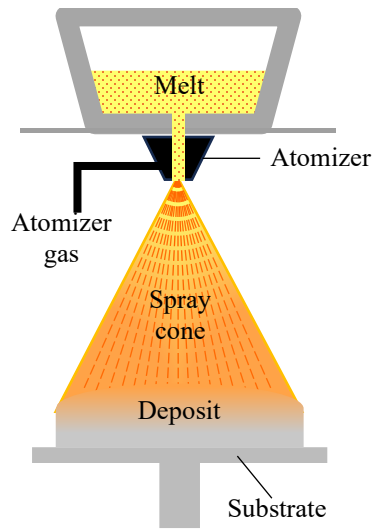


Figure 2.2 Spray forming process illustration.

Defined as “a process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies” [27], additive manufacturing technologies provide the possibility of translating virtual solid model data into fully functional parts of a wide range of materials including metallic, polymers, ceramic, and composites [28]. Overall, additive manufacturing technology creates finished parts by the addition of materials. However, the technique used to layer deposition and how the deposited layers are bonded together differs in each process, see Figure 2.3 [5, 28]. Different methods of AM have been developed and continuously perfected to produce high-performance materials and complex 3D structures. The prompt of AM technologies is mainly due to the necessity to print large structures with fewer printing defects and better mechanical properties [10]. The main advantages of AM over traditional manufacturing are the high degree of customization and personalization, the production of geometrically complex components with minimal material waste, and the optimization of the process through the reduction of time and costs associated with small quantity productions [29, 30]. These benefits open the door to novel innovations in design and functionality, which are necessary for the manufacturing and assembly of any product. Additive manufacturing has also made possible the development of environmentally friendly products by reducing the amount of energy and natural resources that are consumed for its operation. On the other hand, limitations in size, surface imperfections, and the high initial cost of AM equipment are the major limiting factors that do not allow AM to compete with conventional manufacturing [5].

The latest advances and developments in the materials, processing, software, and equipment areas have made possible the implementation of AM technologies in the production of reliable components with adequate physical properties. The direct manufacture of functional products continues to be the main objective of AM technologies, especially for metallic parts, and its use has increased in recent years mainly in the manufacture of small and medium quantities [28].

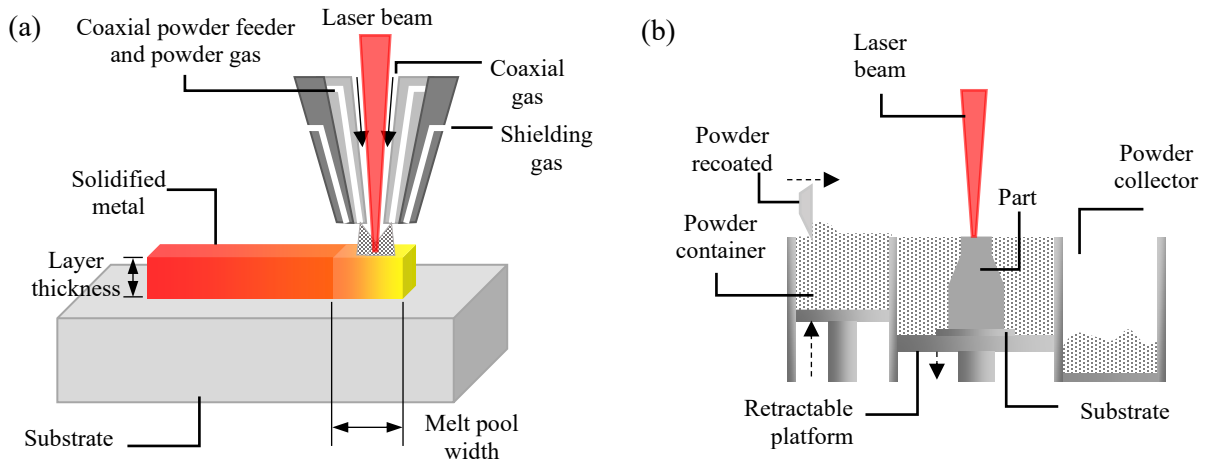


Figure 2.3 Representative scheme of two of the most common additive manufacturing technologies in the production of metals a) DED and b) L-PBF [3].

RESEARCH RESULTS AND DISCUSSION

CHAPTER III

AN INVESTIGATION OF THE MICROSTRUCTURE EVOLUTION OF HEAT-TREATED SPRAY FORMED 440C MARTENSITIC STAINLESS STEEL

Abstract

AISI 440C martensitic stainless steels (MSS) are widely used in industry due to their high strength and toughness in combination with good corrosion resistance. However, segregation of alloying elements and coarse primary carbides are the main concerns in conventional cast 440C MSS. As a rapid solidification technology, spray forming (SF) is a good alternative to conventional casting by producing fine-grain structures without macro-segregations. This study aims to compare the microstructure evolution and mechanical properties of spray-formed AISI 440C MSS under different heat-treatment conditions. The initial part of the research focused on the microstructure evaluation from the as-received to the as-tempered condition. The observations from scanning electron microscopy revealed that the volume fraction of Cr_{23}C_6 carbides decreases with increasing austenitizing temperature and holding time. Moreover, an increase in grain size and amount of retained austenite was observed. For a given holding time, the hardness exhibited an initial increase to a peak at 1050 °C followed by a gradual decrease at higher austenitizing temperatures. The findings of this research successfully determined specific austenitizing and tempering parameters that lead to the optimal combination of hardness and mechanical properties.

Keywords: Spray Forming, AISI 440C MSS, Retained Austenite, Heat Treatment

3.1 Introduction

The 440C MSS is known for being one of the hardest steel in the family of martensitic stainless steels. Its high carbon content allows to accommodate primary strengthening through mechanisms such as solid solution strengthening and precipitation hardening. For this material, a good balance between strength and ductility can be achieved by implementing the proper heat treatment process [31]. The conventional heat treatment sequence for this steel includes austenitizing to fully or partially dissolve carbides, quenching to promote martensitic transformation, and tempering to enhance toughness and ductility [32]. After heat treatment, the typical microstructure of the 440C MSS consists of martensite, undissolved/re-precipitated carbides, and retained austenite [32]. The volume fraction of these phases is mainly influenced by the austenitizing temperature, which determines the partitioning of carbon and alloying elements between austenite and carbide particles. It is well known that high austenitizing temperatures promote the dissolution of carbides, leading to an increase of carbon and carbide-forming elements in solid solution. This has an impact on the martensitic transformation by depressing the martensite start (M_s) and finish (M_f) temperatures. If the M_f temperature is reduced below room temperature, retained austenite is likely to form [32]. Then, the heat treatment plays a crucial role in determining the microstructure of 440C steel, which depends largely on the austenitizing temperature and time, and therefore on the mechanical performance of the steel. Salhi et al. [33] studied the microstructure and mechanical properties of quenched and tempered 440C MSS. They observed that the hardness decreased with increasing the austenitizing temperature due to the partial dissolution of M_7C_3 , which promoted the growth of prior austenite grains due to the loss of carbide pinning effect. Syarif et al. [31] reported that the higher hardness and strength for 440C MSS are achieved at an austenitizing temperature of 950 °C, at which the partial dissolution of carbides is assumed to occur. At this temperature, the microstructure consisted of $M_{23}C_6$ carbide type, martensite, and a small fraction of retained austenite. Puskar et al. [34] measured the response of 440C MSS to the austenitizing process at temperatures ranging between 1038 to 1093 °C. Their results showed that 1066 °C was the minimum austenitizing temperature to achieve a hardness of 58 HRC. On the other hand, microstructural examination suggested that the morphology and distribution of carbides changed with the austenitizing temperature.

Although some studies have focused on determining the effect of heat treatment on the microstructure and mechanical properties of conventional 440C MSS, only a few studies have analyzed in detail the effect of the austenitizing and tempering processes over a wide range of temperatures and holding time. Moreover, there are no previous studies on spray-formed 440C MSS. Therefore, this investigation aimed to determine the effect of austenitizing and tempering processes on the properties of spray-formed 440C MSS.

3.2 Experimental details

3.2.1 Materials

The alloy was produced using the spray-forming manufacturing technique. After the fabrication, the alloy was forged and then annealed. The chemical composition of the as-received (AR) spray-formed AISI 440C MSS as determined by optical emission spectroscopy is listed in Table 3.1.

Table 3.1 Chemical composition of spray formed 440C MSS (wt.%).

Steel grade	Chemical composition in wt. %											
	C	Mn	P	S	Si	Cr	Mo	V	W	Ni	Co	N
AR-440C	1.19	0.45	0.03	0.024	0.57	15.86	0.816	0.55	0.186	0.33	0.14	0.1
440C ref [35]	0.95- 1.20	≤1.00	≤0.04	≤0.03	≤1.00	16.0- 18.0	≤0.75	---	---	---	---	---

3.2.2 Heat treatment process

Two sets of small samples ($6 \times 6 \times 6 \text{ mm}^3$) were austenitized at temperatures between 1000 and 1100 °C. Then, one set was held for 0.5 h and the other one for 1 h, followed by oil quenching. Different austenitizing temperatures and soaking times were chosen to ensure the phase transformation of austenite into martensite upon quenching and to observe variations in phase fractions. Thereafter, the as-quenched specimens were tempered in the temperature range of 150-550 °C and maintained for 0.5, 1, and 2 h (separately) before undergoing air cooling to room temperature. All the heat treatments were performed in a horizontal tube furnace under an argon-controlled atmosphere.

3.2.3 Microstructural characterization

After heat treatment, all samples were mechanically ground and polished using conventional metallographic techniques. To develop the different microstructures, the samples were etched using Villella's reagent. The microstructural analysis of the samples was performed by scanning electron microscopy (SEM) using lower secondary electron and backscattered electron detectors. The element composition of the phases was determined using energy-dispersive X-ray spectroscopy (EDS). For electron backscattered diffraction (EBSD) analysis, the samples were electropolished using a solution of 60 ml perchloric acid in 940 ml acetic acid solution at 15 V. Subsequently, EBSD analysis was carried out in a field emission gun scanning electron microscope (JEOL JSM-7600F FEG/SEM) using a QUANTAX CrystAlign 400i-EBSD system with a tilt angle of 70°, an acceleration voltage of 20 kV, and a scan step-size of 39 nm. The data was further post-processed using the ESPRIT 2 Quantax software. Thereafter, the surfaces were examined by X-ray diffraction on a Bruker D8 Advance with Cu-K α radiation using the Bragg-Brentano geometry. The diffraction patterns were recorded in the range of 40 to 125° 2 θ with angular steps of 0.05° and a counting time of 3 s per step. The integrated intensities of the peaks (200) $_{\gamma}$, (220) $_{\gamma}$, (311) $_{\gamma}$, (200) $_{\alpha'}$, (211) $_{\alpha'}$, and (220) $_{\alpha'}$ were used to determine the volume fraction of austenite according to equation (3.1) [31].

$$V_{\gamma} = \frac{I_{\gamma}}{(I_{\gamma} + 3.38 I_{\alpha'})} \quad (3.1)$$

Where V_{γ} is the volume fraction of austenite, I_{γ} is the average integrated intensity of the austenite peaks and $I_{\alpha'}$ is the average integrated intensity of the martensite peaks.

Also, the carbon content of reversed austenite was calculated by equation (3.2) [36].

$$C_{\gamma} = (a_{\gamma} - 3.556 - 0.00095X_{Mn} - 0.0056X_{Al}) / 0.04 \quad (3.2)$$

Where a_{γ} is the lattice parameter of the austenite and X_{Mn} and X_{Al} are the weight percent of manganese and aluminum respectively.

Vickers hardness measurements were performed on the heat-treated samples using a computer-controlled tester HM-220B Mitutoyo, equipped with a manually controlled xy stage and digital micrometer heads with a resolution of 1 μm . Vickers hardness of the steel samples was determined under a constant load of 200 g (1.96 N) and a holding time of 15 s. A total of 10 indentations were made to determine the average hardness of each specimen and to verify the homogeneity of the microstructure. For the tensile tests, dog-bone samples of $4.8 \times 5.5 \text{ mm}^2$ cross-section were tested using an MTS[®] 100 kN servo-hydraulic testing machine. The specimens were tested in load control mode at a strain rate of 0.005 s^{-1} . The axial deformation was measured using an MTS 634.31F-24 extensometer with a gauge length of 20 mm.

3.3 Results and discussion

3.3.1 Characterization of the as-received (AR) microstructure

Figure 3.1(a) illustrates the microstructure of the spray-formed AR steel. The sample exhibits intergranular and intragranular carbides, that are homogeneously distributed in the matrix. As shown in Figure 3.1(b), the XRD results show that the microstructure of the AR sample consists of α -ferrite as well as primary Cr_7C_3 and secondary Cr_{23}C_6 carbides. These results are consistent with the EBSD phase analysis in Figure 3.1(c). It can also be seen from the figure that the eutectic Cr_7C_3 carbides mainly precipitate along the grain boundaries either in the form of plates or irregular blocks, while the relatively small secondary Cr_{23}C_6 carbides are observed within the ferrite grains. This type of carbide is found to be better distributed throughout the matrix and in higher amounts than those located at the grain boundaries. In the map colored according to the inverse pole figure observed in Figure 3.1(d), it can be seen that the material has randomly oriented equiaxed grains.

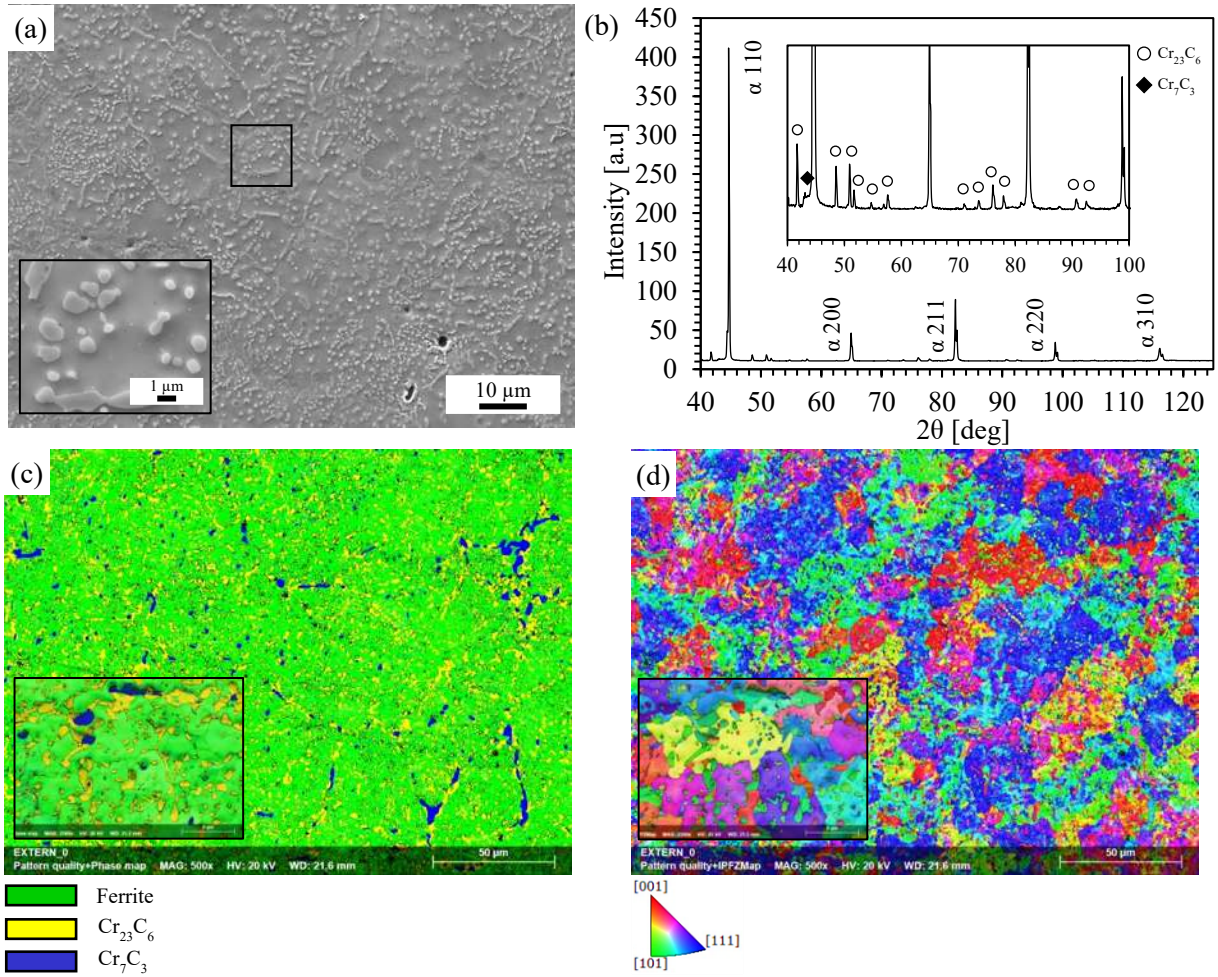


Figure 3.1 (a) Secondary electron SEM micrograph of SF 440C in the AR condition, (b) XRD diffractogram in which characteristic peaks are identified, (c) phase map, and (d) IPFZ map of the ferrite phase and carbide particles.

3.3.2 Effect of austenitizing temperature and time on the microstructure and hardness

Figure 3.2(a) shows the variation of prior austenite grain size as a function of the austenitizing temperature, where an increase in the prior austenite grain size was observed with increasing the austenitizing temperature as the carbides are taken into dissolution at higher austenitizing temperatures. After heat treatment, the average prior austenite grain size is between 40 and 55 μm . The slight variation in size indicates that the undissolved carbide particles effectively hinder the growth of prior austenite grain size during austenitizing. The size distribution of prior austenite grain size is shown in Figure 3.2(b). The results were then fitted to a log-normal distribution curve representing the mean and variance of the grain size.

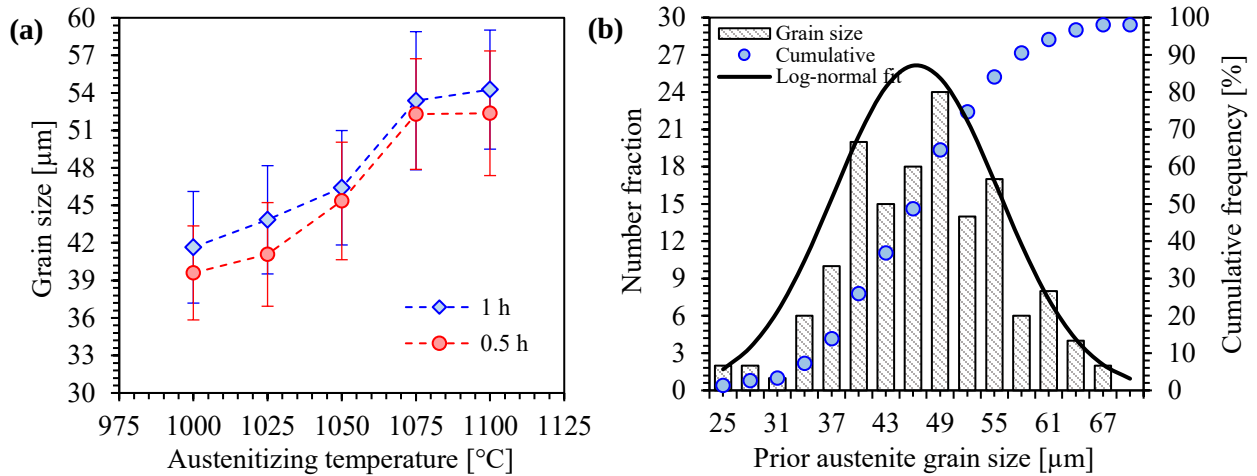


Figure 3.2 (a) Prior austenite grain size as a function of austenitizing temperature and time and (b) normal distribution of grain size in sample austenitized at 1050 $^{\circ}\text{C}$ for 1 h.

From the corresponding XRD patterns in Figure 3.3, it can be observed that the transformation from ferrite to martensite occurs (see (110) reflection), followed by the appearance of austenite in the (111) reflection. After quenching, a decrease in the intensity and a broadening of the peaks is observed. The fitting of diffractograms indicates a degree of crystallographic texture that is mainly observed along the [110] direction. This may be related to the level of strain present in the sample due to phase transformation. In addition, a shift of the peaks to the left can be observed. The shift to the left implies an increase in the interplanar distance and therefore an increase in the lattice parameter, indicating tensile residual stresses. This phenomenon can be explained by changes in the supersaturated carbon structure and changes in the stress state that occur during the martensitic transformation [37]. The detail $\alpha'(001)$ peaks in the XRD diffractograms of Figures 3.3(a) and 3.3(b) indicate that the samples treated at higher austenitizing temperatures for 1 h exhibit a larger amount of retained austenite and a smaller fraction of carbides.

The indexed XRD pattern in Figure 3.3(c) confirms the presence of carbides of the type Cr_7C_3 and Cr_{23}C_6 in the microstructure. Here, the intensity and number of peaks provide an approximation of phase fraction [38]. The measured retained austenite content of the as-quenched samples is shown in Figure 3.3(d). At the austenitizing temperature of 1000 $^{\circ}\text{C}$, only a small amount of Cr_{23}C_6 carbides can be dissolved, and a small amount of retained austenite is formed after quenching. It can be seen that for the holding time of 0.5 h, the austenite fraction shows a small variation at the

different austenitizing temperatures. On the other hand, for the holding time of 1 h, a small variation is perceived before 1075 °C, and a significant increase can be observed from 1100 °C.

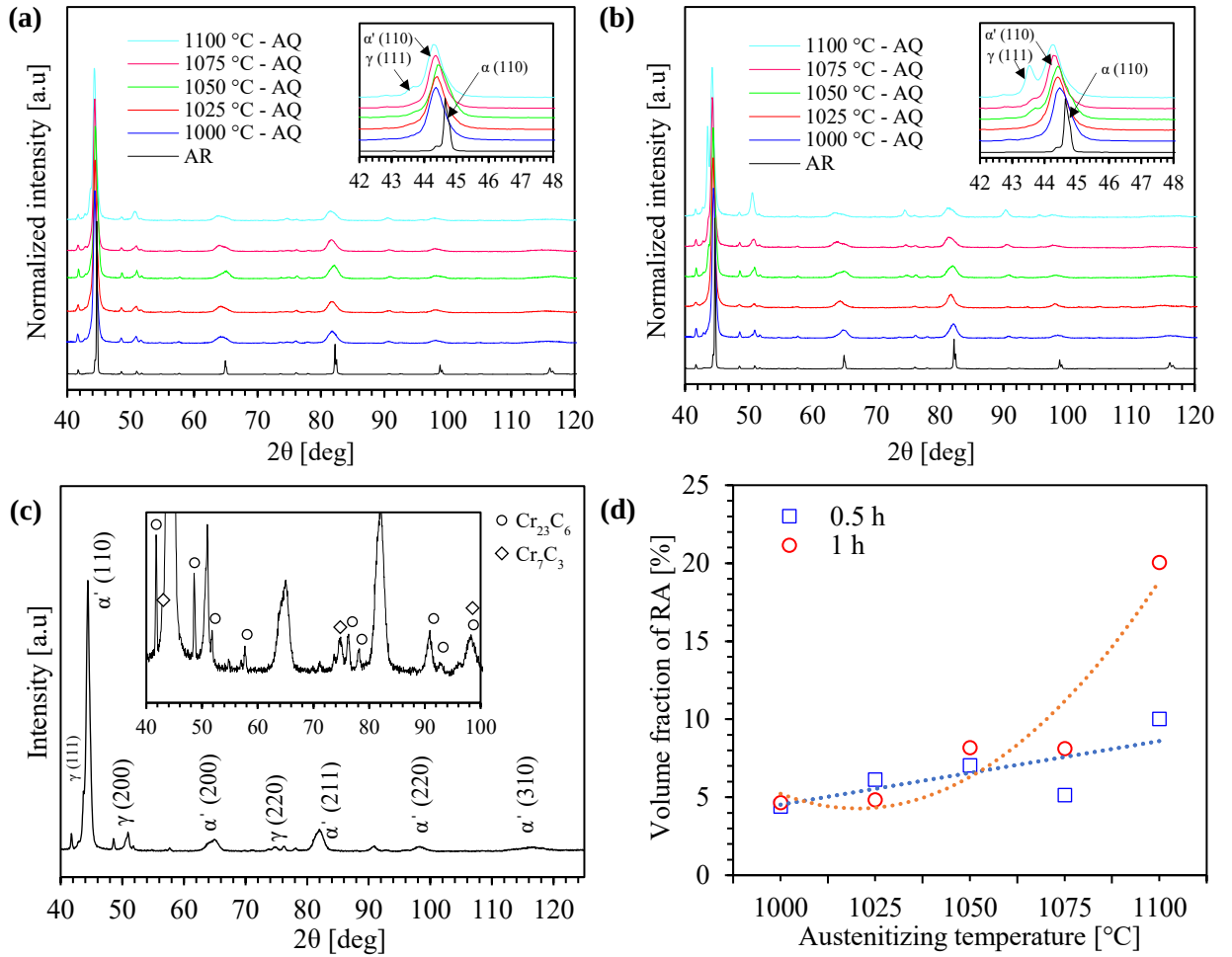


Figure 3.3 XRD pattern of the as-quenched samples austenitized at different temperatures for (a) 0.5 h, and (b) 1 h. (c) Pattern indexation of sample austenitized at 1050 °C for 1 h. (d) Retained austenite % in the as-quenched samples as a function of the austenitizing temperature and time.

The effects of austenitizing temperature and holding time on the microstructure of the SF 440C MSS are shown in Figure 3.4. The microstructure of the as-quenched samples consists of martensite and undissolved Cr₇C₃ and Cr₂₃C₆ carbide particles. It is expected that higher austenitization temperatures and longer holding time will partially dissolve Cr₂₃C₆ carbides into the matrix during the heat treatment. As shown in Figure 3.4(e-f), the higher austenitizing temperature of 1100 °C is not sufficient to completely dissolve the carbides present in the as-received SF material. However, at the austenitizing temperature of 1100 °C, the microstructure under both holding times exhibits

more dispersed globular carbide particles. Then the temperature of 1100 °C promotes partial carbide dissolution and/or carbide coarsening. After quenching, the microstructure of the SF 440C MSS also shows the presence of retained austenite. This is due to the decrease in M_s temperature that occurs when the amount of carbon and alloying elements in solid solution increases during the partial dissolution of the carbide particles [32].

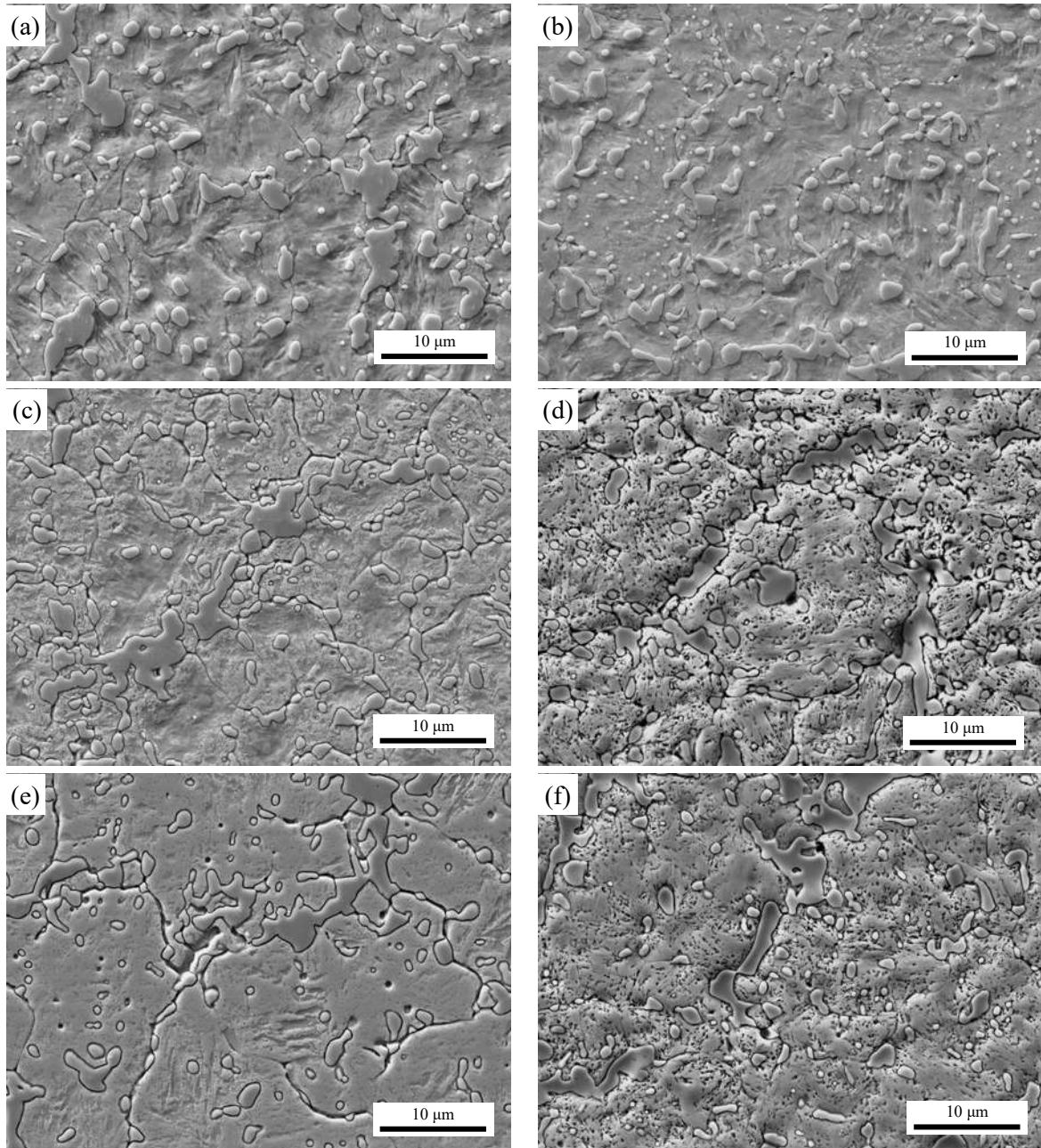


Figure 3.4 SEM micrographs of AISI 440C after austenitizing at (a) 1000, (c) 1050, and (e) 1100 °C for 0.5 h and (b) 1000, (d) 1050, and (f) 1100 °C for 1 h.

The EBSD phase maps of the AQ conditions are shown in Figure 3.5 (a). The overall microstructure of the sample austenitized at 1050 °C in Figure 3.5(a) shows a fully lenticular martensitic structure dominated by Cr_{23}C_6 and a small amount of Cr_7C_3 precipitation. Comparison of the detailed microstructures of samples austenitized at 1050 °C and 1100 °C in Figure 3.5(a) and (b), respectively, shows that at 1100 °C the sample exhibits a smaller Cr_{23}C_6 carbide size. This finding is consistent with the measured increase in retained austenite as well as the decrease in the volume fraction of Cr_{23}C_6 carbide with increasing the austenitizing temperature. Figure 3.5(c) shows the formation of retained austenite between the martensite lenses. Fine and dispersed particles identified as Cr_7C_3 and Cr_{23}C_6 carbides were also found along the grain boundaries and martensite lenses. Since the plate martensite structure is usually formed in nonparallel arrays and has irrational habit planes of high multiplicity, its microstructural arrangement is quite irregular [39]. Dark regions with low contrast of Kikuchi bands were found in the as-quenched samples. This phenomenon can be attributed to high defect density, in this case, dislocations [40].

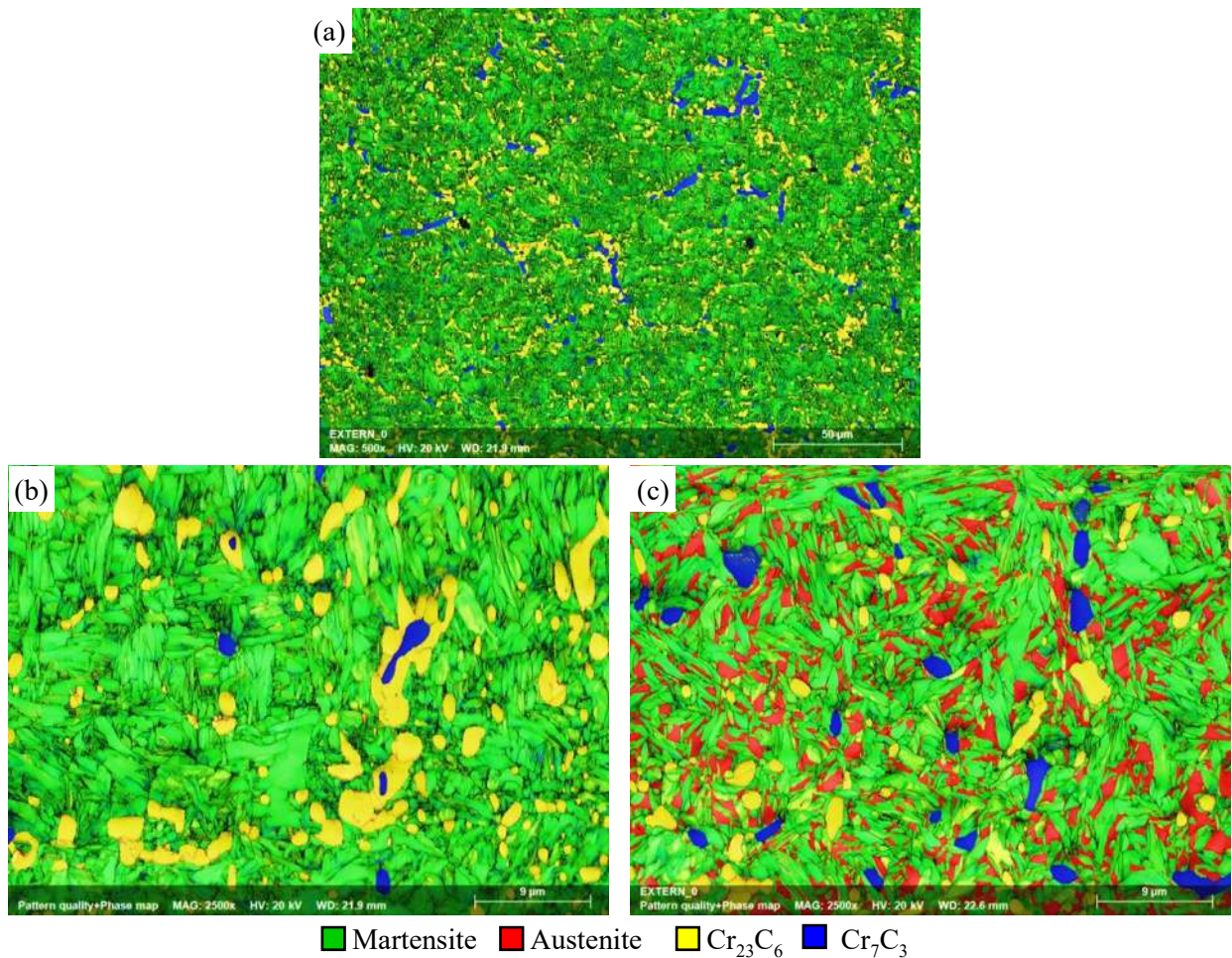


Figure 3.5 EBSD phase map (a) overall microstructure of the sample austenitized at 1050 °C for 1 h and comparison of the as-quenched samples austenitized at (b) 1050 °C for 1 h and (c) 1100 °C for 1 h.

Figure 3.6(a) shows the hardness measurements as a function of austenitizing temperature and holding time. It can be observed that the hardness continuously increases with increasing austenitizing temperature until the maximum hardness is reached at 1050 °C. This is due to the low level of retained austenite and the partial dissolution of Cr_{23}C_6 carbide, which leads to an increase in the carbon supersaturation and promotes the transformation of a higher volume fraction of martensite without depressing the martensite transformation range at sub-zero temperatures [31-33, 41]. At the same time, as the austenitizing temperature increases, the Cr_{23}C_6 carbides partially dissolve, leading to a decrease of the carbides pinning effect and promoting the growth of prior austenite grains, and a decrease in hardness [33, 42].

Among the five temperatures and two holding times studied, the hardness histogram indicates that the equilibrium temperature of carbide dissolution is 1050 °C, which exhibits the maximum hardness. On the other hand, the sample austenitized at 1100 °C for 1 h has a lower hardness and a higher amount of retained austenite. The XRD plots in Figure 3.6(b) and (c) show the asymmetric $\alpha'(022)$ reflection, which is characteristic of supersaturated martensite. The peaks were deconvoluted into two curves by fitting using the pseudo-Voigt distribution. In both cases, peak broadening is observed, which is related to the decrease in the crystallite size and the accumulation of mechanical strain. At the austenitizing temperature of 1100 °C in Figure 3.6(c), the martensite peak is wider and has a lower intensity due to the effects of crystal defects and micro-stress-strain in the sample. Also, the shift of peak (002) to lower Bragg angles indicates the presence of large tensile stress in the martensite.

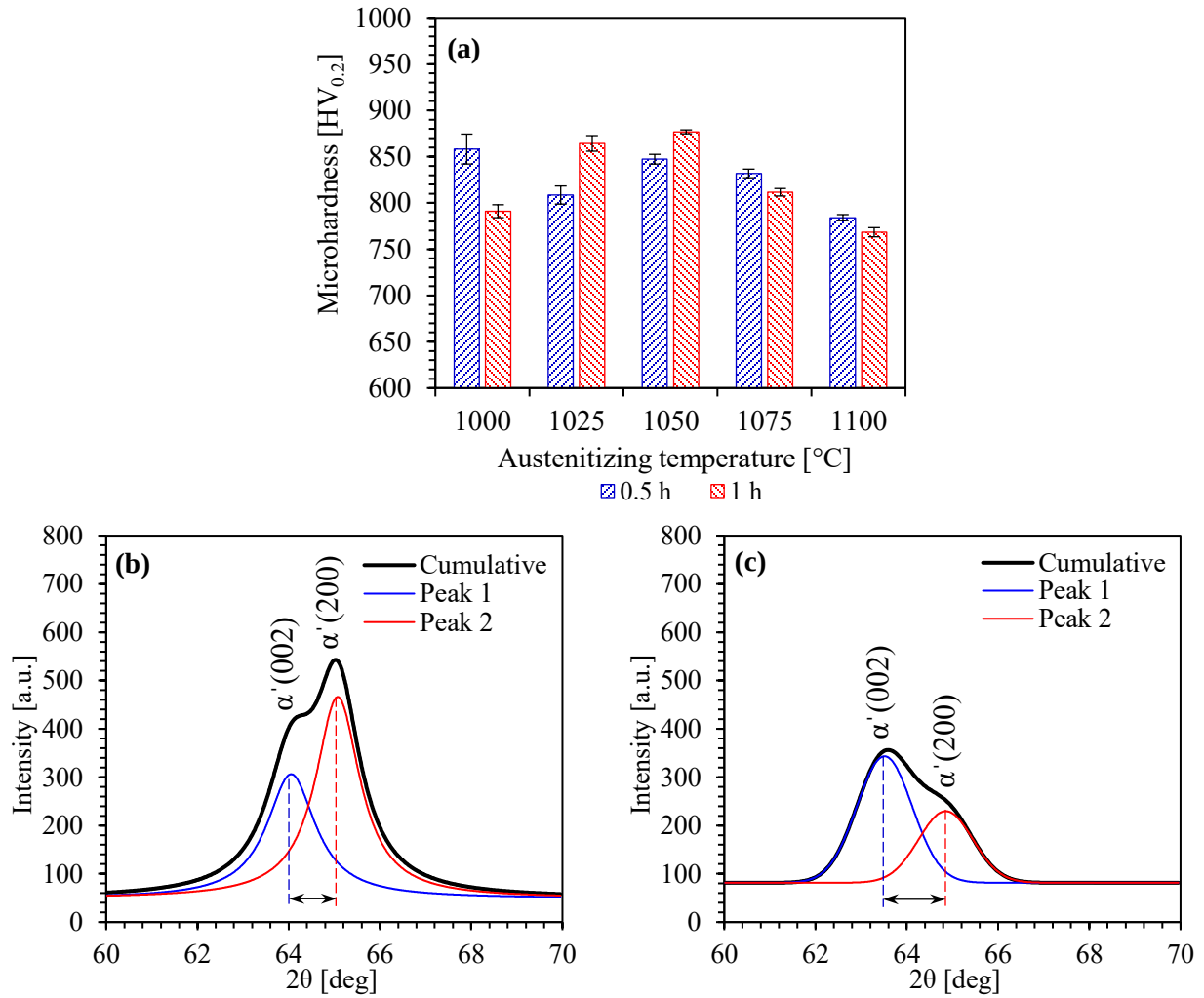


Figure 3.6 (a) Hardness values of the as-quenched AISI 440C SS as a function of austenitizing temperature and time. Peak deconvolution of the second martensite reflection in sample austenitized for 1 h at (b) 1050 °C and (c) 1100 °C.

For further analysis, the temperature of 1050 °C and holding time of 1 h were set as the optimal parameters for the austenitizing process.

3.3.3 Effect of tempering temperature and time on the microstructure and mechanical properties

Figure 3.7 shows the changes in the microstructure of the tempered steel as a function of temperature and time. The microstructure of the as-tempered samples is very similar to that of the as-quenched condition, both showing a martensitic matrix with lenticular shape and zig-zag array. Even at low tempering temperatures, the mobility of carbon is enough to diffuse and precipitate as carbides. During tempering, carbon in the supersaturated state martensitic structure precipitates

into carbides. The presence of small-size secondary carbides embedded in the martensitic structure is also noted. The carbides were mainly needle-like morphology, and some others showed spherical and roundish shapes. Thermal exposure at relatively high temperatures (550 °C) promotes the coarsening of Cr_{23}C_6 carbides, as shown in Figure 3.7(c), (f), and (i).

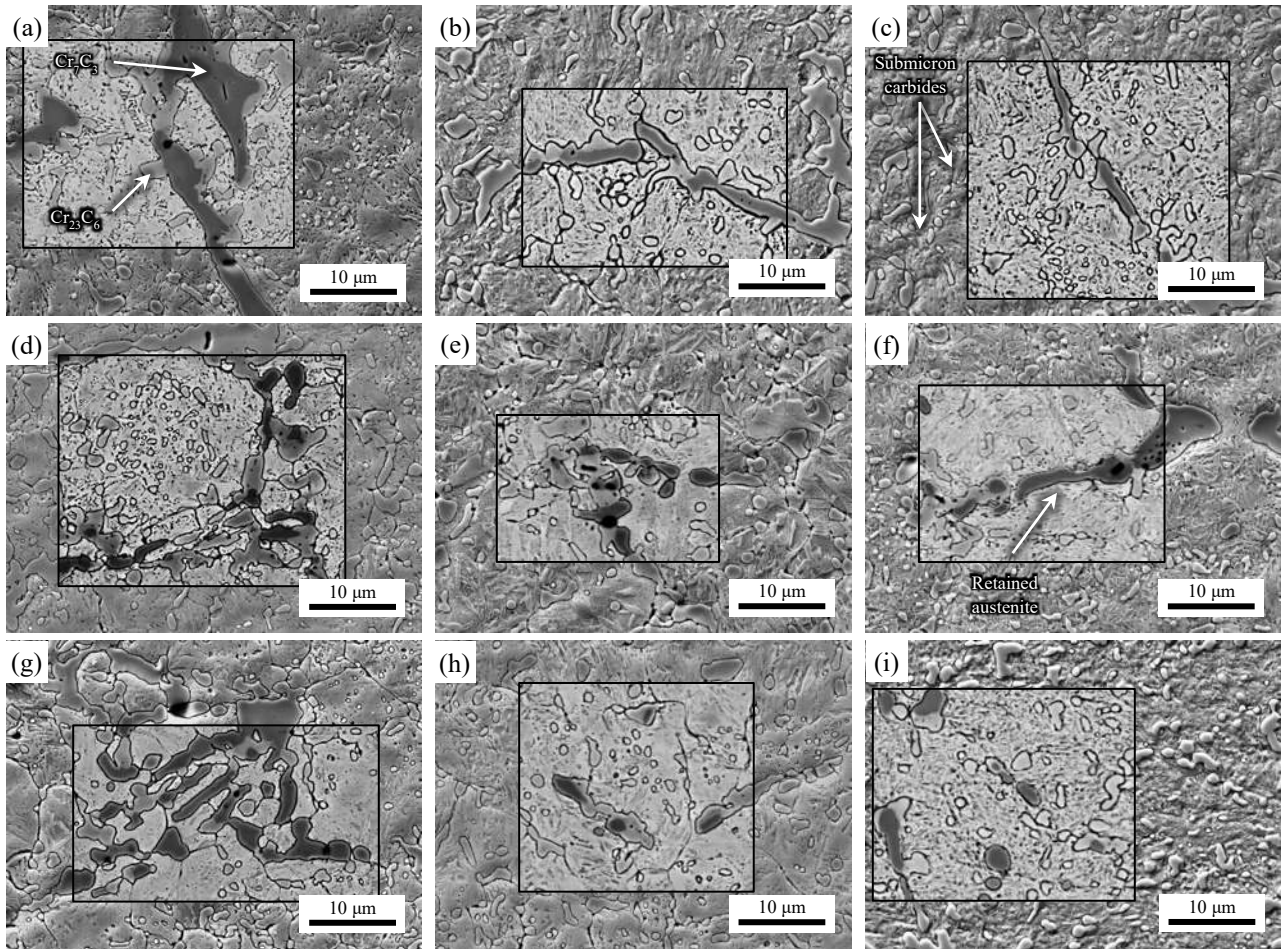


Figure 3.7 SEM/BSE micrographs showing the microstructure of the as-tempered AISI 440C SS for 0.5 h at (a) 150, (d) 350 (g) 550 °C, 1 h at (b) 150, (e) 350, (h) 550 °C, and 2 h at (c) 150, (f) 350 (i) 550 °C.

From the corresponding XRD patterns in Figure 3.8, it can be seen that part of the retained austenite transformed into martensite. In addition, the types of carbides identified are similar to those in the as-quenched state. It is seen that as the tempering temperature increases, the characteristic martensite peaks shift to higher Bragg angles, which suggests tetragonality loss as the lattice parameter c decreases due to stress relaxation of the matrix. An increase of secondary carbides at

tempering temperatures of 450 °C and higher is barely seen due to the low volume. Peak sharpening also occurs at higher tempering temperatures, indicating a reduction in lattice strain.

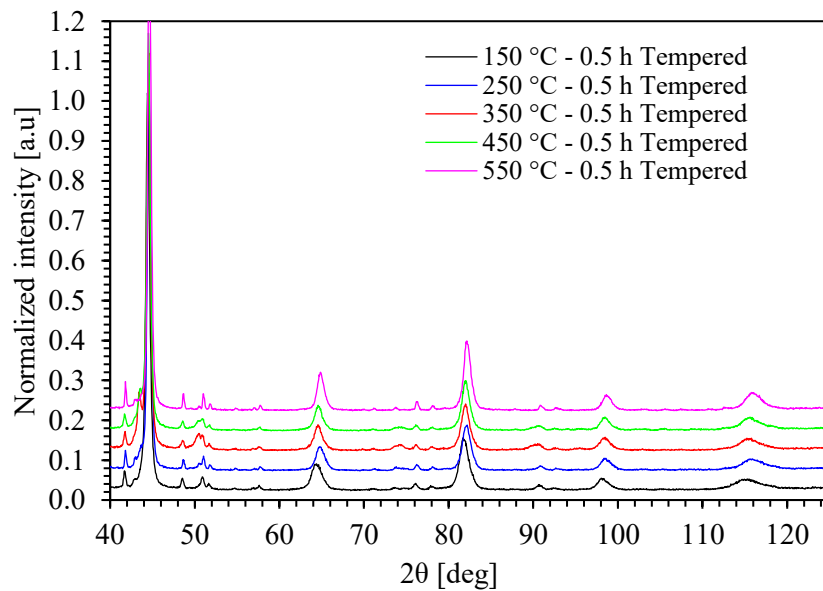


Figure 3.8 XRD patterns for the 440C MSS tempered samples as a function of temperature and time.

The EDS maps of the as-tempered condition at 150 °C for 0.5 h presented in Figure 3.9 reveal the presence of chromium-rich carbides with small vanadium and molybdenum contents as part of their main composition. In Figure 3.9(a), two different contrasts can be seen in the carbides, namely light and dark, which differ in atomic compositions. The EDS maps in Figure 3.9(c-f) show that the light carbides are Fe-rich carbides containing Cr and small amounts of Mo and V. On the other hand, the dark carbides are Cr-rich carbides that contain Fe and small quantities of Mo and V. It is worth noting that the V content in the darker carbides is considerably higher than that in the light carbides. The qualitative elemental composition of carbides and the matrix determined by ESD microanalysis is shown in Figure 3.9(a-b) and Table 3.2. The EDS analysis of particle 6 is shown in Figure 3.9(b).

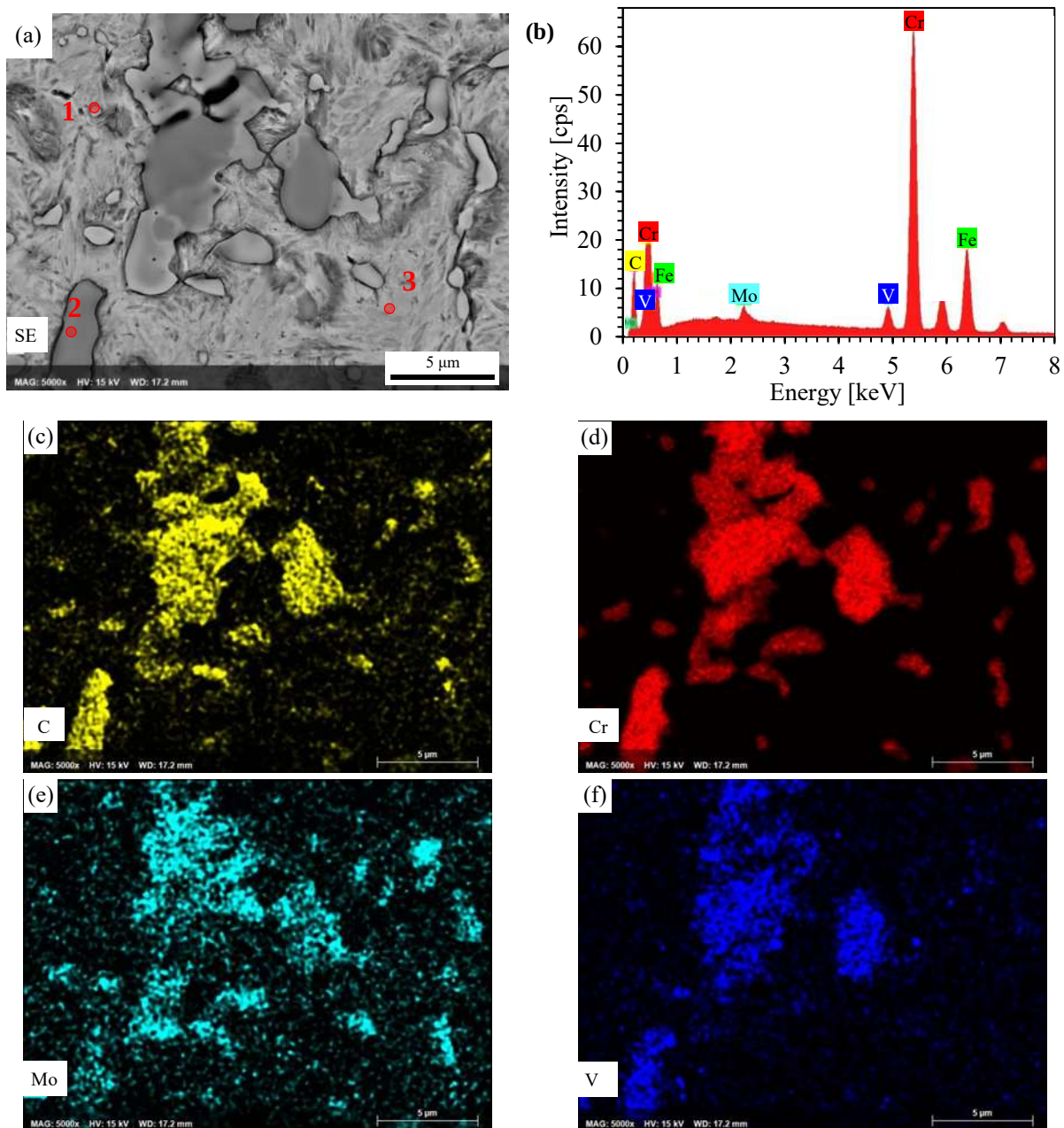


Figure 3.9 (a) SEM image of the sample cryo treated and tempered for 0.5 h at 350 °C, (b) EDS spectra of particle 2 in (a), and (c-f) EDS mapping composition.

Table 3.2 SEM-EDS data of carbides in the sample austenitized at 1050 °C for 1 h.

Phase	Spectrum	Element composition (at. %)				
		Fe	Cr	Mo	V	Si
Carbide	1	61.1	36.8	1.1	1.0	---
Carbide	2	29.3	65.5	1.1	4.1	---
Matrix	3	84.8	13.1	0.3	0.2	1.5

The variations of Vickers microhardness as a function of tempering temperature and time are shown in the histogram in Figure 3.10. At the low tempering temperature (LTT) of 150 °C, most of the samples preserve the hardness of the as-quenched martensite, but it changes continuously as the tempering time increases to 350 °C. During tempering, it is plausible that carbon diffuses from the supersaturated martensite at the same time that static recovery by a reduction in the dislocation density in the martensitic matrix occurs via carbon redistribution and reconstruction of partial dislocations [43]. At tempering temperatures above 250 °C, the formation of fine carbide occurs as a diffusion-controlled transformation of the retained austenite [39]. This phenomenon is known as secondary hardening, and in this case, occurs at a tempering temperature of 450 °C. Some studies have reported that secondary hardening during tempering is accomplished through primary strengthening mechanisms, namely solid-solution strengthening and precipitation-hardening effects of chromium and molybdenum carbides [31, 44, 45]. At tempering temperatures above 500 °C, the hardness drops drastically for the tempering time of 2 h. This is due to the matrix softening that takes place when Cr_7C_3 partially decomposes into Cr_{23}C_6 carbides, which are more stable and remain at all temperatures, and also due to the degradation of the martensite microstructure as carbon diffuses and grain boundary precipitates become coarser, which lead to a reduction in the pinning effect and promotes grain growth [16, 33, 42]. The coarsening of Cr_{23}C_6 carbides occurs due to the high solubility of iron and chromium, the main constituents of this carbide [46]. The measurable decline in hardness can also be attributed to the recovery of metastable martensite and carbide spheroidization [45, 47].

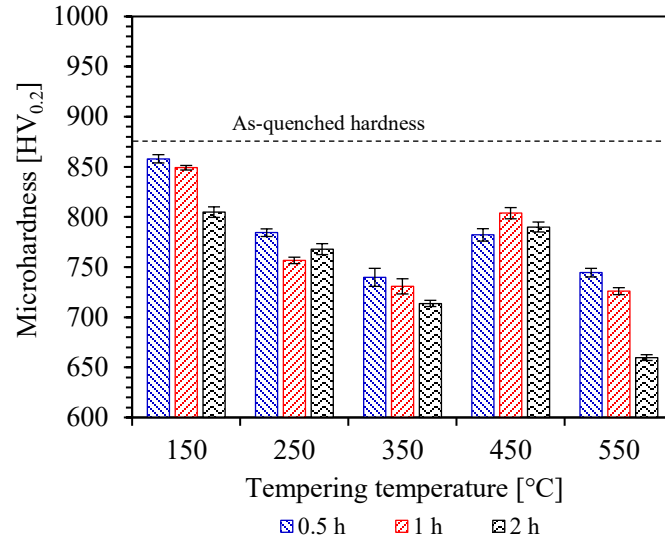


Figure 3.10 Effect of tempering temperature and time on the hardness of the as-quenched samples at 1050 °C for 1 h.

The engineering strain-stress curves in Figure 3.11(a) show that all the as-tempered samples failed before reaching the ultimate tensile stress (UTS). This limitation under tensile and bending loads is caused by the various embrittlement phenomena associated with hardened high-carbon steels [39, 48]. As shown earlier, the hardness of the 440C MSS is deeply related to the heat-treatment conditions. However, due to the embrittlement phenomena of this material, the tensile properties are not directly correlated to these parameters. During the hardness tests, the compressive load is less likely to cause a premature failure of the steel because the intergranular network of carbides does not act as a site for crack nucleation and propagation. Therefore, it is not sensitive to the brittle-fracture phenomena that limit the useful application of these steels [39]. As a result, the most representative mechanical properties such as yield stress σ_y , ultimate tensile stress σ_{UTS} , and strain hardening behavior cannot be inferred from tensile strength data; similar conclusions were made by Bhadeshia [49] for 52100 high-carbon steel.

On the other hand, the low ductility exhibited by the samples tempered at 150 and 250 °C can also be explained in terms of the remaining high state of stress and dislocation density that remains in the samples after quenching from the austenitizing temperature. For the sample tempered at 350 °C, the stress-strain behavior shows perceptible change in strength and ductility, which can be attributed to the relief of internal stresses [50, 51]. These results suggest that stress relief during tempering between 250 and 450 °C is required to improve the tensile strength. In addition, as seen

in Figure 3.11(a), at the tempering temperature of 550 °C, an elastic-plastic transition begins to develop and the fracture strength decreases. The slight decrease in strength may be related to the recovery of the microstructure and the gradual coarsening undergone by secondary hardening carbides at higher tempering temperatures. Despite the embrittlement phenomena, the material exhibits high strength. Also, there are no significant changes in the stress to rupture at tempering temperatures above 350 °C. To determine whether the SF 440C MSS alloy can further exhibit tensile plastic behavior, a series of alternative heat treatments were carried out. The effects of holding time and an alternative double tempering treatment were investigated and the results are shown in Figure 3.11(b) and (c), respectively. As can be seen, the holding time and double tempering do not show any significant effect on the tensile properties of the steel.

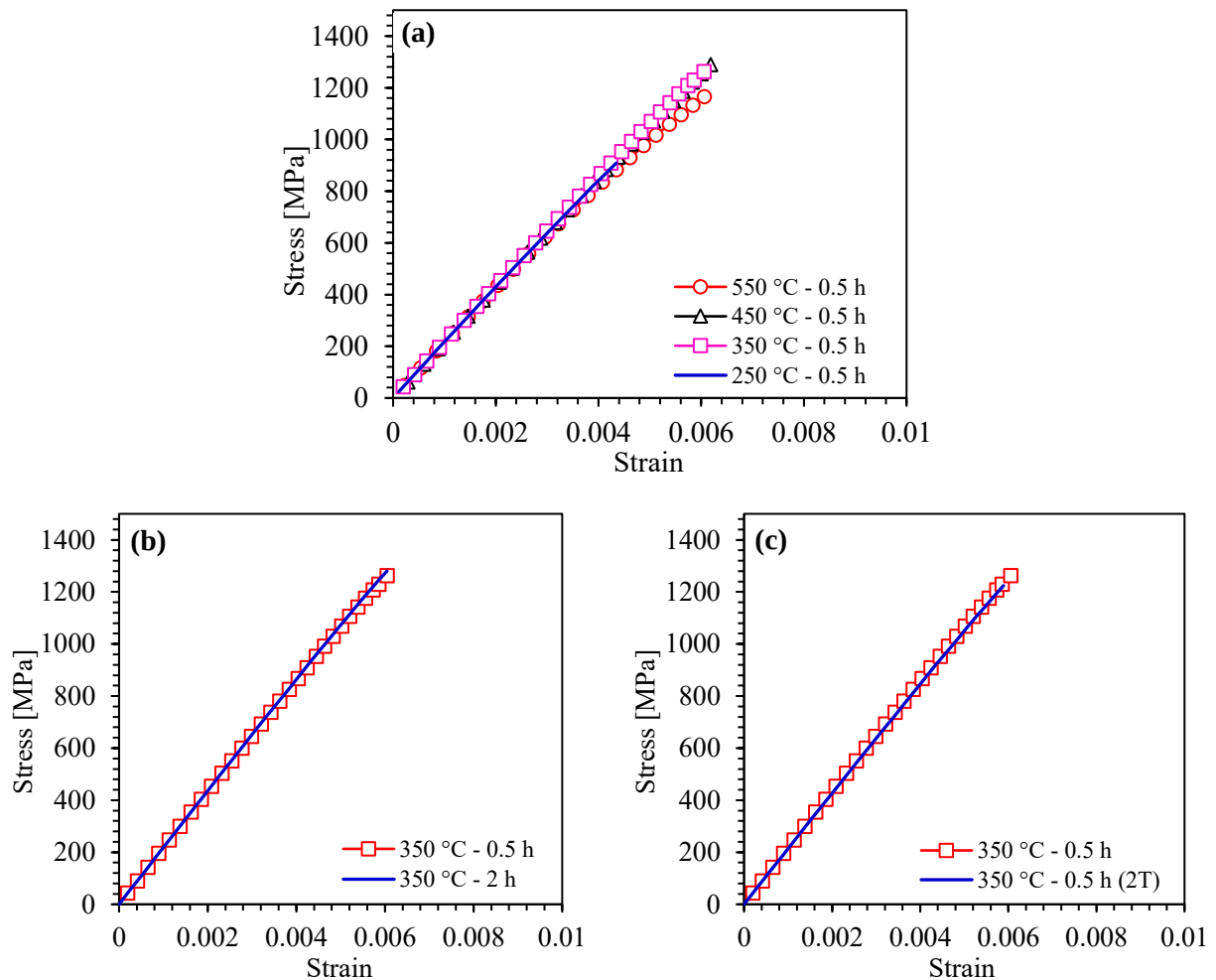


Figure 3.11 Stress-strain curves for SF 440C MSS quenched at 1050 °C for 1 h and tempered at different temperatures. Effect of (a) tempering temperature, (b) tempering time, and (c) double tempering cycle on tensile elastic-plastic behavior of SF 440C MSS.

Brittle intergranular fracture in high-carbon steels has been attributed to high strain-hardening rates that lead to higher ultimate tensile strengths and little post-uniform stresses to produce ductile fracture [39, 48]. Figure 3.12(a) shows the fracture images of the samples, which exhibit brittle intergranular fracture that propagates along prior austenite grain boundaries. However, small-scale microvoids suggest evidence of plastic deformation, see Figure 3.12(b). In each specimen, fracture happened after negligible plastic deformation and the specimens failed before any signs of necking appeared. Fracture analysis of cracks in the surface parallel to the direction of the applied load corroborates that failure occurred through intergranular fracture along prior austenite grain boundaries, as illustrated in Figure 3.12(c) and (d). The fact that an intergranular fracture occurred under tensile stresses, indicates brittle fracture promoted by fractured carbides at the prior austenite grain boundaries.

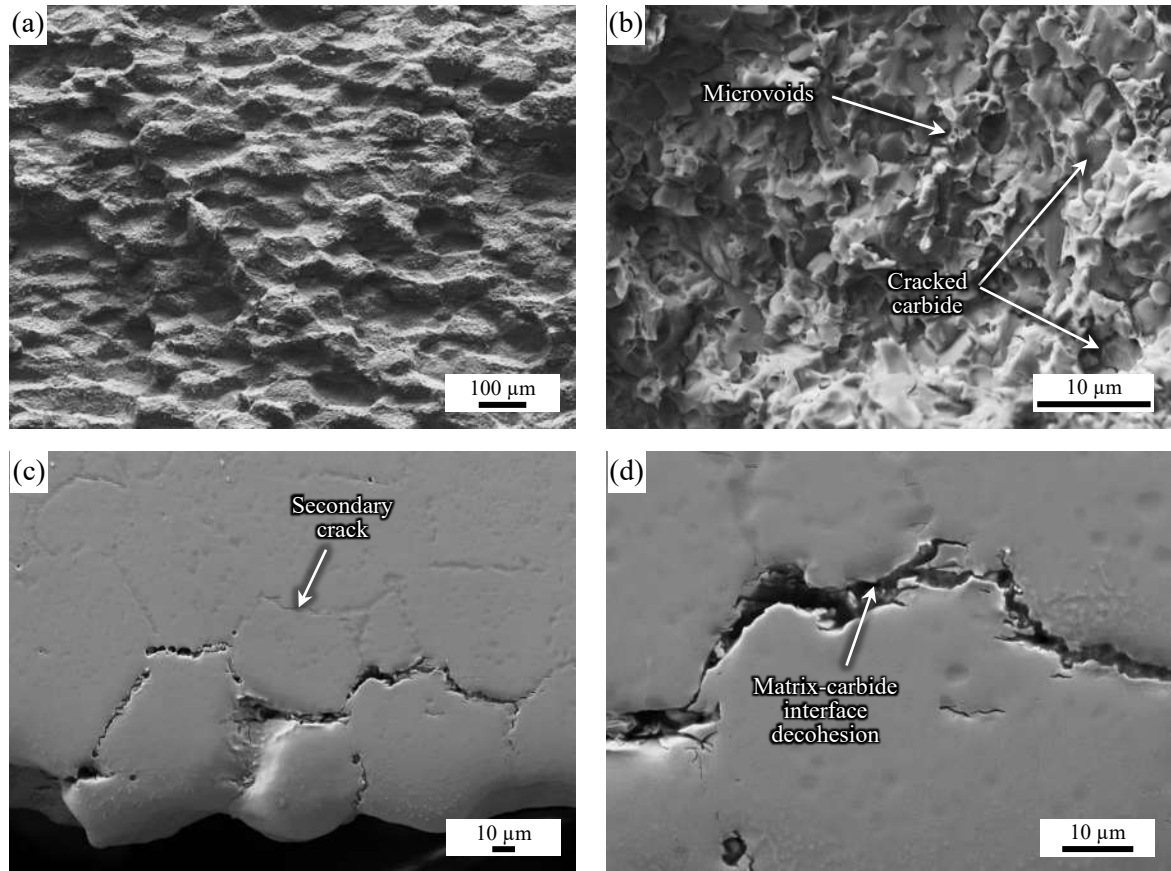


Figure 3.12 SEM images of (a) fracture surface, (b) detail image of the fracture surface, (c) image of intergranular cracks produced during tensile tests, and (d) crack detail. All images correspond to the as-tempered sample at 150 °C for 0.5 h.

3.4 Conclusions

- High austenitizing temperatures promote carbide dissolution, thereby increasing the amount of carbon and alloying elements in solid solution, leading to a decrease in the M_s temperature, which increases the retained austenite content and the prior austenite grain size, and decreases the as-quenched hardness.
- Secondary hardening occurred at the tempering temperature of 450 °C, due to the formation of sub-micron alloy carbides (Cr, V, Mo) that cause the hardness to increase as they form.
- At high tempering temperatures (above 550 °C), the sub-micron carbide particles coarsen at the expense of intra-plate particles and promote recovery of the dislocation structure, which eventually leads to a drop in hardness.
- At 1050 °C austenitizing temperature and further tempering between 150 and 450 °C, it was not possible to determine the main tensile properties, and no yielding was observed due to the quenching embrittlement phenomenon of the samples, which is related to the formation of coarse carbides along prior austenite grain boundaries. The sample tempered at 550 °C showed a slight transition from elastic to plastic, due to the recovery of the structure that results from the decrease in the tetragonality of the martensite.
- The optimal combination of strength and toughness was achieved at an austenitizing temperature of 1050 °C for 1 h followed by tempering at 350 °C for 0.5 h.

CHAPTER IV

EFFECT OF HEAT TREATMENT PROCESSES ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF SPRAY-FORMED 440C MARTENSITIC STAINLESS STEEL

Abstract

In the present work, 440C martensitic stainless steel (440C MSS) was manufactured by spray forming (SF) technology. Microstructural and mechanical properties such as strength, ductility, and toughness were evaluated after quenching and tempering-partitioning (Q-T^P) and quenching-intercritical quenching-tempering (Q-IQ-T) heat treatments. The microstructural features that control the deformation and fracture behavior are discussed for the different heat treatment conditions. The experimental results showed that after austenitizing at 1050 °C the material exhibits no apparent plastic deformation before fracture. However, specimens austenitized above 1050 °C and the specimen subjected to Q-IQ-T exhibit an improvement in the tensile properties by showing an elastic-plastic transition. This improvement of ductility and strength is related to the strain-induced martensitic transformation of retained austenite formed during the Q-T^P process and to a decrease in the volume fraction of martensite with increasing the austenitizing temperature. Also, it was observed that the strain-hardening rate decreases with increasing austenitizing temperature. Furthermore, the stress-strain data suggests that the Q-IQ-T heat treatment effectively improves the toughness and ductility of the steel without compromising strength. The results indicate, that the mechanical response of the SF-440C MSS can be tailored by adjusting the heat treatment parameters which will enable better design for industrial applications.

Keywords: Spray-Forming, AISI 440C, Martensitic Stainless Steel, Retained Austenite, Stress-Strain Induced Transformation

4.1 Introduction

Martensitic stainless steels are extensively used in the tool industry for applications where a combination of high strength, high hardness, wear resistance, and good corrosion resistance is needed [31-33]. In this class of steels, AISI 440C high-carbon steel exhibits high strength and hardness as well as excellent wear resistance, making it an ideal alloy for heavy-duty products, including cutlery, bearings, tools, blades, and valve components [31, 34, 41, 52]. The favorable properties are realized by a large volume fraction of primary and secondary carbides (up to 30 %) distributed in the martensitic matrix [53]. Besides their good properties and performance, a drawback of high-carbon martensitic stainless steels is the balance between strength and ductility as compared to conventional low-alloy martensitic steels [43, 54]. To mitigate this drawback, different approaches have been developed in steel research that focus on improving the performance of these materials by optimizing the chemical composition, manufacturing procedure, and heat treatment sequences [31, 33, 39, 55, 56].

In conventional manufacturing of high-alloyed steels containing alloying elements such as Cr, Mo, W, and V macro-segregation occurs during the solidification of the ingot, leading to an inhomogeneous distribution of coarse and brittle carbides [53]. Alternative advanced manufacturing processing, such as spray forming, has been implemented successfully for several engineering alloys with complex compositions to mitigate this inhomogeneous carbide distribution [23-25, 53, 57]. It was found that SF offers a high degree of control over the process parameters, the resulting microstructure, and the mechanical properties. Spray-formed steels have a more homogeneous and finer microstructure free of macro-segregation and therefore, exhibit superior mechanical performance as compared to their conventionally manufactured counterpart [23-25, 57, 58].

A typical heat treatment sequence for AISI 440C consists of austenitizing, quenching to form martensite, and subsequent tempering of martensite to improve ductility and impact toughness, as well as to reduce residual stresses that develop during quenching due to inhomogeneous martensite formation [31]. A drawback is that the high carbon content makes the steel susceptible to brittle intergranular fracture during quenching. This phenomenon has been reported in martensitic steels with carbon contents exceeding 0.5 wt%, wherein the formation of a network of carbides along prior austenite grain boundaries (PAGB) is promoted [39, 48, 59, 60]. Several attempts have been

reported to reduce the effect of quenching embrittlement in high-carbon steels [61, 62]. The quenching and tempering-partitioning heat treatment has been implemented over the last few years and differs from conventional quenching and tempering (Q-T) [63]. During Q-T^P, the steel is quenched to a temperature between M_s and M_f to obtain a mixture of martensite and austenite in the microstructure. Subsequently, the alloy is tempered at a so-called partitioning temperature, where carbon is partitioned over martensite and austenite, i.e. carbon diffuses out of martensite to enrich and further stabilize retained austenite. Residual austenite stable at room temperature might transform into martensite during loading as either stress- (i.e. elastic) or strain (i.e. plastic)-induced transformation mechanisms, leading to an improvement of yield strength, work hardening rate, and ductility [43, 50, 63-66].

Another heat treatment procedure is the so-called intercritical quenching, which consists of quenching from a solution treatment temperature (Q), heating the steel to a temperature between A_{CI} and A_{CM} for a certain holding time, followed by quenching to room temperature (IQ), and subsequent tempering (T). Li et al. [67] employed the Q-IQ-T treatment on a 25MnSiCr super-bainitic steel and observed that the intercritical quenching step promotes grain size refinement, which improves the toughness without compromising the strength. Kim et al. [68] studied the microstructural features of intercritical treatment and its effect on the toughening of 5-6Ni steel. Their results showed that the Q-IQ-T step leads to grain refinement due to the precipitation of thermally stable austenite distributed along prior martensite lath boundaries, which improves the mechanical properties of the steel by decreasing the ductile-brittle transition temperature. Moreover, it is well established that grain refinement, carbide dissolution, and carbon content have a beneficial influence on the toughness of steels [67, 69-71]. On the other hand, research carried out on medium manganese, lightweight steel reported that intercritical quenching dramatically improves the mechanical properties of the steel by a good combination of strength and ductility. This is mainly attributed to the amount of ferrite that forms upon quenching, which has good plasticity and ductility, but also to the volume fraction of austenite and its stability as it transforms into martensite during plastic deformation [36]. Several studies on dual-phase (DP) steels have successfully implemented the intercritical annealing treatment [72, 73]. The results revealed that an increase in the ductility and toughness is mainly attributed to the final microstructure, which consisted of ferrite, martensite, and retained austenite. Despite all previous work regarding the

effect of heat treatment of 440C MSS manufactured by conventional techniques, the effect of alternative heat treatment procedures on the mechanical behavior of spray-formed high-carbon steel like the 440C MSS appears unexploited. The present research presents an alternative approach to designing high-carbon steels by investigating in detail the effect of Q-T^P and Q-IQ-T heat treatments on the structure-property relations of spray-formed 440C MSS.

4.2 Experimental details

4.2.1 Materials manufacturing

The steel was produced by spray forming according to a proprietary process of Nordic Steel. The chemical composition of the spray-formed 440C MSS is given in Table 4.1.

Table 4.1 Nominal chemical composition (wt. %) of the spray-formed 440C MSS as determined by optical emission spectroscopy.

C	Mn	P	S	Si	Cr	Mo	V	W	Ni	N	Fe
1.19	0.448	0.0307	0.0237	0.571	15.86	0.816	0.549	0.186	0.33	0.100	Bal.

4.2.2 Heat treatment

To investigate the effect of the Q-T^P treatment, a set of samples was austenitized at 1050 °C for 1 h, followed by oil quenching (OQ) to obtain a martensitic microstructure. After oil-quenching, the specimens were subjected to tempering (T^P) for 0.5 h at 350 °C for carbon partitioning, followed by air-cooling to room temperature. Also, an alternative Q-IQ-T heat treatment was performed first by a solution treatment at 1200 °C for 1 h followed by OQ. After this, the samples were heat treated at an intercritical temperature of 900 °C for 1 h terminated by OQ. Finally, the specimens were tempered at 350 °C for 0.5 h and air-cooled to room temperature. All heat treatments were carried out under an argon atmosphere in a tube furnace.

4.2.3 Microstructural characterization

After heat treatment, all specimens were mechanically ground and polished using conventional metallographic techniques. The microstructures of the samples were investigated with scanning electron microscopy (SEM), using secondary and backscatter electrons. For this, the samples were

polished to 0.05 μm alumina and etched in Villella's reagent. The composition of the phases was determined using energy-dispersive X-ray spectroscopy (EDS). Electron backscatter diffraction (EBSD) was used to determine the amount of the different phases present in the steel after electropolishing in an electrolyte solution of 60 ml perchloric acid in 940 ml acetic acid at 15 V. The EBSD analyses were carried out with a field emission gun scanning electron microscope (JEOL JSM-7600F FEG/SEM) at a tilt angle of 70° , using a QUANTAX CrystAlign 400i-EBSD system, an acceleration voltage of 20 kV, and a scan step-size of 39 nm. The data was post-processed using the ESPRIT 2 Quantax software. Thereafter, surfaces were examined with X-ray diffraction using a Bruker D8 Advance using Cu-K α radiation in Bragg-Brentano focusing geometry. Diffractograms were recorded from 40 to $125^\circ 2\theta$ at a step size of 0.05° and a counting time of 3 s per step. Phase identification and quantitative analysis for the heat-treated samples (before tensile testing) were performed by Rietveld refinement using the GSAS II software. The integrated intensities I_{γ_1} , I_{γ_2} and $I_{\alpha'}$ of 220_γ , 311_γ , and $211_{\alpha'}$ peaks, respectively, were used to determine the volume fraction of austenite, V_γ , (after tensile testing) using [74]:

$$V_\gamma = \frac{I_{\gamma_1} + I_{\gamma_2}}{(I_{\gamma_1} + I_{\gamma_2}) + 0.5324I_{\alpha'}} \quad (4.1)$$

4.2.4 Mechanical characterization

After heat treatment, micro-hardness, tensile testing, and compression tests were carried out. Vickers hardness measurements were performed on an HM-220B Mitutoyo computer-controlled tester, equipped with a manually controlled xy stage and digital micrometer heads with 1 μm resolution. Vickers hardness of the steel samples was determined using a constant load of 200 g (1.96 N), and a holding time of 15 s. For each specimen, 10 independent indents were performed to provide an average hardness and to verify the homogeneity of the microstructure.

For the tensile tests, dog-bone samples of $4.8 \times 5.5 \text{ mm}^2$ cross-section were cut from the spray-formed plate by electrical discharge machining. Quasi-static uniaxial tensile tests were performed at room temperature using an MTS[®] 100 kN servo-hydraulic testing machine with load frame

model Landmark Series 370 and equipped with a FlexTest-40 controller and TestSuite Multipurpose Elite™ Software. All specimens were tested in load control mode at a strain rate of 0.005 s^{-1} . The axial deformation was measured using an MTS 634.31F-24 extensometer with a gauge length of 20 mm. Compression tests were conducted on a Zwick/Roell Z100 tensile testing machine on standard cylindrical samples of 6 mm diameter and 16 mm length. Standard Charpy V-Notch (CVN) specimens with a $(10 \times 10 \text{ mm}^2)$ cross-section and a central 45° V-notch of 2 mm depth were used for Charpy impact tests using an INSTRON impact testing machine at room temperature.

4.3 Results and discussion

4.3.1 Microstructural characterization

Figure 4.1(a-d) shows representative microstructures that resulted from the different heat treatments. It is observed that the microstructure mainly consists of tempered lenticular martensite with a zig-zag array, retained austenite, and undissolved carbides. As observed in Figure 4.1(a-c), the fraction, morphology, and distribution of the carbide particles change as a function of the austenitizing temperature. In these samples, large and coarse carbides are distributed as a semi-continuous network along prior austenite grain boundaries, while small carbide particles remain dispersed within the matrix. Moreover, it is possible to observe that higher austenitizing temperatures promote partial carbide dissolution as well as a decrease in particle size. This finding could be due to the instability of M_{23}C_6 carbides at temperatures above 950°C , as predicted by ThermoCalc® simulations. Retained austenite is also visible in Figure 4.1(a-c) as clear areas. The formation of this phase is attributed to the low solubility of carbon in ferrite/martensite, which forces carbon partitioning in austenite [64]. The amount of austenite increases whereas the volume fraction of carbides decreases on increasing the austenitizing temperature. This is in good agreement with previous work performed by Puskar et al. [34]. The Q-IQ-T sample in Figure 4.1(d) exhibits different microstructural features compared to the Q-T^P heat treatment. Coarse carbides with irregular shapes are present at the grain boundaries, while fine round carbides are dispersed within the grains, along former twin boundaries in austenite, and near the large grain boundary carbides. Carbide precipitation along grain boundaries can be attributed to chromium diffusion from the surroundings into the grain boundaries [47].

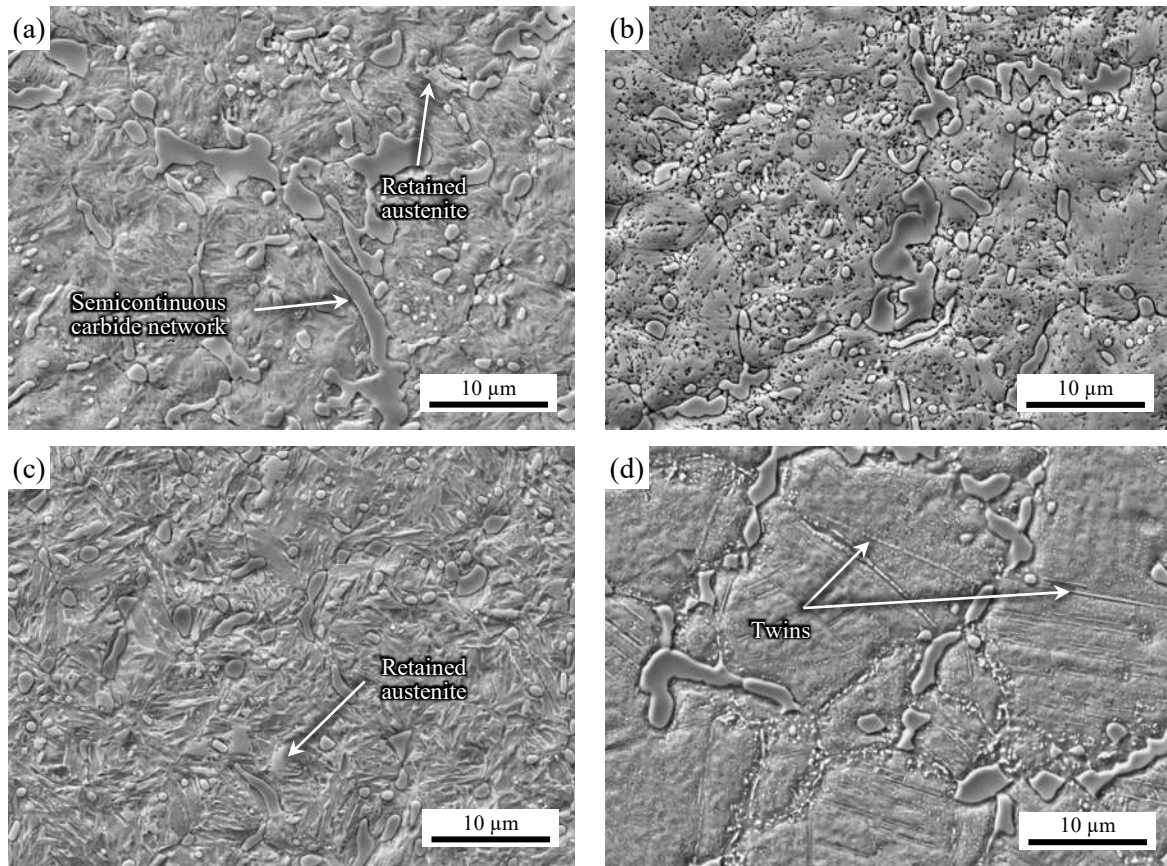


Figure 4.1 SEM images of samples subjected to different heat treatments: (a) austenitizing at 1050 °C, (b) austenitizing at 1100 °C, (c) austenitizing at 1125 °C, and (d) Q-IQ at 1200 and 900 °C. All the samples were tempered at 350 °C for 0.5 h.

Figure 4.2(a) shows a backscatter electron micrograph of the sample austenitized for 1 h at 1050 °C. The difference in contrast between particles 1 and 2 is thought to be caused by differences in particle composition, e.g., darker particles contain a lower content of relatively heavy elements than lighter particles, as corroborated by the EDS maps in Figure 4.2(b-f). The dark carbides contain Fe, Cr, V, and some Mo, while the light carbides contain less Cr and V and more Fe and Mo. SEM/EDS analysis of particles in Figure 4.2(a) revealed the presence of austenite and corroborates the precipitation of carbides within the matrix, as seen in Table 4.2. It is worth mentioning that point analysis with EDS was normalized to 100% excluding carbon and alloying elements that were found in concentrations lower than 0.5 at. %, because of the limitations of this technique in the quantitative analysis of either light elements or low concentrations.

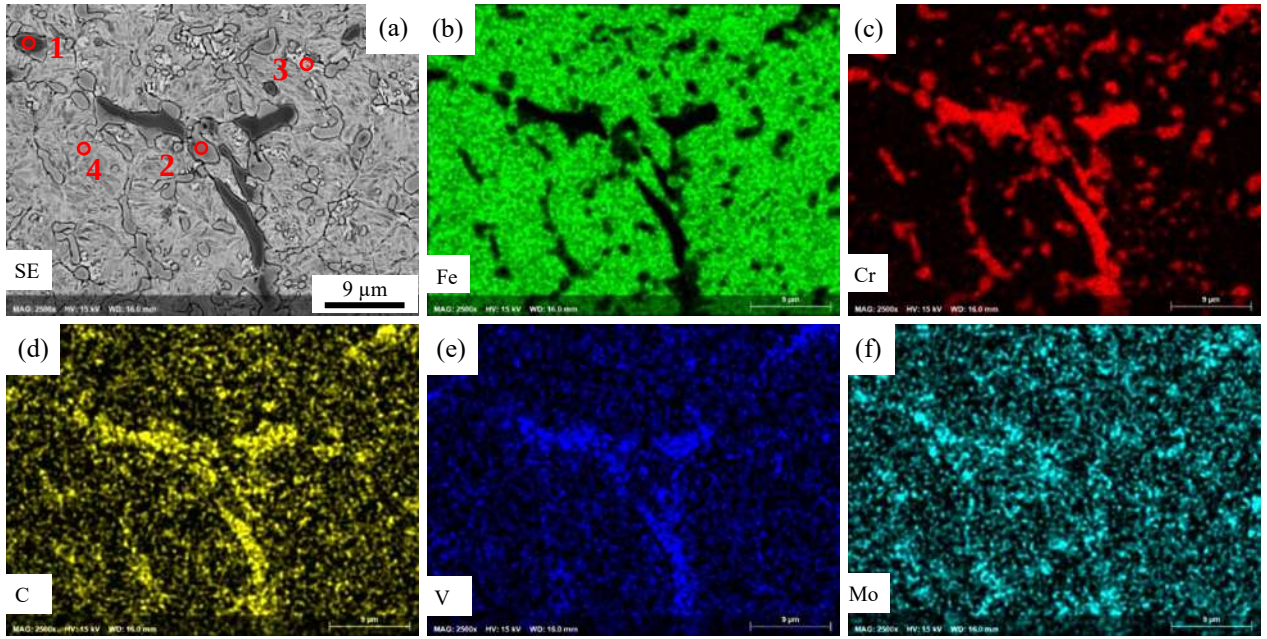


Figure 4.2 (a) SEM/BSE image of the sample austenitized at 1050 °C for 1 h and tempered for 0.5 h at 350 °C, (b-f) EDS maps of the sample indicating K_{α} radiation.

Table 4.2 SEM-EDS data of carbides in the sample austenitized at 1050 °C for 1 h.

Phase	Spectrum	Element composition (at. %)					
		Fe	Cr	Mo	V	Si	Mn
Carbide	1	31	65	0.7	3.8	---	---
Carbide	2	41	55	1.6	2.9	---	---
Matrix	3	83	14	0.3	0.3	1.3	0.6
Matrix	4	86	12	---	---	1.4	0.5

X-ray diffractograms for the different heat treatment conditions are shown in Figure 4.3(a). The diffraction peaks confirm the presence of M_7C_3 and $M_{23}C_6$ carbides, along with martensite and austenite. The presence of retained austenite after quenching reflects the relatively high carbon content in solid solution, which has lowered M_s [32]. The results indicate that samples treated at a higher austenitizing temperature contain a higher fraction of retained austenite and a lower fraction of carbides, as seen in Figure 4.3(b). More dissolved carbides for a higher austenitizing temperature imply a less effective pinning effect on grain boundary migration, causing grain growth.

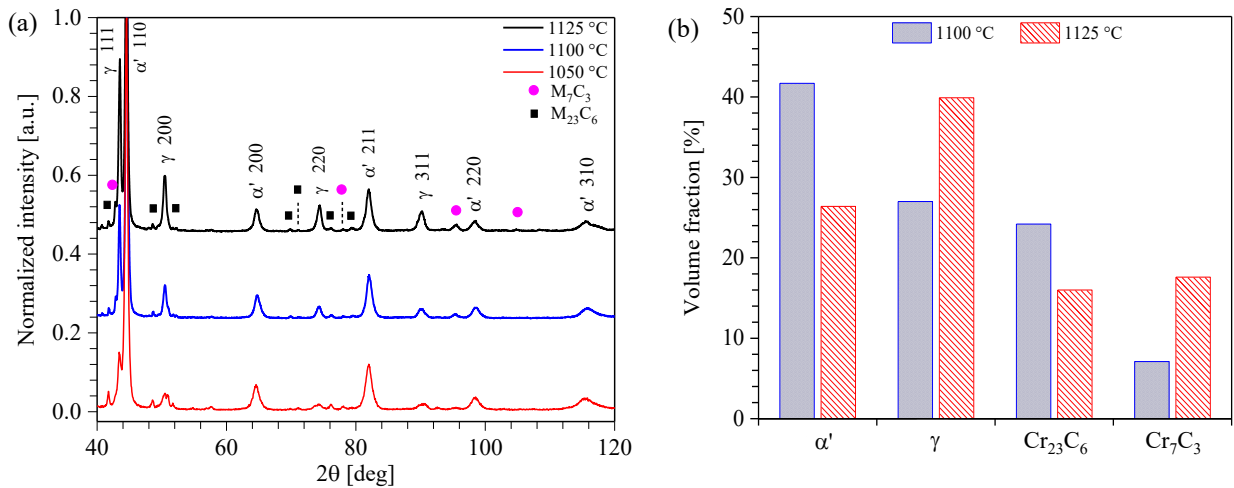


Figure 4.3 (a) X-ray diffractograms of samples austenitized at different temperatures and tempered at 350 °C for 0.5 h. (b) Volume fractions of the present phases, as determined by Rietveld refinement.

4.3.2 Mechanical behavior

Figure 4.4(a) shows the hardness obtained after different heat treatment conditions. It is clearly seen that the hardness decreases with increasing austenitizing temperature. This can be attributed to the partial dissolution of carbides that leads to higher contents of carbon and alloying elements in solid solution and promotes the formation of retained austenite after quenching. It is expected then, that the final hardness is mainly controlled by the fraction of retained austenite. The results also reveal that the reduction in hardness upon tempering is larger for the lower austenitizing temperatures. This is directly related to the lower martensite content, albeit with a higher C content, and higher retained austenite content. The hardness reduction on tempering is mainly caused by the tempering of martensite. Note that for the specimens austenitized at different temperatures, the hardness after tempering is in the range of 700-740 HV.

Typical strain-stress curves and tensile properties are presented in Figure 4.4(b). For the specimens that were austenitized at 1100 and 1125 °C, a defined and clear transition from elastic to plastic straining is observed compared to the specimen austenitized at 1050 °C. The yield stress corresponding to 0.1% plastic strain is ~1340 MPa (for 1100 °C) and 1070 MPa (for 1125 °C). These higher temperatures lead to a change in carbide size and distribution; however, the large carbides do not contribute to strengthening under tensile loading. The yield stress is mainly influenced by the amount of carbon in solid solution, and the phase fractions of martensite and

retained austenite. Austenite deforms plastically before martensite, and the deformation of martensite begins once the austenite has been strain-hardened sufficiently to transfer load, leading to continuous yielding [75]. For this reason, the curves for 1100 and 1125 °C deviate earlier from linearity than the 1050 °C curve in Figure 4.4(b), which implies elastic straining of martensite and plastic straining of austenite, potentially leading to strain-induced martensite. The effect of the intercritical annealing treatment is also shown in Figure 4.4(b). Evidently, this treatment improves the elongation (ductility) and strength, showing a similar elastoplastic behavior as the 1100 °C Q-T^P heat treatment. This improvement in the mechanical properties can be attributed to both the resulting microstructure and the refined grain size. A comparison with the as-sprayed specimen (AR) shows, that before heat treatment, the material exhibits good ductility and strength. This is reasonable because the mechanical properties of the steel are mainly influenced by its microstructure, i.e. grain size, phase morphology, and distribution. For the as-sprayed specimen, the microstructural analysis revealed that the microstructure consists of a ferritic matrix with fine carbides distributed within the grains and coarse carbide networks precipitated along grain boundaries. The improvement in ductility is then related to the elastic properties of ferrite compared to the brittle martensite of the heat-treated samples.

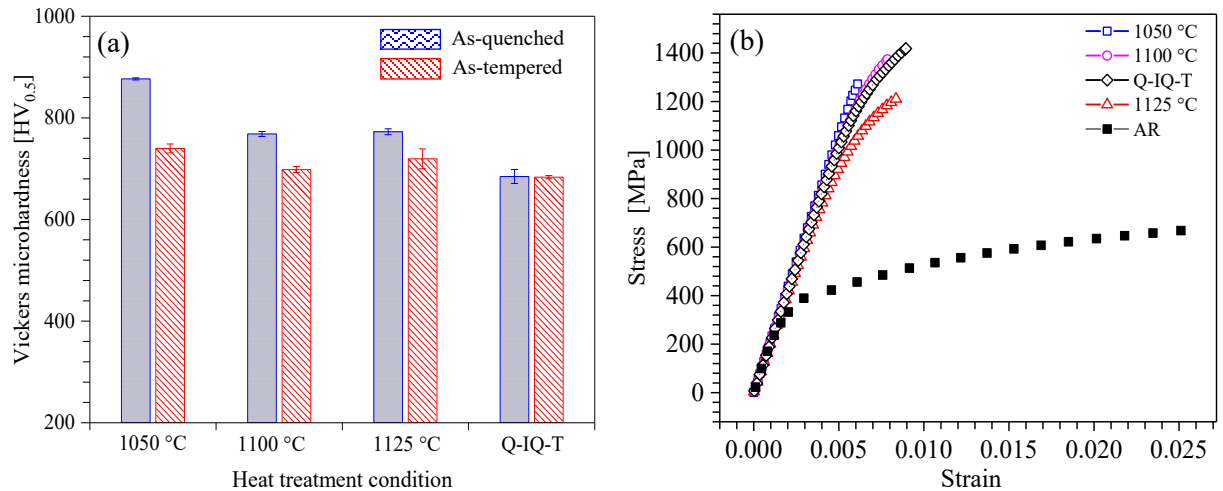


Figure 4.4 (a) Hardness comparison as a function of Q-T^P, and Q-IQ-T heat treatment processes, (b) strain-stress curves of the as-tempered samples for the different heat treatment conditions and the as-sprayed sample (AR).

Representative fracture surfaces for the different heat treatment conditions are presented in Figure 4.5, which shows the fracture morphologies of the tensile samples at a micro and macroscopic level. All the samples show intergranular fracture that is commonly found in materials that are embrittled as a consequence of large grains with low toughness grain boundaries. Such boundaries offer the least resistance to crack propagation. It is seen that for the lowest austenitizing temperature (Figure 4.5(b)) the predominating fracture mode is by cleavage (yellow arrows) with cracks that are initiated at carbide precipitates (black arrows). This is expected since the volume fraction of Cr_{23}C_6 carbide is the highest for this austenitizing temperature. For higher austenitizing temperatures, the volume fraction of carbide is reduced along with a higher phase fraction of austenite. This leads to a smooth fracture surface with quasi-cleavage facets (see Figures (b') and (c')). The presence of micrometer-sized dimples is also observed, which suggests that small-scale plastic deformation with localized yielding occurs. For the Q-IQ-T specimen (Figure 4.5(d')), the size of the micro-voids in the fractured surface decreased (blue arrows) while the micro-void nucleation increased. This can be attributed to a larger phase fraction of retained austenite and the characteristic refined structure of the intercritical heat treatment, which improves ductility. It should be noted that even when the number of micro-voids increased as a function of the austenitizing temperature and for the intercritical treatment, the presence of higher cleavage areas clearly indicates that all the specimens exhibited brittle fracture. As a result, fracture happened after negligible plastic deformation and the specimens fail (long) before necking.

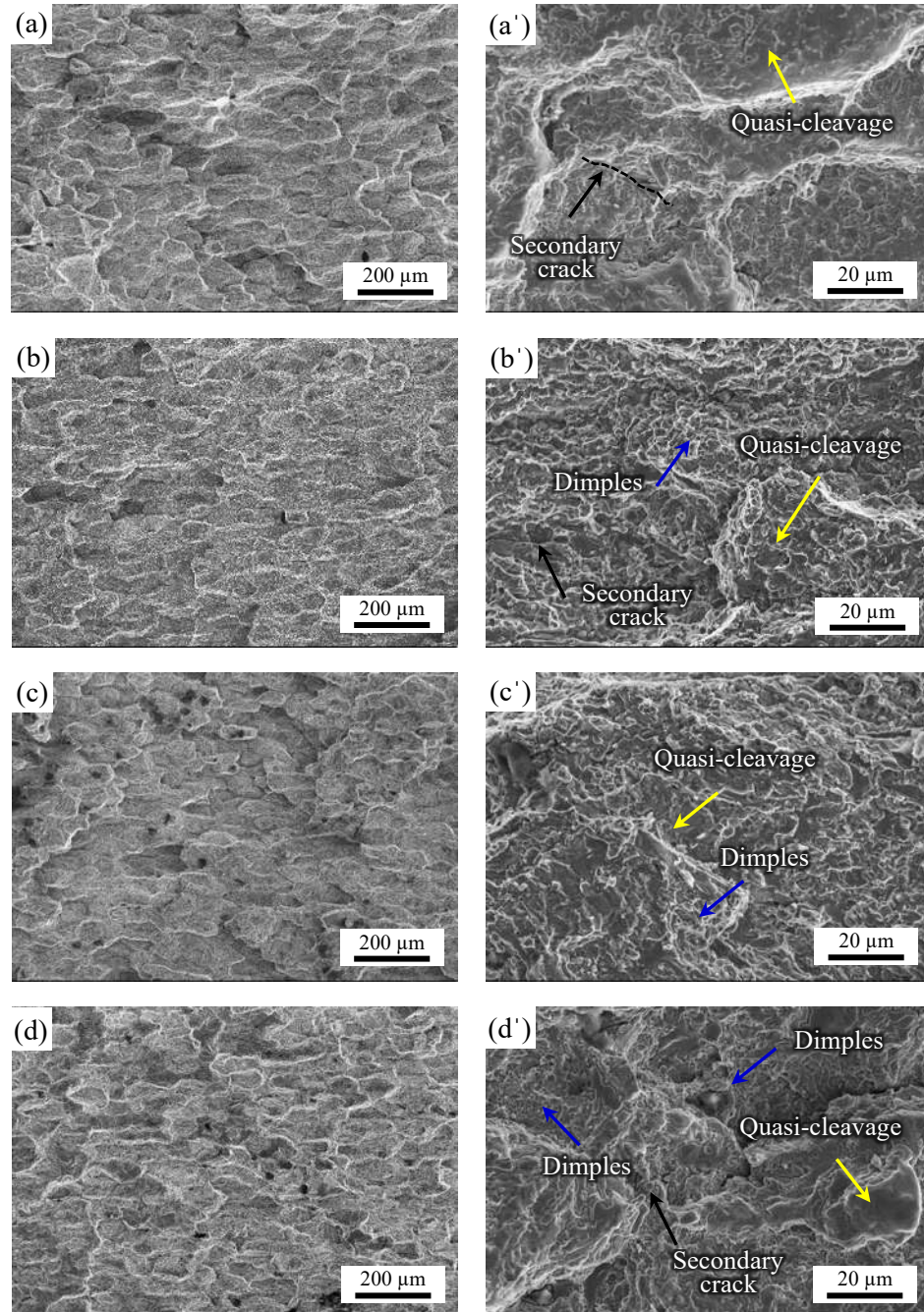


Figure 4.5 Fracture surface of tensile samples at (a-d) macroscopic and (a'-d') microscopic levels at (a) 1050 °C, (b) 1100 °C, (c) 1125 °C, and (d) Q-IQ-T. All the samples were tempered at 350 °C for 0.5 h.

Figure 4.6(a) is a cross-sectional micrograph just below the fracture surface (which is visible on the right-hand side of the micrograph) that shows an intergranular brittle fracture. The crack front runs along grain boundaries (mostly) perpendicular to the loading direction. The higher resolution image in Figure 4.6(b) confirms that fracture occurred in the brittle carbides along prior austenite grain boundaries. This failure is common in steels with high chromium and high carbon content and its effect can be pronounced by the segregation of impurity elements such as P, Sn, and Pb at grain boundaries [19,20,30,32].

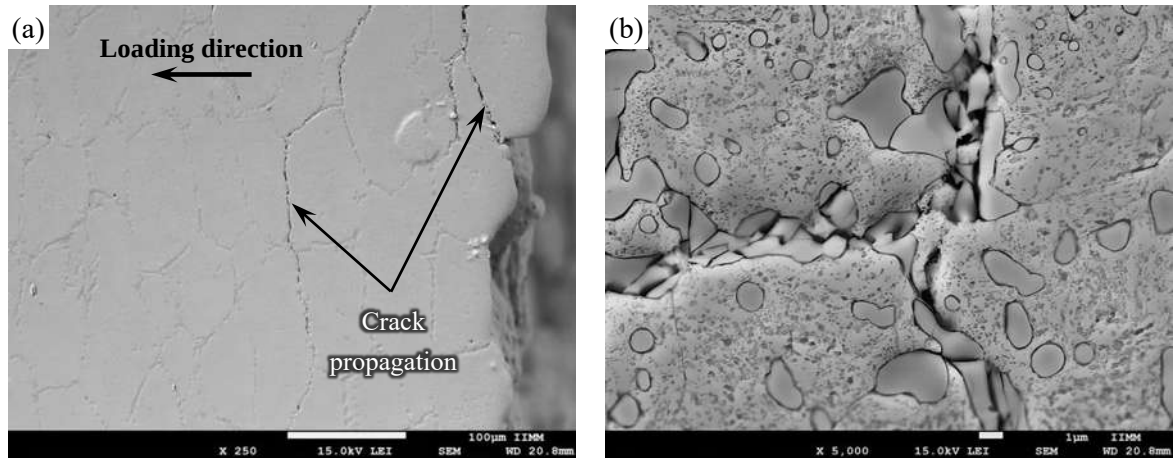


Figure 4.6 SEM/BSE images of intergranular cracks after tensile testing on sample austenitized at 1050 °C for 1 h (a) longitudinal section and (b) high magnification image of crack within the carbide.

To evaluate the effect of the heat treatments on the stress-strain plastic behavior of the different heat treatments, the Hollomon equation [16]:

$$\sigma = K\varepsilon^n \quad (4.2)$$

was fitted to the true stress-strain data, where n is Hollomon's strain hardening exponent and K is the strength coefficient. In the evaluation, the data was taken starting from the onset of plastic deformation up to the maximum strain value. The results are plotted in Figure 4.7(a) for the three conditions that exhibited plastic deformation; the results for the fit parameters are given in Table 4.3. Obviously, the 1100 °C heat treatment has the highest Hollomon exponent and strength coefficient, while the lowest values correspond to the 1125 °C heat treatment.

Table 4.3 Best fitting of Hollomon exponents n and constant K values of samples tempered for 0.5 h at a temperature of 350 °C and intercritical treatment.

Fitting parameter	1100 °C	1125 °C	Q-IQ-T
n_1	0.58	0.42	0.49
K_1 [GPa]	22.7	8.9	14.2

For the SF 440C MSS, the experimental results show that an increase in the austenitizing temperature reduces the strain-hardening rate $d\sigma/d\varepsilon$. This is shown in Figure 4.7(b), where the sample austenitized at 1100 °C exhibits a higher rate compared to the sample austenitized at 1125 °C. This might be attributed to the lower martensite phase fraction of the sample austenitized at 1125 °C. Also, from Figure 4.7(b), the intercritical sample shows strain-hardening behavior similar to that of the sample austenitized at 1100 °C. Therefore, experimental results corroborate that, during uniaxial tensile testing, the strengthening mechanisms are related to the resulting microstructure produced by the heat treatment. It is worth mentioning that high-carbon steels exhibit higher strain hardening rates than those with lower carbon content and, that higher strain hardening rates lead to an increase in the ultimate tensile strength [39].

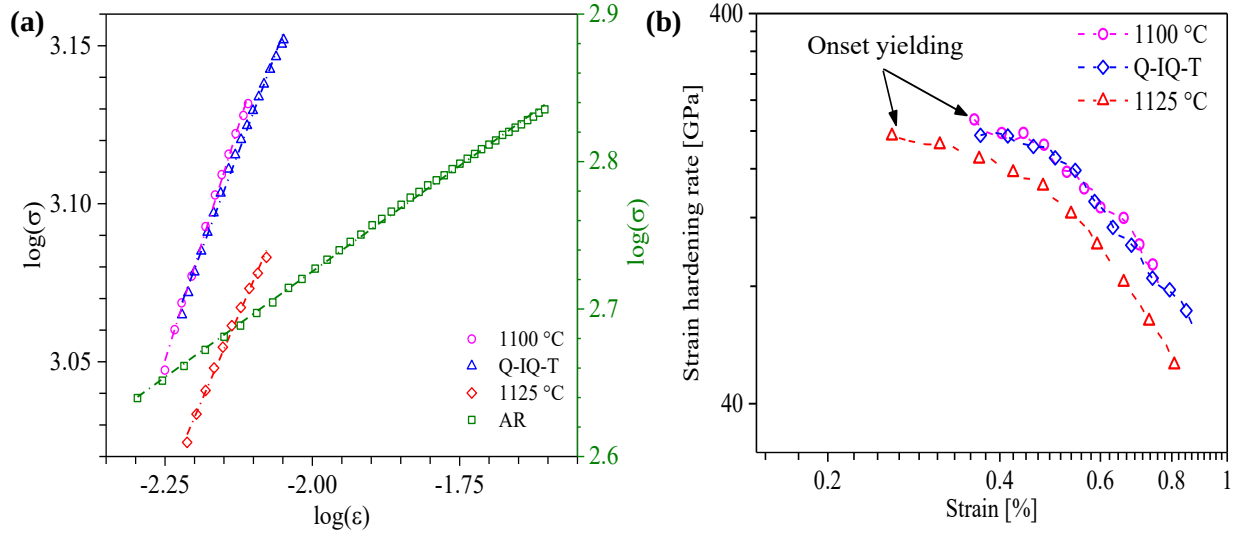
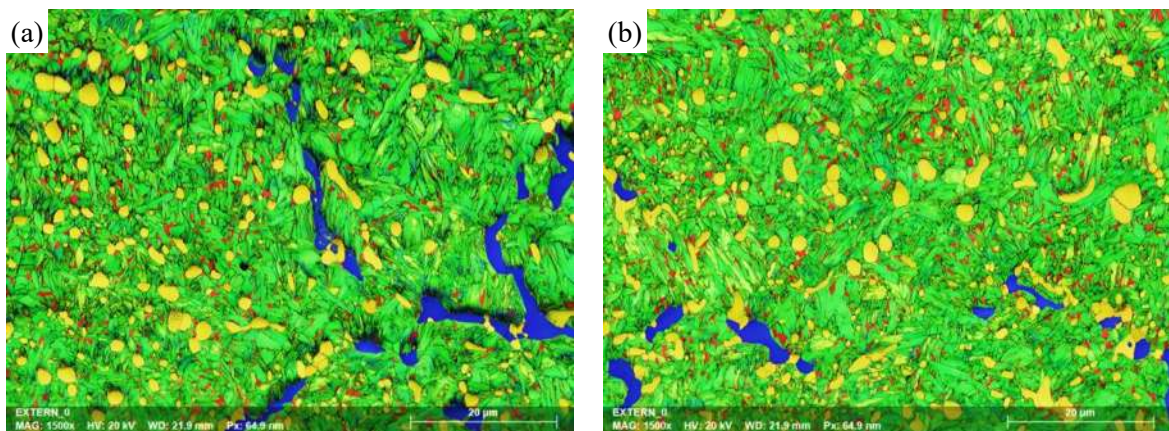


Figure 4.7 (a) Hollomon plot of the plastic regime for the different heat treatments and (b) strain hardening rates as a function of the true plastic strain for the different heat treatment conditions.

EBSD phase maps for the different heat treatments before and after tensile testing are collected in Figure 4.8. The microstructure of the samples contains bcc (martensite) and fcc (austenite) phases, with Cr_{23}C_6 and Cr_7C_3 carbides distributed along PAGB and within the grains. The volume fraction of retained austenite increases with the austenitizing temperature as follows from comparing Figures 4.8(a) and (c). Also, the intercritical heat treatment is associated with the presence of retained austenite, which can be attributed to the (partial) dissolution of Cr_{23}C_6 carbides during the first stage of the heat treatment at 1200 °C.

To track the TRIP effect, a comparison of phase distributions and volume fractions before and after tensile testing was performed by EBSD and the results are illustrated in Figure 4.8. It is worth mentioning that the TRIP effect depends strongly on the mechanical stability of austenite, which is mainly affected by its chemical composition, morphology, size, and distribution. To guarantee an effective TRIP effect, the austenite should be moderately stable. If austenite is too stable, high shear stress would be necessary for stress-induced transformation and even a high volume fraction of this phase will not guarantee the transformation [39, 49, 64, 75, 76]. The results indicate that the transformation of retained austenite into martensite cannot be accomplished for the specimen austenitized at the lowest temperature of 1050 °C. This may be a result of the small grain size of the austenite which increases the energy barrier for martensitic transformation [77]. In contrast, it was observed that the grain size of the austenite increases with increasing the austenitizing temperature, so that, for the 1100 °C sample a small fraction of retained austenite (9 %) transformed into martensite upon straining.



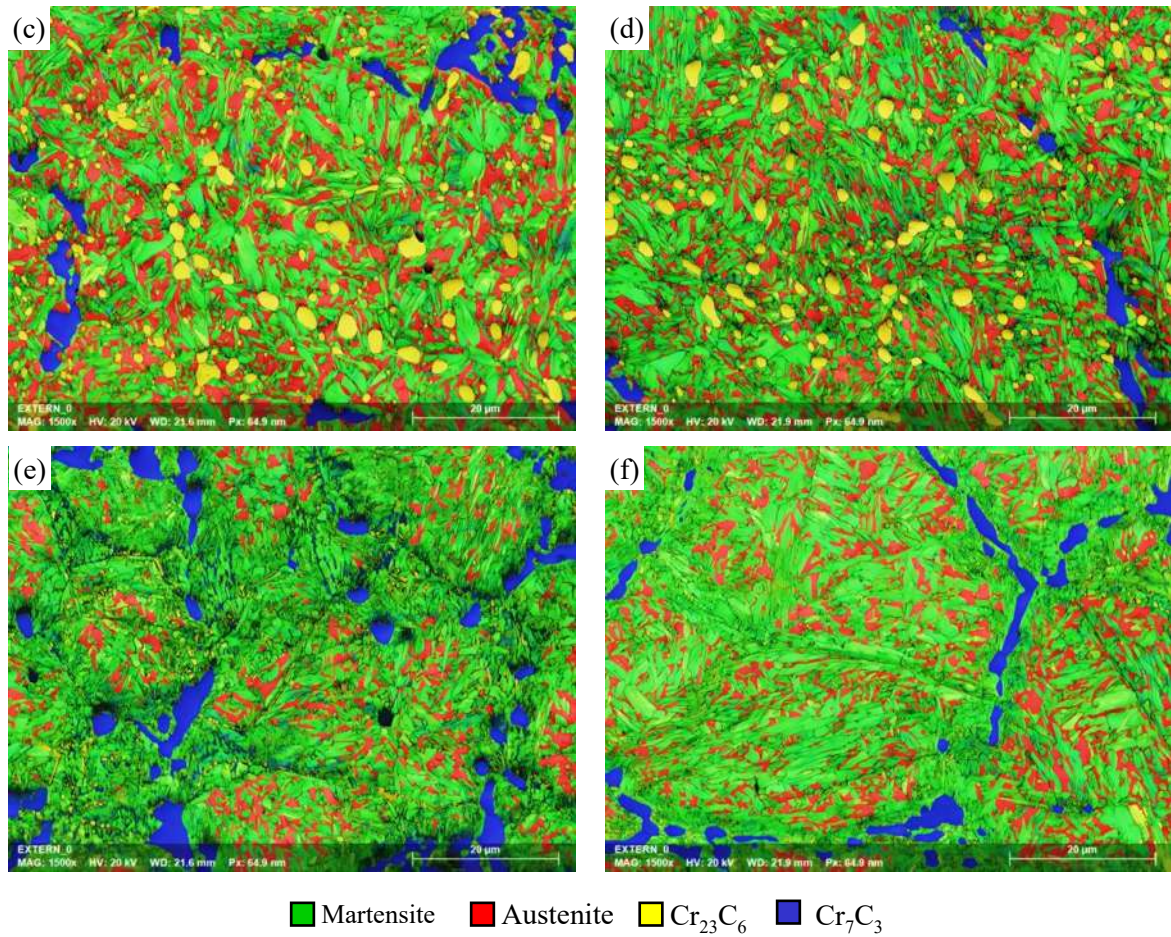


Figure 4.8 EBSD phase map comparison of samples austenitized at 1050 °C for 1 h (a) before and (b) after tensile testing, austenitized at 1100 °C for 1 h (c) before and (d) after tensile testing, Q-IQ-T samples (e) before and (f) after tensile testing.

To corroborate the EBSD analysis, XRD measurements were performed for the different heat treatments after tensile testing (see Figure 4.9(a)). The results indicate that at the lowest austenitizing temperature of 1050 °C, no TRIP effect is obtained. However, it is possible to observe from Figure 4.9(b) that austenite starts to transform into martensite during the tensile tests for the specimens austenitized at higher temperatures. This variation in the volume fraction of austenite after tensile testing is attributed to the higher volume fraction of austenite with increasing the austenitizing temperature. The results are consistent with EBSD.

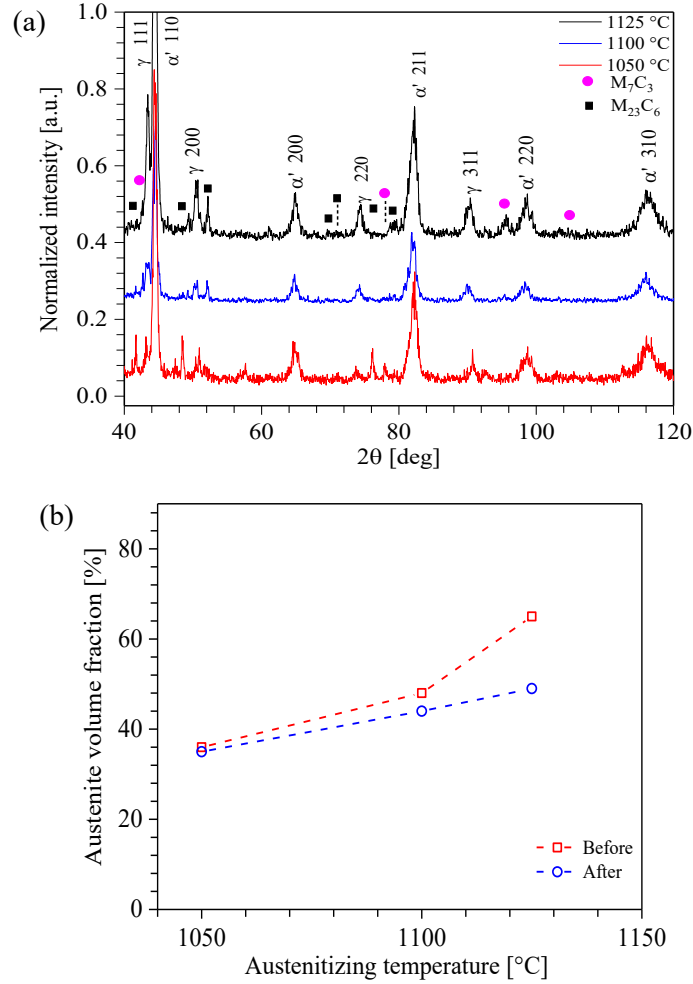


Figure 4.9 (a) XRD pattern comparison of samples after tensile testing for the different heat treatments. (b) retained austenite content, as determined by Eq. (1), before and after straining in dependence on the austenitizing temperature.

High-carbon steels offer an excellent alternative for applications of components that work under compressive loads [39, 48, 49]. As quenching embrittlement limits the applicability of the tensile testing to establish the elastic-plastic behavior of the alloy, a series of compression tests were conducted. Figure 4.10 shows the stress-compression graphs of samples austenitized at 1050 °C for 1 h and tempered at 350 and 450 °C for 0.5 h. Evidently, more plastic deformation can be accommodated in compression testing than in tensile testing. In compression testing, a reduction in ductility is observed in the sample tempered at 450 °C. This result was anticipated as a consequence of secondary hardening that occurs at this tempering temperature.

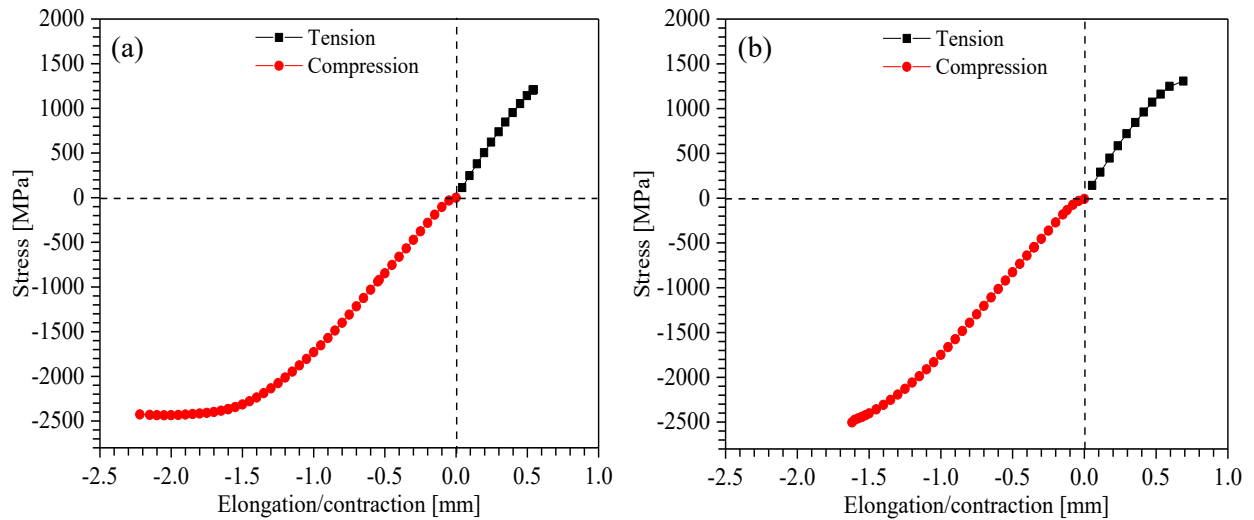


Figure 4.10 Stress-displacement curves for the samples austenitized at 1050 °C for 1 h and tempered for 0.5 h at (a) 350 and (b) 450 °C.

Since the UTS could not be assessed from tensile tests due to the brittle behavior of the steel, an empirical relation to predicting the ultimate tensile strength UTS (σ_{UTS}) from the microhardness was applied: $HV [MPa] = C \cdot \sigma_{UTS}$ [78], where C is a constant with a value ≈ 3 . To predict the UTS of samples tempered for 0.5 h at 350 and 450 °C, this equation was adopted using $C = 3$. The predicted UTS and stress at failure under compression are compared in Table 4.4. A surprisingly good correspondence is observed between these values, suggesting that the stress at failure under compression represents the UTS.

Table 4.4 Estimated compressive strength from the indentation hardness and real data obtained from compression tests.

Tempering temperature [°C]	Measured Vickers microhardness [MPa]	Measured compressive strength [MPa]	Predicted UTS [MPa]
350	7247	2440	2415
450	7669	2500	2556

A summary of the hardness, tension, compression, and Charpy impact results for the different heat treatments is given in Table 4.5. It is observed that the effect of increasing the austenitizing temperature is an apparent decrease in Young's modulus and yield stress. The decrease in Young's

modulus is apparent; it is interpreted as the result of plastic deformation in austenite, while martensite still accommodates the load elastically. If a C value of 3 is used in the relationship between UTS and hardness, it could be predicted that the sample austenitized at 1050 °C has the highest ultimate compressive strength and lowest ductility. On the other hand, the samples austenitized at 1100 °C and intercritically treated (Q-IQ-T) would exhibit similar mechanical properties. Charpy impact energy values for the different austenitizing temperatures are also listed in Table 4.5. Since toughness is directly related to the carbide network, it is expected that the impact energy is at a minimum due to the high strain rate of the test, leading to crack propagation through the carbide network along grain boundaries. Such crack propagation by-passes the more ductile phases in the matrix.

Table 4.5 Effect of different heat treatments on the mechanical and elastic properties of SF 440C MSS. All the samples were tempered for 0.5 h at 350 °C.

Austenitizing temperature [°C]	Hardness [HV _{0.2}]	E [MPa]	$\sigma_{y(0.2\%)}$ [MPa]	σ_f [MPa]	Elongation [%]	UCS [MPa]	Impact [J]
1050	739	212	---	1272	3	2440	1.8
1100	698	203.7	1340*	1361	3.4	---	2
1125	719	195.8	1175	1210	3.1	---	2
Q-IQ-T	683	203	1419	1419	4	---	---

* $\sigma_{y(0.1\%)}$

4.4 Conclusions

The effect of different heat treatment sequences on the microstructure and mechanical properties of spray-formed AISI 440C martensitic stainless steel was investigated by combining different characterization techniques. The conclusions can be summarized as follows:

- Different heat treatments lead to changes in the fraction and distribution of primary and secondary carbides. Higher austenitizing temperatures lead to a lower volume fraction and smaller size of Cr_{23}C_6 carbides. Further, the higher austenitizing temperature leads to a higher content of retained austenite.
- For the austenitizing heat treatment temperature of 1050 °C followed by the partitioning tempering temperatures, no yielding was observed due to quenching embrittlement, originating from the carbide network along prior austenite grain boundaries.
- For austenitizing temperatures of 1100 and 1125 °C, it was possible to change the stress-strain response of the alloy with a well-defined elastic to plastic transition that allowed assessment of the yield stress.
- Using uniaxial compression tests, it was possible to establish the maximum compression strength, the magnitude of the compression stress corresponds to the value of the ultimate tensile strength predicted by the empirical relation $\sigma_{\text{UTS}} = 3\text{HV}$.
- The results indicate that the ductility of the steel is influenced by the (meta-)stability of austenite by the TRIP effect. Higher austenitizing temperatures and associated higher austenite fractions lead to a higher strain-induced transformation of austenite into martensite.

CHAPTER V

MICROSTRUCTURAL AND MECHANICAL CHARACTERIZATION OF SPRAY-FORMED AND CONVENTIONALLY CAST AISI 440C MARTENSITIC STAINLESS STEEL

Abstract

The spray-forming process is a promising processing route for producing high-performance high-carbon steels. In this study, as-received and hardened/tempered spray-formed (SF) AISI 440C steel is compared to its conventionally cast (CC) counterpart. For materials microstructure characterization scanning electron microscopy, X-ray diffraction analysis, energy dispersive spectroscopy, and electron back scatter diffraction were utilized. For the characterization of the mechanical properties, hardness, tensile, and compression tests were performed. The results show that the SF steel has a microstructure that is very different from the CC condition. The differences in the microstructure of the steels after the different processing routes can be explained consistently by differences in the solidification rate and subsequent cooling rate of the solidified structure. In particular, the identity, morphology, and size of the primary carbides depend strongly on the combination of solidification and cooling rates. The differences in microstructures have a decisive influence on the mechanical properties of as-manufactured and hardened/tempered steels. The present findings demonstrate the potential of spray forming to produce high-performance AISI 440C martensitic stainless steel with superior mechanical properties.

Keywords: Spray-Forming, VIM, 440C MSS, Microstructure, Mechanical Properties

5.1 Introduction

Martensitic stainless steels (MSS) are high-performance materials that are used in a wide range of industrial applications. This type of steel is well known for its excellent combination of strength, hardness, and corrosion resistance [79]. 440C MSS is a high-carbon martensitic stainless steel that is particularly well suited for applications requiring high strength and wear resistance, making it an ideal choice for various industrial components such as cutlery, hand tools, bearings, injection molds, pump impellers, and valve seats [31, 33, 34, 80, 81]. The microstructure and properties of high-carbon and highly alloyed stainless steels, such as 440C MSS, are largely determined by the manufacturing process. It is well known that conventional casting and machining of 440C MSS is challenging because the refractory alloying elements segregate during solidification and form coarse primary carbides, which result in poor ductility and toughness [53, 82].

Spray-forming is a relatively new process in the manufacturing of complex alloys with optimized microstructures [53, 83-86]. In essence, spray-forming is a powder metallurgical process that uses rapid solidification to obtain solid components. In spray-forming, a high-velocity gas stream sprays atomized molten metal onto a moving substrate. Solidification during spray forming occurs in two stages. First, during gas atomization, part of the latent heat of the alloy is rapidly removed from the droplet spray (rapid solidification). Upon deposition of the droplets onto a billet, the remaining liquid fraction solidifies [87]. Spray-formed (SF) materials are characterized by a relatively fine and homogeneous microstructure that is free of macro-segregation compared to conventionally cast materials. As a result, the final product exhibits mechanical properties similar to those of the wrought alloys [88, 89]. Spray forming has been successfully used in the production of highly alloyed AISI M3 and AISI D2 tool steels, resulting in a fine microstructure, uniform carbide distribution, and low levels of macro-segregation [90].

Kumar et al. [83] found that the tensile properties of spray-formed H13 tool steel were comparable to its conventional equivalent. Mesquita et al. [91] reported that M3:2 high-speed steel produced through spray forming had a finer and more uniform carbide distribution and considerably improved isotropy of mechanical properties compared to conventional steels. Yan et al. [92] optimized the microstructure of spray-formed Uddeholm Vanadis 4 cold-worked steel by controlling the post-processing parameters during hot rolling and annealing, which strongly affect the evolution, morphology, and distribution of carbides. According to Zhang, et al.[53], the

mechanical properties of T15 high-speed steel, such as bending strength, hardness, and impact toughness were improved through the refinement and globularization of carbides and the homogeneous distribution of carbides by thermo-mechanical processing. Due to the complex solidification process of high-carbon and high-alloyed steel grades produced through spray forming, the study of the evolution of microstructure and resulting mechanical properties deserves special attention. In this work, we compare the process-structure-properties relationships of 440C MSS in spray-formed (SF) and conventionally cast (CC) conditions.

5.2 Experimental details

5.2.1 Materials Manufacturing

Martensitic stainless steel 440C (EN 1.4125) was manufactured through the spray-forming technique at Nordic Steel (Now Asgaard Metals ApS.) using a proprietary process. A conventional equivalent was produced by melting and casting SF 440C in a vacuum induction melting (VIM) furnace. Both materials were analyzed in the as-sprayed and as-cast conditions as well as in heat-treated conditions. The chemical compositions of the steels as determined by optical emission spectroscopy are listed in Table 5.1.

Table 5.1 Mean chemical composition (wt.%) of the two applied steels.

Material	C	Mn	P	S	Si	Cr	Mo	V	W	Ni	N	Fe
SF	1.19	0.448	0.0307	0.0237	0.571	15.86	0.816	0.549	0.186	0.33	0.100	Bal.
Cast (VIM)	1.29	0.433	0.016	0.018	0.57	15.71	0.861	0.43	0.173	0.32	0.06	Bal.

5.2.2 Conventional casting (VIM)

For the conventionally cast alloy, spray-formed 440C ingots were melted in a vacuum induction furnace (VIF-CONSARC) in a 10 kg capacity alumina crucible. Vacuum melting occurred at 1600 °C to ensure the complete melting of the SF ingots, at a pressure of 10^{-3} Torr (0.133 Pa). The molten steel was cast into a preheated metal mold to obtain an ingot of approximately 5 kg. The ingot was cooled to room temperature under vacuum in the furnace chamber.

5.2.3 Heat treatment

To investigate the effect of austenitizing and tempering-partitioning heat treatment on the steel, a set of samples with dimensions of $7 \times 7 \times 7 \text{ mm}^3$ were austenitized at 1050°C for 1 h for both manufacturing routes and then oil quenched (OQ) to obtain a martensitic microstructure. After oil-quenching, tempering was performed (T^P) at temperatures ranging from 150 to 550°C for 0.5 h; tempering was terminated by air-cooling to room temperature. The heating rate to reach the tempering temperatures was performed at $0.083^\circ\text{C s}^{-1}$. All heat treatments were carried out in a horizontal tube furnace under flowing argon. The heat treatment process was selected based on previous research on spray-formed 440C [12].

5.2.4 Microstructural characterization

After quenching and tempering, the samples were mechanically ground and polished using conventional metallographic techniques. To reveal the different phases in the microstructure, the samples were etched in Villella's reagent with a chemistry consisting of 5 ml HCl, 1 g picric acid, and 95 ml ethanol. The microstructural features of the materials were characterized using a field emission gun scanning electron microscope (JEOL JSM-7600F FEG/SEM) equipped with an Xflash 6-30 detector. Energy dispersive X-ray spectroscopy and elemental mapping were performed to determine the chemical composition of the various phases.

Further microstructural analysis was performed by electron backscatter diffraction (EBSD) on a JEOL JSM-7600F FEG/SEM, equipped with an e-flash HR+ detector. For this analysis, the samples were electropolished at 15 V in a 60 ml perchloric acid in 940 ml acetic acid solution. EBSD data were collected using a QUANTAX CrystAlign 400i-EBSD system at an acceleration voltage of 20 kV and a scan step size of 64.9 nm at a tilt angle of 70° . The data were post-processed using ESPRIT 2 Quantax software. For X-ray diffraction (XRD), a Bruker D8 Advance with Cu- K_α radiation in Bragg-Brentano focusing geometry was used. The samples were scanned over a scattering angle range of 40 to $125^\circ 2\theta$ at a step size of $0.05^\circ 2\theta$ and a counting time of 3 s per step. Rietveld refinement of the diffractograms was performed using GSAS II software [93].

5.2.5 Mechanical characterization

The mechanical properties of the steel were analyzed through microhardness, tension, compression, and Charpy impact tests. Vickers hardness indentations were performed on a computer-controlled HM-220B Mitutoyo tester. The Vickers hardness of the steel samples was determined using a constant load of 200 g (1.96 N), and a holding time of 15 s. To verify the microstructural homogeneity of each specimen, 10 independent microhardness indents were made, and the average hardness and standard deviation were calculated. A series of dog-bone subsize specimens with a 20 mm gauge length and a cross-section of $4.8 \times 5.5 \text{ mm}^2$ were cut according to ASTM E8 [94] and tested in an MTS[®] 100 kN servo-hydraulic machine of the model Landmark Series 370, equipped with a FlexTest-40 controller and Test Suite Multipurpose Elite[™] Software. Quasi-static uniaxial tensile tests were performed at room temperature in load-controlled mode with a strain rate of 0.005 s^{-1} . Axial deformation was measured using an MTS 634.31F-24 extensometer. Compression tests were conducted on a Zwick/Roell Z100 tensile testing machine on cylindrical samples with a diameter of 6 mm and a length of 16 mm.

5.3 Results and discussion

Figure 5.1(a) shows the phase stability and phase fractions of the studied alloy calculated with the Thermo-Calc[®] software [95]. The graph shows eutectic solidification at $1273 \text{ }^{\circ}\text{C}$ under the formation of austenite and M_7C_3 carbide. At the A_{C1} temperature (approx. $780 \text{ }^{\circ}\text{C}$) M_{23}C_6 and M_7C_3 carbides co-exist, with partial dissolution of the M_{23}C_6 carbide as the temperature increases. The transition from austenite to ferrite occurring below $780 \text{ }^{\circ}\text{C}$ leads to a decrease in the density. Since the carbon solubility in austenite is higher than in ferrite, this transformation affects substantially the kinetics of diffusion-controlled processes such as carbide transformation [96]. After the austenite-to-ferrite transformation is completed, the equilibrium phase fractions are 79% ferrite, 17% M_{23}C_6 , and 4% M_7C_3 carbide. According to Figure 5.1(a), part of the M_7C_3 carbide remains on cooling after its formation during eutectic solidification; another part dissolves to enable M_{23}C_6 carbide formation. As follows from Figure 5.1(b), the chromium and carbon contents in austenite decrease gradually with temperature along with the (trans)formation of carbides.

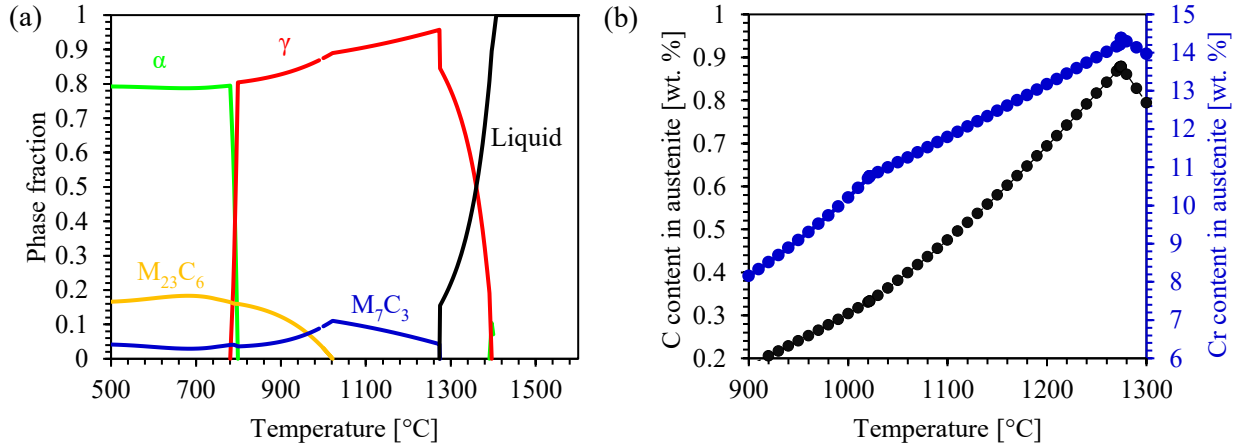


Figure 5.1 Thermodynamic prediction of (a) phase equilibrium diagram showing the volume fraction of the phases and (b) equilibrium carbon and chromium content in austenite as a function of temperature.

5.3.1 Characterization of initial microstructures

The microstructures of the as-cast and as-sprayed 440C MSS are presented in Figure 5.2 and Figure 5.3. The microstructure of the as-cast steel (Figure 5.2(a-c)) shows an equiaxed dendritic morphology and coarse eutectic carbide phase in the inter-dendritic regions. X-ray diffraction and phase fraction analysis (Figure 5.3(a and c), respectively) show that the microstructure of the as-cast material consists of 74% austenite, 4% martensite, 5% $Cr_{23}C_6$, and 17% Cr_7C_3 . These results are corroborated by EBSD, as shown in Figure 5.3(b). The Cr_7C_3 corresponds to the eutectic carbides indicated in Figure 5.2(c). The very small dark spots in Figure 5.2(c) are interpreted as $Cr_{23}C_6$ precipitates that have developed during cooling. As observed in Figure 5.2(e-g), the as-sprayed material consists of small equiaxed ferrite grains with a fine carbide distribution. Phase analysis from Figure 5.3(a and c) showed four major phases in the as-sprayed steel that consisted of 80.5% ferrite, 17.5% $Cr_{23}C_6$, and 2% Cr_7C_3 carbides. The formation of a semi-continuous carbide network along ferrite grains was also identified in the as-sprayed specimen. Compared to the as-cast steel, the as-sprayed microstructure is much finer, which can be attributed to the fast solidification of droplets upon deposition onto the billet, which prevents segregation effects as occurring during equiaxed dendritic solidification [87].

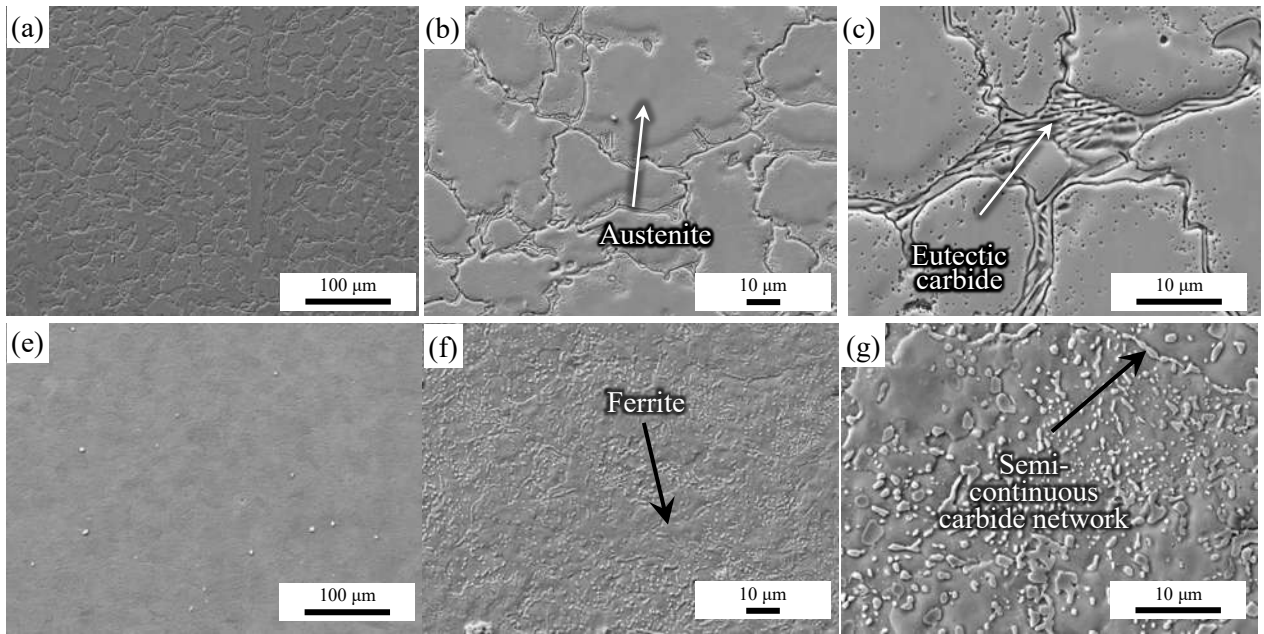


Figure 5.2 SEM representative microstructures of 440C MSS (a-c) as-cast and (e-g) as-sprayed.

The narrow peaks of ferrite and the carbide phases as well as their positions at higher scattering angles than for the as-cast condition, suggest that the as-sprayed steel is closer to equilibrium than that of the as-cast. Also, the much higher phase fraction of Cr_{23}C_6 as compared to Cr_7C_3 is consistent with a condition close to equilibrium (compare Figure 5.1(a) with Figure 5.3(c)). On the other hand, the relatively broad peaks for both austenite and martensite in the as-cast condition in Figure 5.3(a) indicate the presence of micro-strains, possibly caused by composition gradients. The shift of austenite and martensite peaks to relatively low scattering angles as compared to the spray-formed, SF, condition is explained by a relatively high interstitial carbon content in these phases, reflecting a non-equilibrium microstructure.

The microstructural difference between as-cast and as-sprayed conditions can be understood from the very slow cooling of the billet after solidification in the spray-forming process. Despite the rapid solidification of the atomized droplets, all heat is dissipated through the billet. This implies that the solid is cooled very slowly and that austenite can transform into ferrite and carbides, rather than into austenite and supersaturated martensite. Similar observations were reported by Lotta and Hannula for a high-chromium white cast iron [82].

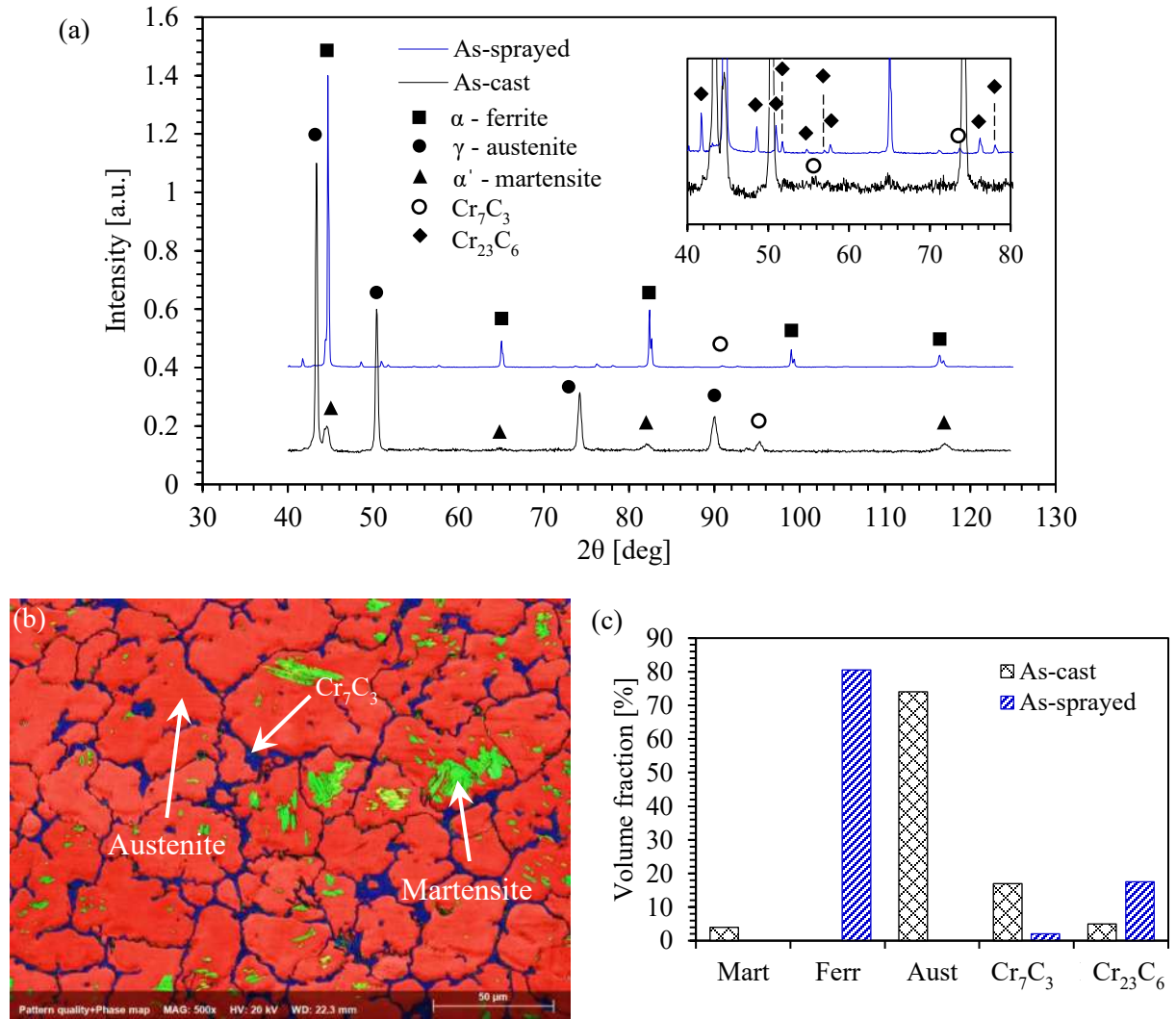


Figure 5.3 (a) XRD diffractograms of as-cast and as-sprayed materials; insert shows magnification to identify carbides. (b) EBSD phase map of the as-cast steel. (c) Volume fractions of the phases that compose the materials.

Backscattered electron (BSE) images of the as-cast and as-sprayed samples (Figure 5.4) reveal a clear difference in contrast between carbide particles. This contrast difference is caused by differences in particle composition. In Figure 5.4(b), particle 2 exhibits a lighter contrast than particle 3. The lighter particles contain a greater amount of Fe and Mo, and less Cr and V, while the darker particles suggest lower Fe and Mo content, and higher concentration of Cr and V.

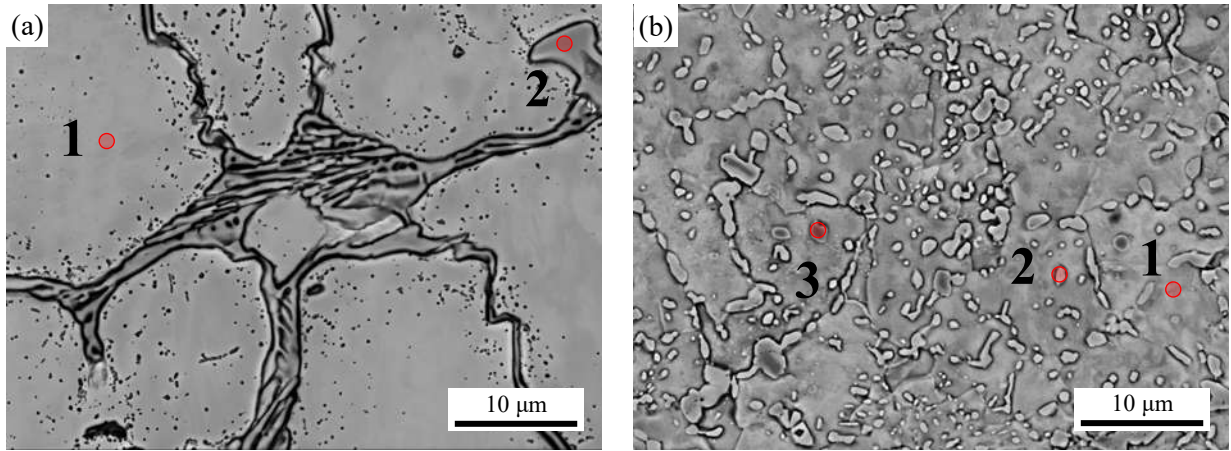


Figure 5.4 SEM/BSE detailed images of (a) as-cast and (b) as-sprayed samples.

EDS point analyses at the locations marked in Figure 5.4 are listed in Table 5.2. The results excluded carbon so only the metallic elements are given. Alloying elements with a content lower than 0.5 at. % were also excluded and the compositions were normalized to 100%. The chemical composition indicates that Fe and Cr were the main alloying elements in the carbides in both materials, with low amounts of Mo and V. The carbide particles in the as-cast steel, have a higher V content than some of the carbides in the as-sprayed material. The carbides with higher V content for the as-cast sample appear to have a lower Cr and a higher Fe content as compared to the as-sprayed steel. Due to the size of the small carbides in the as-cast sample, the EDS technique is not reliable. Therefore, only eutectic carbides are included in the analysis for this sample.

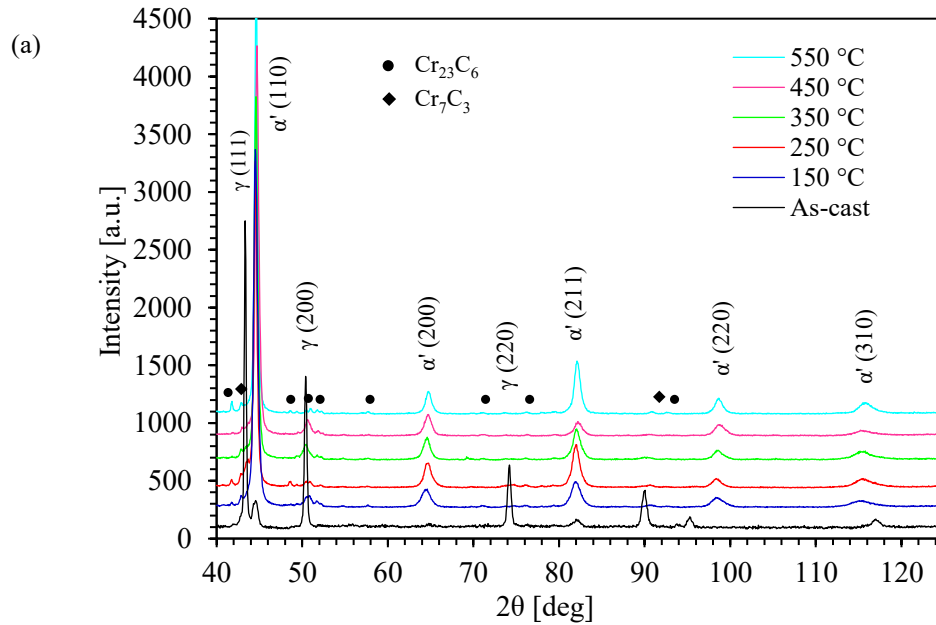
Table 5.2 Quantitative EDS analysis of carbides and matrix.

Material	Phase	Particle	Element composition (at. %)					
			Fe	Cr	Mo	V	Si	Mn
As-cast	Matrix	1	82	16	0.3	0.3	1	0.3
	Carbide	2	41	54	1	4	---	---
As-sprayed	Matrix	1	75	22	0.6	0.6	1	0.6
	Carbide	2	39	58	1.3	1.5	---	---
	Carbide	3	29	66	1	4	---	---

5.3.2 Characterization of heat-treated microstructures

X-ray diffraction

Figure 5.5 shows the X-ray diffractograms in the initial condition and after quenching and tempering for both materials. The results confirm the presence of Cr_7C_3 and Cr_{23}C_6 carbides, martensite, and retained austenite. It is seen that the fraction of retained austenite is lower for a higher tempering temperature, along with an increase in the phase fraction of, tempered and newly formed, martensite. The matrix of the as-cast specimen is austenitic, while it is largely ferritic for the as-sprayed condition. Subsequent heat treatment of the SF steel leads to the dissolution of carbides and martensite formation during cooling. The higher C content in martensite as compared to ferrite causes the matrix reflections to shift to lower Bragg angles.



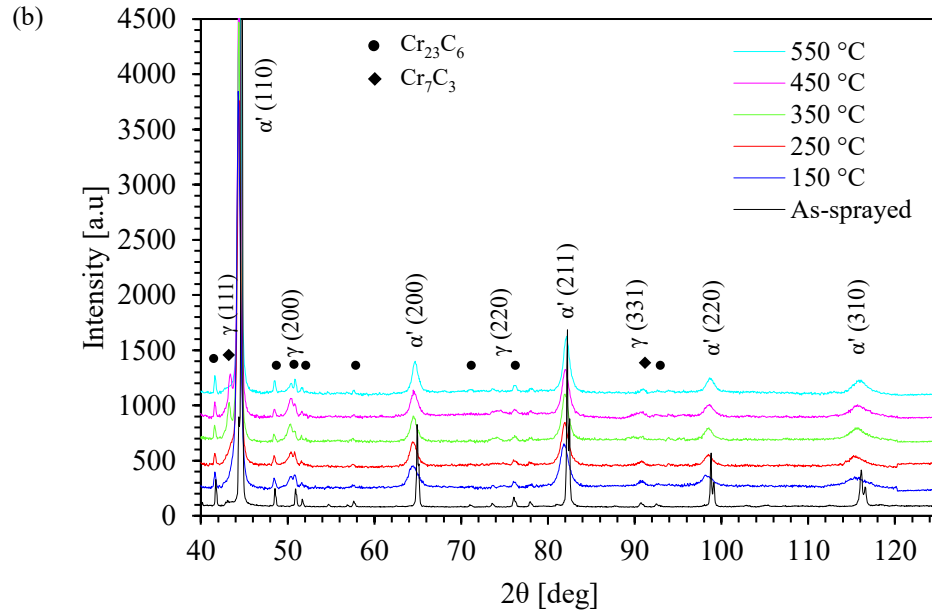


Figure 5.5 XRD diffractograms of the (a) as-cast and heat-treated (quenched and tempered) conventional cast material and (b) as-sprayed and heat-treated (quenched and tempered) SF steel.

For the conventional cast (CC) material, the heat treatment leads to a change in the carbide population along with a reduction in the carbon content in the matrix, as evidenced by a shift to higher Bragg angles. Also, residual stresses affect the peak position. Generally, compositional changes have a larger effect on the peak position than lattice strains. Figure 6 compares the carbide volume fraction of the cast and SF materials after austenitizing at 1050 °C for 1 h and tempering at 350 °C for 0.5 h, as determined by Rietveld refinement. For the cast steel, the volume fraction of Cr_7C_3 carbide decreased by 29% after heat treatment while the volume fraction of Cr_{23}C_6 carbide increased by 130%. This is explained by the low stability of the Cr_7C_3 carbide at the chosen austenitizing temperature and the higher stability of the Cr_{23}C_6 carbide (cf. Figure 1(a)). Consequently, during austenitizing partial decomposition of the non-stable Cr_7C_3 carbide occurs, to enable the formation of the more stable Cr_{23}C_6 carbide. On the other hand, after heat treatment, the SF material shows only small changes in the volume fractions of the carbides, because the as-sprayed condition already had a relatively low volume fraction of Cr_7C_3 carbide. The Cr_7C_3 carbide contains more C per metal atom (5.8 wt% C) than Cr_{23}C_6 (4.8 wt% C). From the carbide fractions

reported in Figure 6, it is estimated that the SF steel contains 0.46 wt% C in solid solution and the cast steel 0.22 wt% C.

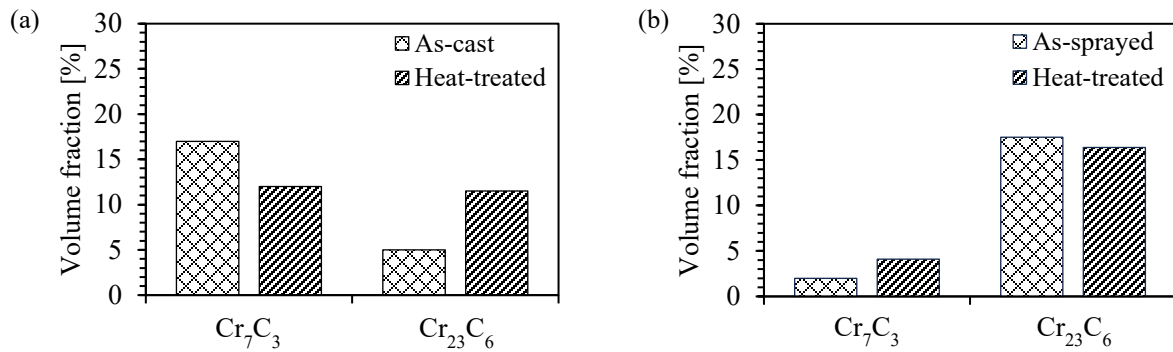


Figure 5.6 Comparison of carbide volume fractions after austenitizing for 1 h at 1050 °C and subsequent tempering for 0.5 h at 350 °C for (a) cast and (b) SF material. The volume fractions were determined by Rietveld refinement of the corresponding X-ray diffractograms.

The tetragonality of the martensite peaks in the heat-treated samples were attempted analyzed by fitting the $\{200/002\}$ and $\{112/211\}$ line profiles. Only for the SF specimen in the quenched condition, the mentioned line profiles were reconcilable with a tetragonal lattice (Figure 5.7) all other $\{200/002\}$ and $\{112/211\}$ line profiles, i.e., the cast /quenched and all tempered conditions, did not allow a meaningful interpretation in terms of tetragonality, because the line profiles were symmetrical and could be described by a single Voigt profile. From the peak fits in Figure 5.7 an average tetragonality of 1.012 ± 0.003 was obtained, corresponding to a carbon content of 0.28 ± 0.07 wt%, using the lattice parameter dependencies reported by Cheng, et al. [97], which is slightly lower than expected for thermodynamic equilibrium of austenite at 1050 °C and lower than the estimate based on the carbide fractions (see above). Tempering caused the tetragonality and broadening of the martensite line profiles to decrease and resulted in a shift to higher Bragg angles, consistent with an anticipated reduction in carbon content in solid solution.

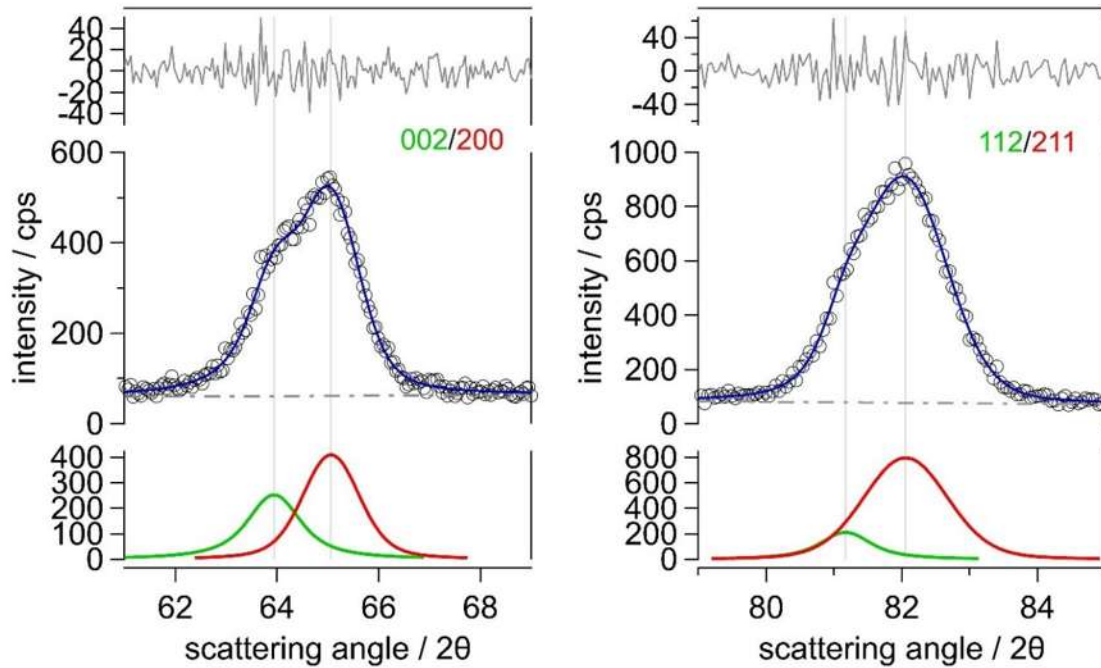


Figure 5.7 Middle: $\{200/002\}$ and $\{211/112\}$ line profiles of SF 440C in austenitized and quenched condition. The data was fitted with two Voigt profiles (bottom) yielding the residual in the top part of the graph.

Energy dispersive spectroscopy

EDS maps are presented in Figure 5.8 for the cast and spray-formed steel in the as-tempered condition (350 °C-0.5 h); corresponding microanalysis results are presented in Table 5.3 and Figure 5.9. Chromium is the main constituent in the carbides; other metallic elements such as Mo and V can substitute Cr and Fe atoms, forming a multi-component complex carbide [42]. The results indicate that despite the considerable difference in the manufacturing history of the two conditions, the carbides are strikingly similar in composition. Backscatter electron images in Figure 5.8(a-a') reveal carbides with two different mean atomic number contrasts. Comparison with the EDS maps and spot analysis in Figures 5.8 and 5.9 and Table 5.3 shows that the dark carbides contain higher contents of chromium and vanadium and a lower content of molybdenum, while the light carbides mainly contain chromium and iron and a slightly higher molybdenum content than the dark carbides.

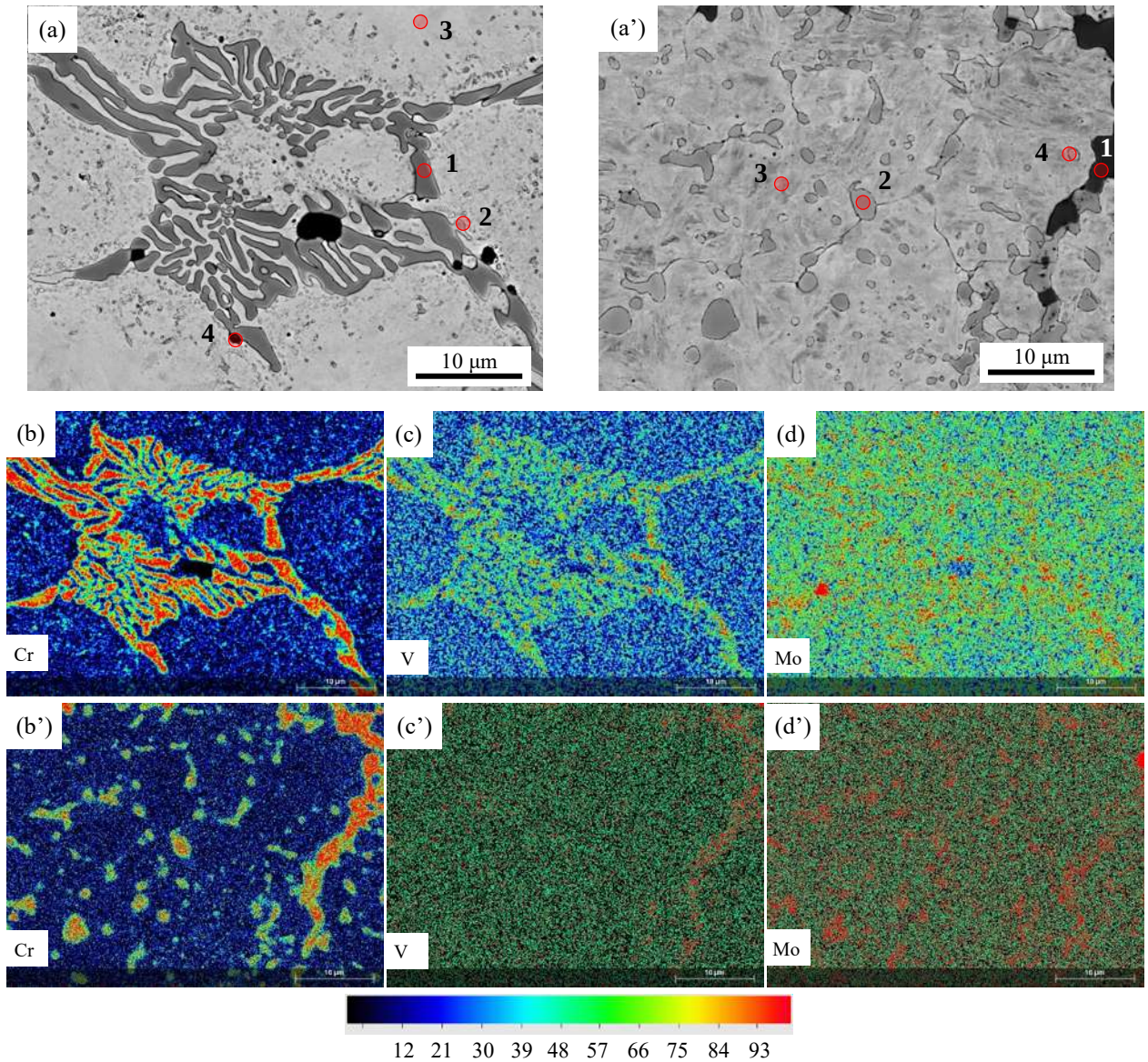


Figure 5.8 SEM/BSE images of (a) as-cast and (a') spray-formed steel. EDS element mapping of (b-d) as-cast and (b'-d') spray-formed specimens. Locations in (a) and (a') correspond to the spot analysis in Table 3. Specimens were austenitized at 1050 °C for 1 h and tempered at 350 °C for 0.5 h.

The skeleton-like coarse carbide morphology in the cast material is anticipated to be harmful to the steel's toughness [98]. Building on previous results, the spray forming technique reduces element segregation compared to the conventional casting, resulting in a more even carbide distribution and, anticipated, enhanced properties.

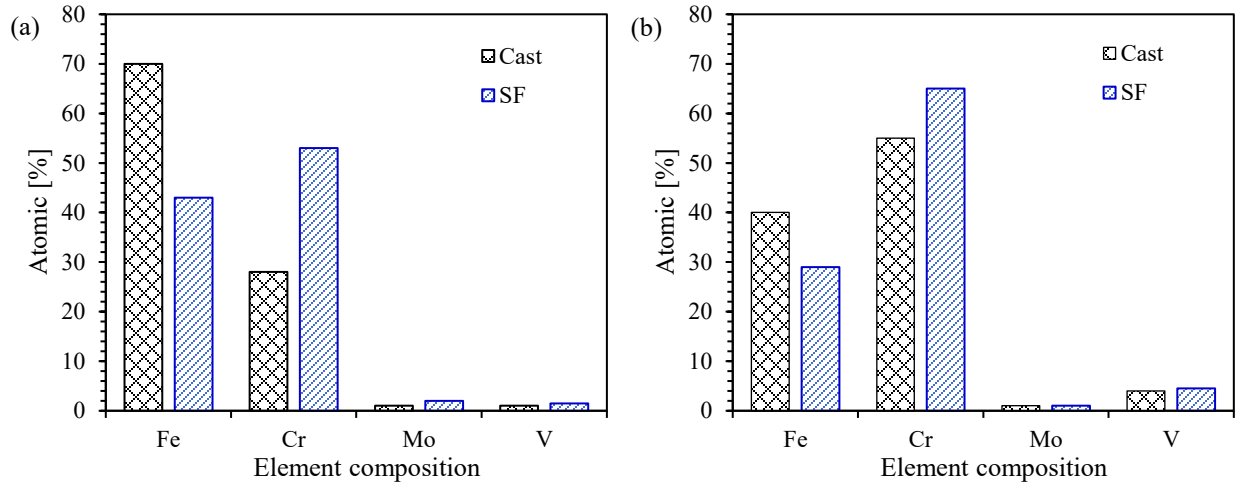


Figure 5.9 Metallic composition of (a) light carbides and (b) dark carbides in the heat-treated conventional cast and spray-formed materials after austenitizing at 1050 °C for 1 h and tempering at 350 °C for 0.5 h.

Table 5.3 Quantitative EDS analysis of carbides and matrix in Figure 6(a, a').

Manufacturing technique	Phase		Element composition (at %)					
			Fe	Cr	Mo	V	Si	Mn
CC	Carbide	1	40	55	1	4	---	---
	Carbide	2	70	28	1	1	---	---
	Matrix	3	79	18	0.4	0.5	1	0.5
	Carbide	4	69	29	1	1	---	---
SF	Carbide	1	29	65.5	1	4.5	---	---
	Carbide	2	43.5	53	2	1.5	---	---
	Matrix	3	84	13	0.3	0.3	1.3	0.7
	Carbide	4	45.5	51	2	1.5	---	---

Scanning electron microscopy

The microstructures of the cast samples after austenitizing at 1050 °C for 1 h followed by OQ and tempering at temperatures ranging from 150-550 °C for 0.5 h are shown in Figure 5.10. For all samples, non-uniformly distributed coarse eutectic carbides are (largely) retained as a result of their sluggish dissolution during austenitizing. These Cr_7C_3 carbides are elongated and irregular in shape with lengths ranging from 1 to 30 μm . In the surrounding matrix, fine carbide particles are homogeneously distributed after austenitizing and OQ (Figure 5.10(a)). Although the austenitizing temperature was chosen as 1050 °C to dissolve Cr_{23}C_6 (cf. Figure 5.1(a)), it is believed that the fine carbides dispersed in the matrix are Cr_{23}C_6 , promoted by the higher Mo content in the matrix,

because the coarse Cr_7C_3 carbides are relatively lean in Mo (cf. Figure 5.9(b)). On subsequent tempering, it is difficult to see any changes in the micrographs presented in Figures 5.10(b-f). In this respect, it is suggested that the finely dispersed Cr_{23}C_6 in the OQ condition grow to accommodate the carbon (and Cr) released on tempering of martensite.

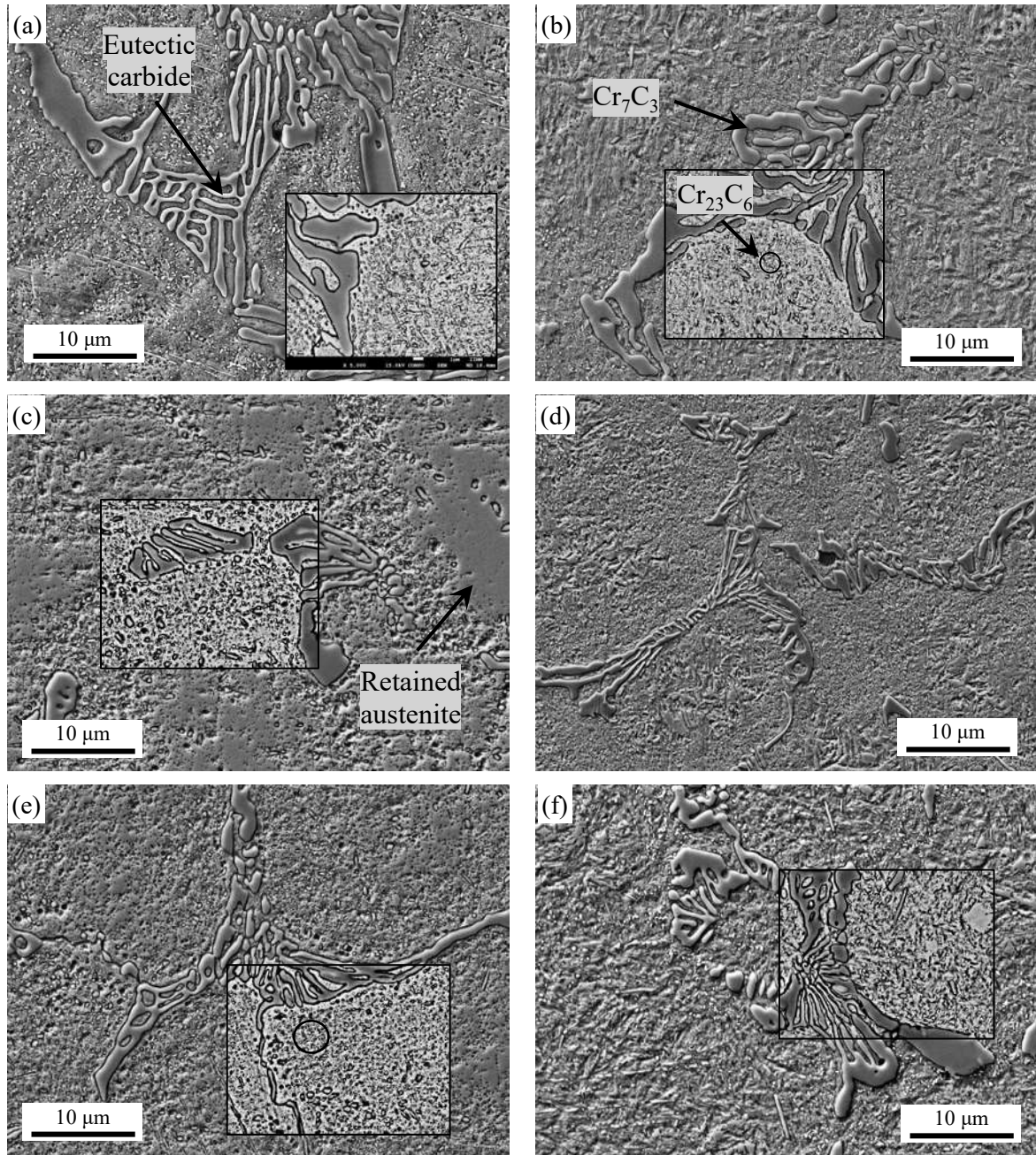


Figure 5.10 SEM/BSE (inserts) micrographs of heat-treated cast 440C MSS (a) after austenitizing at 1050 °C for 1 h and tempering for 0.5 h at 150, 250, 350, 450, and 550 °C in (b) to (f), respectively.

The microstructure of the as-quenched and tempered SF 440C MSS presented in Figure 5.11(a) reveals the presence of Cr_7C_3 , and undissolved Cr_{23}C_6 carbide particles distributed in a martensite matrix. Coarse carbides form a semi-continuous network along (prior) austenite grain boundaries and sub-grain boundaries, while fine carbides are distributed within martensite. Similar results were found in high-carbon steel by Spangel et al. [85]. It is also seen that the large carbides exhibit an elongated and irregular shape as compared to the small carbide particles. The small carbides have a size in the range of a few hundred nanometers up to 15 μm . The matrix appears clearly martensitic and in contrast to Figure 5.10(a) no dispersion of fine carbides is observed in the matrix.

The microstructures of the as-tempered samples are shown in Figure 5.11(b-f). It is observed that the microstructure mainly consists of tempered martensite. The micrographs show the precipitation of sub-micron-sized carbides within the martensitic matrix. At the highest tempering temperature (550 °C), coarser sub-micron-sized carbides are observed, predominantly within the sub-grains (Figure 5.11(f)). A comparison between the microstructures in Figures 5.10 and 5.11 as well as Figure 5.12 shows that the spray-formed material has a considerably finer primary carbide distribution than the cast steel. The large eutectic carbides are prevented due to faster solidification and a correspondingly lower segregation level of alloying elements not present in the coarse Cr_7C_3 carbides. For the cast microstructure the large, non-uniformly distributed eutectic carbides are accompanied by a dispersion of nano-scale carbides. For the SF steel the smaller and more uniformly distributed primary carbides are surrounded by a clearly martensitic matrix, which is a mixture of lath and plate martensite. In the matrix, the very fine nano-scale carbides are difficult to resolve in Figures 5.12(c-d) for SF steel. The difference in finely dispersed carbides in the matrices of austenitized/tempered SF and cast steels is a consequence of the relatively fast cooling after solidification upon casting, leading to more carbon and alloying elements in solid solution in as-cast condition. This supersaturated martensite (Figure 5.5) precipitates Cr_{23}C_6 on austenitizing. On the other hand, slow cooling after solidification in the spray-forming process has led to a closer to equilibrium microstructure (ferrite + carbides; cf. Figure 5.5).

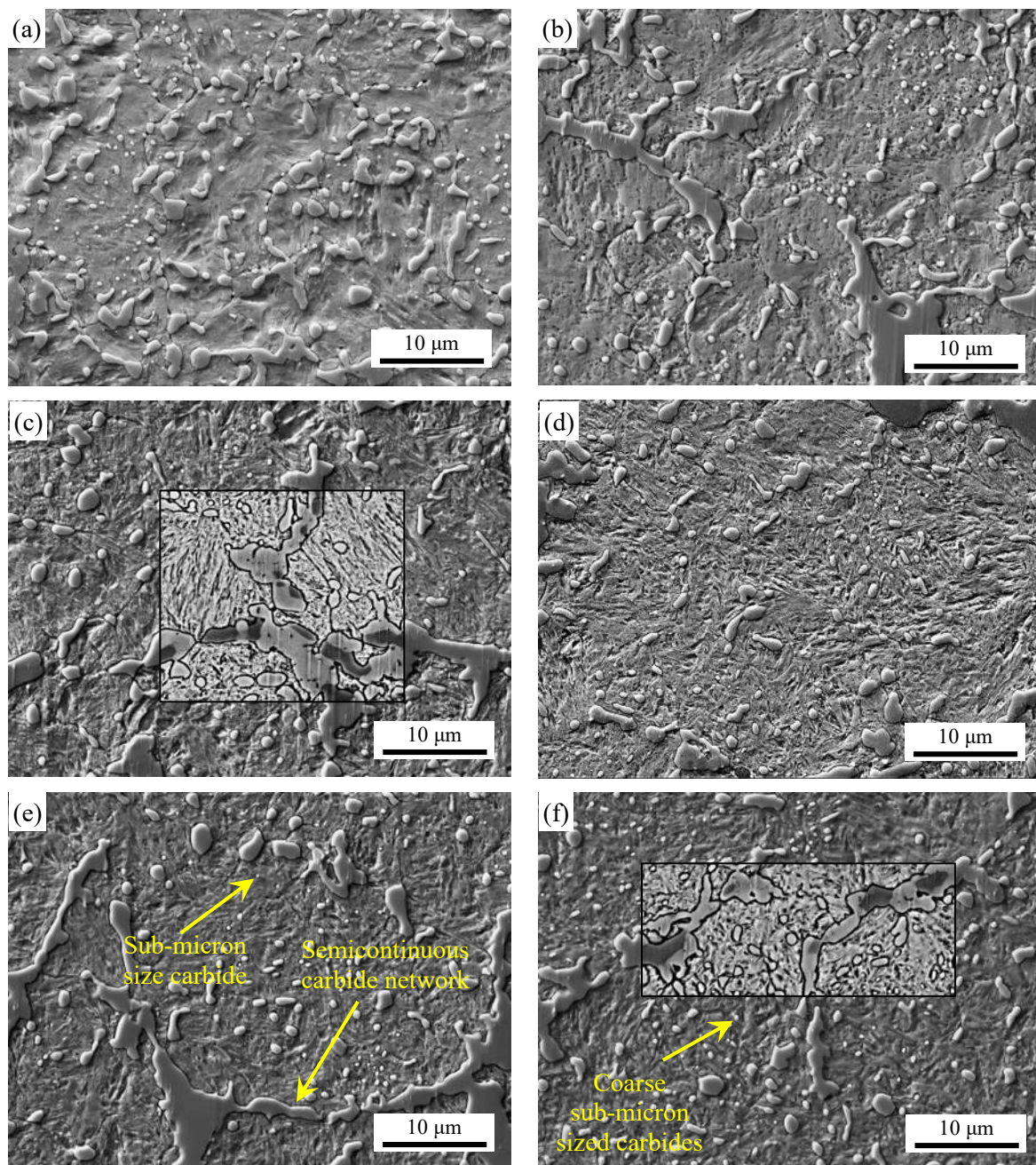


Figure 5.11 SEM/BSE micrographs of heat-treated SF 440C MSS (a) after austenitizing at 1050 °C for 1 h and after tempering for 0.5 h at 150, 250, 350, 450, and 550 °C in (b) to (f), respectively.

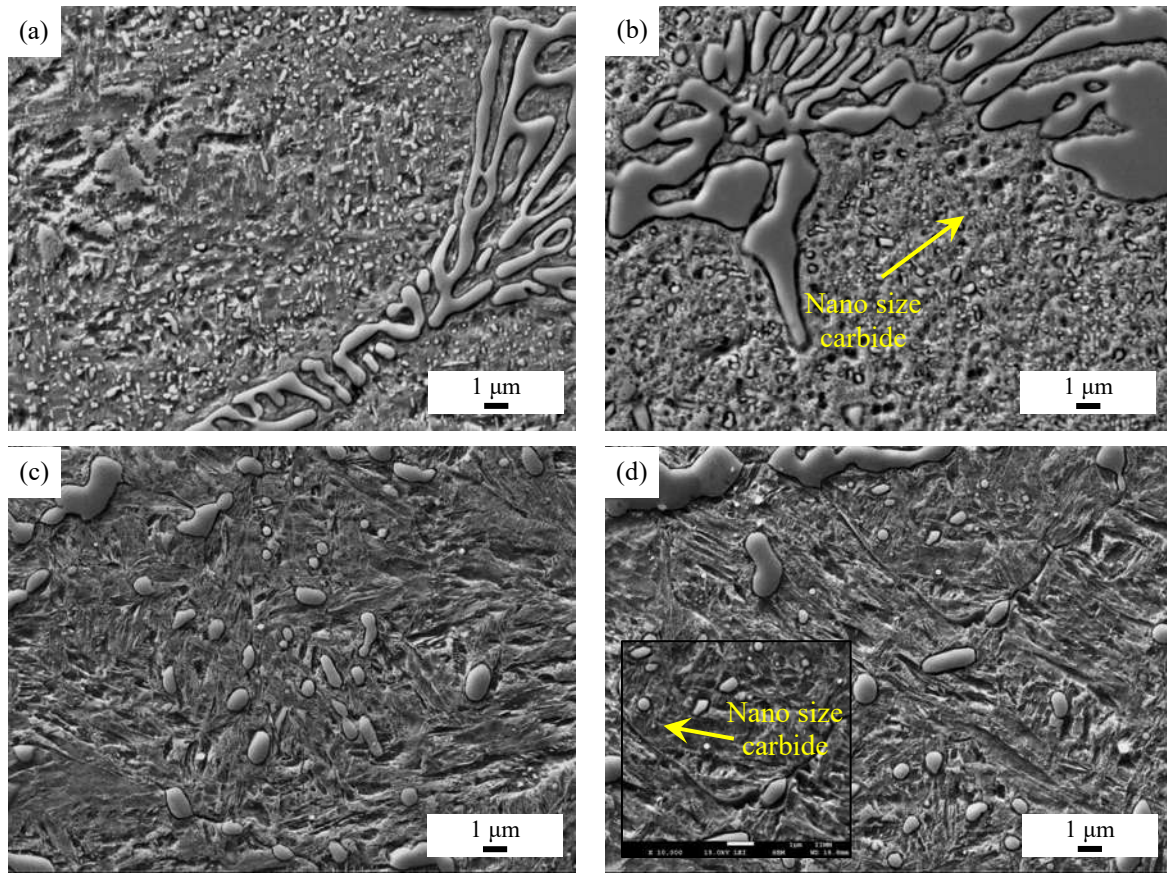
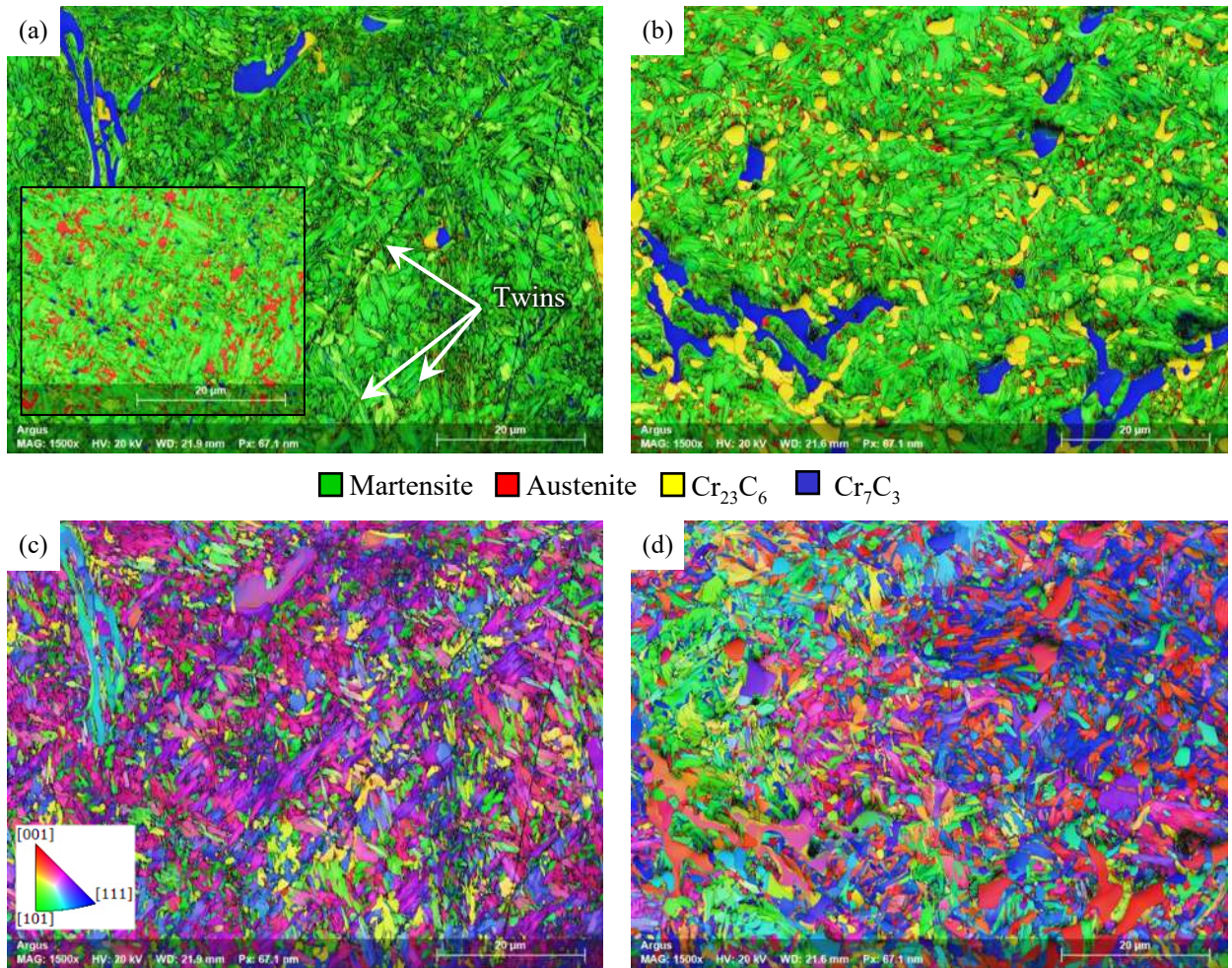


Figure 5.12 Secondary electron images of conventional cast steel tempered for 0.5 h at (a) 350 °C and (b) 450 °C. SF material tempered for 0.5 h at (c) 350 °C and (d) 450 °C.

Electron backscatter diffraction

The phase distribution and morphology were further analyzed with EBSD. In Figure 5.13(a), a lower retained austenite content is observed in the cast steel than in the spray-formed material (Figure 5.13(b)). Analysis of a different area shown in the detailed image in Figure 5.13(a) shows a microstructure with higher retained austenite regions. These large differences in the retained austenite content reflect the rather inhomogeneous microstructure of the cast steel that results from the manufacturing process. Rietveld analysis of the X-ray diffractograms in the as-quenched condition for cast and SF steels revealed that the retained austenite content in the SF steel is slightly higher (10%) than in the cast material (8.6%). If this difference is significant, it may be explained by the finer primary carbides in the SF steel so that more carbide dissolves during austenitizing, leading to more stable austenite [99]. A comparison of the cast and the spray-formed

microstructures in heat-treated conditions (Figure 5.13(c-d)) indicates that the size distributions of martensite units are equal within experimental accuracy. On the other hand, the aspect ratios show a small difference. For SF steel a ratio in the range up to 0.4 is more strongly represented than for the CC steel, while the range 0.45-0.70 is more strongly represented by the CC sample than by SF material. The size distribution and aspect ratio as well as the orientation maps in Figure 5.13(c-d) suggest that the majority of the martensite is of lath type, consistent with the relatively low carbon content in austenite upon austenitizing at 1050 °C (cf. Figure 5.1b) and the low content of retained austenite.



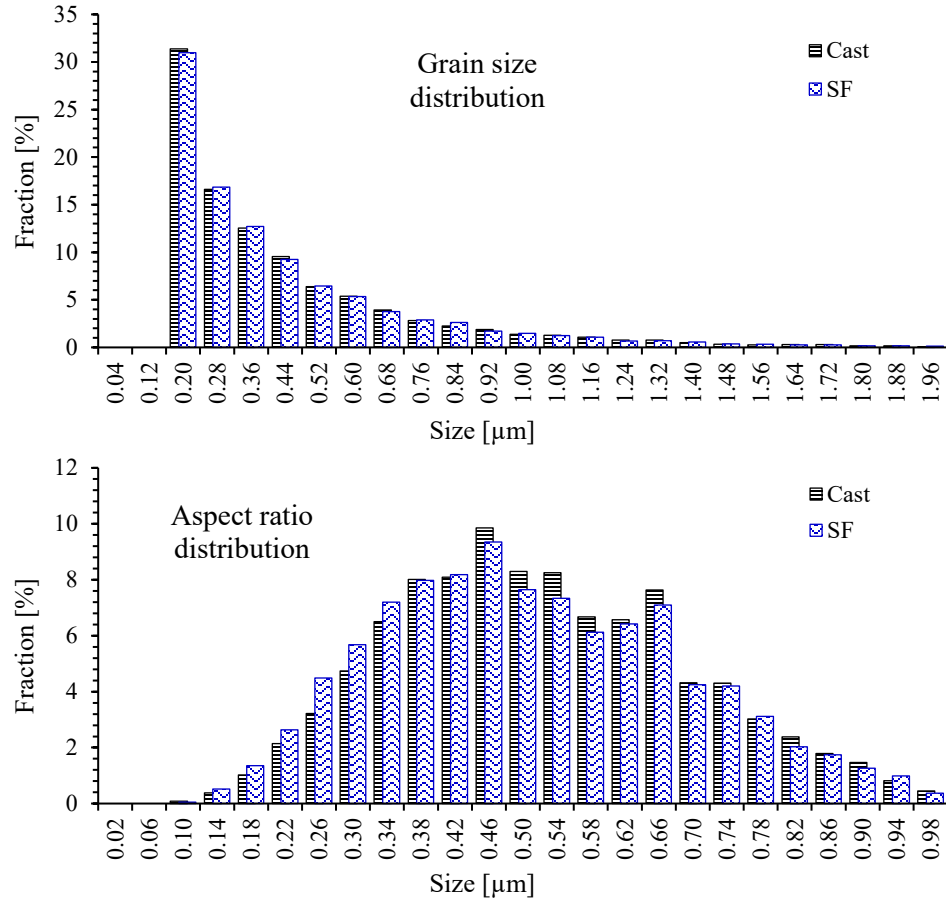


Figure 5.13 EBSD phase map comparison of heat-treated (a) cast and (b) spray-formed specimens. EBSD orientation maps showing microstructure in the (c) cast and (d) spray-formed specimens. The samples were OQ from an austenitizing temperature of 1050 °C and tempered at 350 °C for 0.5 h.

5.3.3 Mechanical properties

Hardness

After quenching, the fresh martensite is brittle and therefore the steel is susceptible to cracking. Generally, tempering is necessary to restore some of the ductility and increase the toughness. Hardness can be used to track the tempering effects and its values can be used as a qualitative estimate of the strength of engineering components. The microhardness evolutions in Figure 5.14 show a trend that the hardness values of the (heat-treated) SF steel are systematically higher than those of the (heat-treated) conventional cast material. These higher values can be attributed to several factors including retained austenite content, carbide size and distribution, and carbon

content in the martensite/austenite, as discussed previously. Vickers microhardness results suggest four partly overlapping stages that occur as follows. For low tempering temperatures (100 to 200 °C) there is a drop in hardness as the tempering temperature increases. This effect can be ascribed to martensite tempering involving carbon redistribution causing loss of tetragonality in the martensite (if present) and the precipitation of C from martensite as transition Fe-based carbides [51]. During tempering at 250 °C partial decomposition of retained austenite into a mixture of (Cr-containing) cementite and ferrite occurs, leading to a lower hardness of martensite and more stable and strengthened retained austenite. Furthermore, a static recovery of the martensite by a reduction in the dislocation density is anticipated [43]. In general, the main applications of low-temperature tempering are those that require high strength, bending fatigue resistance, wear resistance, and contact fatigue resistance [39].

Secondary hardening, referred to as stage IV of tempering, is observed at a tempering temperature of 450 °C. This phenomenon usually occurs in tempered steels that contain strong carbide-forming elements such as Cr, V, Mo, and Nb. During this stage, the hardness begins to increase as fine alloy carbides precipitate when the combination of temperature and time allows the diffusion of substitutional atoms to establish the secondary carbides. The precipitation of these alloy-element carbides requires the diffusion of substitutional atoms (not just diffusion of C as for the transition carbides) so that their precipitation occurs sluggishly. [31, 39, 44, 45]. At temperatures above 500 °C, softening takes place, which is attributed to the degradation of the martensite microstructure as well as the coarsening of carbides [16, 33, 42, 45, 47]. The coarsening of Cr_{23}C_6 carbides is driven by a reduction in the interfacial area between the particles and the matrix [46]. Secondary hardening (stage IV), leads to a hardness increase of 42 HV for the SF material while the cast steel gains 34 HV. The subsequent softening at 550 °C shows a hardness reduction of 37 HV for SF material and 63 HV for the cast steel. For the SF material, the hardness is comparable to that of stage III after tempering at 350 °C. The difference between SF and cast material in the secondary hardening and subsequent softening stage is explained by the difference in initial composition. Spray-formed steel has a substantially higher V content (in wt%) than its cast equivalent; on the other side, the Mo content (in wt.%) in cast 440C is somewhat higher than in SF 440C (Table 5.1). Moreover, the contents of these elements in the Cr_7C_3 and Cr_{23}C_6 carbides are lower for SF than for cast material. Consequently, more abundant secondary carbide precipitation, particularly V-carbides, occurs in

SF material than in cast material, which compensates for the hardness reduction during subsequent coarsening, where large carbides grow at the cost of small carbides.

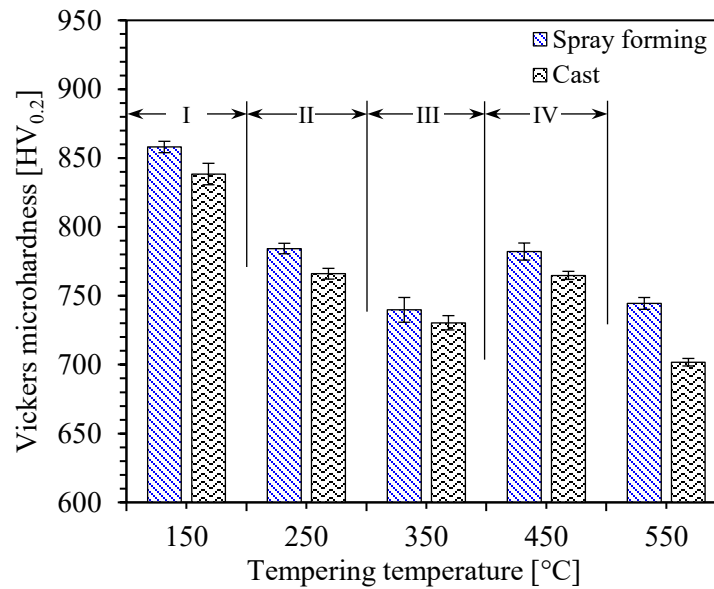


Figure 5.14 Hardness comparison of the tempered-partitioned cast and spray-formed materials.

Tensile and compressive testing

The tensile engineering stress-strain results in Figure 5.15 display a series of graphs that compare the mechanical properties of the as-cast/as-spray-formed and all tempered conditions. For the initial conditions in Figure 5.15(a), the as-cast sample exhibits a higher yield strength and ultimate tensile strength, but a considerably lower ductility as compared to the as-sprayed sample. This can be directly related to differences in the initial microstructures and carbide distributions: i.e., the as-cast sample contains large carbides and has an austenitic/martensitic matrix (higher strength), while SF has finer carbides and a ferrite matrix (high ductility). After heat treatment, the SF samples also exhibited a higher fracture strength than those of the CC material for all tempering temperatures. Nevertheless, it was found that the amount of plastic deformation at fracture is very small for all the tempered conditions. It is observed that secondary hardening upon tempering at 450 °C has a profound effect on the fracture strength of the SF condition, reaching 1307 MPa which is about 72% higher than that of the CC condition (Figure 5.15(e)). Finally, the stress-strain curves of the samples tempered at 550 °C shown in Figure 5.15(f), display a small, yet noticeable, elastoplastic

behavior and a slight reduction in the tensile strength. Regarding the fracture behavior, except for the 550 °C, all tempered samples exhibit brittle fracture before any plasticity is accommodated. In the case of the SF material, it is probable that both stress relief and a loss in the tetragonality of the martensite simultaneously take place and are controlled by the tempering temperature, which contributes to an improvement of the tensile strength of the alloy.

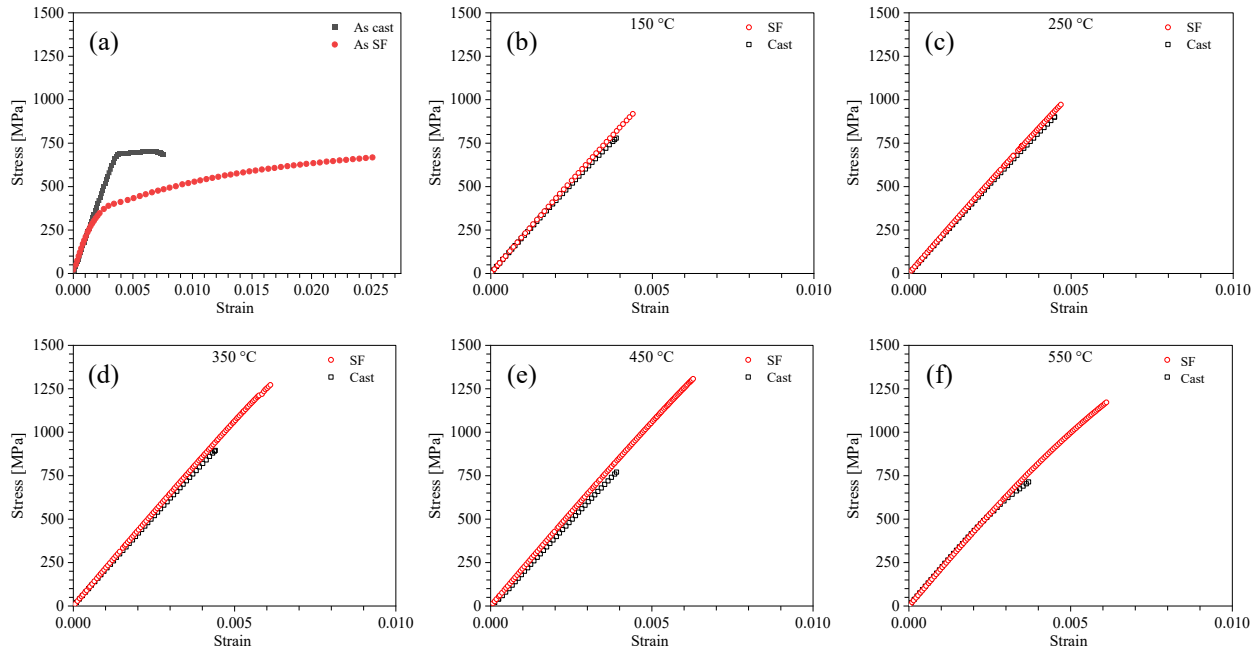


Figure 5.15 Tensile stress-strain curves comparison of CC and SF samples (a) as-cast and as-sprayed conditions. After austenitizing at 1050 °C for 1 h and tempering at (b) 150, (c) 250, (d) 350, (e) 450, and (f) 550 °C.

It is well known that microstructural parameters such as grain size, the volume fraction of phases, and carbide size and distribution greatly influence mechanical properties. The fracture mechanism in martensitic steels involves the nucleation and propagation of microcracks from brittle phases like carbides [83]. It would be expected that a larger carbide size in the CC material leads to lower tensile strength as compared to that of the spray-forming route, see Table 5.4. However, the SF steel possesses better properties compared to the cast steel due to its finer microstructure, which increases the local fracture stress. On the other hand, the experimental results corroborate that the tensile strength of the cast material was highly affected by the carbide size and distribution. Therefore, it can be argued that the improved tensile strength of the SF steel is caused by the

enhanced microstructural features imposed by this manufacturing technique, since carbide morphology, size, and distribution play a crucial role in crack initiation.

The susceptibility of brittle fracture during the tension test obscures insight into the load capacity of materials; here, compression tests may provide a better understanding [100]. Compression tests were performed for the heat-treated conditions of the CC and SF alloys. The experimental results presented in Figure 5.16 show a noticeable effect of the manufacturing history on the mechanical response (the results of the tensile test are also included in the graph to emphasize the significant difference between tensile and compression loading). On compressive loading, the tempered cast alloy shows an elastic-to-plastic transition at about 2,000 MPa and 1 mm compression. In contrast, the SF tempered sample exhibits a significant increase in the elastic-plastic transition at approximately 2,350 MPa and 1.5 mm compression. These findings highlight a clear advantage of the SF steel over the cast material, even when the ultimate compressive strength of the SF steel is slightly lower than that of the cast material (see Table 5.4).

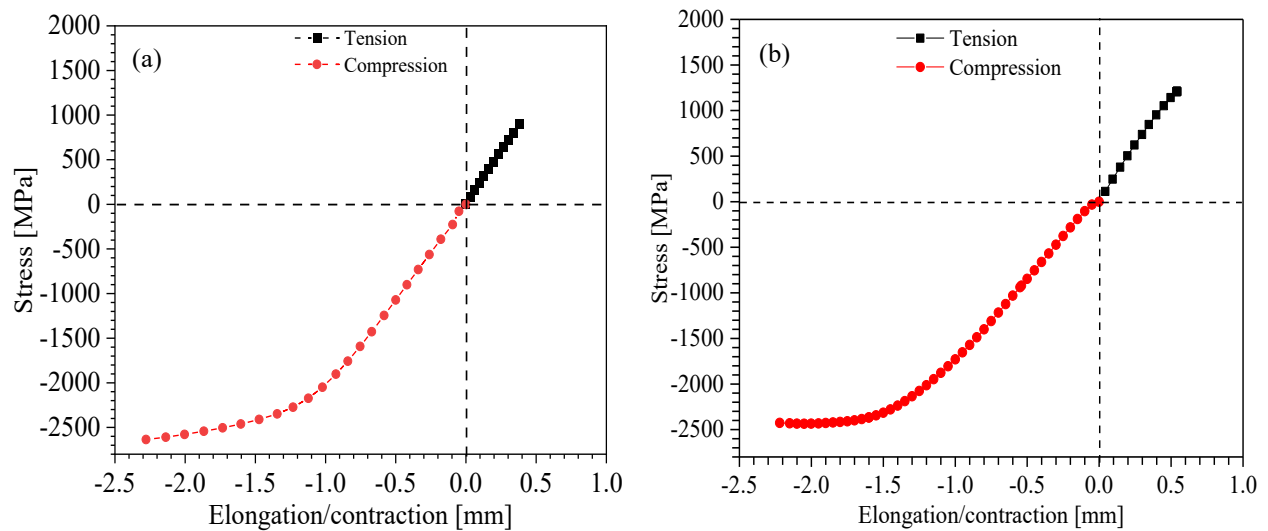


Figure 5.16 Stress-displacement curves for the specimens austenitized at 1050 °C for 1 h and tempered at 350 °C for 0.5 h (a) CC and (b) SF condition.

Table 5.4 Effect of tempering temperature on the mechanical and elastic properties of conventional cast and SF 440C MSS. All the samples were austenitized at 1050 °C for 1 h.

Manufacturing Technique	Tempering T. [°C]	Hardness [HV _{0.2}]	E^* [GPa]	σ_f^* [MPa]	UCS^* [MPa]
CC	150	838	201	779	---
	250	766	201	900	---
	350	730	204	895	2644
	450	764	208	770	---
	550	701	213	713	---
SF	150	858	208	918	---
	250	789	208	971	---
	350	740	206	1272	2428
	450	782	209	1307	---
	550	745	202	1172	---

*Where E stands for elastic modulus, σ_f stress to failure, and UCS for ultimate compressive strength.

Considering the complex state of stresses of real tooling applications, isotropy of the spray-forming microstructure is anticipated to provide better performance than for conventionally cast steels. Mesquita et al. [101] state that coarse carbide distributions may also lead to heat-treating distortions imposed by the difference in the thermal expansion coefficients of the phases.

5.4 Conclusions

The microstructure and mechanical properties of spray-formed martensitic stainless steel 440C were compared to its conventionally cast equivalent. The key findings are:

- In the as-spray-formed condition, the steel's microstructure consists of ferrite and carbides of the types Cr_7C_3 and, mainly, Cr_{23}C_6 , under equilibrium predictions. The carbides are relatively homogeneously distributed. For the as-cast condition, the microstructure is martensitic with retained austenite and coarse Cr_7C_3 , which has formed during eutectic solidification and was retained on subsequent cooling. The amount of Cr_{23}C_6 carbide is much lower than expected from thermodynamic predictions. The difference in initial microstructures is explained by fast solidification in the spray-forming route, which bypasses the eutectic solidification that leads to the large primary carbides in the casting route. After solidification very slow cooling occurs for the spray-forming route, enabling near-equilibrium phase fractions. For casting, cooling after solidification is insufficiently slow to form the equilibrium content of Cr_{23}C_6 carbides.
- Austenitizing terminated by oil quenching causes a change in the phase fractions of Cr_7C_3 and Cr_{23}C_6 for the cast steel although the primary (eutectic) Cr_7C_3 in the cast steel is largely retained; for the SF steel, only marginal changes occur. The steel matrix for the quenched cast steel contains a distribution of finely dispersed Cr_{23}C_6 carbides, while the matrix in the quenched SF steel does not show such finely dispersed carbides. Upon tempering the hardness decreases and secondary hardening occurs at 450 °C. For all conditions, the hardness is highest for the SF steel. The differences in microstructure after quenching and tempering are directly related to the differences between the as-cast and as-sprayed conditions. The higher initial carbon content in the matrix of the as-cast condition leads to the fine distribution of Cr_{23}C_6 carbides on austenitizing. On the other hand, the near-equilibrium starting condition for the SF steel and the lack of coarse Cr_7C_3 carbides causes a higher carbon content in solid solution and harder martensite upon quenching.
- The different microstructures for cast and SF steels lead to different material properties and performance. The SF steel exhibits a more favorable combination of tensile, hardness, and toughness properties.

CHAPTER VI

COMPARISON OF WEAR PROPERTIES OF 440C TOOL STEEL FABRICATED BY SPRAY-FORMING AND CONVENTIONAL CASTING

Abstract

In this investigation, the impact of manufacturing processes and secondary hardening on the wear properties of 440C martensitic stainless steel (MSS), produced through conventional casting and spray-forming, is analyzed comparatively. Wear tests were performed at room temperature using the ball-on-disc configuration without lubrication. The study employs advanced characterization techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and electron backscatter diffraction (EBSD), to comprehensively analyze wear mechanisms. A detailed examination is conducted on how microstructural traits, comprising particle size, carbide distribution, and the phase volume fraction, influence the wear rate, friction coefficient, and the characteristics of wear debris. The investigation highlights the superior wear resistance of the SF process, marked by reduced friction coefficients and enhanced wear rates. This is attributed to the refined and more uniformly distributed microstructure and phase fraction achieved by the spray-forming. Furthermore, adhesion, oxidation, and abrasion are considered to be the main wear mechanisms in both processing methods. The findings of this research provide important insights into the critical role of manufacturing technology in tailoring the wear performance of 440C MSS, thereby helping to optimize tribological applications.

Keywords: 440C MSS, Wear, Microstructure, Spray-Forming, Casting

6.1 Introduction

Martensitic stainless steels (MSSs) are alloys that exhibit high strength and wear resistance combined with moderate corrosion resistance which make them suitable for different applications such as bearings, dies, tools, propellers, impellers, and knives. The microstructure of the 440C steel in the heat-treated condition consists of a tempered martensite, retained austenite as well as bulk primary and fine secondary carbides. The wear behavior of this type of steel is heavily influenced by their microstructure, which relies on the martensite/retained austenite ratio and the fraction, size, and distribution of carbides. The factors governing the final microstructure are (i) the chemical composition of the alloy, (ii) the solidification rate, (iii) hot working, and (iv) heat treatment (with minor changes) [102]. From these, the solidification rate plays a key role in determining the final size and distribution of carbides and may be controlled by the manufacturing process and product size [102, 103]. In the manufacturing of tool steels, the spray-forming technique has been found to yield finer microstructural characteristics compared to conventionally cast steels [82, 91, 104]. This refined microstructure is a consequence of the rapid solidification occurring during the initial stage of the spray-forming process (in-flight stage) and subsequent deposition, where subsequent depositions cause the fragmentation of dendrites by particle impacts [57, 83, 87, 105].

Rodenburg and Rainforth [102] found that large carbides are more prone to fracture, leading to high wear rates. Colaço et al. [106] reported that the wear coefficient of AISI 420 steel increased linearly with the volume fraction of retained austenite. They also found that the stress-induced transformation (retained austenite $\rightarrow$ martensite) and the work hardening of the austenite during the wear test reduces the wear coefficient of the retained austenite as the applied load increases. The effect of spray-forming on the wear behavior of high-speed steel was addressed by Hanlon and Rainforth [104], who showed that an optimum carbide size and distribution reduce the wear rate of steel. Therefore, carbides that are too large lead to high wear because they are prone to fracture, while carbides that are too small cannot protect the matrix from plastic deformation. Although some research has been conducted to improve the wear resistance of different grades of martensitic stainless steel [103, 106-110], most of these studies have focused on either assessing surface treatments and coatings to improve the wear resistance of bulk materials or examining how the carbide size, distribution, and volume fraction induced by a change in chemical composition can affect the wear behavior. Only a few studies have evaluated the effect of the manufacturing process

and secondary hardening on the wear resistance of MSS. Therefore, this work aimed to investigate the effect of the manufacturing route and secondary hardening on the microstructure-wear behavior relationship of conventionally cast and spray formed 440C MSS steel.

6.2 Experimental procedure

6.2.1 Materials and methods

High-carbon AISI 440C martensitic stainless steel with a similar chemical composition was produced by two different processing routes: i) spray-forming and ii) conventional casting. The chemical composition of each material, as determined by optical emission spectroscopy is listed in Table 6.1.

Table 6.1 Mean chemical composition (wt. %) of the two steels.

Material	C	Mn	P	S	Si	Cr	Mo	V	W	Ni	N	Fe
SF	1.24	0.44	0.02	0.013	0.55	15.86	0.89	0.42	0.186	0.33	0.07	Bal.
CC (VIM)	1.29	0.43	0.016	0.018	0.57	15.71	0.86	0.43	0.173	0.32	0.06	Bal.

As-cast and as-sprayed samples were cut and machined from both alloys and subsequently heat-treated. For this, two sets of samples of each material were quenched in oil from an austenitizing temperature of 1050 °C, and afterward one set was tempered at 350 °C for 0.5 h, and the other one was subjected to a tempering temperature of 450 °C for 0.5 h, both followed by air cooling to room temperature. All heat treatments were performed in a tube furnace under a flowing argon atmosphere. After heat treated, the specimens were ground with 220-1500 emery paper and further polished with a 0.05 µm alumina suspension. The microstructure of the samples was revealed by using Vilella's reagent for 10 seconds. The different microstructures were analyzed via light optical microscopy (LOM) in a Zeiss axio observer microscope and scanning electron microscopy (SEM) using an EM: JEOL JSM-7600F FEG/SEM. Then, image processing was done using the ImageJ® software. Energy dispersive spectroscopy (EDS) was performed to analyze the chemical composition of the carbides and wear debris. Further microstructural analysis was conducted by Electron Backscatter Diffraction (EBSD) with a JEOL JSM-7600F FEG/SEM equipped with an e⁻ flash HR+ detector. To perform this analysis, the samples were electropolished in a solution of 60 ml perchloric acid in 940 ml acetic acid solution at 15 V. The EBSD data were collected using a

QUANTAX CrystAlign 400i-EBSD system at a tilt angle of 70°, an acceleration voltage of 20 kV, and a scan step-size of 64.9 nm. The data was post-processed using ESPRIT 2 Quantax software. XRD was performed using a Bruker D8 advanced diffractometer in Bragg-Brentano focusing geometry with Cu K α radiation at 40 kV and 40 mA. The samples were scanned using a step size of 0.05° and a counting time of 3 s per step. Finally, the diffraction patterns were further post-processed by Rietveld refinement using the GSAS II software [93].

Vickers microhardness measurements were performed using a Mitutoyo HM-220B computer-controlled tester equipped with a manually controlled xy stage with digital micrometer and a resolution of 1 μ m. The test parameters were a constant load of 200 g (1.96 N) and a holding time of 15 s. For each sample, 10 independent indentations were made in each sample.

6.2.2 Wear testing

The wear tests were performed on the cast and spray-formed heat-treated samples in a tribometer (TRIBOtechnic®) using the ball-on-disc contact configuration under unlubricated conditions at room temperature. In this configuration, an Al₂O₃ ball of 6 mm was used. The wear parameters were a 12 N normal load (F_N), a Hertz pressure of 1726 MPa, an average sliding speed of 150 mm/s, and a total sliding distance (d_s) of 1000 m. The friction coefficient (μ) was continuously recorded during the test and the tests were performed at least twice on each sample. The material's volume loss (V_l) was determined using a Nanovea® noncontact optical profilometer. Then, the specific wear rate (K) was calculated as

$$K = \frac{V_l}{F_N d_s} \quad (6.1)$$

Finally, the worn surface and cross-section were characterized using SEM, electron backscatter diffraction (EBSD), and Vickers microhardness techniques.

6.3 Results and discussion

6.3.1 Microstructure

Figure 6.1 shows the XRD results of both tempered alloys. The results revealed that the main microstructural constituents are α' -martensite, Cr_{23}C_6 , and Cr_7C_3 carbide phases. Some peaks of γ -austenite were also detected, indicating the presence of a minor amount of retained austenite which was formed after quenching. The SF steel exhibited a clearer identification of austenite, suggesting that the extent of the $\gamma \rightarrow \text{M}$ transformation differs due to the difference in the volume fraction of Cr_{23}C_6 and Cr_7C_3 carbides resulting from the processing route.

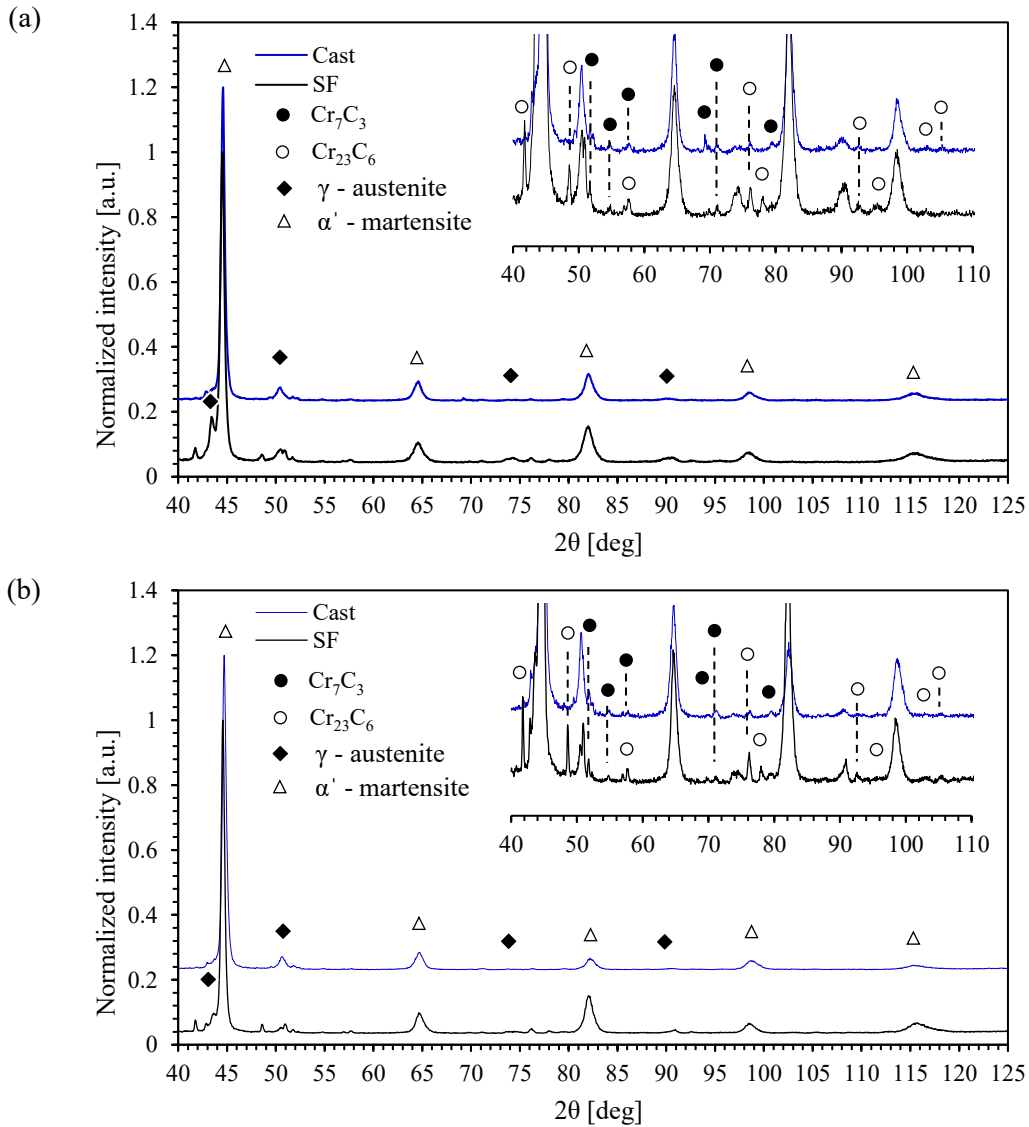


Figure 6.1 XRD patterns of the two materials for the tempering temperatures of (a) 350 and (b) 450 °C.

Figure 6.2 shows the tempered microstructure of the spray-formed (SF) and conventionally cast (CC) materials. As a result of the fabrication process, the carbide shape and size distribution show significant differences. In Figure 6.2(a), the SF steel exhibits a much finer microstructure than the CC material. In the case of the SF alloy, elongated carbides are observed along prior austenite grain boundaries as well as discrete carbides that are present inter- and intragranularly. On the other hand, the CC material (Figure 6.2(b)) has coarser microstructure with large eutectic carbides that form a semi-continuous network along the interdendritic spaces that results from the rejection of chromium and alloying element to the liquid phase during the solidification process. The precipitation of finer carbides distributed evenly within the matrix was also detected. The area distribution of carbides is shown in Figure 6.2(c-d), from the graphs, the average area fraction shows that the VC doubles (56.2%) the area fraction of the SF alloy, indicating the SF induces a smaller carbide size.

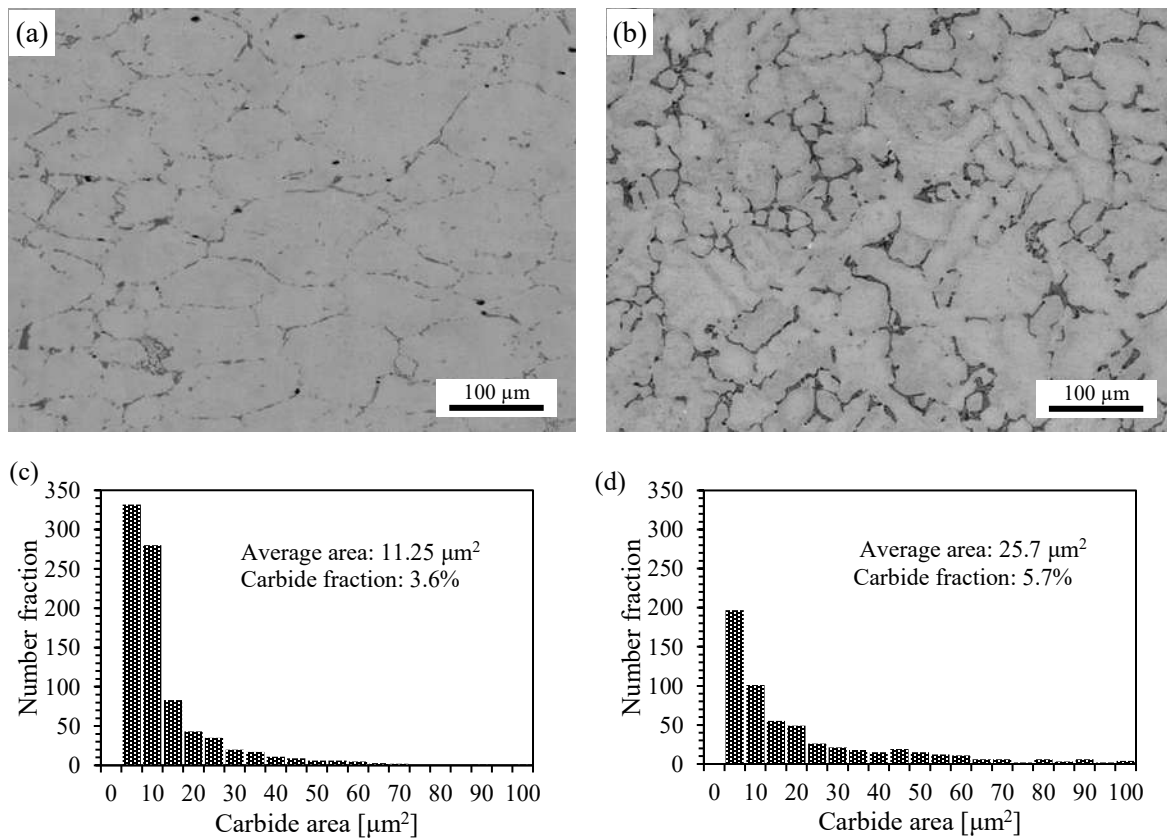


Figure 6.2 SEM/BSE micrographs of specimens after tempering at 350 °C (a) SF and (b) CC alloys. Particle area distributions of eutectic carbides of (c) SF and (d) CC materials.

The high magnification SEM backscattered electron (BSE) images in Figure 6.3 show carbide precipitates embedded in the martensitic matrix. As can be seen, the carbide phases display two different contrasts, where the presence of lightweight carbon in the carbides causes them to appear darker in comparison with the bright matrix. Also, a brighter carbide indicates the presence of heavier alloying elements such as Mo (atomic weight 95.94). The dark carbides may correspond to the Cr_7C_3 type, while the light carbides might be identified as Cr_{23}C_6 type. It has been reported that, during the austenitizing treatment, the large and less stable Cr_7C_3 carbides in the original microstructure partially decompose into the more stable Cr_{23}C_6 carbide [111].

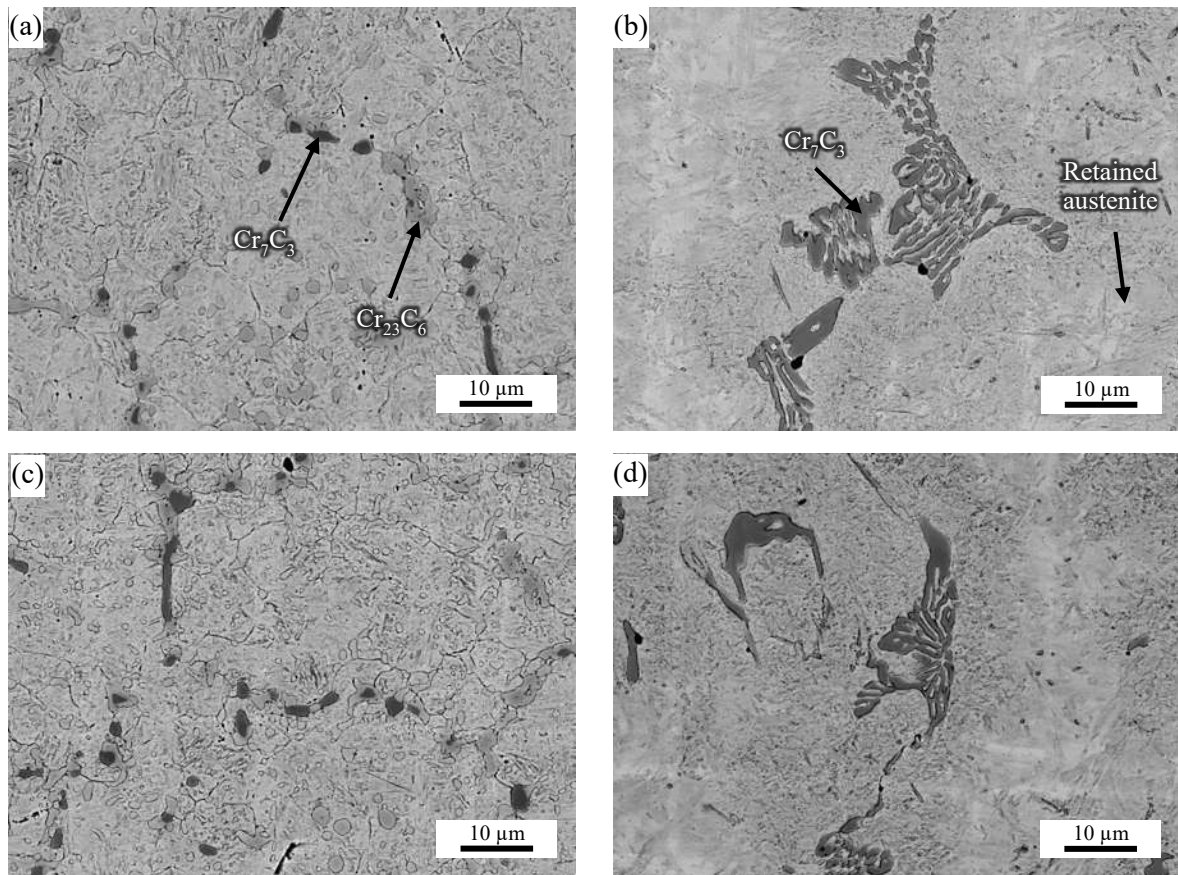


Figure 6.3 SEM/BSE images showing microstructural characteristics of the two alloys after tempering treatment (a) 350 °C-SF, (b) 350 °C-CC, (c) 450 °C-SF, (d) 450 °C-CC.

The SEM/BSE images in Figure 6.4 show a detailed view of the phases and their respective EDS analyses. The dendritic microstructure in the cast steel shows areas that partially transform into martensite (zones A and B).

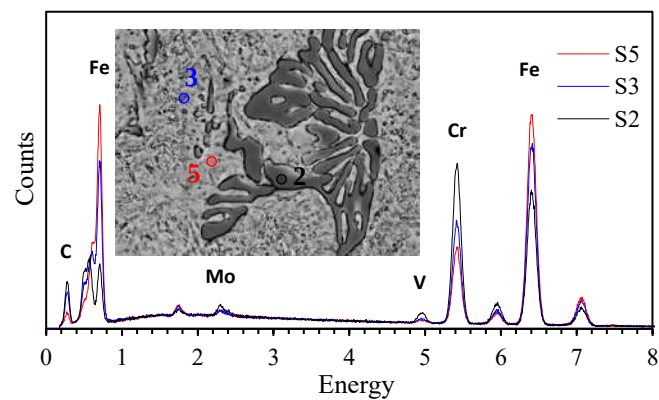
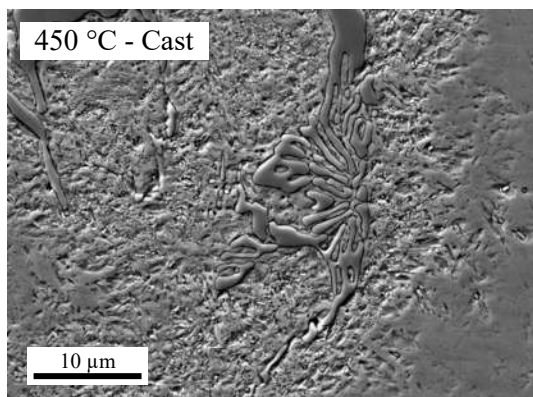
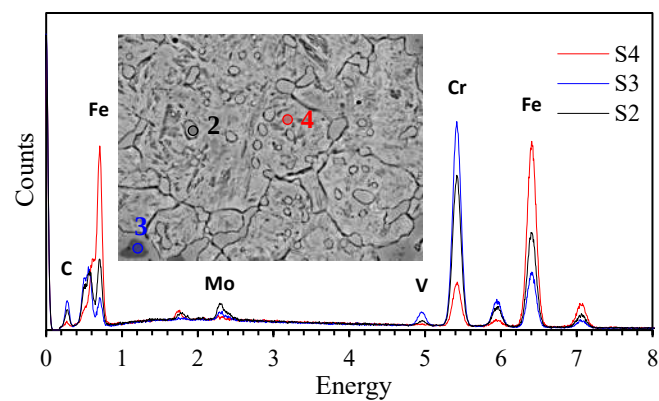
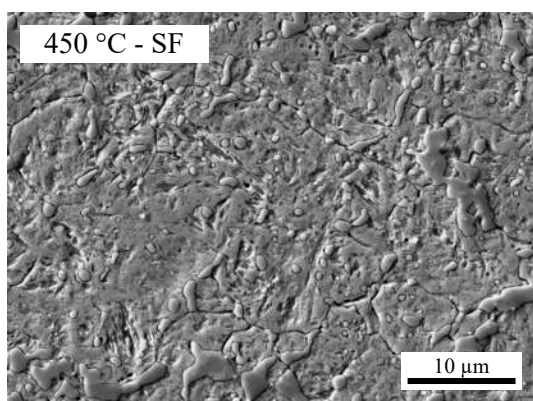
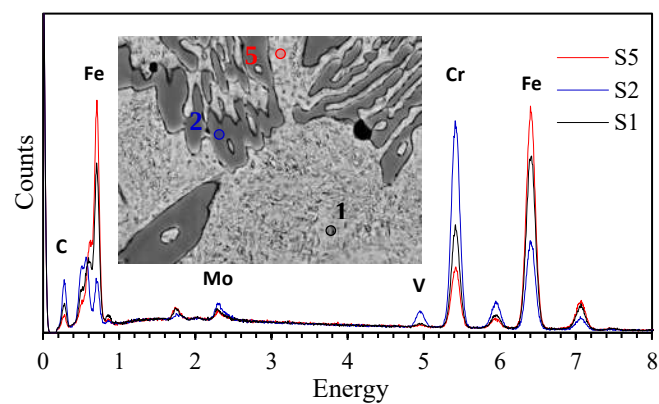
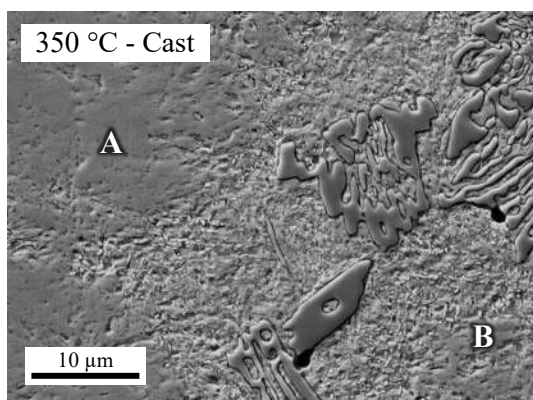
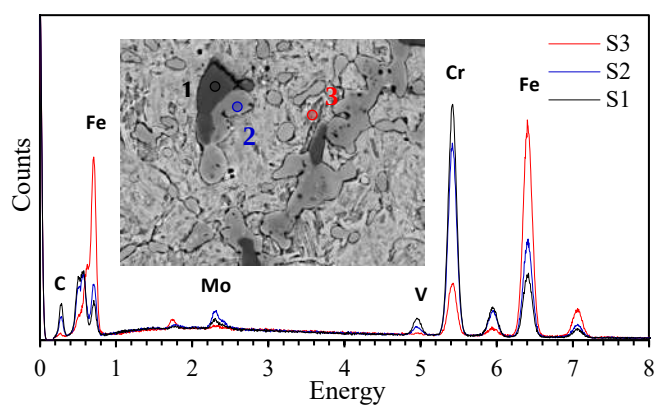
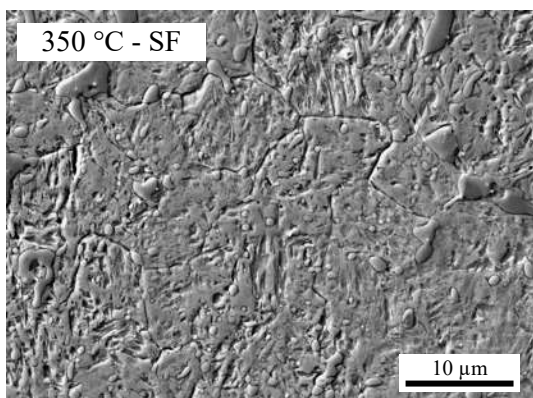


Figure 6.4 (left) SEM micrographs showing microstructural details of tempered alloys and (right) their respective EDS microanalysis.

Both alloys exhibit the presence of carbides mainly composed of Fe, Cr, Mo, and V, as summarized in Table 6.2. The analysis confirms that the darker carbides are Cr_7C_3 with higher Cr content and enriched of V and a low content of Mo. In the case of light carbides, the main alloying composition is Cr and Fe and similar content of V and Mo. Compared to the CC alloy, these particles show a slightly lower content of V and higher Mo. From the chemical composition, these carbides were identified as Cr_{23}C_6 . It was found that the matrix has slight difference in the composition, this can be explained by the difference in the volume fraction of carbides which lead to different concentration of alloying elements in solid solution.

Table 6.2 Quantitative EDS analysis of the worn surface.

Manufacturing technique	Phase	Particle	Element composition (at. %)							
			Fe	Cr	Mo	V	Si	Mn	Ni	W
SF (350 °C)	Carbide	1	29.4	65.5	0.9	4.2	---	---	---	---
	Carbide	2	43.3	53	1.7	2	---	---	---	---
	Matrix	3	83.8	13.3	0.3	0.3	1.4	0.7	0.3	---
Cast (350 °C)	Carbide	1	70	26	1	0.8	1.3	---	1	---
	Carbide	2	38.8	55.8	1.5	3.9	---	---	---	---
	Matrix	5	81.8	14.7	0.7	0.4	1.4	0.8	---	---
SF (450 °C)	Carbide	3	29	66	0.9	3.9	---	---	---	---
	Carbide	2	47.5	49	1.8	1.3	---	---	---	0.3
	Matrix	4	84	13	0.3	0.3	1.4	0.7	0.4	---
Cast (450 °C)	Carbide	3	70.9	26.5	0.5	1	1	---	---	---
	Matrix	5	78.5	18.2	0.5	0.6	1.3	0.5	0.3	---
	Carbide	2	55.2	40.9	0.9	2.3	0.6	---	---	---

6.3.2 Carbide size, morphology, and distribution after tempering

After tempering, the microstructure of the samples consisted of tempered martensite with Cr_7C_3 and Cr_{23}C_6 carbide particles. The higher fraction of Cr_7C_3 carbides can be explained in terms of the slower solidification rate, which promotes segregation of alloying elements to the dendrite boundaries. Also, as seen in Figure 6.5 (b) and (d), large precipitation of cuboidal submicron Cr_{23}C_6 carbides surround the eutectic carbides. This can be explained by the partial decomposition of the

Cr_7C_3 carbide with hexagonal structure that transforms into cubic Cr_{23}C_6 carbide. Then, the preexistent amount of Cr_7C_3 carbides (with high carbon in solid solution for the relation of carbon/metal atoms) promotes an increase in the Cr_{23}C_6 carbide fraction. This is not the case of the SF steel, which has lower volume fraction of Cr_7C_3 carbide, see Figure 6.5(a) and (c).

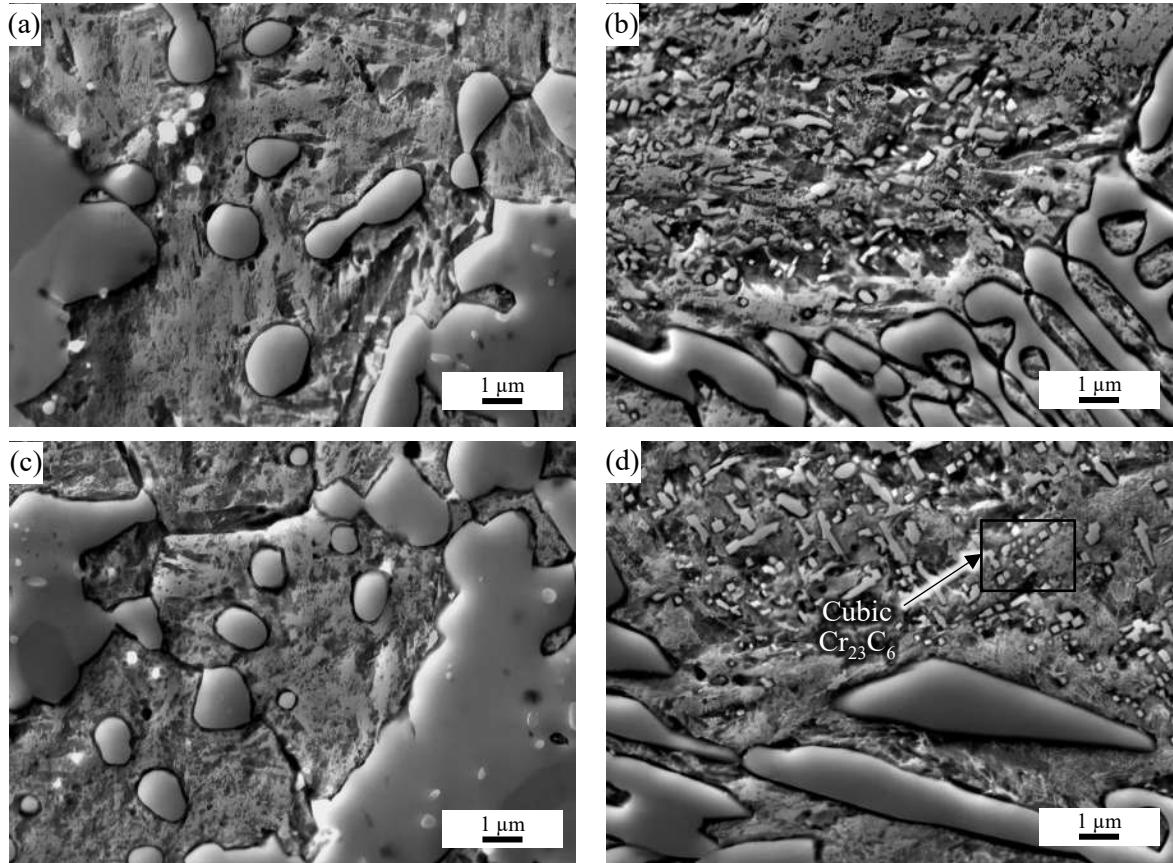


Figure 6.5 High-magnification SEM images showing the presence of chromium-rich carbides (a) 350 °C-SF, (b) 350 °C-CC, (c) 450 °C-SF, and (d) 450 °C-CC samples.

Figure 6.6 shows the comparison between the carbide area distribution (CAD), aspect ratio distribution ARD, and the nearest neighbor carbide distance distribution (NNCD) of the SF and CC alloys. These results indicated that the average carbide area of the SF steel is $\sim 3 \mu\text{m}^2$, while in the case of the CC alloy is $\sim 13 \mu\text{m}^2$. However, the mean area is between $2 \mu\text{m}^2$ and $3 \mu\text{m}^2$ for the SF material and $6 \mu\text{m}^2$ for the CC steel. Also, the number of carbides per area is higher for the SF material than for their CC counterpart. An aspect ratio distribution closer to 1 of the SF material indicates a more homogeneous round shaped carbides compared to the CC steel, which carbides are less spherical. The NNCD showed that the SF alloy exhibits a homogeneous carbide

distribution with a distance between carbides below 3.5, while in the case of the CC alloy, the distance between carbides is larger and their distribution is highly inhomogeneous. Also, the second phase volume fraction, i.e. retained austenite and carbides, is remarkably different in both alloys, as summarized in Table 6.3. These microstructural features play a dominant role in the wear behavior of steels, since wear resistance depends on carbide type and distribution, as well as austenite to martensite transformation relationship [112].

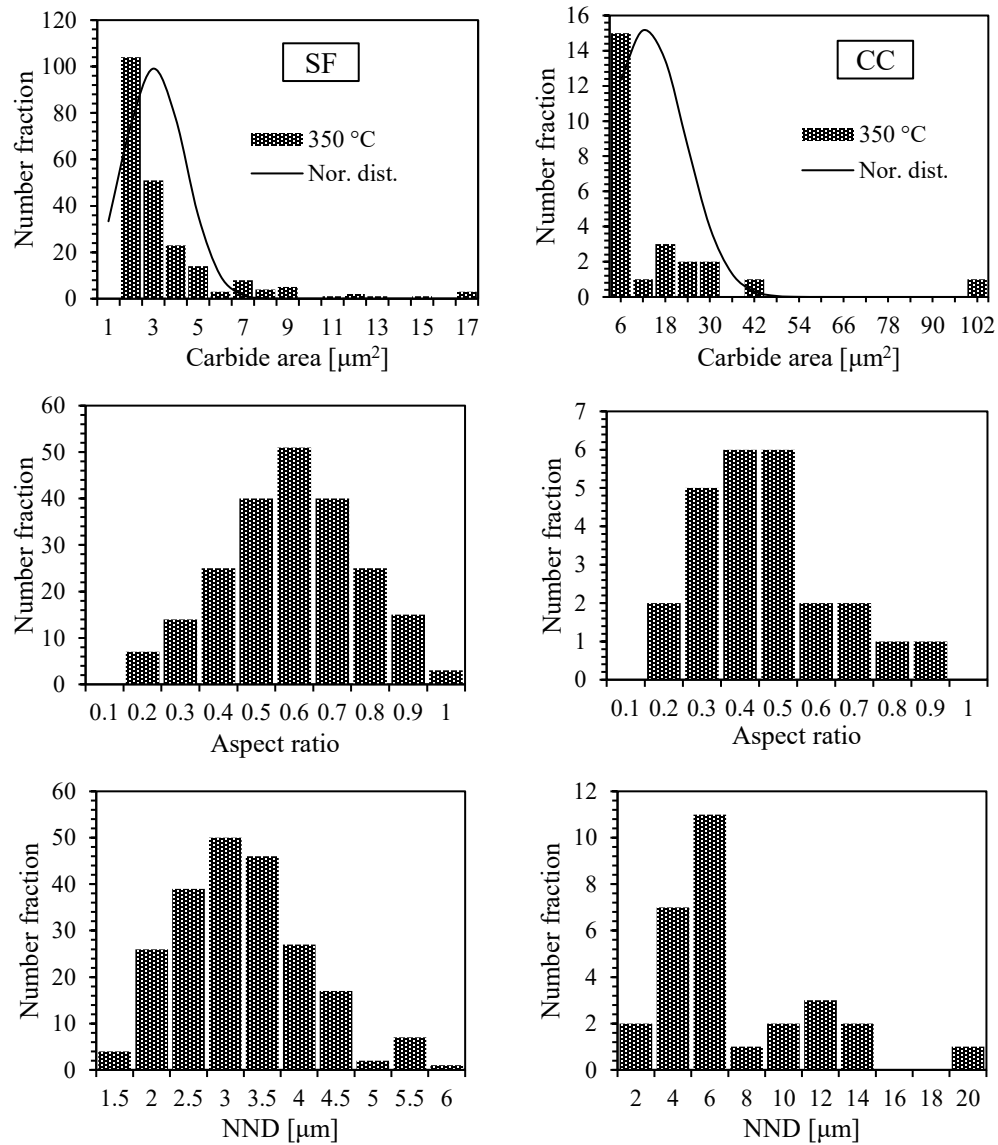


Figure 6.6 Carbide particle analysis: carbide area, aspect ratio, and nearest neighbor distance (NND) between carbides.

Table 6.3 Microstructural features comparison of phases.

Microstructural feature	SF	CC
	350 °C	350 °C
Cr ₂₃ C ₆ Carbide area mean size [μm^2]	3.04	12.8
Cr ₂₃ C ₆ Carbide mean size [μm]	1.8	3.24
Carbide volume fraction Cr ₂₃ C ₆ [%]	16.8	9.3
Cr ₇ C ₃ Carbide area mean size [μm^2]	11.25	25.72
Cr ₇ C ₃ Carbide mean size [μm]	3.35	4.7
Carbide volume fraction Cr ₇ C ₃ [%]	7.1	8.9
Mean distance between carbides ¹ [μm]	2.97	6
Austenite volume fraction [%]	11.9	3.8
Martensite volume fraction [%]	64.2	78

6.3.3 Wear behavior of tempered CC and SF alloys

The friction coefficient (FC) of the SF samples and cast material was compared as a distance function (see Figure 6.7). The findings revealed distinct average FC for each manufacturing technique, with spray-formed samples exhibiting an FC of 0.83, while the CC materials presented a lower FC of 0.71. The SF samples showed a consistent friction coefficient, with a steady state across most of the testing distance, indicating reduced adhesion of ball material onto the disc surface. In contrast, the progression of the friction coefficient of the CC material was less stable, with notable fluctuations at both tempering temperatures, a phenomenon associated with severe adhesion between the sample and the counter body, as elucidated by Podgornik et al. [113], and occasionally surpassing an FC of 1.0. Moreover, a greater scatter of FC measurements was observed in the CC samples compared to the more uniform SF steel. During testing, the FC of the cast samples dropped suddenly in certain instances, a change attributed to the formation of a thick, lubricious tribo-oxide layer. This layer can form when the applied load is insufficient to break it, leading to ceramic-to-ceramic contact which dramatically reduces friction and promotes gradual wear due to the ongoing removal of this oxide layer [114]. The difference in frictional behavior between the SF and the CC material might be attributed to their respective microstructures that result from each manufacturing technique. The spray-forming process yields a finer and more

¹ Submicron Cr₂₃C₆ carbides in the CC samples are not considered in this analysis.

homogeneous structure, leading to higher wear resistance and steadier FC. This variation in the FC is particularly pronounced due to the more erratic dendritic microstructure of the CC material. Additionally, the observed higher FC may be attributed to the effect of the relatively high sliding speed, which may promote an increase in both ploughing and abrasive wear characteristics due to the transfer layer establishment on the contacting surfaces [115, 116].

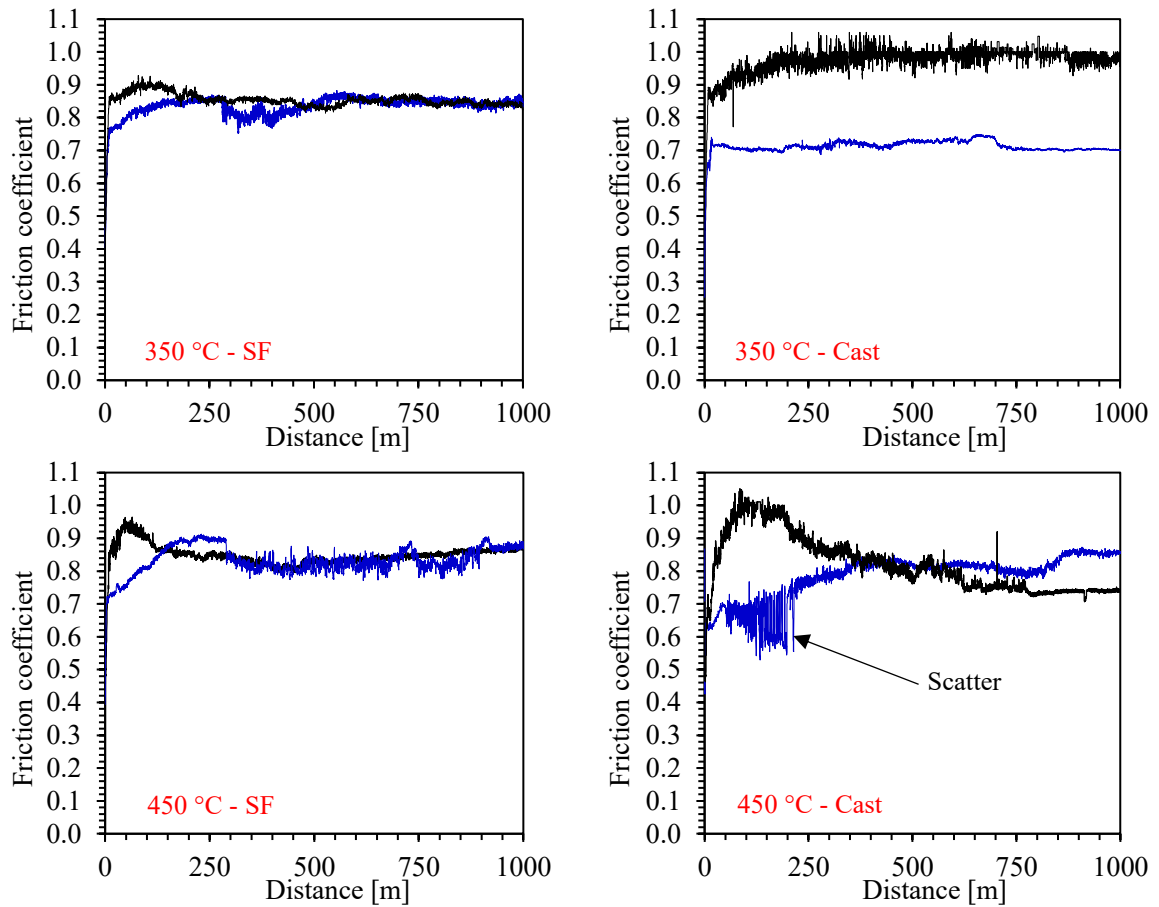


Figure 6.7 Friction coefficient as a function of time for the tempered SF and cast materials. (a) First test (blue) and (b) second test (black).

The wear tracks obtained via optical profilometry of the four wear test conditions are shown in Figure 6.8, indicating the sample condition and volume loss during the test. For this purpose, the volume loss was accurately measured from the digitalized surface after each test, and the results are shown in Table 6.4.

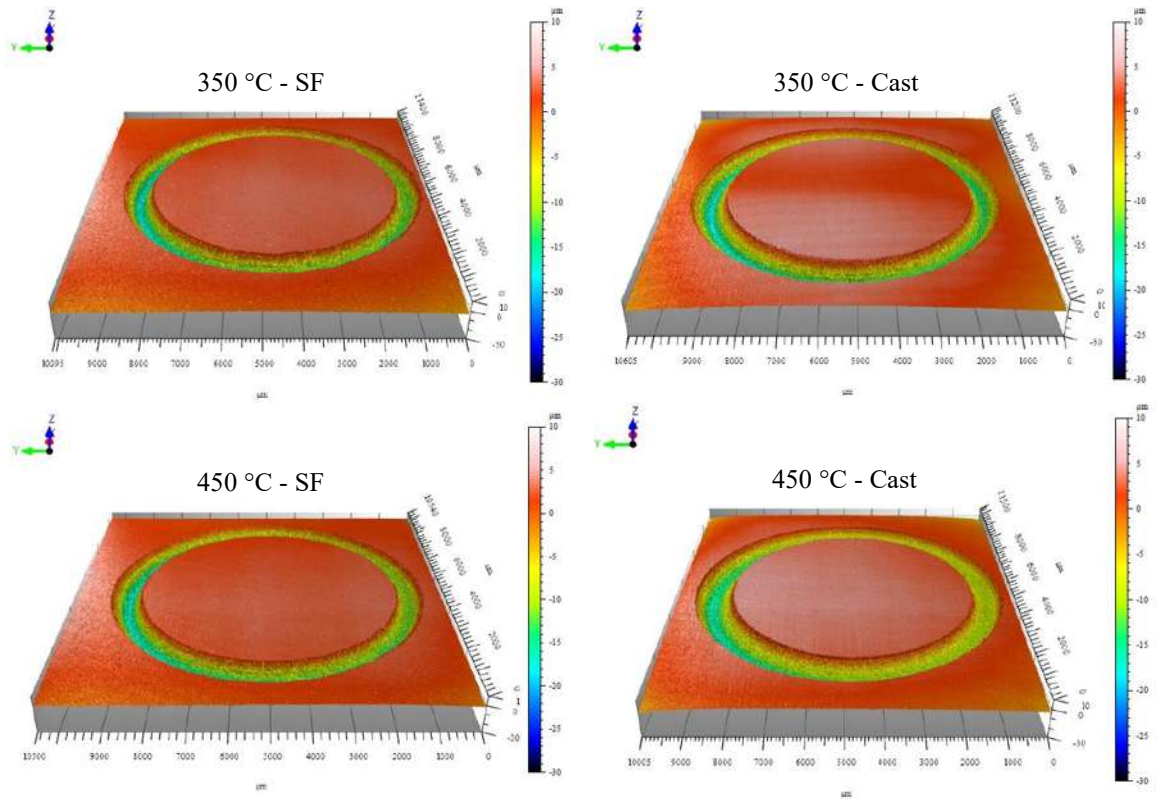


Figure 6.8 3D images of the digitalized wear tracks under different conditions, obtained by the profilometer after the tests.

Although the hardnesses of both CC and SF steels are similar, their wear behavior differs, which could be related to the type, distribution, size, volume fraction, and morphology of the carbide [7]. Kasak and Neumeyer [112] found that for high-hardness steels, the hardness is not one of the main factors in determining the wear behavior as other microstructural features. It is seen from Figure 6.9(a) and (b) that the CC samples exhibit slightly wider and deeper wear tracks than the SF material. This behavior agrees with the hardness values of each sample; i.e., the lower the hardness is, the greater the wear rate (see Figure 6.9(c)).

The average wear rate as a function of the tempering temperature is shown in Figure 6.9(d). As expected, the SF steel exhibited better wear resistance than the cast material for both tempering temperatures. For the 350 °C tempering temperature, the average difference was 24%, while for the tempering temperature of 450 °C, the difference was 12.6%. This seems to be a relatively small change in the wear behavior but can be critical in determining the service life of a mechanical component [112]. As discussed previously, these differences can be attributed to the finer carbide distribution and dispersion that results from the solidification process [112, 117]. Another

important feature is that the wear rate of the SF steel increased only slightly at the tempering temperature of 450 °C. On the other hand, the wear rate of the cast material after tempering at 450 °C decreased by approximately 17% compared to that of the tempering temperature of 350 °C. Also, the wear rates of exhibited by all the samples were on the order of 10^{-6} mm³/Nm, which is described as a mild wear regime [118].

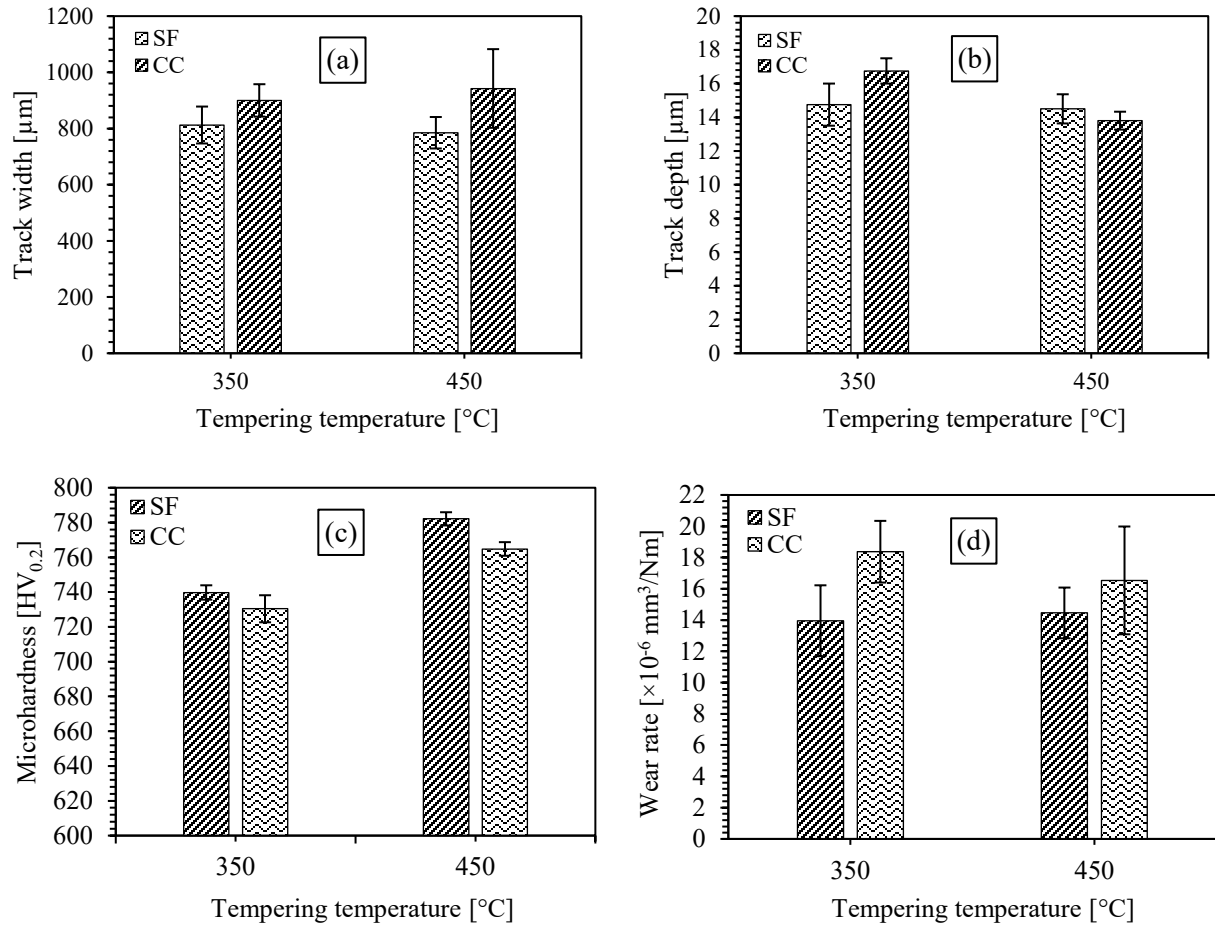


Figure 6.9 (a) Track width, (b) track depth, (c) microhardness and (d) wear rate, of tempered materials after the dry sliding wear test.

Table 6.4 summarizes some of the parameters obtained from the wear tests. A hardness increase is observed on the worn surface due to the work hardening caused by the sliding during the test, as compared to the bulk matrix. The SF sample tempered at 350 °C shows the highest variation in hardness, with an increase of approximately 7.3% compared to the corresponding cast sample which displayed an increase of 3.5%.

Table 6.4 Mean CoF, volume loss, wear rate, and hardness values of the SF and CC samples.

Sample	Mean FC	Average volume loss [mm ³]	Average wear rate [$\times 10^{-6}$ mm ³ /Nm]	Worn surface's hardness [HV _{0.2}]
350 °C (SF)	0.83	0.16 $\pm$ 2.3	13.9 $\pm$ 2.3	794.64 $\pm$ 4.4
450 °C (SF)	0.83	0.17 $\pm$ 1.6	14.5 $\pm$ 1.6	800 $\pm$ 5.4
350 °C (CC)	0.71	0.22 $\pm$ 1.9	18.4 $\pm$ 1.9	756 $\pm$ 12
450 °C (CC)	0.78	0.20 $\pm$ 3.4	16.5 $\pm$ 3.4	791 $\pm$ 11

Figure 6.10 shows SEM images of the worn surfaces of the SF and CC materials after the wear tests. The low magnification micrographs on the left show that the appearance of the wear track was similar for both materials. However, a track widening and increase in the oxide layer thickness are observed in the CC specimens compared to the SF material. The surfaces of the four samples were grooved, where both groups of specimens developed a thin oxide layer on the worn surface. These results suggest that there are differences in the wear mechanisms observed in the SF and CC specimens.

The high magnification images on the right side of Figure 6.10, show the formation of small slivers along the worn surface due to the inherent ratcheting process that occurs during the unidirectional sliding tests. This process contributes to the plastic deformation of the asperities. As the slivers grow due to the plastic deformation, tiny plate-like debris forms, breaks, and then detaches from the surface. Additionally, it was observed that for the CC samples, the worn surface was almost fully covered by the tribo-oxide film compared to that developed by the SF material, which implies that the formation of the tribo-oxide layer in the SF samples was relatively slower in contrast to the CC sample. The reason for this difference is that once a lubricious tribo-oxide film forms, the wear mechanism might be influenced by the abrasive wear of the oxide film (debris) that falls below the contact area. This observation is confirmed by the formation of typical scratches produced by the abrasion mechanism, which was observed in all the samples. Park et al. reported similar results for direct energy deposited M2 tool steel [114].

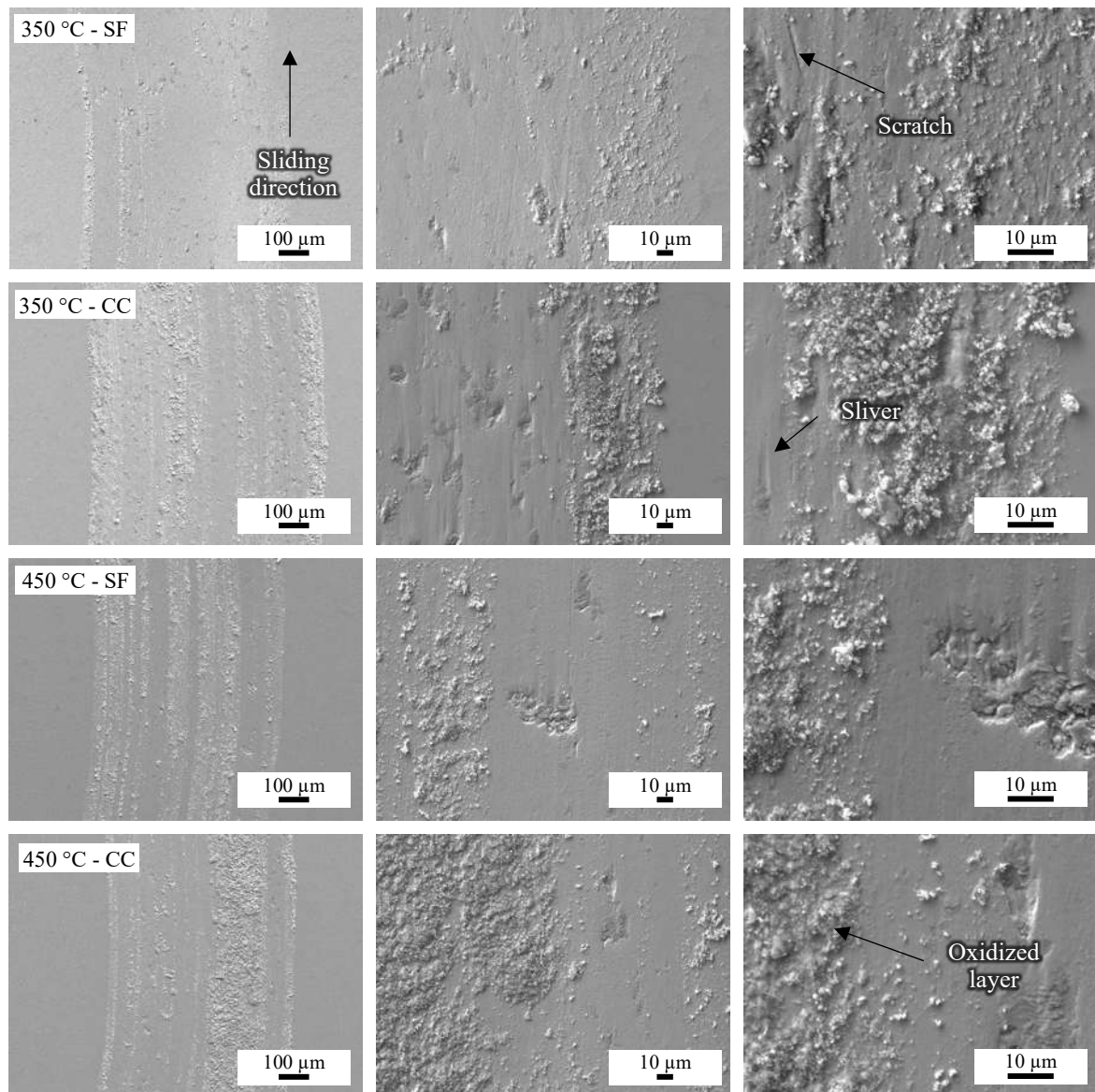


Figure 6.10 SEM images at different magnifications of tempered alloys showing the appearance of the worn surfaces.

In Figure 6.11, it is observed that adhesion also occurred during sliding (to a lesser extent), along with a small amount of plastic deformation on the surface, mainly in the surroundings of the carbide particles. Notably, the worn surface showed signs of oxidation as the tribo-oxide film formed, containing fine wear particles (dark contrast in BSE images), which suggests that the main wear mechanism was tribo-oxidative. As seen in the images, the oxide formation begins at the matrix/carbide interface, and then the oxide layer grows inward to the matrix along the wear track.

All the specimens exhibited similar surface wear features, with the SF steel showing less superficial damage.

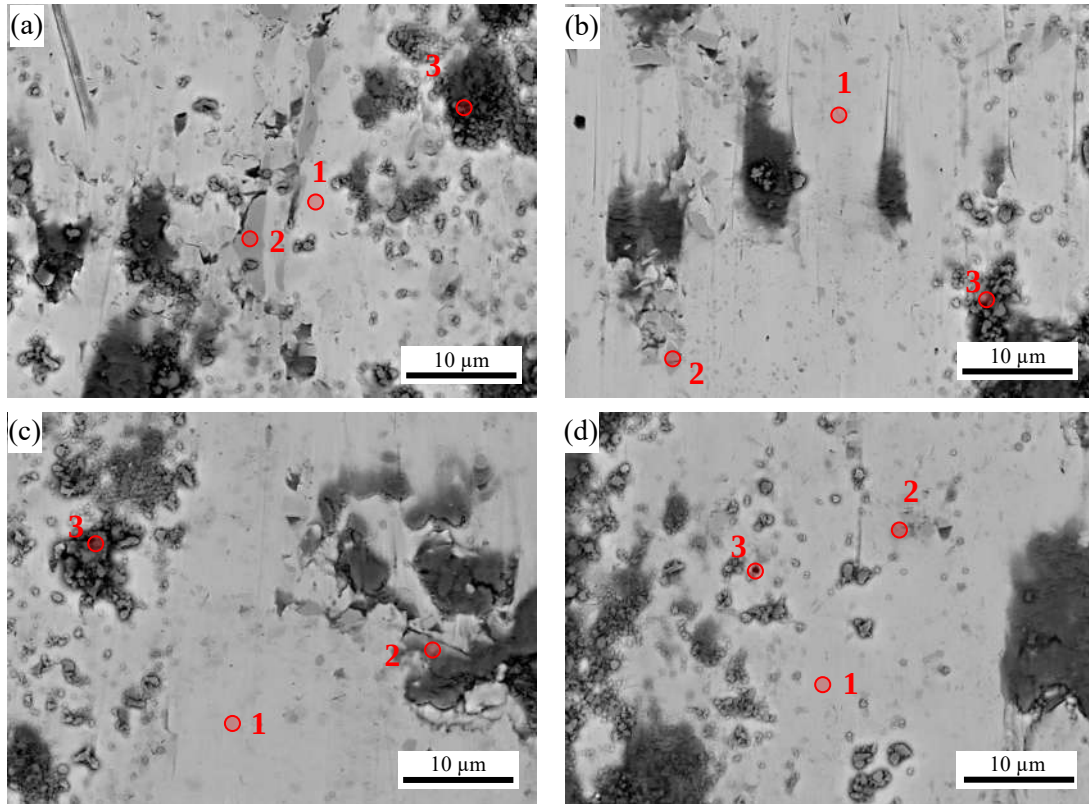


Figure 6.11 SEM/BSE micrographs of the worn surface showing the details of the particles that formed during the wear test and points for EDS microanalysis (a) 350 °C-SF, (b) 350 °C-CC, (c) 450 °C-SF, and (d) 450 °C-CC.

The results of EDS point analysis in Table 6.5 indicate that the tribo-oxide film contains constituents of the MSS, i.e., Fe and Cr complex oxides. The oxide layers of the SF steel contain a higher at. % of Fe and Cr. This supports the idea that the carbide particles and distribution in the SF samples were likely responsible for the better wear performance of the SF steel.

Table 6.5 Quantitative EDS analysis of the worn surface.

Manufacturing technique	Phase	Particle	Element composition (at. %)							
			Fe	Cr	O	Al	Mo	V	Si	Mn
SF (350 °C)	Matrix	1	80.4	13.9	---	---	1	1	2.3	1.3
	Carbide	2	27.7	54.5	7.8	---	3.7	6.1	---	---
	Oxide	3	38.9	9.6	45.9	---	1.2	1.3	1.7	2.3
CC (350 °C)	Matrix	1	72.3	16	5.9	---	1.2	1.2	2	1.2
	Carbide	2	41.2	45.2	4.7	---	3.5	5.3	---	---
	Oxide	3	32.6	8	42.6	13	0.9	0.9	1.1	0.8
SF (450 °C)	Matrix	1	77.1	16.4	---	---	1.4	1.4	2.3	1.3
	Carbide	2	29.5	46.2	16.3	---	2.9	5	---	---
	Oxide	3	39.5	10.8	43.9	---	1.3	1.3	1.7	1.3
CC (450 °C)	Matrix	1	78.9	15.9	---	---	1	1	1.9	1.2
	Carbide	2	32.6	51.6	5.3	---	4	6.4	---	---
	Oxide	3	26.1	7.2	23.1	40.7	0.8	0.5	0.5	1

EDS maps and the elemental composition of the sample's worn surfaces are shown in Figure 6.12. Both materials showed the presence of chromium carbide particles, as indicated by white arrows. In the cast steel, eutectic carbides formed between the dendrite arms and fine precipitates dispersed in the microstructure (white boxes) were observed. On the other hand, the SF steel exhibited a more homogeneous microstructure. Additionally, Fe-Cr oxide islands were observed in zones around the carbides, as shown in the oxygen EDS maps and the EDS analysis comparison.

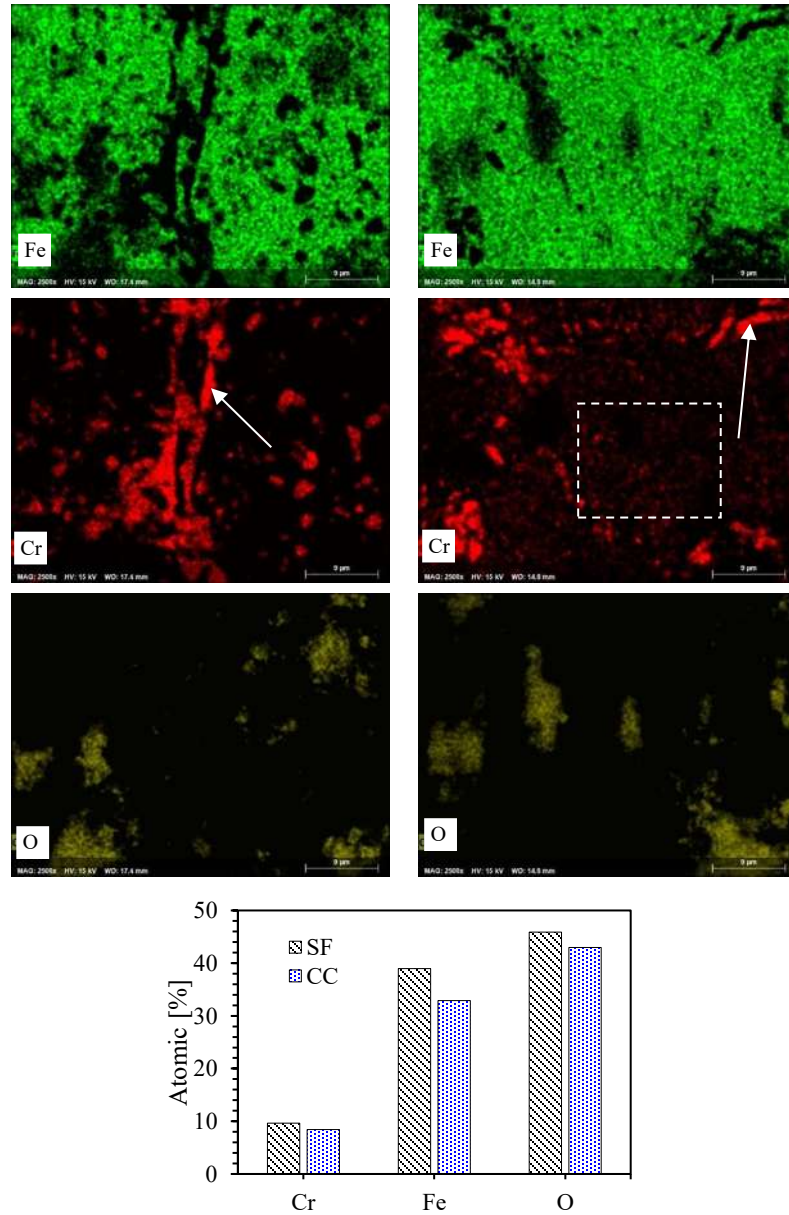


Figure 6.12 EDS maps of the worn surface of samples tempered (left) 350 °C-SF alloy and (right) 350 °C-CC alloy. Matrix (Fe), carbides (Cr), oxide (O), and graph of atomic composition of oxides.

The worn surfaces of the wall were examined to better understanding of the wear mechanisms that occurred on the metallic materials. Figure 6.13 shows that there was mild adhesion transference between the specimens and the counter-body, indicating that adhesive transfer to the counterpart occurred immediately after the asperity rupture of a debris fragment. Additionally, a slight weight loss in the Al_2O_3 counterpart material was observed, forming a small contact area, which suggests

that the hardness of the counterpart was high enough to sustain wear without pronounced damage. The wear of the alumina counterpart was correlated with that of the material, and a lower wear rate of the material led to low counterpart wear.

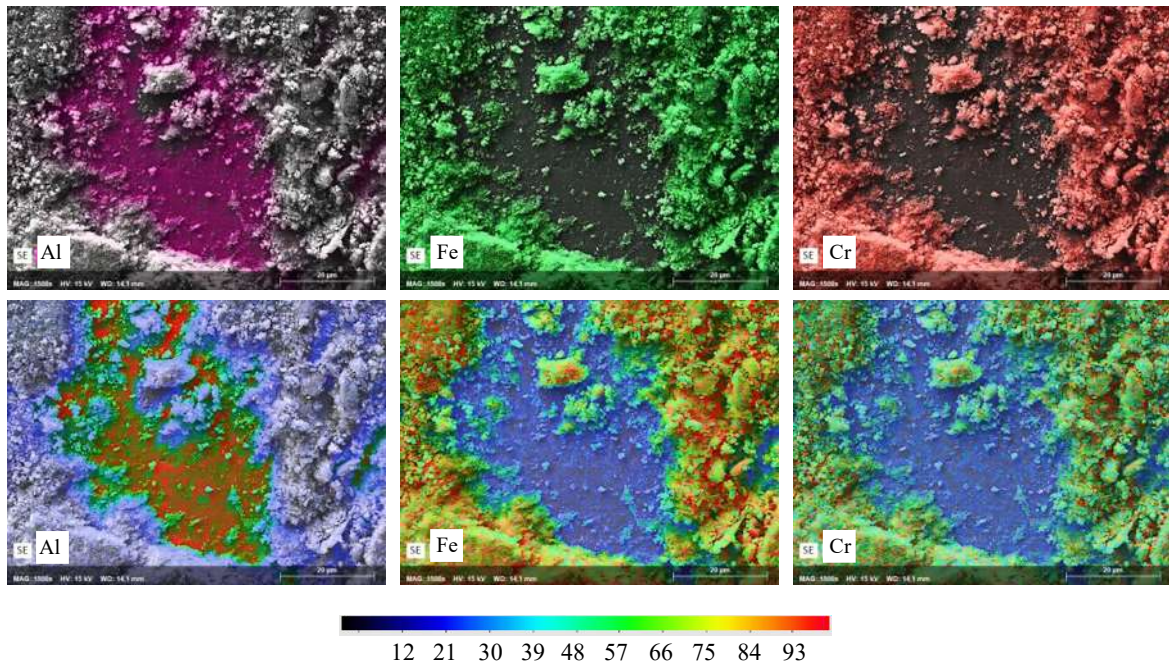


Figure 6.13 EDS element maps of the counter-body (Al_2O_3 ball) after testing the CC 450 °C specimen.

The EDS elemental composition maps of the debris are shown in Figure 6.14. The debris is mainly composed of fine particles that remain either individually or agglomerated and are predominantly metal oxides containing Cr and Fe. Arrows in the Al map show spots with higher color intensity corresponding to small particles that detached from the alumina ball due to the high sliding speed and contact area between the sample and the counterpart, which could promote some abrasive wear during the tests.

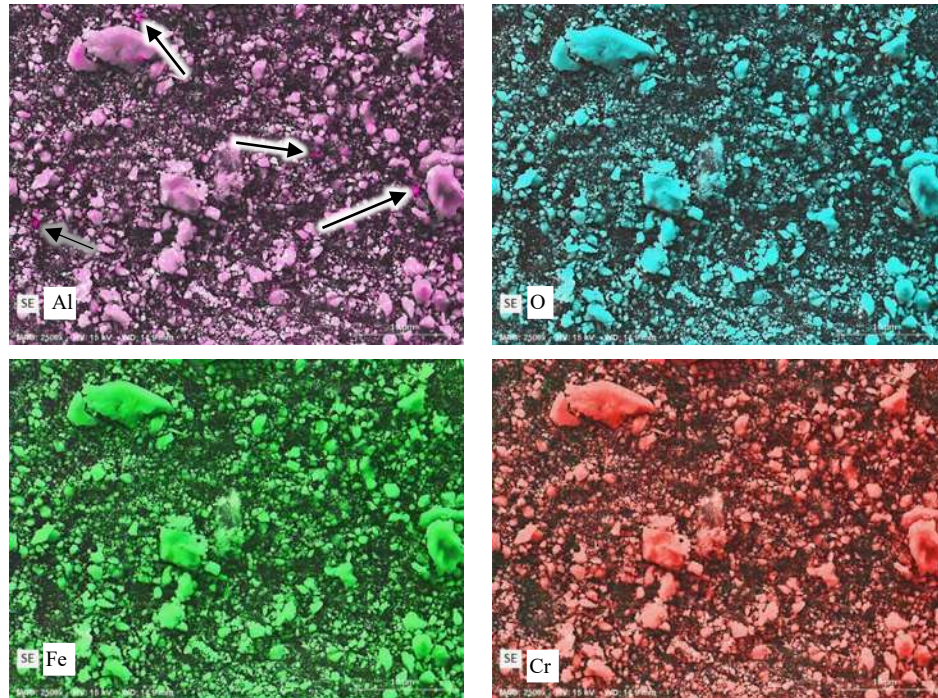


Figure 6.14 EDS mapping of the debris after testing the CC 450 °C specimen.

Figure 6.15 shows SEM micrographs of the microstructures of the longitudinal cross-section, in which damage underneath the worn surface is observed. Noticeable microstructural differences were found between the SF and CC materials. In both materials, the martensitic microstructure was strained along the sliding direction showing a fair amount of plastic deformation. Still, the SF samples exhibited a greater extent of plastic deformation, forming deformed zones with a depth of about 100 μm . Also, in the SF material, individual and cluster carbides were observed near the surface layer. Furthermore, two zones of microstructural modification were identified: Zone 1 with the undeformed bulk material and zone 2 containing the plastically deformed material, with an effective plastic strain increasing toward the worn surface. No evidence of carbide fracture below the worn surface was found, which can be directly attributed to the size and morphology of the carbides.

On the other hand, the large interconnected carbides in the CC material promoted a greater depth of oxidation that mainly occurred at the carbide-matrix interface, similar findings were found by Hanlon et al. [104]. Moreover, the carbides perpendicularly aligned to the shear stress direction were more prone to fracture and could act as hard debris within the worn surface. For both materials, the carbides were also distorted by the shear stress that occurred during sliding. The

highlighted region with a blue box in Figure 15(450 °C - SF) shows sub-superficial cracks that propagated to the surface and caused material detachment (delamination) in a sheet shape. Also, the bright zones near the surface correspond to the oxide layers. This supports the hypothesis that the active wear mechanism for these materials consisted of a combination of oxidation, adhesion, and abrasion.

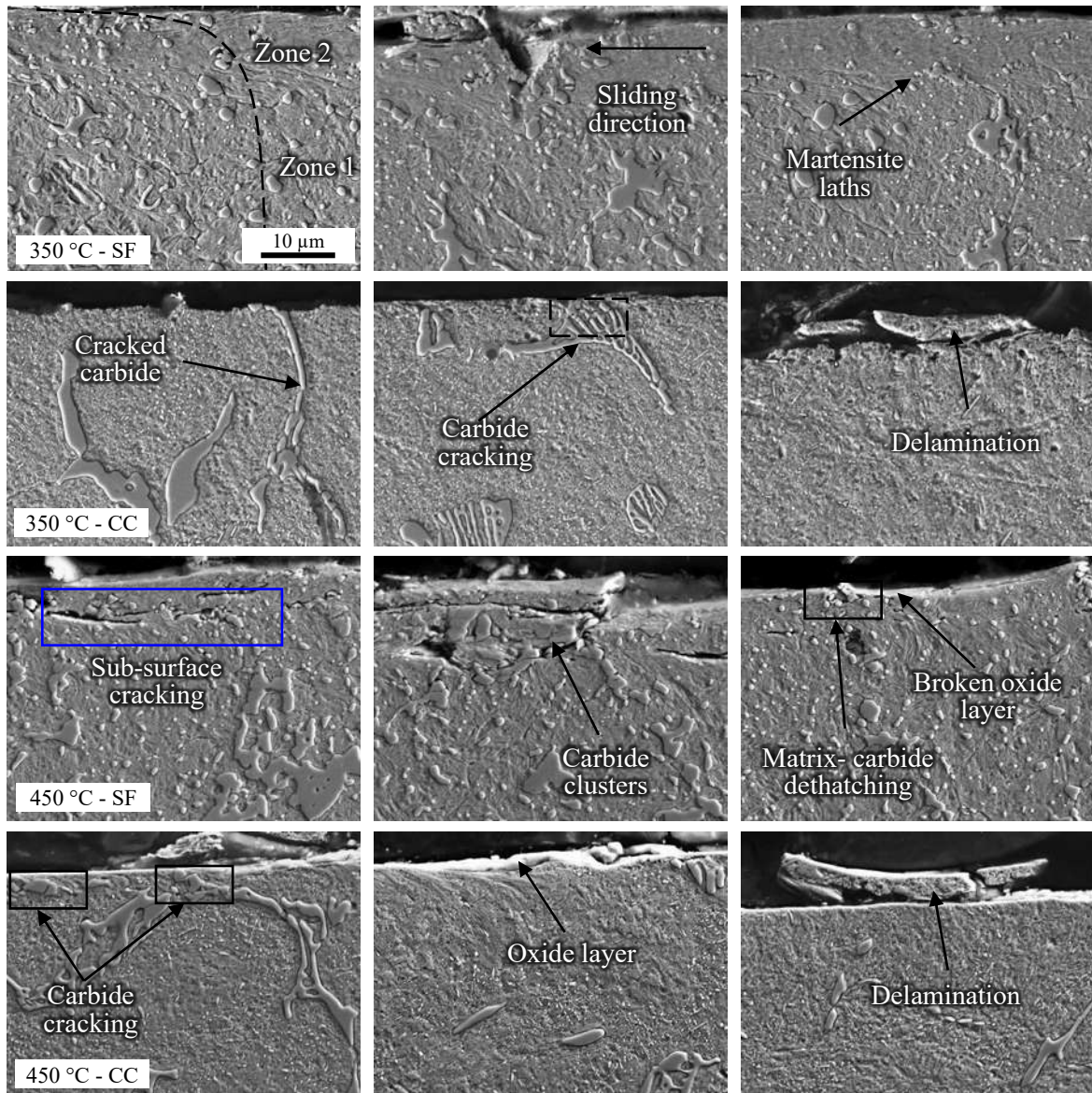
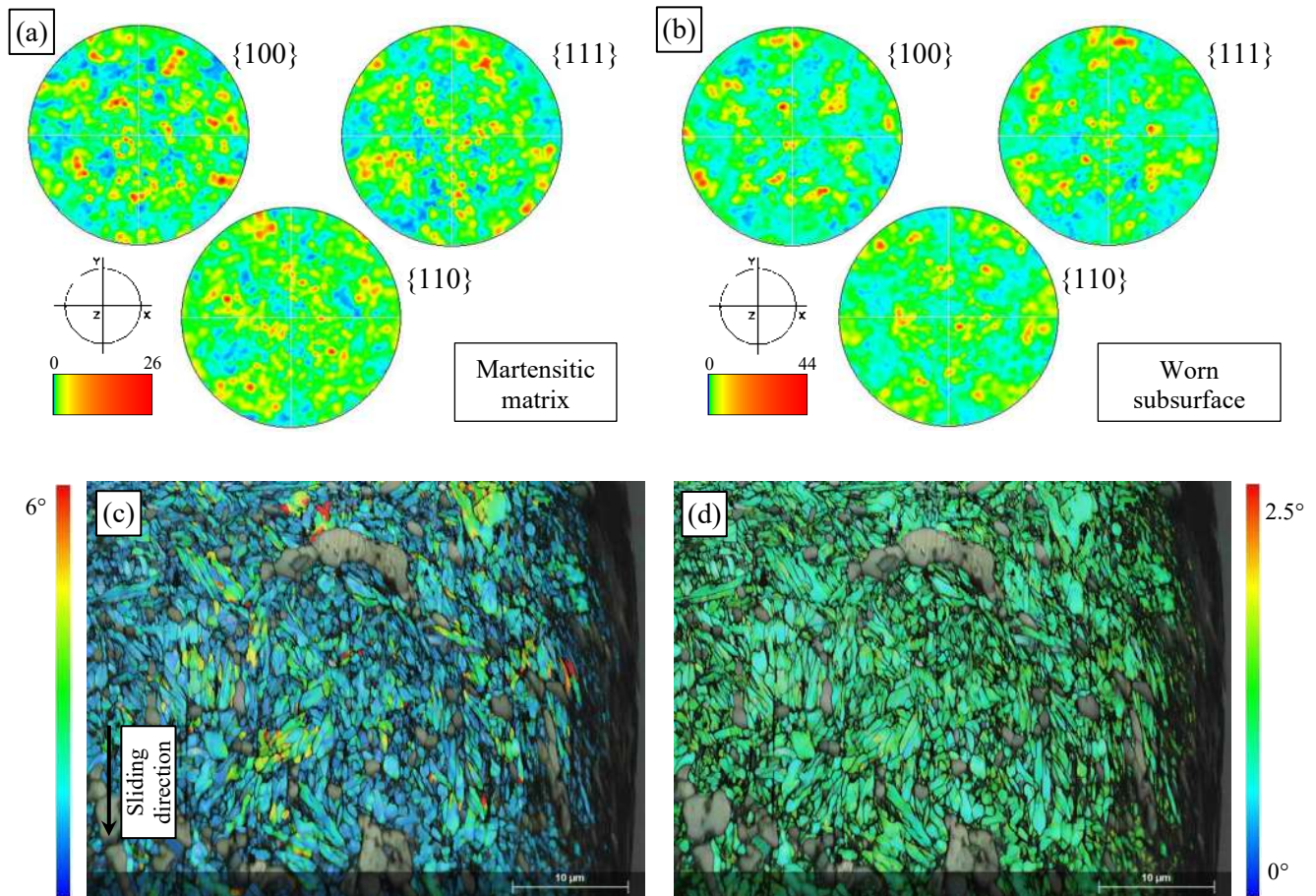


Figure 6.15 Cross-section SEM images of the worn surface of each sample.

The EBSD analysis of the cross-section for the SF and CC materials are shown in Figure 6.16 and Figure 6.17, respectively. The pole figure in Figure 6.16(a-b) shows that compared to the bulk

material, the worn subsurface has a crystallographic texture that is common in most metals subject to wear [119]. The white box in Figure 6.16(c) highlights the misorientation of the grains that were greatly affected by the wear process, as evidenced the black layer below the surface, which exhibits poor diffraction data due to severe deformation. Also, a fine-grained region down to $\sim 10\ \mu\text{m}$ below the worn surface is observed, which is poorly defined due to the fine grain structure.

The corresponding grain average misorientation (GAM) distribution and the Kernel average misorientation (KAM) distributions shifted to higher angles compared to the bulk material. This implies that plastic deformation was induced in the surface layer, leading to strain between and within the grains and an increase in the dislocation density. Similar results were reported by Holmberg et al. who investigated the surface deformation of Inconel 718 after high-speed milling [120]. It is also possible that stress-induced transformation of retained austenite into fresh martensite with higher misorientation, compared to the existing one, contributed to the KAM increase. This transformation process promotes work hardening and enhances wear resistance.



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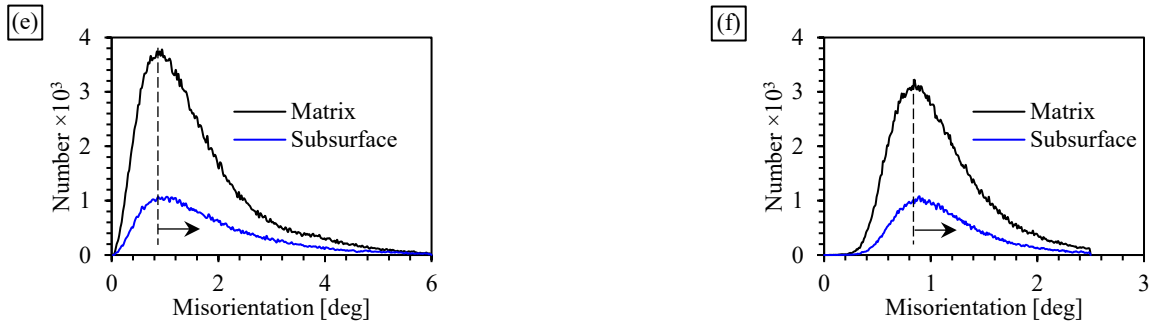
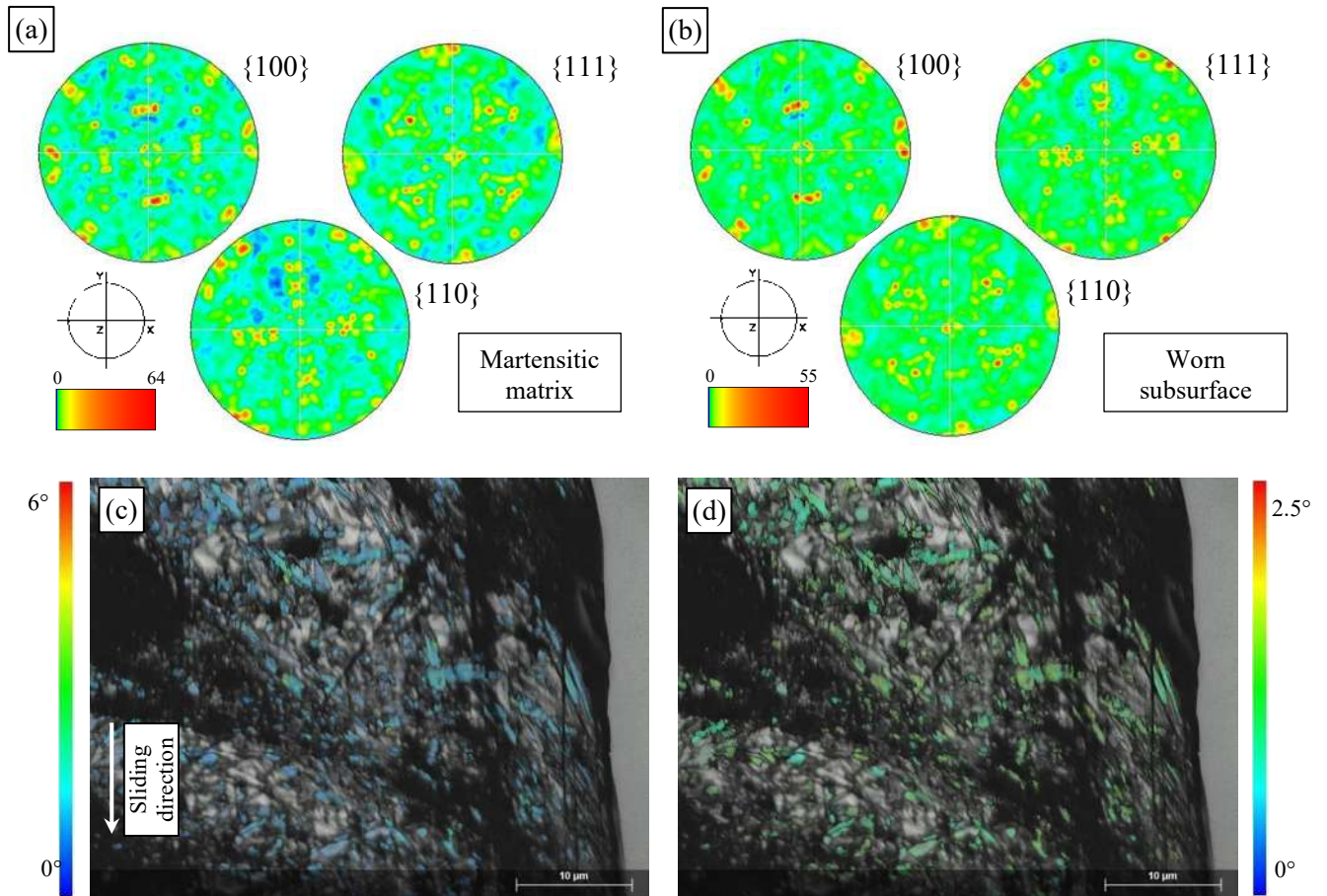


Figure 6.16 EBSD analysis of the SF sample tempered at 350 °C. Pole figure of (a) martensitic matrix and (b) worn subsurface. (c) Grain average misorientation and (d) Kernel average misorientation of the worn cross section surface. (e-f) Grain average misorientation, and Kernel misorientation distributions, respectively.



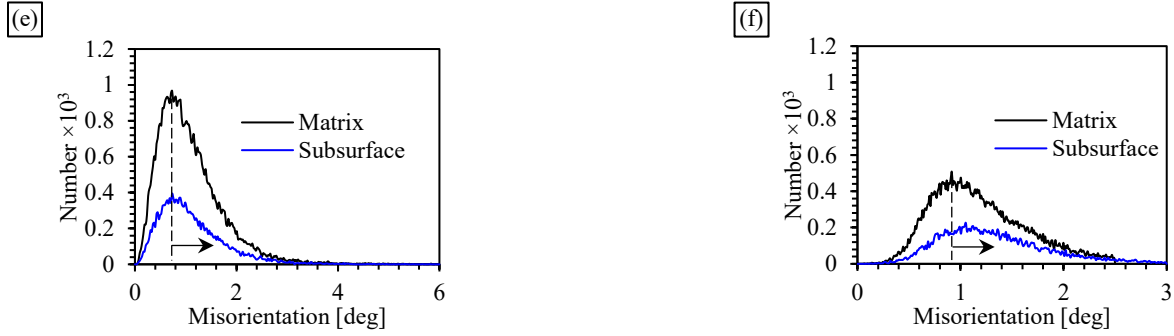


Figure 6.17 EBSD analysis of the SF sample tempered at 350 °C. Pole figure of (a) martensitic matrix and (b) worn subsurface. (c) Grain average misorientation and (d) Kernel average misorientation of the worn cross section surface. (e-f) Grain average misorientation, and Kernel misorientation distributions, respectively.

Based on the previous results, we propose that the improvement in the wear resistance of the SF material is strongly related to the carbide particle size and distribution. This is in accordance with Meng et al. [121], who found that the wear resistance improvement of bearing steel was attributed to the precipitation of small and well distributed carbides after deep cryogenic treatment. Also, the shear modulus mismatch between carbides and the matrix leads to a higher interaction force that reaches a maximum at the interface between the matrix and the carbide: $F_m = 0.05\Delta Gb^2 \left(\langle r \rangle / b \right)^{0.85}$ where r stands for the carbide particle radius and b the Burgers vector [122]. For the CC material (which has a greater particle size), this makes the carbide particles more prone to cracking and detaching from the matrix, leading to a decrease in the wear resistance of the steel due to more intensive abrasive wear. On the other hand, in the SF steel, which has a smaller particle size, the interaction force is lower, and the interface strength is greater, which increases the stability of carbide particles reducing the risk of carbide detachment. This leads to a wear resistance improvement by taking advantage of the shadow effect of the carbides.

6.4 Conclusions

Based on the results obtained from this study, the following conclusions can be drawn:

- The solidification rate during the manufacturing process influences the carbide size and distribution. The spray-forming process can effectively reduce particle size and interconnection of the carbide structure.
- Large differences were found regarding the volume fraction of second phases and carbide particle size, shape, distribution, and dispersion for the two manufacturing routes, being the SF steel the one that showed better microstructural features.
- The refined and more homogeneous microstructure of the SF material significantly influenced the wear resistance of the 440C MSS compared to its CC counterpart, showing an improvement of up to 24% depending on the tempering temperature.
- Both materials presented oxidation as the most dominant wear mechanism. However, abrasion and adhesion also occurred to a lesser extent.
- The probability of carbide fracture is determined by the size of the carbides. If a critical diameter is not reached, the probability of carbide fracture is reduced. The coarser carbides in the cast material exhibited more carbide fracture than those in the SF steel, leading to greater wear.
- An improvement in the tribological performance of the SF specimens is a result of the higher hardness, but mainly due to carbide size, morphology, and distribution which lead to almost absent carbide fracture and internal oxidation at the carbide-matrix interface. This demonstrates the benefits of the spray-forming manufacturing technique on the tribological behavior of high-carbon MSSs.

CHAPTER VII

THE POTENTIAL OF DIRECTED ENERGY DEPOSITION IN THE MANUFACTURING OF HIGH-PERFORMANCE 440C STAINLESS STEEL

Abstract

Additive manufacturing (AM) technology has revolutionized the manufacturing industry by enabling the production of complex geometries and customized components. This study investigated the suitability and effectiveness of direct energy deposition (DED) in the manufacturing of 440C martensitic stainless steel (MSS). The DED process uses either a laser, electron beam, or plasma arc to melt metal powder or wire, which is then deposited layer by layer to create a 3D part. The objective of this study was to compare the mechanical properties, microstructural characteristics, and dimensional accuracy of 440C MSS parts manufactured using the DED process. To evaluate the mechanical properties, hardness, tensile, and compression tests were performed on the manufactured samples. The microstructural analysis was performed using scanning electron microscopy (SEM) and X-ray diffraction (XRD) to assess the grain structure, phase composition, and potential defects. The findings of this study provided valuable insights into the suitability and performance of DED technology for the manufacturing of 440C martensitic stainless steel. The results contributed to advancing the understanding and application of additive manufacturing techniques in the production of high-performance stainless-steel components.

Keywords: Direct Energy Deposition, Additive Manufacturing, 440C Martensitic Stainless Steel, Microstructure, Mechanical Properties

7.1 Introduction

DED is a promising and widely used additive manufacturing (AM) technology that has emerged as a powerful tool in the production of 3D components due to its flexibility. This technology offers several advantages, including high deposition rates, higher material usage efficiency, flexibility to build large-scale and complex parts, and the ability to use a wide range of metallic materials [123, 124]. The DED involves localized melting of metallic feedstock, in the form of wire or powder, using a focused energy source such as a high-power laser or electron beam. The molten material is then deposited onto a substrate, to build up a layer-by-layer solid component with a specific geometry. During the laser deposition processes, parameters such as laser power, travel velocity, and powder flow rate parameters directly influence the thermal history of the deposited material, thereby affecting the microstructural evolution, solid-state phase transformations, porosity, segregation, cells, crystallographic texture, grain structure, distortion, defects, inclusions, residual stresses, and the final physical and mechanical properties of the manufactured components [5, 11]. The complex thermal cycles that the material undergoes during the DED process affect the microstructure of the deposited material. The rapid heating and solidification of the fused material within the melt pool as the laser beam moves on, lead to a series of reheating and re-cooling processes during the subsequent welding of the layers, while the volume continues to be exposed to heat. As a result, non-equilibrium phase compositions and microstructure variations across the final component are usually observed [125]. In addition, the high solidification rates (10^3 - 10^8 K/s), lead to the formation of finer grain structures characterized by a high dislocations density [10, 126, 127]. This refined microstructure follows the Hall-Petch law increasing the strength of the material. The anisotropy of the build component can be influenced by the scanning strategy and the size of the melt pool [5, 127, 128]. This phenomenon can be related to heat conduction, which is typically higher in the build direction, causing the grains to grow on preferred crystallographic orientations, resulting in texture and anisotropic mechanical properties [30, 126]. Therefore, aspects such as process parameters and build direction must be carefully selected as they can produce microstructures with unique properties, which provides exciting possibilities for tailoring the mechanical properties of different materials, as reported in the literature [128, 129]. Another important aspect to consider is the heat treatment and its influence on the resulting material anisotropy and homogeneity.

In recent years, the DED process has become particularly appealing for processing a variety of materials, including stainless steel, producing parts with high strength and high-performance parts efficiently and cost-effectively. Martensitic stainless steel metal parts such as 410, 420, and 440C produced using the DED process are attractive to the industry because of the improved properties such as wear resistance, corrosion resistance, strength, and hardness. These properties can be tailored by controlling the microstructure of the steel during the printing stage. Although there are some reports in the literature regarding the properties of martensitic stainless steel components fabricated by different additive manufacturing technologies [130-135], only limited studies have focused on AM 440C MSS parts. Therefore, there is a need to fully understand the microstructural evolution during the DED process. Several studies have been conducted to investigate the effects of additive manufacturing process parameters on the microstructure and mechanical properties of 440C parts. Bang et al. [124] studied the microstructure and mechanical properties of selective laser melting 440C SS by implementing different energy densities. Samat et al. [136] investigated the effect of sintering parameters on the density and hardness of powder metallurgy 440C steel. Wang et al. [137] analyzed the effect of different steel powders and heat treatment processes on the microstructure and mechanical properties of additively manufactured ultrahigh-strength steel. These research results showed that AM technologies have a promising future in the manufacturing of high-strength steel. Compared to conventional manufacturing methods, these technologies offer many advantages, such as better or equivalent properties than conventionally manufactured steels, design freedom, shorter production time, and reduced material waste. However, the research on high-strength steel parts is still in its early stages.

The present work focused on determining the feasibility of implementing the DED as a processing method in the manufacturing of 440C MSS. The study of the microstructural and mechanical properties of the additively manufactured parts was systematically analyzed in both transverse and longitudinal directions. In addition, a detailed comparison of the microstructure and properties of the as-built and heat-treated samples was performed. The outcome of this research contributes to the limited literature on the process-structure-properties relationship of 440C MSS processed by the DED technique and provides valuable insights into the feasibility of this emerging technology to address the specific industry requirements.

7.2 Experimental details

7.2.1 Material manufacturing techniques

The 440C MSS was produced through the DED additive manufacturing technology. The DED process was performed using an L-DED machine owned by FORCE Technology located in Munkebo Denmark. Multi-tracks were used to produce samples and analyze how the process behaves during the manufacturing of more advanced 3D structures. The feedstock material used in this study was provided in powder form and produced by Nordisk Stal A/S using a proprietary spray-forming process. The particle size of the powder was in the range of 0.2-0.43 μm . The chemical composition of the steel is given in Table 7.1.

Table 7.1 Nominal chemical composition (wt. %) of 440C MSS produced through both routes as determined by optical emission spectroscopy.

C	Mn	P	S	Si	Cr	Mo	V	W	Ni	N	Fe
1.19	0.448	0.0307	0.0237	0.571	15.86	0.816	0.549	0.186	0.33	0.100	Bal.

7.2.2 Heat treatment

A set of DED specimens were heat-treated to determine the effect of heat treatment on the microstructure and mechanical properties of the manufactured structure. A multistep heat treatment was performed starting with a homogenization process at 1130 °C, followed by an austenitizing treatment at 1100 °C and then quenching in gas nitrogen. All heat treatments were carried out under a flowing argon atmosphere in a horizontal tube furnace.

7.2.3 Microstructural characterization

After quenching, the samples were mechanically ground and polished using conventional metallographic techniques. Energy dispersive X-ray spectroscopy and elemental mapping were then performed to determine the chemical composition of the phases. To develop the different microstructures, the samples were etched using Villella's reagent. The microstructure of the samples was analyzed by scanning electron microscopy (SEM) using secondary and backscattered electron detectors. For EBSD analysis, the samples were electropolished using a solution of 60 ml perchloric acid in 940 ml acetic acid solution at 15 V. The EBSD analysis was then performed in

a field emission gun scanning electron microscope (JEOL JSM-7600F FEG/SEM) at a tilt angle of 70°, an acceleration voltage of 20 kV, and a scan step-size of 64.9 nm using a QUANTAX CrystAlign 400i-EBSD system. The data were post-processed using the ESPRIT 2 Quantax software. Thereafter, the electropolished samples were examined by X-ray diffraction in a Bruker D8 Advance in Bragg-Brentano focusing geometry using Cu-K α radiation. The diffractograms were recorded from 40 to 125° 2 θ at a step size of 0.05° and a counting time of 3 s per step.

7.2.4 Mechanical evaluation

The mechanical properties of the steel were analyzed by microhardness, tensile, and compression tests. Vickers hardness measurements were performed on an HM-220B Mitutoyo computer-controlled tester, equipped with a manually controlled xy stage and digital micrometer heads with 1 μ m resolution. Vickers hardness of the steel samples was determined using a constant load of 200 g (1.96 N), and a holding time of 15 s. On each specimen, 10 independent indents were performed to determine the average hardness and to verify the homogeneity of the microstructure. Tensile dog-bone specimens were cut according to ASTM E8 and tested in an MTS® 100 kN servo-hydraulic testing machine with load Frame model Landmark Series 370. Quasi-static uniaxial tensile tests were performed at room temperature in load control mode at a strain rate of 0.005 s⁻¹. The axial deformation was measured using an MTS 634.31F-24 extensometer. Compression tests were performed on a Zwick/Roell Z100 tensile testing machine on standard rectangular samples of 5.8 mm length 3.96 mm width, and 13.6 mm height.

7.3 Results and discussion

7.3.1 Microstructural characterization

The microstructural features of the as-deposited (AP) 440C MSS at different levels are shown in Figure 7.1(a-c), corresponding to the black box in Figure 7.1(d). The interface between two deposits in the center of the sample in Figure 7.1(a) is characterized by fine dendritic equiaxed grains as well as regions with fine cellular grain structure, which is attributed to the solidification rate and the temperature gradient, respectively. In Figure 7.1(b), a transition to a coarser dendritic structure can be observed. This grain coarsening increases when approaching the center of the deposited layer, as shown in Figure 7.1(c).

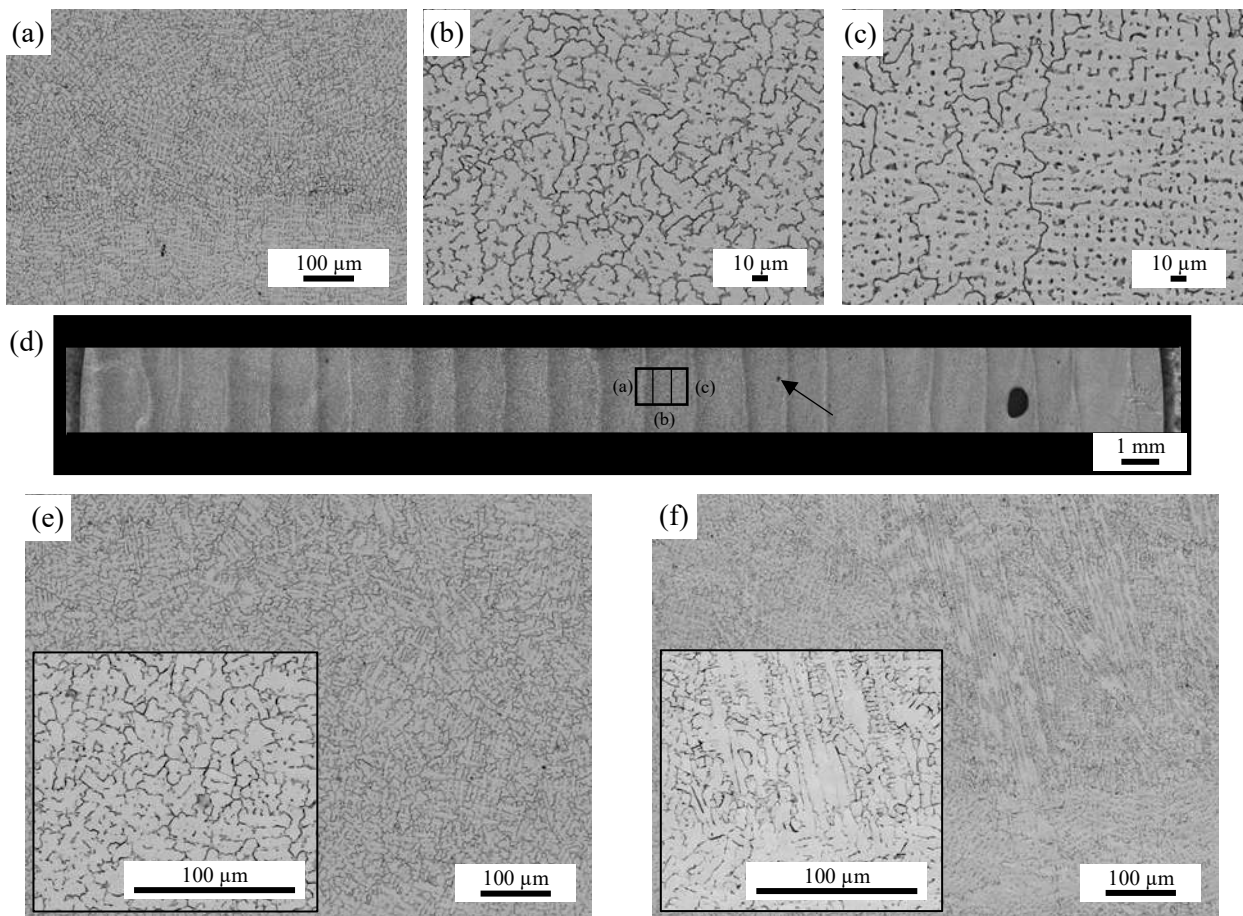


Figure 7.1 OM/SEM images of the microstructure of the 440C MSS. (a-c) detail structure at the interface between two deposits. (d) Macrograph of the as-deposited steel. (e-f). Top and bottom layers, respectively.

A macrograph of the as-deposited material showing the overall microstructure along the build direction is seen in Figure 7.1(d). Figure 7.1(e) shows the microstructure of the top layer, whose

structural morphology is characterized by relatively fine dendritic grains. On the other hand, Figure 7.1(f) shows that columnar grains grow in the bottom layer along the heat transfer direction (from the hot to the cold zone). The fine and equiaxed grains are the result of the rapid solidification and nucleation process, while the transition from equiaxed to columnar grains indicates a slower solidification process. This transition microstructure persists along the sample and shows a prevail equiaxed structure that becomes coarser as a function of the solidification rate from the lowest bottom layer to the highest top layer.

A certain degree of porosity is also observed in the sample, majorly found at the interface of each track (see black arrow in Figure 7.1(d)). This type of defect is common in additively manufactured components and occurs as a result of insufficient energy to fully melt the powder particles. The shape of these porosities is irregular with sharp edges, which act as a local stress concentrator. Porosity also can originate from gas bubbles trapped within the melt during the metal deposition process. Gas porosities exhibit a spherical shape and do not form in specific locations.

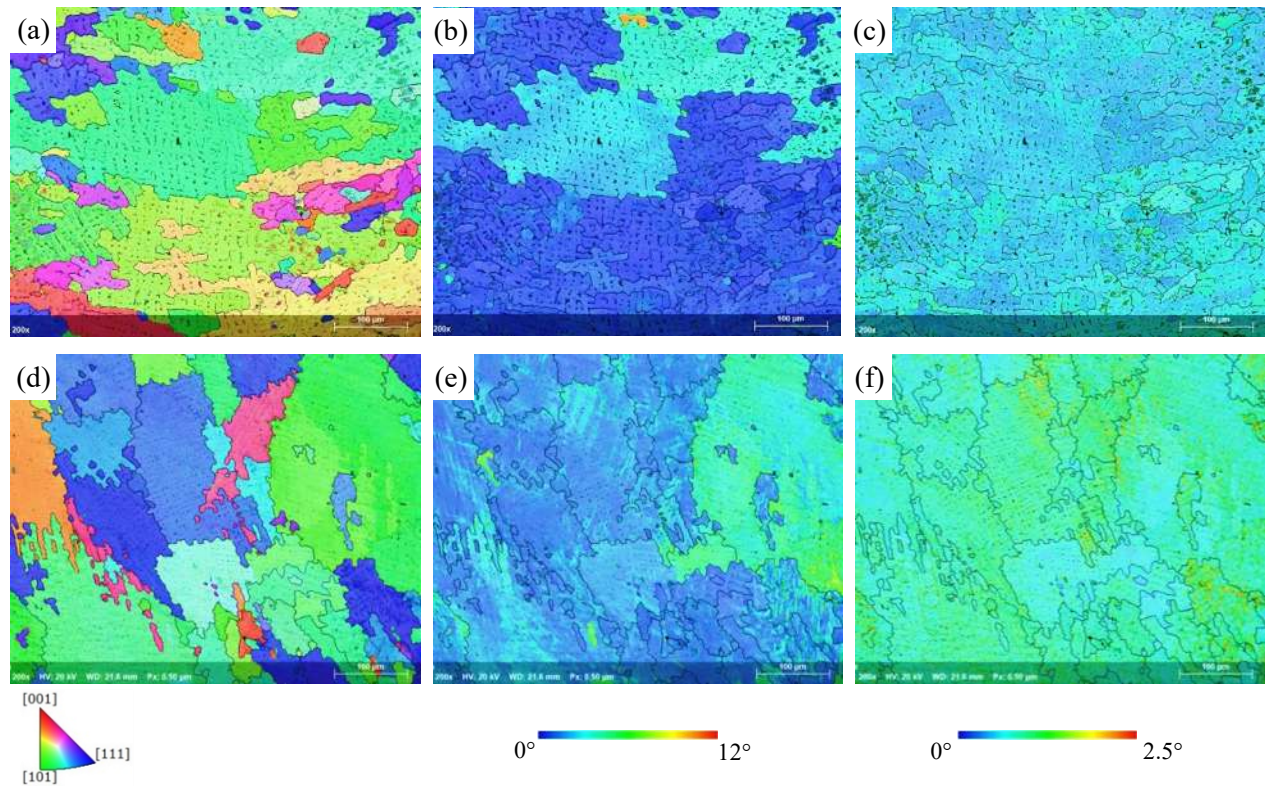


Figure 7.2 EBSD orientation maps of the AP (a) horizontal and (d) vertical samples. Grain average misorientation of (b) horizontal and (e) vertical samples. Kernel average misorientation of (c) horizontal and (f) vertical samples.

The EBSD orientation maps in Figure 7.2(a) and (d) show a non-uniform distribution of grain size and fine dendritic subgrains. The grains exhibit an elongated shape in the direction of the heat transfer during solidification. A comparison of grain average misorientation (GAM) of the horizontal and vertical samples is shown in Figure 7.2(b) and (e). The intragranular GAM is higher for the vertical sample. The distribution of local misorientation in the Kernel average misorientation (KAM) map in Figure 7.2(c) and (f) also shows a higher misorientation in the vertical sample compared to that of the horizontal. In addition, a high dislocation density in the material is observed due to grain distortion during printing.

7.3.2 Mechanical characterization

Hardness

Figure 7.3 shows the Vickers microhardness measurements of the horizontal and vertical samples in the as-printed and heat-treated conditions. The results show a clear advantage of the heat-treated samples. However, the as-printed samples exhibit unusual hardness values for conventional austenitic structures. The high hardness of the AP samples might be attributed to the reduced grain size that follows the Hall-Petch relationship. Similar hardness values are observed for the heat-treated samples, regardless of the build direction. On the other hand, the vertically as-printed samples exhibited higher hardness than the horizontally-built ones. This might be due to the distinct solidification and thermal cycles produced during the building process [138].

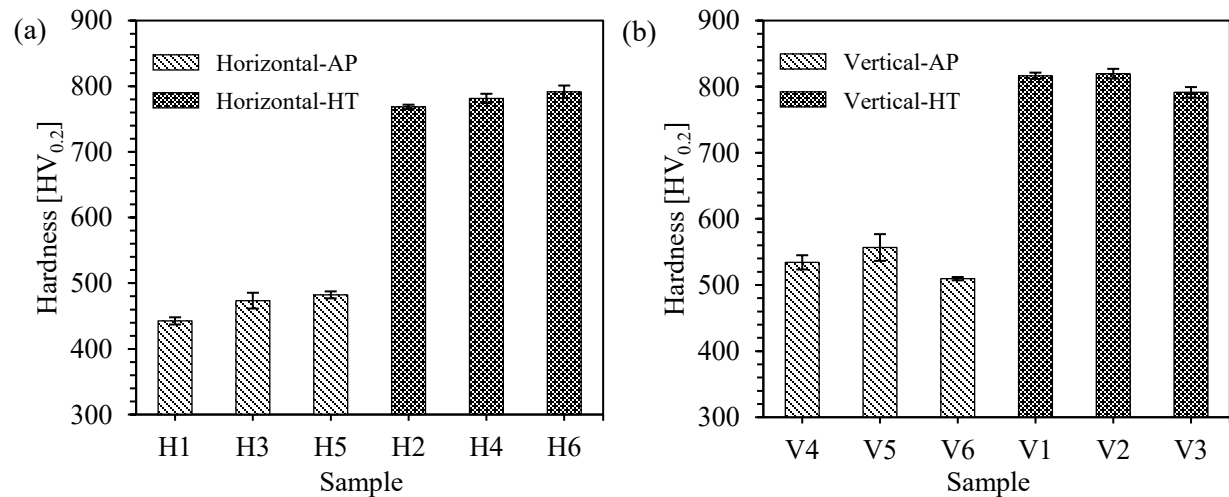


Figure 7.3 Vickers micro-hardness (a) horizontal as-printed and heat-treated and (b) vertical as-printed and heat-treated samples. The numbers in the sample designation stand for the position from which the samples were taken from the built part.

Tensile tests

The microstructural characterization showed that the microstructure is significantly influenced by the DEP process and the direction in which the material is printed. This is evident in the stress-strain curves of Figure 7.4(a-b). Regardless of the direction, the samples exhibit similar ductility (strain $\approx 3.5\%$). In Figure 7.4(a), the stress-strain curves of as-printed samples obtained in the horizontal printing direction show different mechanical responses, which can be attributed to the microstructural anisotropy caused by the printing process. The sample denoted as H1-AP exhibits higher strength but lower ductility, possibly caused due to defects such as porosity or lack of fusion. These defects promote stress concentration around them leading to premature failure. Samples tested in the vertical printing direction also show the effects of microstructural anisotropy, although the ductility is very similar in all three samples.

The heat treatment tends to homogenize the mechanical response of the samples. However, the yield strength of the HT sample increases while the ductility decreases. The fracture strength of both AP and HT conditions are quite similar. On the other hand, the strength of vertical and horizontal samples in Figure 7.4(c-d) does not differ significantly, showing almost the same mechanical behavior. The horizontal samples exhibit slightly better mechanical properties such as ductility, yield strength, and tensile strength. The as-printed DED 440C material showed a fracture strength (σ_f) of 783 ± 14 MPa, a yield strength (YS) of 750 ± 25 MPa, and an elongation of $3.5 \pm 0.2\%$. On the other hand, the DED-HT 440C material exhibited values of 800 ± 10 MPa (σ_f), 750 ± 43 MPa (YS), and $2.2 \pm 0.2\%$ (elongation).

In terms of elongation, both the DED-AP and DED-HT 440C materials exhibited slightly lower values when compared to annealed [139, 140] and heat-treated [141, 142] wrought AISI 440C materials. However, it is important to consider that elongation is typically reduced in additive manufacturing processes due to the intrinsic microstructural characteristics and residual stresses associated with the manufacturing method. Overall, the tensile properties of the DED-AP and DED-HT materials demonstrate their potential for relatively high-strength applications.

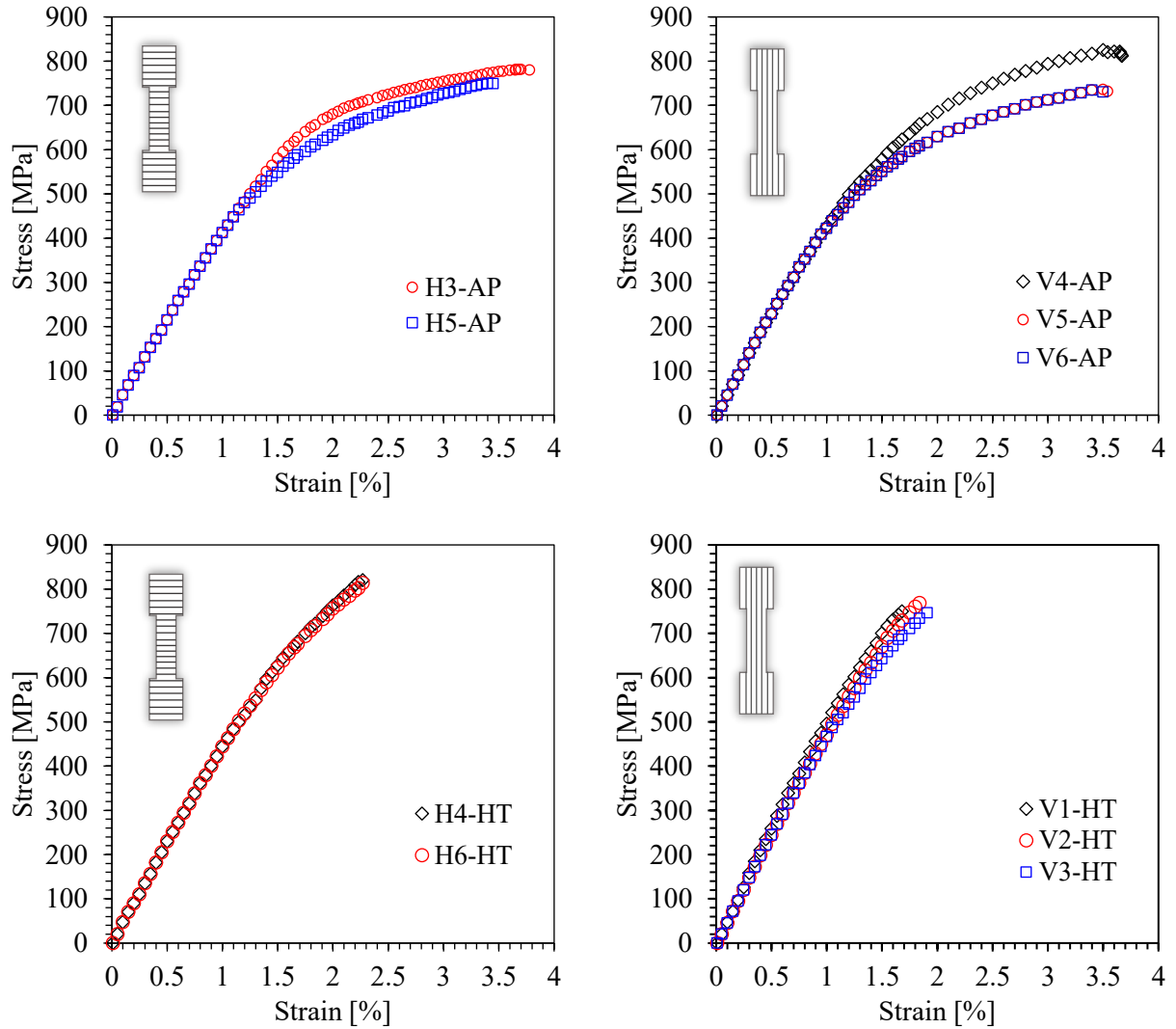
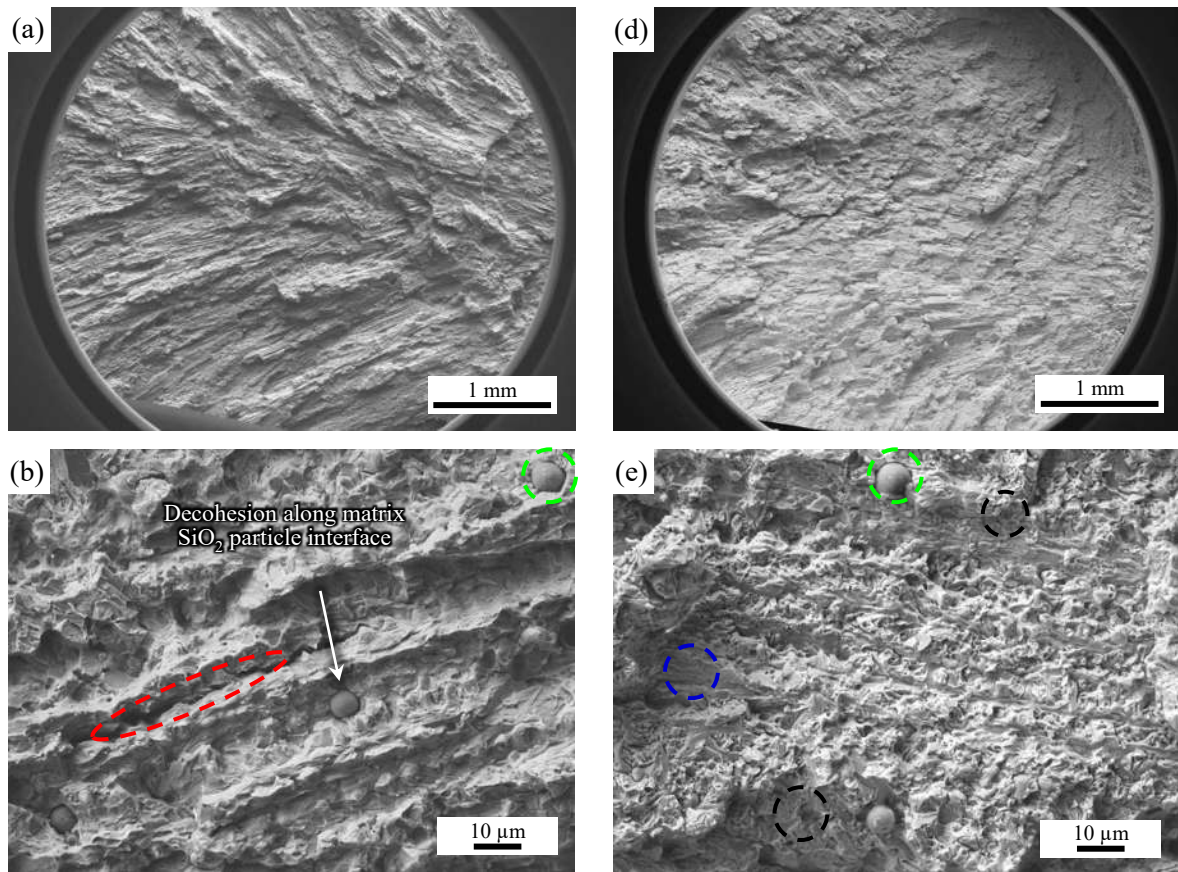


Figure 7.4 Stress-strain tension curves for DED AISI 440C steel as a function of printing direction (a-b) as-printed and (c-d) heat treated.

Figure 7.5 shows the microstructural characteristics of the fracture surfaces after conducting tension tests on the DED AISI 440C material. Both the DED-AP and DED-HT specimens displayed brittle or cleavage fracture modes. For the case of DED-AP 440C, the fractured surfaces primarily exhibited dendrite structures, see Figure 7.5(a). Closer examination at higher magnification Figure 7.5(b) revealed fractured eutectic structures in focused areas (highlighted by red ellipse). This suggests that the eutectic region observed in the initial microstructures plays a significant role in the fracture behavior.

In contrast, DED-HT 440C exhibited a relatively smoother fracture surface compared to DED-AP 440C, with dendrite structures observed only in certain parts of the fracture surface (Figure 7.5(d)). Further magnification in Figure 7.5(e) revealed numerous fine carbides highlighted by dark circles on the fractured surface. Areas without carbides exhibited fine dimples. Based on the results, it can be inferred that brittle fractures occur within the network-shaped and needle-type carbides formed in the martensite. These carbides contribute to a low elongation property, as they act as sites for crack initiation and propagation during the fracture process [143, 144]. Additionally, the HT samples showed a cleavage fracture mode (blue circle). Quasi-spherical SiO_2 inclusions with sizes of a few micrometers were observed in both the AP and HT samples (green circles). These particles can affect the strength of the samples by creating stress concentration fields that prompt the decohesion of these particles to form voids at the onset of fracture. Figure 7.5(c) y (f) also shows a lack of fusion defect with a diameter of about 900 μm , which results from the incomplete fusion of particle powder.



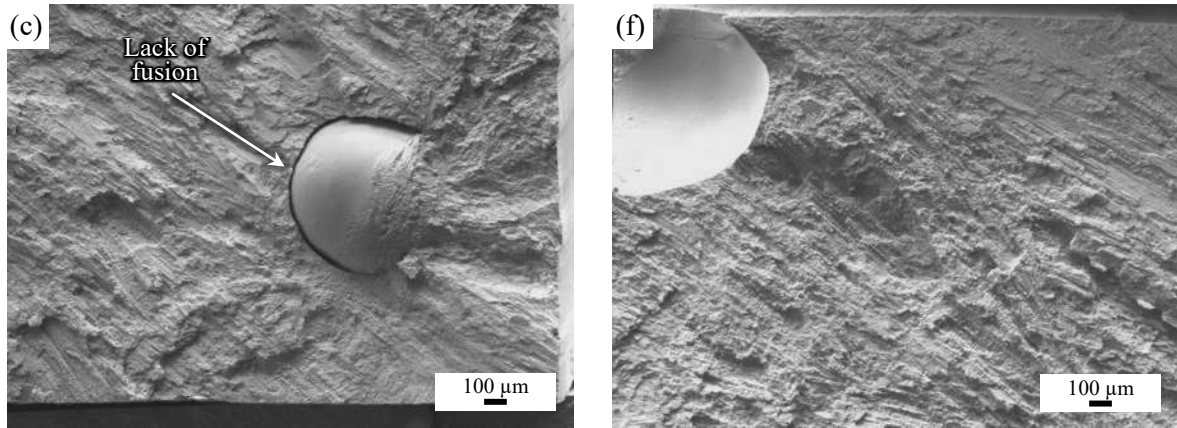
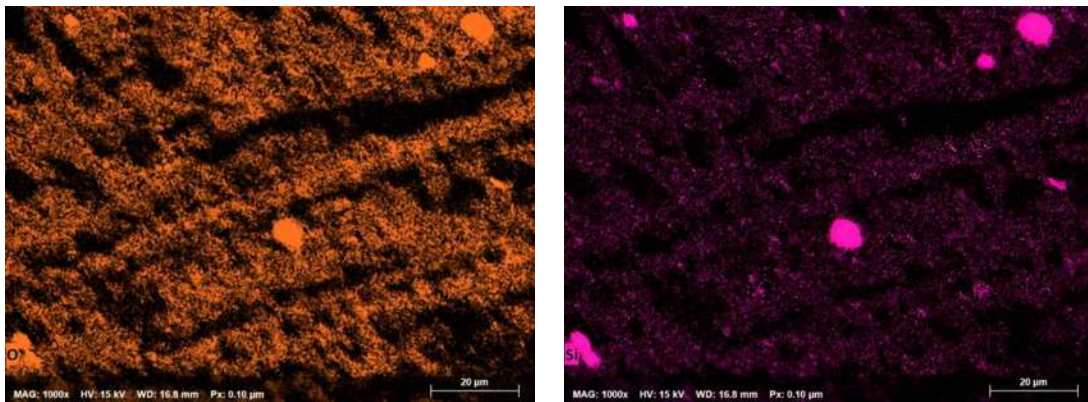


Figure 7.5 Fractographies of the horizontal DED tensile fractured samples (a-c) AP and (d-f) HT samples.

Figure 7.6 and Table 7.2 show the elemental mapping of typical oxide inclusions on the surface fracture and their respective EDS analysis, respectively. These oxide inclusions are common microstructural features in the DED process and are formed when the solubility of oxygen dissolved in the molten pool decreases [128]. It can be seen that the inclusions have a semi-spherical shape and size range of 2-9 μm , and the EDS analyses corroborate that the oxide inclusions are all enriched in Si and Mn.



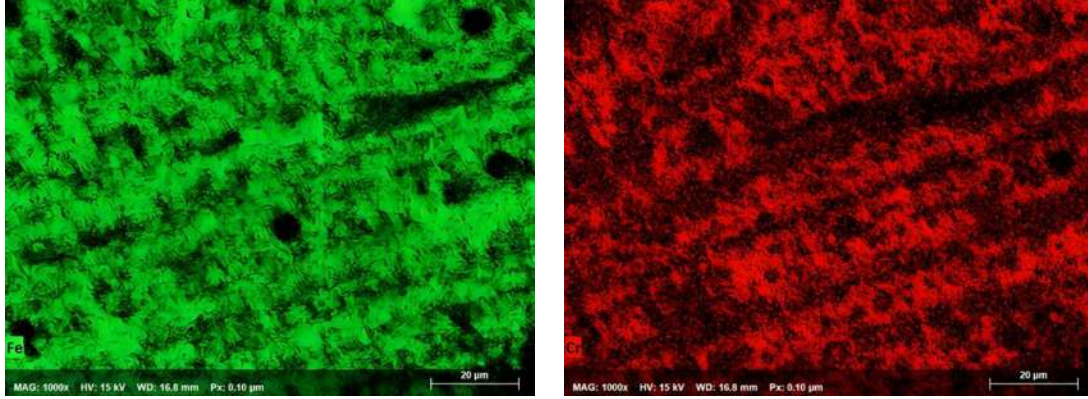


Figure 7.6 EDS mapping images of the fracture surface of the as-printed horizontal specimen.

Table 7.2 EDS point analysis of oxides in the as-printed horizontal specimen.

Phase	Element composition (at. %)							
	Fe	Cr	Mo	V	Si	C	O	Mn
Matrix	73.2	14.9	0.7	0.8	1.0	9.29	---	---
Oxide	1.87	10.4	0.4	0.6	24.7	1.6	50.2	10.2

The stress-assisted and the strain-induced transformations are the two mechanisms of martensitic transformation, which for FCC materials, are intrinsically related to the stacking faults energy (SFE), as this value determines whether twinning, martensite transformation, or dislocation slip dominates the deformation [145]. During severe deformation, materials with low SFE lead to the formation of primary and secondary twins. On the other hand, as the SFE increases, the activity of twins decreases, and dislocation slip increases. In materials with high SFE, microstructural refinement occurs due to the interaction, evolution, and rearrangement of dislocations [146]. The stability of austenite is strongly affected by the chemical composition, particularly carbon, which is a strong austenite stabilizer element. From Figure 7.7(a) and (b) it is seen that some degree of stress-strain-induced transformation occurred in the samples. It is worth mentioning that, since the material failed prematurely, the evolution of this process did not reach its final stage. A comparison between the horizontal and the vertical samples shows that the austenite is more likely to transform in the vertical samples, which can be attributed to the stability of the austenite that varies according to the building direction [147]. The results suggest that the austenite of the horizontal samples is more stable than that of the vertical samples.

The grain deformation resistance is associated with their respective orientations. From the orientation maps in Figure 7.7(c) and (d), the formation of some slip bands is appreciated. Furthermore, the grains oriented towards $[111]$ direction exhibit less deformation resistance, than those oriented in the $[110]$. Also, the orientation of the grains is closely related to the slip systems in the crystal. To properly understand the mechanism of slip propagation through grain boundaries, a description of the lattice rotation of the crystal is essential [148], as depicted in Figure 7.7(e).

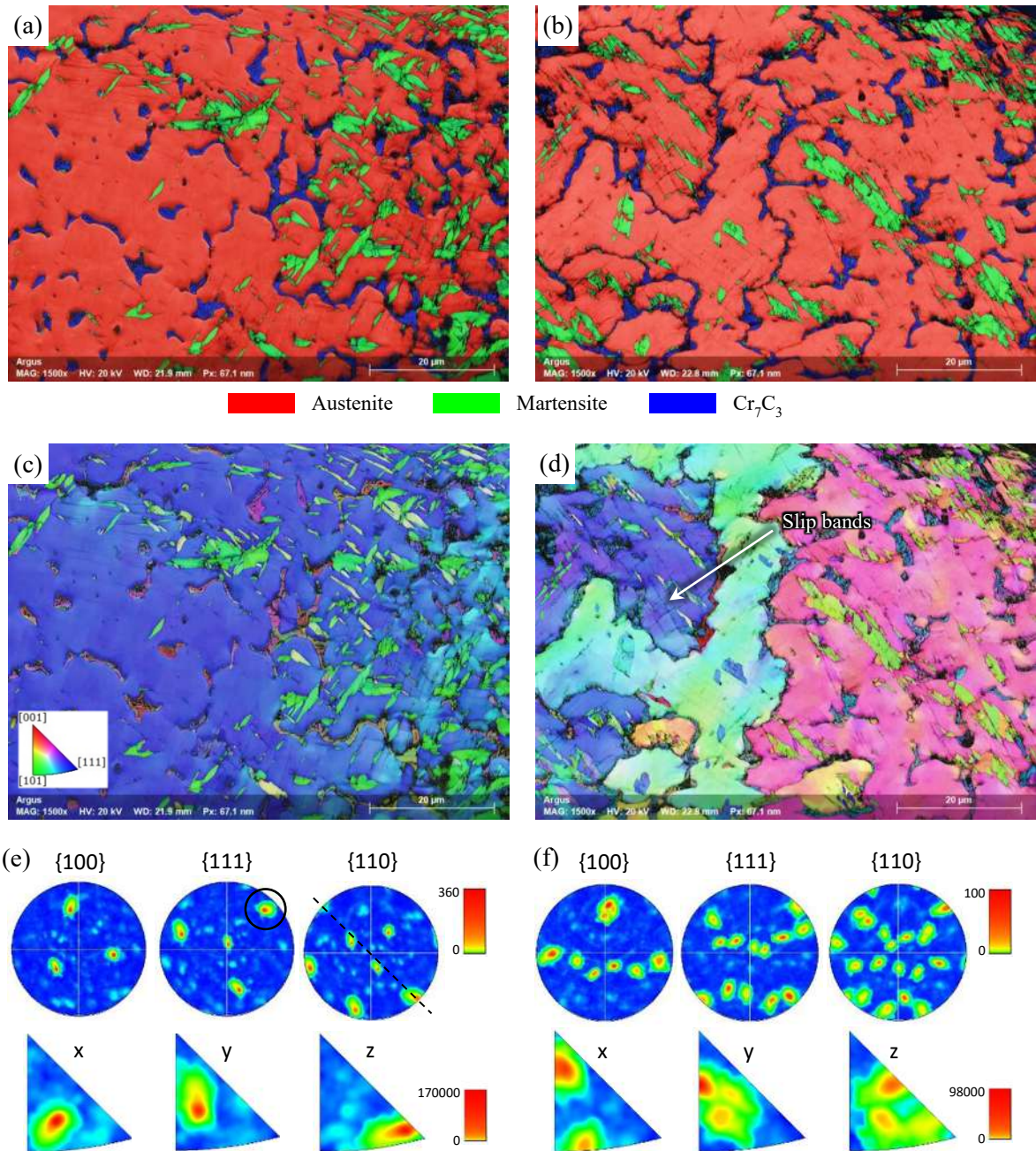


Figure 7.7 EBSD analysis results of the AP DED steel after tensile testing: (a-b) Phase distribution in the horizontal and vertical specimens respectively. (c-d) Orientation maps colored according to the inverse pole figure in the horizontal and vertical specimens respectively. (e-f) Pole figure and inverse pole figure in the horizontal and vertical specimens respectively.

The grain average misorientation (GAM) and Kernel average misorientation (KAM) maps in Figure 7.8 show a high misorientation in the samples after mechanical testing, with the horizontal samples exhibiting more severe deformation, see Figure 7.8(a) and (b). The results suggest that a higher degree of misorientation occurs in the surroundings of the martensite that formed as a result of the TRIP effect. As seen in Figure 7.8(c) and (d), a higher dislocation density is observed in the material after mechanical testing. Moreover, the dislocations seem to be piled up along the grain boundaries of the martensite and carbides. These factors, combined with the fine structure and dislocation strengthening mechanisms, contribute to the improved mechanical properties and strength of the material [9].

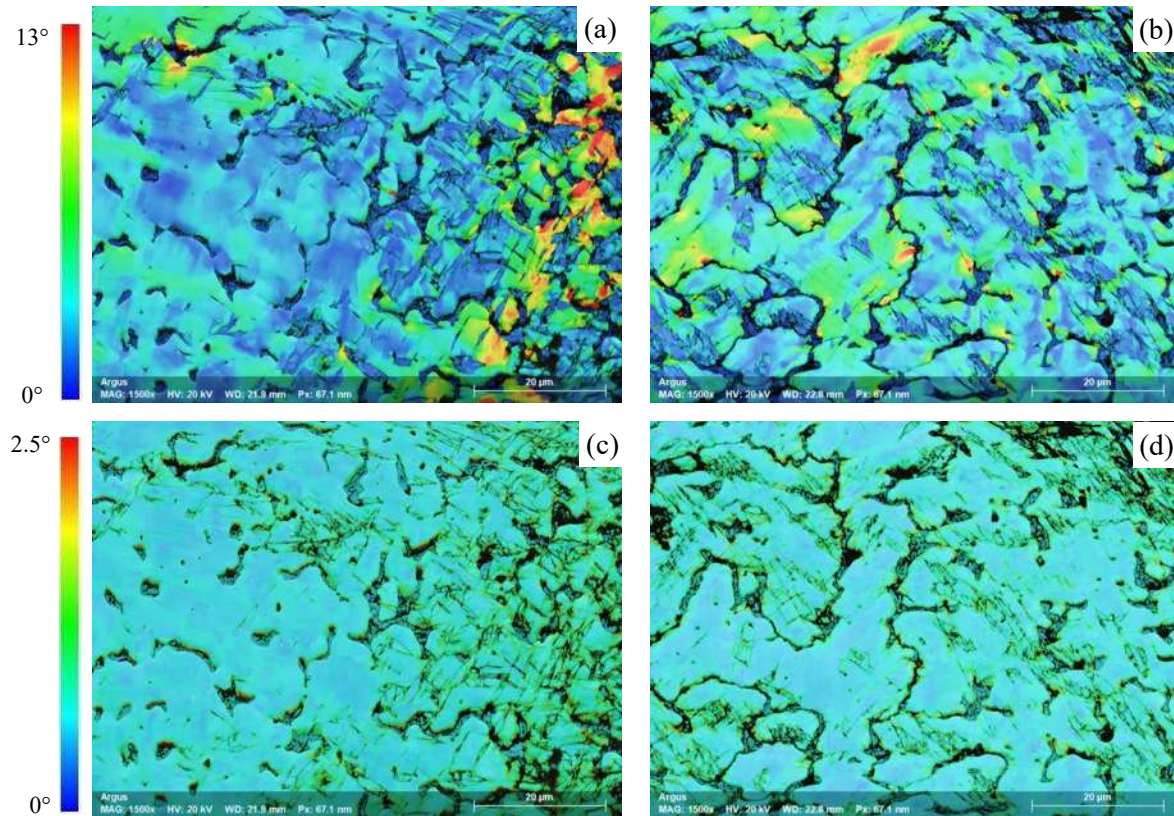


Figure 7.8 Grain average misorientation distribution of AP DED specimen after tensile testing, (a) horizontal and (b) vertical building directions. Kernel average misorientation distribution of AP DED specimen after tensile testing, (c) horizontal and (d) vertical building directions.

Vickers hardness maps below the fracture surface of the horizontal and vertical AP samples after tensile testing are shown in Figure 7.9. The average hardness values increased near the deformed fracture zone for both conditions, confirming that the TRIP effect occurred during the testing, as supported by the EBSD analysis in Figure 7.7(a) and (b). Notably, the vertical AP sample exhibits higher average hardness than the horizontal sample.

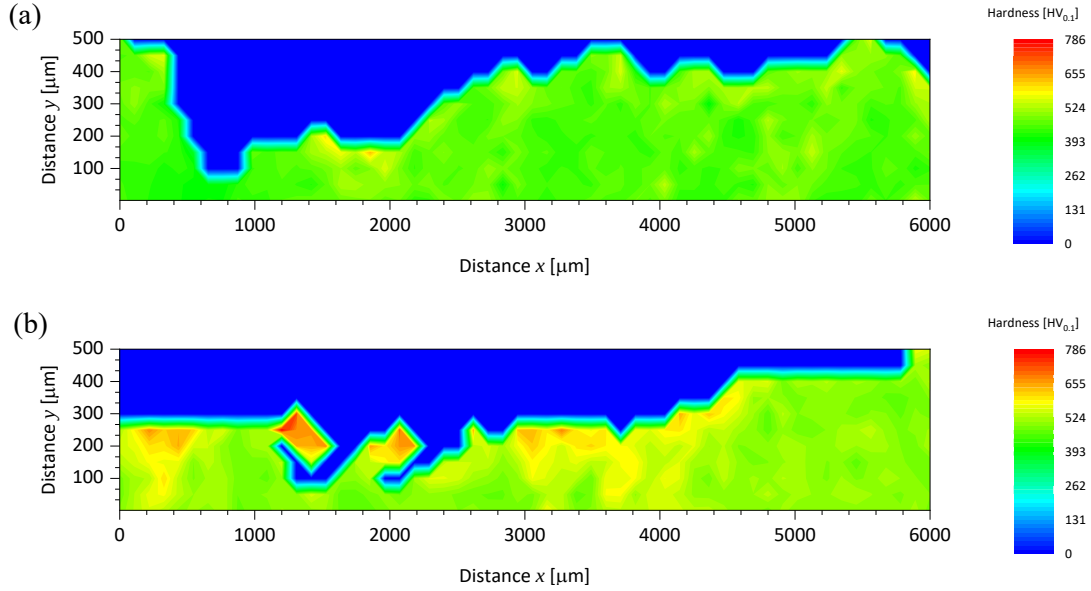


Figure 7.9 Vickers hardness map below the fracture surface after the tensile test (a) horizontal-AP and (b) vertical-AP.

Compression test

As the defects found in the DED material limit the applicability of the tensile testing to establish the elastic-plastic behavior of the alloy, compression tests were conducted in a set of both AP and HT representative samples in the horizontal and vertical building direction. The results of the compression test are shown in Figure 7.10, indicating a reduction in ductility in the HT samples. This result was anticipated as a consequence of the martensitic transformation that occurs during the quenching process. Interestingly, the AP samples exhibited an elastic-plastic linear hardening behavior with a relatively high work hardening. This implies that the yield strength and flow stress increase with plastic strain [149]. During uniaxial compression, a larger number of grains in the sample promotes better coordination of individual grains as plastic deformation occurs. Therefore, a smaller critical shear stress can activate multiple slip systems and slip occurs easily.

The activation of slip systems is also governed by the orientation of individual grains. When the orientation is favorable for slip motion, the resistance of grains to deformation decreases, accompanied by a reduction in flow stress. Conversely, if the orientation of the grains difficult slip motion, both the resistance of grains to deformation and the flow stress increase. During linear hardening, as the flow stress increases, the density of secondary dislocations also increases, which makes them a stronger obstacle and increases their range of interaction. At this point, new obstacles are formed blocking thoroughly the slip lines. Then, new slip lines form with increasing stress, allowing the movement of dislocation until a new obstacle blocks the slip line. Consequently, the dislocations will pile up making the stress sufficient to activate secondary slip systems. Therefore, each new slip line will act as an obstacle for slip promoting the formation of dislocation clusters that trap more dislocations. Because the dislocations on secondary systems only move small distances, the plastic strain on secondary systems is small but with a high density of dislocations [150, 151].

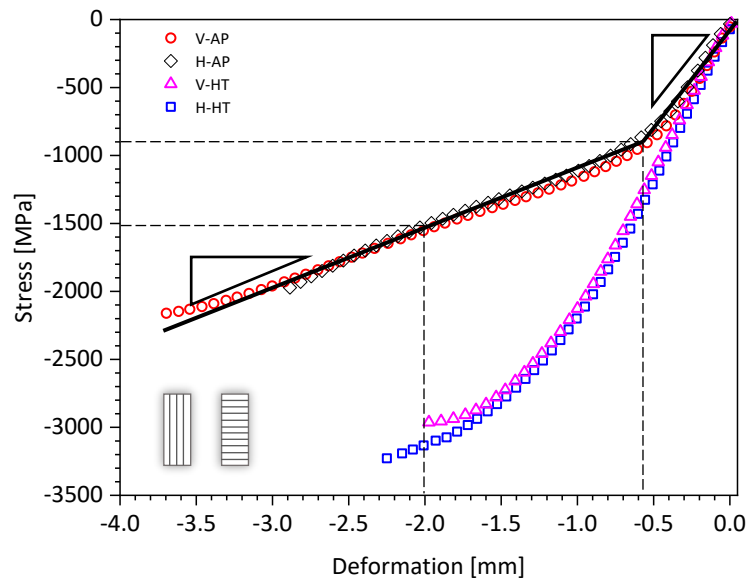


Figure 7.10 (a) Stress-displacement curves for horizontal and vertical DED 440C AP and HT samples.

Figure 7.11(a) displays the fractography of the vertical HT sample after failure during the compression test. The surface fracture in Figure 7.11(b) exhibits some ductile dimples along with cleavage facets, indicating a decrease in ductility. An analysis of the surface fracture suggests a brittle mechanism behavior with some degree of plastic deformation.

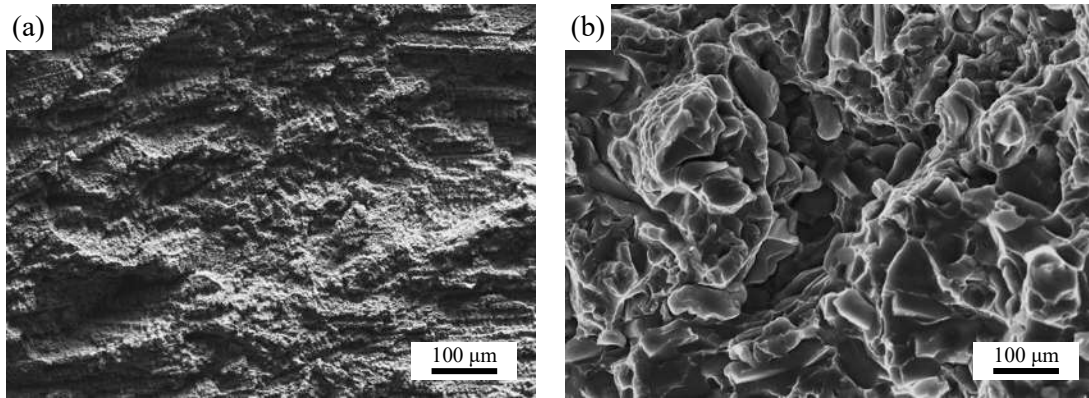
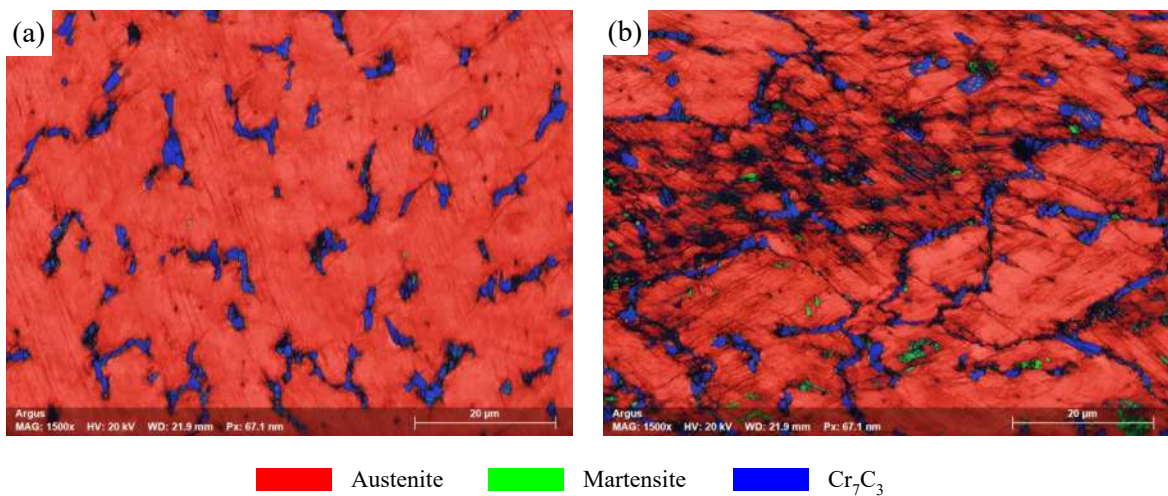


Figure 7.11 Surface fracture of HT vertical sample after failure under compression.

EBSD maps of the horizontal and vertical samples after compression strain are presented in Figure 7.12. The main differences between the two samples lie in the density of slip bands and the stress-strain-induced transformation of metastable austenite into martensite, which is more pronounced in the vertical sample, see Figure 7.12(a) and (b). The grain misorientation analysis in Figure 7.12(c) and (d) confirms that the austenite of the vertical sample allows a higher degree of deformation, observed in the increased fraction of slip bands formed after the mechanical tests were performed. Analysis of the pole figures shows that the texture in the horizontal samples is dominated by the C component $\{001\}\langle 110\rangle$ based on ideal torsion fiber texture representation [152]. On the other hand, the vertical samples exhibit a combination of components A $\{111\}\langle 110\rangle$ and B $\{112\}\langle 110\rangle$ according to reference [152]. Compared to the pole figure in Figure 7.7, the crystal lattice is rotating in such a way that the $\{111\}$ slip planes are close to the direction of the maximum shear stress.



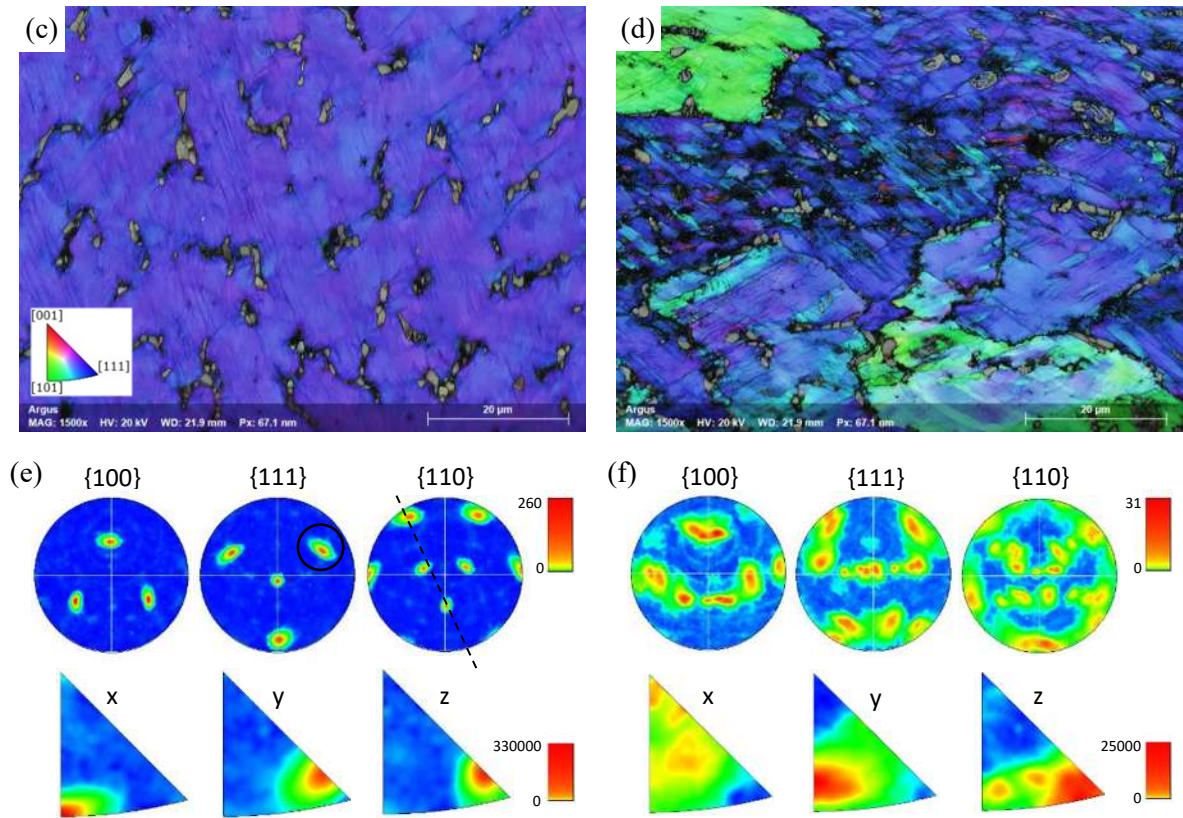


Figure 7.12 EBSD analysis results of the AP DED steel after compression test: (a-b) Phase distribution in the horizontal and vertical specimens respectively. (c-d) Orientation maps colored according to the inverse pole figure in the horizontal and vertical specimens respectively. (e-f) Pole figure and inverse pole figure in the horizontal and vertical specimens respectively.

The Kernel average misorientation maps presented in Figure 7.13 (c) and (d) highlight the regions of higher deformation, showing the developments of local misorientation associated with an increase in the effective strain (plastic deformation). Higher KAM values are also related to plastic deformation and an increase in the dislocation density [153]. A comparison of the misorientation in the AP horizontal and vertical samples shows that before deformation, the local misorientation is in the range from 0.18 to 1.4° and 0.18 to 2.0° , respectively. After the deformation imposed for the mechanical tests, the formation and accumulation of dislocation densities promote misorientation in the highly deformed regions. As mentioned previously, since the tensile samples failed before reaching the maximum stress, the compression samples exhibited a higher effective strain.

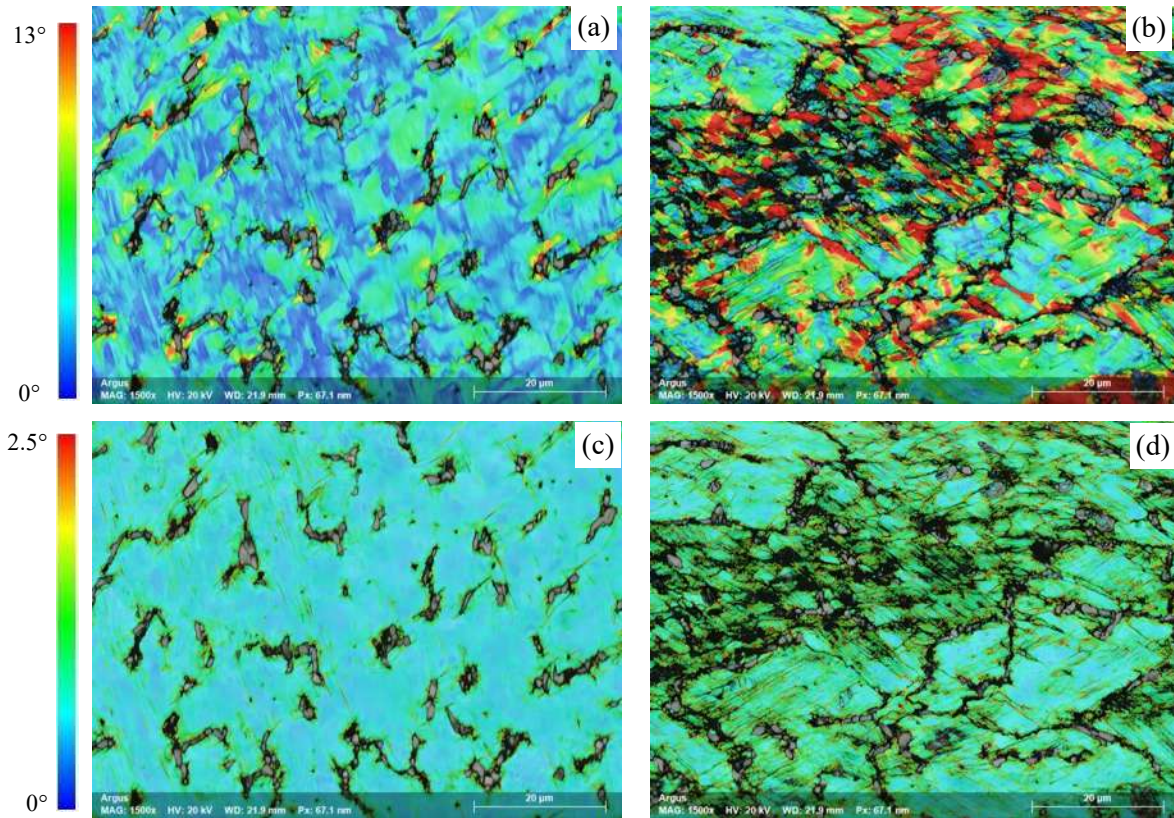


Figure 7.13 Grain average misorientation distribution of AP DED specimen after tensile testing, (a) horizontal and (b) vertical building directions. Kernel average misorientation distribution of AP DED specimen after tensile testing, (c) horizontal and (d) vertical building directions.

Results from GAM analysis in Figure 7.14(a) and (b) indicate that the misorientation angles for the horizontal samples increased by two units after strain, compared to the as-printed condition. For the vertical samples, the shift towards higher misorientation angles is more pronounced. These higher GAM values indicate higher dislocation densities. From Figure 7.14(c) and (d), it is seen that KAM values have similar distributions after tensile and compression testing for the horizontal samples. On the other hand, the KAM distribution for the compression test in the vertical sample exhibits a clear shift to higher misorientation angles, suggesting a change in the arrangement of dislocations accompanied by an increase in the dislocation density.

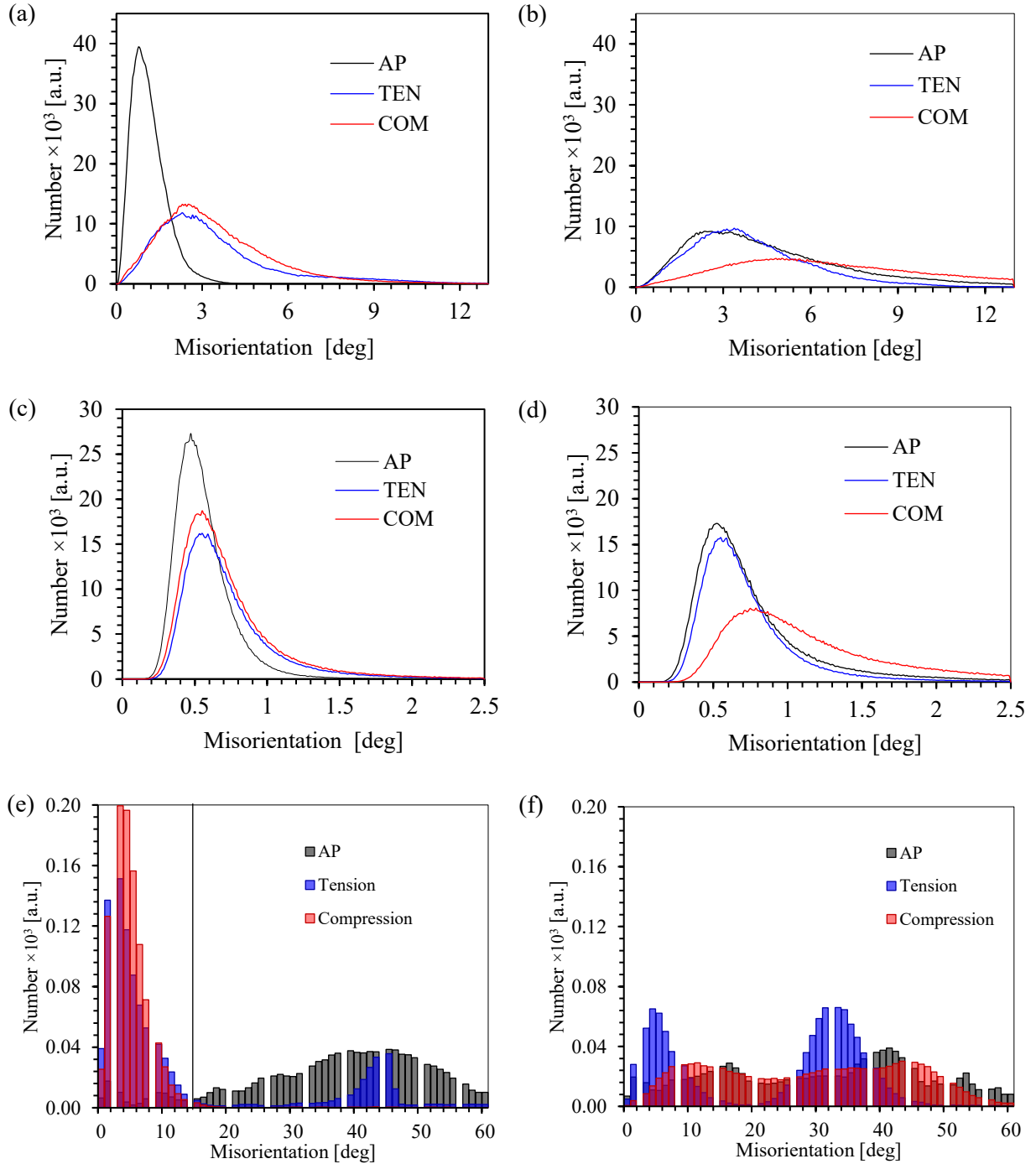


Figure 7.14 Frequency distribution of grain average misorientation for the (a) horizontal and (b) vertical samples. Kernel average misorientation frequency distribution of (c) horizontal and (d) vertical samples. Misorientation frequency distribution of (e) horizontal and (f) vertical samples.

The different strain levels for each mechanical test are clearly reflected in the grain boundary misorientation distributions in Figure 7.14(e) and (f). For the AP horizontal samples, the misorientation distributions evolved to small angles below 10° after tension and compression, typically associated with plastic deformation (deformation-induced boundaries) [154]. On the other hand, the AP vertical counterparts exhibited different behavior, characterized by both small and large misorientation angles. For the compression test, misorientations evolved to angles around 45° as a result of martensitic transformation during compression testing. This is consistent with the predicted orientation relationship between austenite and martensite by Kurdjumov-Sachs and Nishiyama-Wasserman, which is close to 42.9° and 46° , respectively. Misorientations close to 60° are produced by deformation twinning since the twin boundary misorientation in austenite is 60° around $\langle 111 \rangle$. In the AP vertical samples, the grain boundaries exhibit random misorientation distribution that results from large strains, where deformation sub-boundaries continuously develop (low angles) and martensitic transformation occurs (angles of 45°). This behavior is common in largely strained metals and alloys [154]. In the case of the horizontal samples, the AP condition exhibits a peak for misorientations between 40° and 50° , which shifts towards boundaries with misorientation angles below 10° after deformation. This subgrain structure with LAGBs is less stable than those with medium or high orientation angles, which highly influences the final microstructure after plastic deformation [155]. On the other hand, the vertical samples are characterized by a more even distribution of misorientation angles, implying the presence of strong texture [155].

The XRD patterns of the as-printed and deformed (after compression) samples in Figure 7.15 identify the phase constituents and texture. The microstructure that results from the DED process is nearly a single phase that consists of austenite, with only a small fraction of primary Cr_7C_3 carbide and martensite. Furthermore, the XRD diffractograms show that the initial texture of the material is higher for the vertical sample (Figure 7.15 (b)), especially for the $(111)\gamma$ and $(200)\gamma$ peaks, indicating preferential crystallographic orientations compared to the horizontal one in Figure 7.15(a). The horizontal and vertical deformed samples also exhibit strong crystallographic texture towards the $(111)\gamma$. It is worth mentioning that a small amount of martensite phase appears in the specimens after deformation, showing evidence that some level of phase transformation occurred during the test.

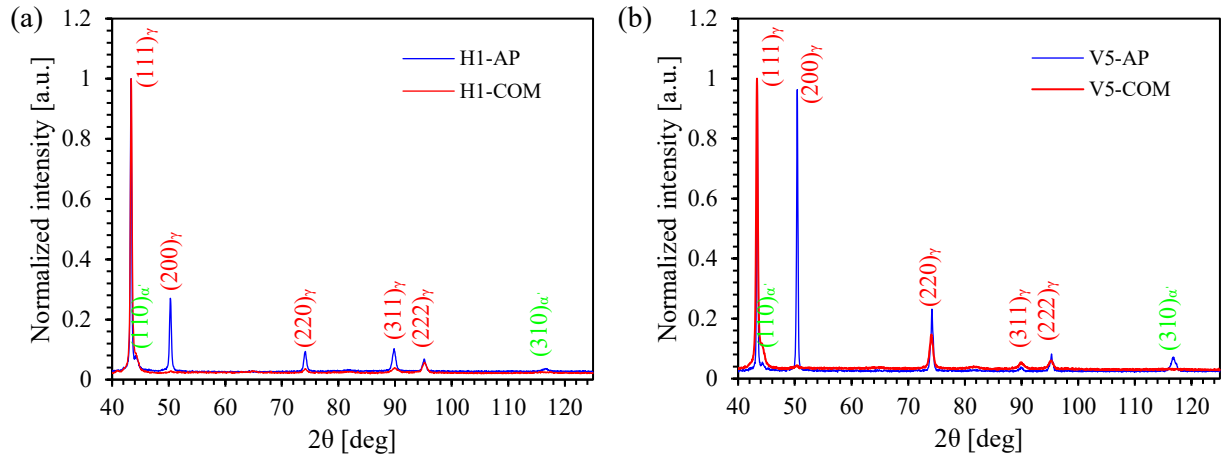


Figure 7.15 XRD diffractograms of the AISI 440C DED as-printed and after compression samples in the (a) horizontal and (b) vertical building directions.

7.4 Conclusions

By employing the DED additive manufacturing process, significant advancements have been made in overcoming the inherent challenges associated with the manufacturing of high-carbon stainless steel alloys like 440C. Several key conclusions can be drawn from this study:

- The DED as-printed material was found to be almost fully austenitic with eutectic carbides in the interdendritic region. The microstructure consisted of a fine equiaxed and columnar dendritic structure.
- The average hardness of the as-printed vertical samples was higher compared to the horizontal ones, which resulted from the heat transfer during the building process. No significant differences in hardness were found in the heat-treated horizontal and vertical samples.
- Tensile results were not representative of the mechanical properties of the steel since the material failed prematurely due to macroscopic defects formed during the deposition process. Compression strength and elongation gave more representative values regarding the mechanical response of the steel.
- The fracture surfaces of tensile and compression specimens showed a dendritic structure where interdendritic carbides acted as sites for crack propagation. Fine dimples were also observed in some areas. The fracture mode was fragile with some degree of plastic deformation.
- The deformed structure after the tensile test exhibited martensite-induced transformation near the fracture zone, especially in the vertical samples. In the case of the specimens deformed under compression uniaxial loading, only a small fraction of martensite formed, but the amount of slip bands increased compared to the tensile samples.

CHAPTER VIII

SUMMARY AND CONCLUDING REMARKS

In this work a comparative investigation of the process-structure-properties relationship of conventional and advanced manufacturing techniques in the production of 440C MSS was performed. This research has demonstrated that the manufacturing process allows the tailoring of martensitic stainless steel properties to optimize its performance. For instance, conventional casting is a well-established manufacturing technique that often produce coarse microstructures with inherent limitations in property control. On the other hand, additive manufacturing techniques such as DED, offer a higher flexibility in tailoring the microstructure and properties to specific applications through the optimization of the process parameters. The DED process has demonstrated the ability to produce 440C steel components with enhanced material properties. The microstructure analysis revealed a refined and uniform grain structure, leading to improved mechanical strength compared to conventionally manufactured counterparts.

The findings of this research offer a deeper understanding on the structure-property relationship, and provide insights for the development of advanced materials. Future research could explore the potential of other additive manufacturing techniques in the production of martensitic stainless steels.

It is worth mentioning that while this investigation initially included research on D2 and M42 tool steels, the results of these steels have been omitted from this thesis to keep it shorter and more focused. However, such research will be used for future publications and/or future work.

REFERENCES

- [1] Roberts G H J, Johnson A *Tool steels*. 3rd edn. Ohio, USA.Metals Park. 1962.
- [2] Totten G E. *Steel heat treatment handbook*. 2nd edition. Oregon, USA.Taylor & Francis. 2007.
- [3] Doñate-Buendía C, Streubel R, Kürnsteiner P, Wilms M, Stern F, Tenkamp J, Bruder E, Barcikowski S, Gault B, Durst K, Schleifenbaum J, Walther F,Gökce B. *Effect of nanoparticle additivation on the microstructure and microhardness of oxide dispersion strengthened steels produced by laser powder bed fusion and directed energy deposition*. 2020.
- [4] !!! INVALID CITATION !!! [1-4].
- [5] Srivatsan T S,Sudarshan T S. *Additive manufacturing : innovations, advances, and applications*. Boca Raton, Fla.CRC Press. 2016.
- [6] Mesquita R A. *Tool Steels Properties and Performance*. London.CRC Press. 2017.
- [7] Spiegelhaue C. *Industrial production of tool steels using the spray forming technology*. In; 6th International Tooling Conference. 1101-1109.
- [8] Park J S, Lee M-G, Cho Y-J, Sung J H, Jeong M-S, Lee S-K, Choi Y-J,Kim D H. *Effect of heat treatment on the characteristics of tool steel deposited by the directed energy deposition process*. **Metals and Materials International**. (22). 143-147. 2016.
- [9] Liu Z, Chua C, Leong K F, Kempen K, Thijs L, Yasa E, Van-Humbeeck J,Kruth J-P. In; **A preliminary investigation on Selective Laser Melting of M2 high speed steel**. 339-346. 2011.
- [10] Ngo T D, Kashani A, Imbalzano G, Nguyen K T Q,Hui D. *Additive manufacturing (3D printing): A review of materials, methods, applications and challenges*. **Composites Part B: Engineering**. (143). 172-196. 2018.
- [11] Haghdadi N, Laleh M, Moyle M,Primig S. *Additive manufacturing of steels: a review of achievements and challenges*. **Journal of Materials Science**. 1 (56). 64-107. 2021.
- [12] Rodríguez V M, López-Morelos V H, Nadimpalli V K, Bue Pedersen D, Ruiz A,Somers M A J. *Effect of Heat Treatment Processes on the Microstructure and Mechanical Properties of Spray-Formed 440C Martensitic Stainless Steel*. **steel research international**. 6 (94). 2200749. 2023.
- [13] Garrison W M. *Encyclopedia of Materials: Science and Technology*. In; **Stainless Steels: Martensitic**. Oxford.Elsevier. 8804-8810. 2001.
- [14] Mesquita R A, Barbosa C A,Machado A R. *Heat Treatment of Tool Steels*. 2016.
- [15] G. Aggen F W A, C. Michael Allen, H.S. Avery. *ASM Handbook, Volume 1, Properties and Selection: Irons, Steels, and High Performance Alloys*. 10. 2005.
- [16] Dossett J,Totten G E. *Heat Treating of Martensitic Stainless Steels*. **AMS International**. (4D). 382-396. 2014.
- [17] Avner S H. *Introduction to Physical Metallurgy*. 2nd edition. London.McGRAW-HILL. 1974.
- [18] George Roberts G K, Richard Kennedy. *Tool Steels*. 5th Edition. OH.ASM International. 1998.
- [19] Jarczyk G,Franz H. *Vacuum melting equipment and technologies for advanced materials*. **Archives of materials science and engineering**. 2 (56). 82-88. 2012.

- [20] ASM. *Casting: Vacuum Induction Melting*. **ASM International**. (Volume 15). 1-8. 2008.
- [21] Sen S, Stefanescu D M. *Melting and casting processes for high-temperature intermetallics*. **JOM**. 5 (43). 30-34. 1991.
- [22] Schlatter R. *Vacuum induction melting*. **JOM**. 5 (24). 17-25. 1972.
- [23] Bolfarini C, Srivastava V C. *Metal Sprays and Spray Deposition*. In; **Spray Forming of Novel Materials**. Cham. Springer International Publishing. 521-561. 2017.
- [24] Lachenicht V, Scharf G, Zebrowski D, Shalimov A. *Spray forming: a promising process for making high-quality steels and alloys*. **Metallurgist**. 9 (54). 656-668. 2011.
- [25] Grant P S. *Solidification in Spray Forming*. **Metallurgical and Materials Transactions A**. 7 (38). 1520-1529. 2007.
- [26] Zepon G, Ellendt N, Uhlenwinkel V, Bolfarini C. *Solidification Sequence of Spray-Formed Steels*. **Metallurgical and Materials Transactions A**. 2 (47). 842-851. 2016.
- [27] ASTM International. ASTM F2792. Standard Terminology for Additive Manufacturing Technologies. 2012.
- [28] Huang Y, Leu M, Mazumder J, Donmez M. *Additive Manufacturing: Current State, Future Potential, Gaps and Needs, and Recommendations*. **Journal of Manufacturing Science and Engineering**. (137). 014001. 2015.
- [29] Yang L, Hsu K, Baughman B, Godfrey D, Medina F, Menon M, Wiener S. *Additive Manufacturing of Metals: The Technology, Materials, Design and Production*. 2017.
- [30] Zadi-Maad A, Rohib R, Irawan A. *Additive manufacturing for steels: a review*. **IOP Conference Series: Materials Science and Engineering**. (285). 012028. 2018.
- [31] Syarif J, H. Yousuf M, Sajuri Z, Baghdadi A H, Merabtene M, Omar M Z. *Effect of Partial Solution Treatment Temperature on Microstructure and Tensile Properties of 440C Martensitic Stainless Steel*. **Metals**. 5 (10). 2020.
- [32] Barlow L D, Du Toit M. *Effect of Austenitizing Heat Treatment on the Microstructure and Hardness of Martensitic Stainless Steel AISI 420*. **Journal of Materials Engineering and Performance**. 7 (21). 1327-1336. 2012.
- [33] Salih A, Omar M Z, Junaidi S, Sajuri Z. *An investigation on the microstructure and mechanical properties of quenched and tempered SS440C martensitic stainless steel*. **International Journal of Mechanical and Materials Engineering**. (7). 119-123. 2012.
- [34] Puskar J, Hanson R, Chidester A, Houghton R. *Effects of Varying Austenitizing Temperatures on Vacuum Hardening of Type 440C Stainless Steel*. 2009.
- [35] ASTM International. ASTM A276. Standard Specification for Stainless Steel Bars and Shapes. 2006.
- [36] Cao R, Liang J, Li F, Li C, Zhao Z. *Intercritical Annealing Processing and a New Type of Quenching and Partitioning Processing, Actualized by Combining Intercritical Quenching and Tempering, for Medium Manganese Lightweight Steel*. **steel research international**. 1 (91). 1900335. 2020.
- [37] Bénéteau A, Aeby-Gautier E, Geandier G, P W, Redjaïmia A, Appolaire B. *Tempering of a martensitic stainless steel: Investigation by in situ synchrotron X-ray diffraction*. **Acta Materialia**. (81). 30-40. 2014.
- [38] Anantha K, Örnek C, Ejnermark S, Medvedeva A, Sjöström J, Pan J. *Correlative Microstructure Analysis and In Situ Corrosion Study of AISI 420 Martensitic Stainless Steel for Plastic Molding Applications*. **Journal of The Electrochemical Society**. (164). C85-C93. 2017.

- [39] Krauss G. *Deformation and fracture in martensitic carbon steels tempered at low temperatures*. **Metallurgical and Materials Transactions B**. 2 (32). 205-221. 2001.
- [40] Gushev M N, Leonard K J. *In situ SEM-EBSD analysis of plastic deformation mechanisms in neutron-irradiated austenitic steel*. **Journal of Nuclear Materials**. (517). 45-56. 2019.
- [41] Pan L, Kwok C T, Lo K H. *Friction-stir processing of AISI 440C high-carbon martensitic stainless steel for improving hardness and corrosion resistance*. **Journal of Materials Processing Technology**. (277). 116448. 2020.
- [42] Baltusnikas A, Grybėnas A, Kriukiene R, Lukosiute I, Makarevicius V. *Evolution of Crystallographic Structure of M23C6 Carbide Under Thermal Aging of P91 Steel*. **Journal of Materials Engineering and Performance**. (28). 2019.
- [43] Deng B, Hou Z Y, Wang G D, Yi H L. *Toughness Improvement in a Novel Martensitic Stainless Steel Achieved by Quenching–Tempering and Partitioning*. **Metallurgical and Materials Transactions A**. 11 (52). 4852-4864. 2021.
- [44] Chidester A J, Darragh C V, Hoff R C, Imundo J R, Maloney J L, III, Nitescu D. *Heat Treating of Irons and Steels*. In; **Heat Treatment of Bearings**. ASM International. 2014.
- [45] Channa I, Shah A A, Abro S, Siddiqui M, Mujahid M, Chandio A. *Effect of Tempering Temperature on the Properties of Martensitic stainless steel (AISI 420)*. 2019.
- [46] Hidalgo J, Vittorietti M, Farahani H, Vercruyse F, Petrov R, Sietsma J. *Influence of M23C6 carbides on the heterogeneous strain development in annealed 420 stainless steel*. **Acta Materialia**. (200). 74-90. 2020.
- [47] Khazaei B, Mollaahmadi A. *Rapid Tempering of Martensitic Stainless Steel AISI420: Microstructure, Mechanical and Corrosion Properties*. **Journal of Materials Engineering and Performance**. (26). 2017.
- [48] Krauss G. *Heat Treated Martensitic Steels: Microstructural Systems for Advanced Manufacture*. **ISIJ International**. 4 (35). 349-359. 1995.
- [49] Bhadeshia H K D H. *Steel for Bearings*. **Progress in Materials Science**. (57). 268–435. 2012.
- [50] Zurnadzhy V, Efremenko V, Wu K M, Azarkhov A Y, Chabak Y, Greshta V L, Isayev O B, Pomazkov M V. *Effects of stress relief tempering on microstructure and tensile/impact behavior of quenched and partitioned commercial spring steel*. **Materials Science and Engineering: A**. (745). 2018.
- [51] Bhadeshia H K D H, Honeycombe S. In; **The Tempering of Martensite**. 183-208. 2006.
- [52] Yu W-T, Li J, Shi C, Zhu Q-T. *Effect of Titanium on the Microstructure and Mechanical Properties of High-Carbon Martensitic Stainless Steel 8Cr13MoV*. **Metals**. (6). 2016.
- [53] Zhang G, Yuan H, Jiao D, Li Z, Zhang Y, Liu Z. *Microstructure evolution and mechanical properties of T15 high speed steel prepared by twin-atomiser spray forming and thermo-mechanical processing*. **Materials Science and Engineering: A**. (558). 566-571. 2012.
- [54] Tsuchiyama T, Tobata J, Tao T, Nakada N, Takaki S. *Quenching and partitioning treatment of a low-carbon martensitic stainless steel*. **Materials Science and Engineering: A**. (532). 585-592. 2012.
- [55] Idayan A, Gnanavelbabu A, Rajkumar K. *Influence of Deep Cryogenic Treatment on the Mechanical Properties of AISI 440C Bearing Steel*. **Procedia Engineering**. (97). 1683-1691. 2014.
- [56] Mohamed Salleh S H, Derman M N B, Omar M Z, Syarif J, Abdullah S. *Microstructure and Properties of Heat-Treated 440C Martensitic Stainless Steel*. **Defect and Diffusion Forum**. (334-335). 105-110. 2013.

- [57] Lotta J, Spiegelhauer C, Hannula S-P. In; **Spray Forming of Steels**. 463-495. 2017.
- [58] Mesquita R A, Barbosa C A. *Spray forming high speed steel - properties and processing*. **Materials Science and Engineering A, Structural Materials: Properties, Microstructure and Processing**. 1 (383). 87-95. 2004.
- [59] Zia-Ebrahimi F, Krauss G. *Mechanisms of tempered martensite embrittlement in medium-carbon steels*. **Acta Metallurgica**. (32). 1767-1778. 1984.
- [60] Reguly A, Strohaecker T R, Krauss G, Matlock D K. *Quench embrittlement of hardened 5160 steel as a function of austenitizing temperature*. **Metallurgical and Materials Transactions A**. 1 (35). 153-162. 2004.
- [61] Meyer H, Spice J, Greer J, Krauss G, Matlock D. *Effects of Silicon and Boron Additions on the Susceptibility to Quench Embrittlement and the Bending Fatigue Performance of Vacuum Carburized Modified 4320 Steel*. **SAE Transactions**. 2007.
- [62] Krauss G, Matlock D, Reguly A. *Microstructural Elements and Fracture of Hardened High-Carbon Steels*. **Materials Science Forum - MATER SCI FORUM**. (426-432). 835-840. 2003.
- [63] Yuan L, Ponge D, Wittig J, Choi P, Jiménez J, Raabe D. *Nanoscale austenite reversion through partitioning, segregation and kinetic freezing: Example of a ductile 2 GPa Fe-Cr-C steel*. **Acta Materialia**. (60). 2790-2804. 2012.
- [64] Gennari C, Pezzato L, Franceschi M, Fabrizi A, Brunelli K, Dabalà M, Polyakova M, Konstantinov D. *Effect of Intercritical Annealing and Austempering on the Microstructure and Mechanical Properties of a High Silicon Manganese Steel*. **Metals**. (10). 2020.
- [65] Bhadeshia H, Honeycombe R. *Steels: Microstructure and Properties (Fourth Edition)*. In; **Chapter 9 - Tempering of Martensite**. Butterworth-Heinemann. 237-270. 2017.
- [66] Eres-Castellanos A, Caballero F G, Garcia-Mateo C. *Stress or strain induced martensitic and bainitic transformations during ausforming processes*. **Acta Materialia**. (189). 60-72. 2020.
- [67] Li J, Tan Z, Zhang M, Gao G, Misra R D K, Bai B. *Effect of Intercritical Austenitizing Temperature during Quenching–Intercritical Quenching–Tempering Process on Toughness of 25Mn2Si2Cr Bainitic Steel*. **Steel Research International**. 6 (90). 1800573. 2019.
- [68] Kim J I, Syn C K, Morris J W. *Microstructural sources of toughness in QLT-Treated 5.5Ni cryogenic steel*. **Metallurgical Transactions A**. 1 (14). 93-103. 1983.
- [69] Kim J I, Morris J W. *On the scavenging effect of precipitated austenite in a low carbon Fe-5.5Ni alloy*. **Metallurgical Transactions A**. 8 (11). 1401-1406. 1980.
- [70] Wu S J, Sun G J, Ma Q S, Shen Q Y, Xu L. *Influence of QLT treatment on microstructure and mechanical properties of a high nickel steel*. **Journal of Materials Processing Technology**. 1 (213). 120-128. 2013.
- [71] Soleimani M, Mirzadeh H. *Enhanced mechanical properties of dual phase steel via cross rolling and intercritical annealing*. **Materials Science and Engineering: A**. (804). 140778. 2021.
- [72] Dulucleanu C, Severin T, Potorac A, Irimescu L. *Influence of intercritical quenching on the structure and mechanical properties of a dual-phase steel with low manganese content*. **Materials Today: Proceedings**. (19). 941-948. 2019.

- [73] Maleki M, Mirzadeh H, Zamani M. *Effect of Intercritical Annealing on Mechanical Properties and Work-Hardening Response of High Formability Dual Phase Steel*. **steel research international**. 4 (89). 1700412. 2018.
- [74] Jateczak C F. *Retained Austenite and Its Measurement by X-Ray Diffraction*. **SAE Transactions**. (89). 1657-1676. 1980.
- [75] Avishan B, Garcia-Mateo C, Morales-Rivas L, Yazdani S, Caballero F. *Strengthening and mechanical stability mechanisms in nanostructured bainite*. **Journal of Materials Science**. (48). 1-12. 2013.
- [76] Mukherjee M, Hashimoto S-i, Hojo T, Sugimoto K-i. *Strain-induced Transformation Behaviour of Retained Austenite and Tensile Properties of TRIP-aided Steels with Different Matrix Microstructure*. **Isij International - ISIJ INT**. (46). 316-324. 2006.
- [77] Waitz T, Antretter T, Fischer F, Karnthaler H. *Size effects on martensitic phase transformations in nanocrystalline NiTi shape memory alloys*. **Materials Science and Technology**. (24). 934-940. 2008.
- [78] Zhang P, Li S X, Zhang Z F. *General relationship between strength and hardness*. **Materials Science and Engineering: A**. (529). 62-73. 2011.
- [79] Garrison W M, Amuda M O H. *Reference Module in Materials Science and Materials Engineering*. In; **Stainless Steels: Martensitic**. Elsevier. 2017.
- [80] Salleh S H. *Investigation of Microstructures and Properties of 440C Martensitic Stainless Steel*. **International Journal of Mechanical and Materials Engineering**. (4). 21-24. 2009.
- [81] Yang J-R, Yu T H, Wang C H. *Martensitic transformations in AISI 440C stainless steel*. **Materials Science and Engineering A-structural Materials Properties Microstructure and Processing - MATER SCI ENG A-STRUCT MATER**. (438). 276-280. 2006.
- [82] Lotta J, Hannula S-P. *Microstructural Comparison of Spray-Formed and Conventionally Cast 2.5C–19Cr High-Chromium White Iron*. **Metallography, Microstructure, and Analysis**. 4 (4). 261-272. 2015.
- [83] Kumar S, Jadhav P, Patil A, Kirwai S, Singh R. *An Investigation of Performance of Spray Formed H13 Tool Steel*. **Procedia Structural Integrity**. (14). 872-882. 2019.
- [84] Jesus E R B, Jesus Filho E S, Rossi J L. *Performance Assessment of Spray Formed AISI M2 High-Speed Steel Tools*. **Materials Science Forum**. (530-531). 315-320. 2006.
- [85] Spangel S, Matthaei-Schulz E, Schulz A, Vethers H, Mayr P. *Influence of carbon and chromium content and preform shape on the microstructure of spray formed steel deposits*. **Materials Science and Engineering: A**. 1 (326). 26-39. 2002.
- [86] Zepon G, Nascimento A R C, Kasama A H, Nogueira R P, Kiminami C S, Botta W J, Bolfarini C. *Design of wear resistant boron-modified supermartensitic stainless steel by spray forming process*. **Materials & Design**. (83). 214-223. 2015.
- [87] Grant P. *Solidification in Spray Forming*. **Metallurgical and Materials Transactions A**. (38). 1520-1529. 2007.
- [88] Doherty R D, Khalfalla Y E, Benyounis K Y. *Reference Module in Materials Science and Materials Engineering*. In; **Spray Casting: Fundamentals**. Elsevier. 2016.
- [89] Wang H, Hou L, Ou P, Wang X, Li Y, Shen L, Zhao H, Cui H, Zhang J. *Enhanced microstructures and properties of spray-formed M3:2 high-speed steels by niobium addition and thermal-mechanical treatment*. **Journal of Materials Research**. 6 (34). 1043-1053. 2019.

- [90] Schulz A, Uhlenwinkel V, Escher C, Kohlmann R, Kulmburg A, Montero M C, Rabitsch R, Schützenhöfer W, Stocchi D, Viale D. *Opportunities and challenges of spray forming high-alloyed steels*. **Materials Science and Engineering: A**. 1 (477). 69-79. 2008.
- [91] Mesquita R, Barbosa C. *High-Speed Steels Produced by Conventional Casting, Spray Forming and Powder Metallurgy*. **Materials Science Forum - Mater SCI Forum**. (498-499). 244-250. 2005.
- [92] Yan F, Shi H, Jin B, Fan J, Xu Z. *Microstructure evolution during hot rolling and heat treatment of the spray formed Vanadis 4 cold work steel*. **Materials Characterization**. 8 (59). 1007-1014. 2008.
- [93] Toby B H, Von Dreele R B. *GSAS-II: the genesis of a modern open-source all purpose crystallography software package*. **Journal of Applied Crystallography**. 2 (46). 544-549. 2013.
- [94] ASTM International. *ASTM E8. Standard Test Methods for Tension Testing of Metallic Materials*. 2016.
- [95] Andersson J O, Helander T, Höglund L, Shi P, Sundman B. *Thermo-Calc & DICTRA, computational tools for materials science*. **Calphad**. 2 (26). 273-312. 2002.
- [96] Asensio J, Pero-Sanz J A, Verdeja J I. *Microstructure selection criteria for cast irons with more than 10 wt.% chromium for wear applications*. **Materials Characterization**. 2 (49). 83-93. 2002.
- [97] Cheng L, Böttger A, de Keijser T H, Mittemeijer E J. *Lattice parameters of iron-carbon and iron-nitrogen martensites and austenites*. **Scripta Metallurgica et Materialia**. 3 (24). 509-514. 1990.
- [98] Choudhary S K, Ganguly S, Sengupta A, Sharma V. *Solidification morphology and segregation in continuously cast steel slab*. **Journal of Materials Processing Technology**. (243). 312-321. 2017.
- [99] Verdiere A, Castro Cerda F, Béjar Llanes A, Wu J, Crebolder L, Petrov R H. *Effect of the austenitizing parameters on the microstructure and mechanical properties of 75Cr1 tool steel*. **Materials Science and Engineering: A**. (785). 139331. 2020.
- [100] Clemons K, Lorraine C, Salgado G, Taylor A, Ogren J, Umin P, Es-Said O. *Effects of Heat Treatments on Steels for Bearing Applications*. **Journal of Materials Engineering and Performance**. (16). 592-596. 2007.
- [101] Mesquita R, Barbosa C. *Spray forming high speed steel - Properties and processing*. **Materials Science and Engineering: A**. (383). 87-95. 2004.
- [102] Rodenburg C, Rainforth W M. *A quantitative analysis of the influence of carbides size distributions on wear behaviour of high-speed steel in dry rolling/sliding contact*. **Acta Materialia**. 7 (55). 2443-2454. 2007.
- [103] Dalmau A, Rmili W, Joly D, Richard C, Igual-Muñoz A. *Tribological Behavior of New Martensitic Stainless Steels Using Scratch and Dry Wear Test*. **Tribology Letters**. 3 (56). 517-529. 2014.
- [104] Hanlon D N, Rainforth W M. *The rolling sliding wear response of conventionally processed and spray formed high speed steel at ambient and elevated temperature*. **Wear**. 7 (255). 956-966. 2003.
- [105] Kjeldsteen P. *Development of high alloyed tool steels using spray forming on an industrial scale*. **Powder Metallurgy**. (46). 297-298. 2003.
- [106] Colaço R, Vilar R. *On the influence of retained austenite in the abrasive wear behaviour of a laser surface melted tool steel*. **Wear**. (258). 225-231. 2005.

- [107] Kikuchi S, Sasago A, Komotori J. *Effect of simultaneous surface modification process on wear resistance of martensitic stainless steel*. **Journal of Materials Processing Technology**. 20 (209). 6156-6160. 2009.
- [108] Prieto G, Tuckart W. *Influence of Cryogenic Treatments on the Wear Behavior of AISI 420 Martensitic Stainless Steel*. **Journal of Materials Engineering and Performance**. (26). 2017.
- [109] Li Y, He Y, Xiu J, Wang W, Zhu Y, Hu B. *Wear and corrosion properties of AISI 420 martensitic stainless steel treated by active screen plasma nitriding*. **Surface and Coatings Technology**. (329). 184-192. 2017.
- [110] Leonard A J, Rainforth W M. *Wear behaviour of tool steels with added (W,Ti)C particles*. **Wear**. 1 (255). 517-526. 2003.
- [111] Jovičević-Klug P, Jovičević-Klug M, Podgornik B. *Effectiveness of deep cryogenic treatment on carbide precipitation*. **Journal of Materials Research and Technology**. 6 (9). 13014-13026. 2020.
- [112] Kasak A, Neumeyer T A. *Observations on wear of high-hardness steels*. **Wear**. 6 (14). 445-454. 1969.
- [113] Podgornik B, Hogmark S, Pezdernik J. *Comparison between different test methods for evaluation of galling properties of surface engineered tool surfaces*. **Wear**. (257). 843-851. 2004.
- [114] Park Y K, Ha K, Shin K Y, Lee K Y, Kim D J, Kwon S-H, Lee W. *Wear resistance of direct-energy-deposited AISI M2 tool steel with and without post-heat treatment*. **The International Journal of Advanced Manufacturing Technology**. 11 (116). 3917-3931. 2021.
- [115] Okonkwo P C, Kelly G, Rolfe B F, Pereira M P. *The effect of sliding speed on the wear of steel-tool steel pairs*. **Tribology International**. (97). 218-227. 2016.
- [116] Okonkwo P, Kelly G, Rolfe B, Pereira M. *The effect of temperature on sliding wear of steel-tool steel pairs*. **Wear**. (s 282–283). 22–30. 2012.
- [117] Aksoy M, Yilmaz O, Korkut M H. *The effect of strong carbide-forming elements on the adhesive wear resistance of ferritic stainless steel*. **Wear**. 8 (249). 639-646. 2001.
- [118] Archard J F, Hirst W, Allibone T E. *The wear of metals under unlubricated conditions*. **Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences**. 1206 (236). 397-410. 1997.
- [119] Prasad S V, Michael J R, Christenson T R. *EBS D studies on wear-induced subsurface regions in LIGA nickel*. **Scripta Materialia**. 3 (48). 255-260. 2003.
- [120] Holmberg J, Wretland A, Berglund J, Beno T. *Selection of milling strategy based on surface integrity investigations of highly deformed Alloy 718 after ceramic and cemented carbide milling*. **Journal of Manufacturing Processes**. (58). 193-207. 2020.
- [121] Meng F, Tagashira K, Sohma H. *Wear resistance and microstructure of cryogenic treated Fe-1.4Cr-1C bearing steel*. **Scripta Metallurgica et Materialia**. 7 (31). 865-868. 1994.
- [122] Ardell A J J M T A. *Precipitation hardening*. (16). 2131-2165. 1985.
- [123] Tian W P, Jin Z Q, Wang X R, Xie G M. *Wire-arc directed energy deposition super martensitic stainless steel with excellent strength and plasticity*. **Journal of Manufacturing Processes**. (103). 11-22. 2023.
- [124] Bang G B, Hwang Y J, Kim W R, Song Y H, Kim G H, Hyun S-K, Cha S C, Park H J, Lee T W, Kim H G. *Microstructural and mechanical properties of AISI 440C stainless*

- steel fabricated using selective laser melting. **Materials Science and Engineering: A**. (860). 144259. 2022.
- [125] Collins P, Brice D, Samimi P, Ghamarian I, Fraser H L. *Microstructural Control of Additively Manufactured Metallic Materials*. **Annual Review of Materials Research**. (46). 2016.
- [126] Herzog D, Seyda V, Wycisk E, Emmelmann C. *Additive manufacturing of metals*. **Acta Materialia**. (117). 2016.
- [127] Krakhmalev P, Fredriksson G, Svensson K, Yadroitsev I, Yadroitsava I, Thuvander M, Peng R. *Microstructure, Solidification Texture, and Thermal Stability of 316 L Stainless Steel Manufactured by Laser Powder Bed Fusion*. **Metals**. (8). 643. 2018.
- [128] Smith T R, Sugar J D, San Marchi C, Schoenung J M. *Microstructural development in DED stainless steels: applying welding models to elucidate the impact of processing and alloy composition*. **Journal of Materials Science**. 1 (56). 762-780. 2021.
- [129] Pacheco J T, Meura V H, Bloemer P R A, Veiga M T, de Moura Filho O C, Cunha A, Teixeira M F. *Laser directed energy deposition of AISI 316L stainless steel: The effect of build direction on mechanical properties in as-built and heat-treated conditions*. **Advances in Industrial and Manufacturing Engineering**. (4). 100079. 2022.
- [130] du Plessis A, Yadroitsava I, Yadroitsev I. *Effects of defects on mechanical properties in metal additive manufacturing: A review focusing on X-ray tomography insights*. **Materials & Design**. (187). 108385. 2020.
- [131] Geenen K, Röttger A, Feld F, Theisen W. *Microstructure, mechanical, and tribological properties of M3:2 high-speed steel processed by selective laser melting, hot-isostatic pressing, and casting*. **Additive Manufacturing**. (28). 585-599. 2019.
- [132] Iakovakis E, Roy M J, Gee M, Matthews A. *Evaluation of wear mechanisms in additive manufactured carbide-rich tool steels*. **Wear**. (462-463). 203449. 2020.
- [133] Kim Y-K, Lee K-A. *Direct energy deposition of high strength austenitic stainless steel matrix nanocomposite with superior ductility: Microstructure, tensile properties, and deformation behavior*. **Materials Characterization**. (179). 111358. 2021.
- [134] Mao Y, Li J, Li W, Cai D, Wei Q. *Binder jetting additive manufacturing of 316L stainless-steel green parts with high strength and low binder content: Binder preparation and process optimization*. **Journal of Materials Processing Technology**. (291). 117020. 2021.
- [135] Nadimpalli V K D T, Valente E H, Mohanty S, Pedersen D B. *Multi-material additive manufacturing of steels using laser powder bed fusion*. In; Euspen's 19th International Conference and Exhibition. 240-243. 2019.
- [136] Samal P K, Valko J C, Pannell J D J A i P M, Materials P. *Processing and properties of PM 440C stainless steel*. Part 7 112-121. 2009.
- [137] Wang M, Zhang Q, Li W, Zhang Z, Chui P, Yu Z, Zhang K. *Investigation of the Microstructure and Mechanical Properties of an Ultrahigh Strength Martensitic Steel Fabricated Using Laser Metal Deposition Additive Manufacturing*. **Metals**. 10 (12). 2022.
- [138] Lee J-R, Lee M-S, Chae H, Lee S Y, Na T, Kim W-S, Jun T-S. *Effects of building direction and heat treatment on the local mechanical properties of direct metal laser sintered 15-5 PH stainless steel*. **Materials Characterization**. (167). 110468. 2020.
- [139] Lesyk D A, Martinez S, Dzhemelinskyy V V, Lamikiz A, Mordyuk B N, Prokopenko G I. *Surface microrelief and hardness of laser hardened and ultrasonically peened AISI D2 tool steel*. **Surface and Coatings Technology**. (278). 108-120. 2015.

- [140] Davim J, Maranhão C, Faria P, Abrao A, Campos Rubio J, Silva L. *Precision radial turning of AISI D2 steel*. **International Journal of Advanced Manufacturing Technology**. (42). 842-849. 2009.
- [141] Torkamani H, Raygan S, Rassizadehghani J. *Comparing microstructure and mechanical properties of AISI D2 steel after bright hardening and oil quenching*. **Materials & Design**. (54). 1049-1055. 2014.
- [142] Ben fathallah B, Dakhli C, Terres M A. *The effect of grinding parameters and gas nitriding depth on the grindability and surface integrity of AISI D2 tool steel*. **The International Journal of Advanced Manufacturing Technology**. (104). 2019.
- [143] Sander J, Hufenbach J, Giebeler L, Wendrock H, Kühn U, Eckert J. *Microstructure and properties of FeCrMoVC tool steel produced by selective laser melting*. **Materials & Design**. (89). 335-341. 2016.
- [144] Baek G Y, Shin G Y, Lee E M, Shim D S, Lee K Y, Yoon H-S, Kim M H. *Mechanical characteristics of a tool steel layer deposited by using direct energy deposition*. **Metals and Materials International**. (23). 770-777. 2017.
- [145] Shen Y F, Dong X X, Song X T, Jia N. *Carbon content-tuned martensite transformation in low-alloy TRIP steels*. **Scientific Reports**. 1 (9). 7559. 2019.
- [146] Roy B, Maity T, Das J. *Tuning of nanostructure by the control of twin density, dislocation density, crystallite size, and stacking fault energy in Cu100-xZnx (0≤x≤30wt%)*. **Materials Science and Engineering: A**. (672). 203-215. 2016.
- [147] Wang G, Ouyang H, Fan C, Guo Q, Li Z, Yan W, Li Z. *The origin of high-density dislocations in additively manufactured metals*. **Materials Research Letters**. 8 (8). 283-290. 2020.
- [148] Mania I, Paul H, Chulist R, Petrzak P, Miszczyk M M, Prażmowski M. *Crystal Lattice Rotations Induced by Shear Banding in fcc Metals Deformed at High Strain Rates*. **Archives of Metallurgy and Materials**. 319-329. 2022.
- [149] Yu H, He Z, Shen J. *Experimental Study of the Plasticity Responses of TRIP780 Steel Subjected to Strain-Path Changes*. **SAE International Journal of Materials and Manufacturing**. 3 (9). 558-564. 2016.
- [150] Hirsch P B. *A theory of linear strain hardening in crystals*. **Discussions of the Faraday Society**. 0 (38). 111-122. 1964.
- [151] Schoeck G. *Remarks on a theory of linear strain hardening*. **The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics**. 123 (13). 635-640. 1966.
- [152] Liu F C, Nelson T W. *In-situ grain structure and texture evolution during friction stir welding of austenite stainless steel*. **Materials & Design**. (115). 467-478. 2017.
- [153] Goran D. *Full Characterization of a Tool Steel Texture and Microstructure by Using Fast Simultaneous EBSD/EDS Measurements*. **Solid State Phenomena**. (172-174). 1290-1295. 2011.
- [154] Marina O, Belyakov A, Kaibyshev R. *Development of Nanocrystalline 304L Stainless Steel by Large Strain Cold Working*. **Metals**. (2015). 656-668. 2015.
- [155] Lipińska M, Brynk T, Hütter A, Golinski J, Enzinger N, Olejnik L, Lewandowska M. *Similar and dissimilar welds of ultrafine grained aluminium obtained by friction stir welding*. **Materials Science and Engineering A**. 139076. 2020.

NOMBRE DEL TRABAJO

EFFECT OF ADVANCED MANUFACTURING TECHNOLOGIES ON THE MICROSTRUCTURE-PROPERTY RELATIONSHIP OF 40C MA

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Título del trabajo	EFFECT OF ADVANCED MANUFACTURING TECHNOLOGIES ON THE MICROSTRUCTURE-PROPERTY RELATIONSHIP OF 440C MARTENSITIC STAINLESS STEEL	
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